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WASTE MANAGEMENT TECHNICAL MANUAL

Edited by

J. S. Buckingham

Waste Management Process Engineering
Research and Engineering

August 31, 1967

ISOICHEM INC.

RICHLAND, WASHINGTON

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CHAPTER I
INTRODUCTION

By

J. S. Buckingham

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PART ICHAPTER I INTRODUCTIONA. PURPOSE, SCOPE AND ARRANGEMENT OF THE MANUAL1. Purpose and Scope

The Waste Management Technical Manual has been prepared to provide a documented compendium of the technical bases and general physical features of Isochem Incorporated's Waste Management Program. The manual is intended to be used as a means of training and educating personnel unfamiliar with the Waste Management Program and as a reference handbook for use by personnel responsible for executing (carrying out) the Waste Management Program. The material in this manual was assembled by members of Isochem's Chemical Processing Division, Battelle Northwest Laboratory, and Hanford Engineering Services between September 1965 and March 1967.

2. Arrangement

The manual is divided into parts as follows:

Part I, Introduction, contains a summary of the overall Waste Management Program. It is written to provide the reader with a synoptic view and as an aid in understanding the subsequent parts.

Part II, Feed Material, contains detailed discussion of the types and sources of feed material used in the Waste Management Program, including a chapter on nuclear reactions and the formation of fission products.

Part III, Waste Fractionization Plant Processing, contains detailed discussions of the processes used in the Waste Fractionization Plant with supporting data and documentation of the technology employed.

Part IV, Waste Fractionization Plant Product and Waste Effluent Handling, contains detailed discussions of the methods of handling the product and waste material generated by the Waste Fractionization Plant.

Part V, Plant and Equipment, describes the layout of the Waste Management facilities, arrangement of equipment, and individual equipment pieces.

Part VI, Process Control, describes the instruments and analytical methods used for process control.

Part VII, Safety, describes process hazards and the methods used to safeguard against them.

Each part contains one or more chapters. A total of eighteen chapters is included in the seven parts. Pages are numbered to designate chapter number (i.e., Chapter I page numbers begin with 101, Chapter II with 201, etc.). Figures and Tables are numbered in series for each chapter. References to documents containing more detailed information are listed at the end of each chapter.

B. PURPOSE OF THE WASTE MANAGEMENT PROGRAM

The Atomic Energy Commission's nuclear reactors at Hanford are operated primarily to produce plutonium. Substantial quantities of other radioactive elements are also produced as a result of fission and other reactions in the reactors. Plutonium, uranium, selected fission products, and certain transuranium elements are isolated in Isochem Incorporated's Chemical Separations Plants for a variety of uses. Virtually everything else that leaves the chemical processing plants is considered to be a radioactive waste. Following is a brief description of these radioactive wastes and the ways these wastes have been handled in the past.

1. Description of Wastes and Past Handling Practices

1.1 Gaseous Waste

The chemical processing of irradiated fuel elements results in contaminated gaseous effluents which are discharged to the atmosphere after being treated to reduce contamination to acceptable levels. The principle sources of airborne radioactive contamination are the dusts and mists evolved during fuel dissolution, waste concentration, and jet transfer of process solutions. Some of the radioactive elements such as iodine-131 and krypton-85 exist as a gas. The past practice of handling gaseous effluents before they were discharged to the atmosphere was to remove the dusts and mists with filters which retained virtually all particles greater than one micron in diameter. Gaseous iodine-131 was removed through the use of silver reactors, acid absorption towers, and caustic scrubbers.

1.2 Solid Wastes

Solid materials which become contaminated with radioactive material are buried when their useful life is ended. If a significant amount of plutonium is present, the combustible waste is burned and the plutonium is recovered from the ash. In the past, large pieces of plant equipment which failed beyond repair were placed in special wooden or concrete boxes for burial. That equipment from the Purex Plant too large to box was stored in special railroad tunnels adjoining the Purex Plant.

1.3 Low Activity Level Liquid Wastes

Low activity level liquid wastes are those that do not create a hazard when discharged to the ground surface. These wastes are essentially free of radioactivity, but may become contaminated if a process leak were to occur. In general, the radionuclide concentrations are below their MPC (maximum permissible concentration in water). In the past, large ^w volumes of low activity level wastes were discharged to natural surface depressions where they formed ponds or swamps. The water evaporated or seeped through the soil to the ground water below.

1.4 Intermediate Activity Level Liquid Wastes

Intermediate activity level liquid wastes such as process condensate, tank farm condensate, and process heat exchanger steam condensate, are those with radionuclide concentrations up to several times their MPC_w, and have a potential for contaminating the environment. The past practice was to discharge intermediate activity level liquid wastes to drainage fields called cribs built below the surface of the ground. The safety of this technique relies on the ion exchange properties of the soil and on the radionuclide decaying to innocuous levels before migrating to the edge of the Hanford reservation.

1.5 High Activity Level Liquid Wastes

High activity level liquid wastes are those solutions containing virtually all of the fission products and salts from chemical processing. Over the years of operation at Hanford, the high activity level liquid wastes were made alkaline and stored in underground tanks. In the storage tanks, solids settled to the bottom forming a sludge layer. Most of the fission products are contained in the sludge layer. The supernatant liquid over the sludge is composed mainly of solutions of sodium salts and contains the fission products cesium-137 and technetium-99. Those wastes which generate sufficient heat to self-boil are called "boiling wastes." Wastes which have a sufficiently low heat generation rate to allow the waste to be safely concentrated to a salt cake in underground tanks are called "solidifiable waste." Coating wastes are an example of solidifiable waste. Those high activity level wastes that do not generate enough heat to self-boil, but still generate too much heat to store as a salt cake are called "warm or simmering wastes."

2. Objectives of the Program

Through the years of experience in storing and disposing of radioactive wastes at Hanford, a high degree of safety has been provided at a reasonable cost. Studies have indicated that these practices could

have been continued almost indefinitely without jeopardizing environmental safety provided the stored liquid wastes and their sludges were periodically transferred to new tanks. A risk of contaminating the environment still existed, however, as the fission products were stored in a mobile form. Continuous surveillance was required to assure that the stored materials were in fact safely contained. In view of these considerations, the in-tank storage of radioactive liquids was considered to be a temporary practice and the Waste Management Program was established to implement improved methods of waste immobilization.

Research and development activities in support of the Waste Management program complemented Fission Product Recovery research and development activities. While the objectives of the two programs were different, the end results were nearly the same - the removal of long-lived fission products from the mobile waste streams. In one case, the isolated fission products were considered a waste requiring long-term storage and surveillance, and in the other case, the fission products were considered a concentrated source of radioisotopes for beneficial use.

The Waste Management Program as formulated by the Chemical Processing Division has four objectives:

1. Assure the safe confinement of the radioactive materials for centuries.
2. Minimize the long-term cost of the storage and surveillance operations.
3. Make selected fission products and other reactor-produced isotopes available for beneficial use.
4. Reduce to a minimum the amount of radioactive waste dispersed to the environs.

3. Outline of the Waste Management Program

3.1 Gaseous and solid wastes

The Waste Management Program will continue to handle solid and gaseous wastes the same way that they have been handled in the past. Development efforts are being directed toward methods for improved iodine removal from plant waste streams. Studies are being conducted to more fully understand the complex nature of iodine and to develop adsorbers of high performance and efficiency. The practice of burying solid wastes in trenches and tunnels will be continued.

3.2 Low Activity Level Liquid Waste

Low activity level liquid waste will continue to be discharged to ponds and swamps as has been done in the past. An operating limit of 5×10^{-5} microcuries of mixed fission products per cubic centimeter is the established limit for swamp disposal. Cooling towers have been considered as a way of reducing the volume of water discharged to the ground; however, the cost to benefit ratio was not favorable at the time this manual was written.

3.3 Intermediate Activity Level Liquid Waste

Intermediate activity level liquid wastes will continue to be discharged to the ground via cribs. The safety of this technique relies primarily on the ion exchange properties of the soil and on the fission product decay in transit to the Columbia River. In general, a well to the ground water is drilled adjacent to each crib. The appearance of the 30-year half-life cesium-137, the 28-year half-life strontium-90, or the 5-year half-life cobalt-60 in samples of ground water taken from beneath the crib in concentrations approaching one-tenth of the maximum permissible concentration (MPC) for drinking water is cause for abandonment. Hydrogen-3 (tritium) and ruthenium-106 are decayed and diluted to less than one-tenth MPC before they migrate to the Columbia River and are diluted to background when blended with the river.

Some intermediate activity level liquid wastes are disposed of by a technique which relies solely on the physical ability of the soil to retain the liquid. This is called disposal by specific retention. The volume of waste routed to a specific retention disposal site is limited to six percent of the soil column volume beneath the site. The waste types so disposed include organics, depleted uranium solutions, solutions with a somewhat higher than usual radioisotope concentration and those with poor or unknown ion exchange properties.

3.4 Stored High Activity Level Liquid Wastes That Can Be Solidified

Stored high activity level liquid wastes that generate heat at a sufficiently low rate are concentrated to a salt cake within an underground waste storage tank. Solidification is accomplished by using electrically powered In-Tank Solidification (ITS) units described in detail in Chapter VIII.

3.5 Stored High Activity Level Liquid Wastes That Cannot Be Solidified

Stored high activity level liquid wastes that generate enough heat from radioactive decay to self-boil are allowed to self-concentrate under controlled conditions. After about five years the short-lived fission products have decayed to the point where the waste storage tank is simmering rather than boiling. A sludge layer, composed of low solubility salts, forms in the bottom of the tank. This sludge layer contains a majority of the fission products, except for cesium which is in the supernatant liquid above the sludge.

The supernatant liquid is decanted from the sludge layer and pumped to the Waste Fractionization Plant (B Plant) where the cesium is removed by ion exchange techniques. The cesium-free supernatant liquid is then a waste that can be solidified in an ITS facility. The cesium is eluted from the ion exchanger, concentrated, and stored in tanks located in B-Plant. The stored cesium can also be made available for use in a fission products program.

The sludge layer is sluiced from the tank, acidified and transferred to the Waste Fractionization Plant where strontium is removed by precipitation and solvent extraction techniques. A rare earth fraction containing promethium-147 may also be recovered from the sludge by the same techniques. If the strontium is needed for a fission products program, it is purified further by solvent extraction.

3.6 Current High Activity Level Liquid Wastes

Current high activity level liquid wastes from the Purex Plant are processed immediately, or after only a few weeks of lag storage, in the Waste Fractionization Plant. Wastes generated by an processing that may be done in the Redox Plant will be sent to underground storage and considered as stored high activity level wastes.

In the Waste Fractionization Plant, Purex wastes are separated into a strontium fraction, a rare earth fraction, a cerium fraction, (or alternately a cerium-rare earth fraction) and a salt waste fraction. The salt waste fraction, containing cesium and short-lived fission products, is sent to underground waste storage for two to five years to allow the short-lived fission products to decay. The cesium is then removed by ion exchange as is done with high activity stored waste. The strontium fraction is stored for about a year to allow the 50.4-day half-life strontium-89 to decay. The "aged" strontium may then be purified further by solvent extraction for use in a fission products program. The cerium fraction may either be made available for use in a fission products program, or sent to underground storage for five to seven years, then solidified. The rare earth fraction may be purified further and stored in B-Plant for use in a fission products program, or sent to a non-boiling waste tank for eventual solidification.

A flow pattern for the Waste Management Program is shown schematically in Figure I-1.

Alternate flow schemes have been devised that remove the cesium from current waste at the same time that strontium and the rare earths are being removed. These alternate flow schemes are discussed in more detail in a later section.

FIGURE I-1

Flow Pattern for Waste Management Program

C. FUNCTION OF THE WASTE FRACTIONIZATION PLANT

The function of the Waste Fractionization Plant is to remove the long-lived heat producing fission products, such as strontium-90 and cesium-137, from current and stored waste, and to recover strontium-90, cesium-137, promethium-147, and cerium-144 for beneficial use. Removal of the long-lived heat producing fission products from the wastes permits concentrating the wastes to a salt cake for long-term storage.

The wastes handled by the Waste Fractionization Plant are generally categorized by difference in physical and chemical properties into 1) current acid waste, 2) stored alkaline sludge wastes, and 3) stored alkaline supernatant liquid wastes. For convenience in describing the various process streams, a system of letter designations has been developed. These designations are also used in flowsheets and flow diagrams. Table I-1 is a glossary of these terms.

TABLE I-1

GLOSSARY OF LETTER DESIGNATIONS

A. WASTE STREAMS WHICH MAY BE PROCESSED

- PAW - Purex Acid Waste - Current high-level acid waste from the Purex plant solvent extraction process.
- ZAW - Zircflex Acid Waste - Current high-level acid waste from processing zirconium clad fuel elements.
- RAW - Redox Acid Waste - Current high-level acid waste from the Redox plant solvent extraction process.
- PAS - Purex Acid Sludge - Acid stream resulting from acid dissolution of water insoluble sludge solids sluiced from the Purex plant high-level underground waste storage tanks (241-A and 241-AN Tank Farms.)
- RAS - Redox Acid Sludge - Acid stream resulting from acid dissolution of water insoluble sludge solids sluiced from the Redox plant high-level underground waste storage tanks, (241-S and 241-SX Tank Farms.)
- PSN - Purex Supernatants - Alkaline supernatant liquid pumped from the Purex plant high-level waste storage tanks, (241-A and 241-AN Tank Farms.)
- RSN - Redox Supernatants - Alkaline supernatant liquid pumped from the Redox plant high-level waste storage tanks, (241-S and 241-SX Tank Farms.)
- PSS - Purex Sludge Supernatants - Alkaline liquid resulting from water leaching the sludge solids remaining after removing PSN from Purex plant high-level waste storage tanks.
- RSS - Redox Sludge Supernatants - Alkaline liquid resulting from water leaching the sludge solids remaining after removing RSN from Redox plant high-level waste storage tanks.

B. SOLVENT EXTRACTION STREAMS

- 1AF - Aqueous feed to the 1A column.
- 1AX - Organic extractant to the bottom of the 1A column.
- 1AW - Aqueous raffinate from the 1A column; 1A column waste stream.
- 1AP - Organic raffinate from the 1A column containing extracted materials. 1A column product stream.
- 1SS - Aqueous scrub to the 1S column. Flows sequentially to the top of the 1A column.
- 1SP - Organic raffinate containing product material from top of the 1S column.
- 1BX - Aqueous strip to the top of the 1B column. Used to strip strontium from the organic phase.
- 1BP - Aqueous strontium product from the bottom of the 1B column.
- 1BW-1CF - Organic raffinate from the top of the 1B column. Contains the rare earth fraction.
- 1CX-1 Persulfate-acid oxidant for cerium-promethium separation.
- 1CX-2 Silver-acid catalyst for cerium-promethium separation. Added with 1CX-1 to the top of the 1C column.
- 1CS - Aqueous strip to top of 1C column. Used when cerium is not separated from promethium and other rare earths.
- 1CP-Pm - Aqueous raffinate from bottom of the 1C column containing promethium and rare earth product.
- 1CP-Ce - Organic raffinate from top of the 1C column containing cerium separated from the rare earth product.
- 1CP - Aqueous raffinate from the bottom of the 1C column containing unseparated cerium and rare earths.
- 1CW - Organic raffinate from top of the 1C column, stripped of cerium and rare earths. Organic waste stream.
- Ce-Strip - Nitric acid solution added to batch contactor to strip cerium from the organic phase.
- Ce-Prod. - Aqueous cerium nitrate fraction stripped from the organic phase in a batch contactor.
- 1OS - Aqueous scrub used to clean up the organic stream.
- 1OO - Washed organic stream.
- 1OW - Aqueous waste from the organic washing process.
- Sr-1AF - Aqueous feed to 1A column during strontium purification cycle.
- Sr-1AX - Organic extractant to 1A column during strontium purification cycle.
- Sr-1SS - Aqueous scrub to 1S column during strontium purification cycle.
- Sr-1AW - Aqueous raffinate from 1A column during strontium purification cycle. 1A column waste stream.
- Sr-1BX - Aqueous strip to top of 1B column used to strip strontium from organic phase during strontium purification cycle.
- Sr-1BP - Aqueous product raffinate from bottom of 1B column. Contains purified strontium product during strontium purification cycle.
- Sr-1BW - Organic raffinate stripped of strontium from top of 1B column during strontium purification cycle. 1B column organic waste stream.
- Sr-1OS - Aqueous scrub used to clean up organic stream during strontium purification cycle.
- Sr-1OW - Aqueous waste from organic washing step during strontium purification cycle.
- Sr-1OO - Washed organic during strontium purification cycle.

C. ION EXCHANGE STREAMS

- C&NE - Alkaline supernatant feed to the cesium ion exchange column.
- C&NW - Cesium ion exchange column waste effluent generated during column wash cycle.
- C&NP - Cesium ion exchange column product effluent.
- E&E - Effluent from cesium ion exchange column during loading cycle. Feed material for processed technetium, rhodium, and palladium recovery processes.

1. Source and Composition of Feed Material

1.1 Current Waste

Current acid waste is the high activity acid waste generated by the Purex Plant. There are two types of current acid waste: Purex Acid Waste (PAW) is generated during the processing of aluminum-jacketed normal and enriched uranium fuel elements. Zirflex Acid Waste (ZAW) is generated by the Purex Plant during the processing of zirconium-jacketed fuel elements. Both PAW and ZAW are the bottoms of the Purex waste concentrator and have been treated with sugar to reduce the nitric acid concentration. PAW and ZAW do not include coating waste or solvent washes. PAW and ZAW do contain the entire spectrum of fission products produced by the Hanford reactors; however, only strontium-90, cesium-137, promethium-147, and cerium-144 are of primary interest in the Waste Management Program. The estimated composition of PAW and ZAW are shown in Table I-2.

1.2 Stored Sludge Waste

High activity alkaline waste solutions generated by the separations plants prior to the startup of the Waste Fractionization Plant were stored in underground steel-lined concrete tanks. These wastes contained solids and had a high inert salt content. In the storage tanks, these solids have settled to the bottom forming a sludge layer. A majority of the fission products, including strontium-90, promethium-147, and cerium-144, which constitute but a small fraction of the total salts present, are contained in the sludge layer. The composition of a typical Purex sludge waste is shown in Table I-2. Because the composition of various radioactive isotopes varies widely from tank to tank, the concentration of the radioisotopes is not included in the table. Sludge waste is identified as Purex Acid Sludge waste (PAS) and Redox Acid Sludge waste (RAS). Purex sludge wastes are stored in the A and AX Tank Farms. Redox sludge wastes are stored in the S and SX Tank Farms.

1.3 Stored Supernates

The supernatant liquid associated with the sludge layer in the underground waste storage tanks is called stored supernates and designated Purex Supernates (PSN) or Redox Supernates (RSN). A major portion of the cesium-137 associated with the alkaline wastes is found in the waste supernates. Other isotopes of interest found in the supernatant liquid are technetium-99, rhodium-103, and palladium. Technetium-99 has potential beneficial use and means of recovering it have been developed. Rhodium and palladium are precious metals used in industry. Ways of recovering rhodium and palladium are being developed.

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A third supernatant liquid waste, other than PSN and RSN, is generated by water leaching stored sludge after decanting the supernatant liquid. The designation for this waste is Purex or Redox Sludge Supernate (PSS or RSS). The compositions of PSN, RSN, and PSS are shown in Table I-2.

TABLE I-2
COMPOSITION OF WASTES

<u>Purex Acid Waste</u> (PAW)		<u>Zirflex Acid Waste</u> (ZAW)		<u>Purex Sludge Waste</u> (PAS)	
H	0.5 M	H	0.235 M	H	0.1 M
Na	0.7	Na	0.35	Na	0.42
Fe	0.315	Fe	0.39	Fe	0.36
Al	0.08	Al	0.78	Al	0.55
Cr	0.032	Cr	0.016	Cr	0.021
Ni	0.016	Ni	0.0078	Ni	0.012
Ca	0.0013	Ca	0.0015	Ca	0.031
Sr	0.0013	Sr	0.0013	Sr	0.0017
RE + Am	0.0077	Zr	0.005	Mn	0.01
SO ₄ ⁼	0.24	RE + Am	0.0078	Mg	0.009
NO ₃ ⁻	2.06	F ⁻	0.3	RE	0.0085
Sr-90	36.6 Ci/gal.	SO ₄ ⁼	0.119	SO ₄ ⁼	0.026
Cs-137	396	NO ₃ ⁻	0.9	NO ₃ ⁻	2.42
Pm-147	141	Sr-90	79 Ci/gal.		
Ce-144	881	Cs-137	800		
		Pm-147	300		
		Ce-144	1900		

<u>Purex Sludge Supernatant</u> (PSS)		<u>Purex Supernatant</u> (PSN)		<u>Redox Supernatant</u> (RSN)	
Na	5.4 M	<u>A Farm</u>		<u>S Farm</u>	<u>SX Farm</u>
Fe	--	Na	4.57 M	Na	5.49 M
Al	0.04	NO ₃ ⁻	0.58	Al	0.34
Cr	0.002	NO ₂ ⁻	2.25	NO ₃ ⁻	3.53
NO ₃ ⁻	4.2	SO ₄ ⁼	0.10	NO ₂ ⁻	--
NO ₂ ⁻	0.22	CO ₃ ⁼	0.77	SO ₄ ⁼	--
SO ₄ ⁼	0.25	Cs-137	13.1 Ci/gal.	OH ⁻	1.59
CO ₃ ⁼	0.24	RuRh-106	0.5	Cs-137	0.33 Ci/gal.
		Tc-99	100 mg/gal.	RuRh-106	0.013
				Tc-99	2.8 mg/gal.
					16.8 mg/gal.

2. Basis of Design

The design of the Waste Management Fractionization Plant (B-Plant) is based on processing current Purex acid waste (PAW and ZAW), Purex aged supernate (PSN), Purex sludge waste (PAS), and Redox aged supernate (RSN). The equipment is sized to permit processing of the stored high level waste concurrently with fresh waste so as to work off the stored waste inventory within five to seven years.

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The alkaline supernate containing the cesium is processed by ion exchange using synthetic zeolites (aluminum silicates) as the ion exchange medium. Cesium is eluted from the ion exchange medium with a mixture of ammonium hydroxide and ammonium carbonate. At least 95 percent of the cesium is removed from the alkaline supernates by the ion exchange process.

Current acid waste and acidified sludge waste is fractionized in common equipment on a campaign basis using a solvent extraction process. Greater than 95 percent of the strontium-90 is removed from the waste. About 75 percent of the promethium-147 can be recovered from both current and stored waste, and made available for use in a fission products program. Approximately 75 percent of the cerium in current waste can be recovered and supplied to a fission product program on demand. Rates for processing current acid waste and stored sludge waste are based on campaign cycles allowing twice as much time for processing current waste as is allowed for sludge waste. The amount of waste processed is based on a plant operating efficiency of 72 percent.

3. Product material

The Waste Management Waste Fractionization Plant (B-Plant) has capabilities for recovering and purifying four major fission products: strontium-90, cesium-137, cerium-144, and promethium-147. Capabilities to recover seven additional products - technetium-99, rhodium, palladium, americium-241, plutonium-239, neptunium-237, and antimony-125 have been or are being developed. Each of the product materials is discussed below.

3.1 Strontium-90

Strontium-90 has a half-life of 28 years. It is a pure beta emitter; however, its daughter, yttrium-90, emits a 0.2 and a 1.7 Mev gamma. Together, strontium-90 and yttrium-90 produce 6.8 thermal watts of energy per kilocurie of strontium-90, which is 23.2 Btu/hr. per kilocurie. Because of its high heat generation and long half-life, strontium-90 must be removed from waste before the waste is concentrated to a salt cake. The strontium separated from the waste may be put to beneficial use as a heat source. Strontium-90 which cannot be put to beneficial use will eventually be contained in high-integrity containers for long-term storage. Because of its relatively long half-life, strontium-90 is found in stored sludge waste as well as current waste. The isotopic content of the strontium will vary from less than 25 weight percent strontium-90 for well-aged sludge to greater than 60 weight percent from the waste generated during the processing of high exposure reactor fuels. A major portion of any strontium used for beneficial purposes will have an isotopic content greater than 50 weight percent strontium-90.

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3.2 Cesium-137

Cesium-137 has a half-life of 30 years. The decay of cesium-137 produces both beta and gamma radiations. Cesium produces 4.8 thermal watts of energy per kilocurie during radioactive decay which amounts to 16.4 Btu/hr. Cesium-137 generates sufficient heat during decay that it must be removed from the salt wastes before they are concentrated to a salt cake. Cesium-137 has beneficial use as a heat source or as a radiation source. Cesium-137 which cannot be put to beneficial use will eventually be contained in high-integrity containers for long-term storage. The isotopic content of the cesium recovered from waste will range from 30 to 40 weight percent cesium-137, depending on the age of the material. The cesium will be recovered from stored supernatant liquid waste, and from a water leach of the stored sludge waste. Flow-sheets exist for the recovery of cesium from current waste; however, economies favor the nitric storage of current waste and recovery of cesium from waste aged two to five years.

3.3 Cerium-144

The half-life of cerium-144 is a comparatively short 285 days. Cerium-144 produces moderately energetic beta and gamma radiation as it decays. However, cerium-144 in equilibrium with its daughter, praseodymium-144 produces extremely energetic beta and gamma radiation as it decays. The combination of cerium-praseodymium-144 produces 8.05 thermal watts or 27.5 Btu/hr per kilocurie of cerium-144 during decay. Because of its relatively short half-life, cerium-144 is present in considerable amounts only in current waste and in stored sludge waste aged less than five years. For any fission products program requirements, cerium will be recovered on demand from current waste. Separated cerium-144 not required for a fission products program will be returned to underground storage with the salt waste for five to ten-year aging before being concentrated to a salt cake. because of its short half-life, the isotopic content of the cerium-144 product changes quite rapidly; however, it is estimated that cerium with an isotopic content of 18 percent cerium-144 can be made available.

3.4 Promethium-147

Promethium-147 has a half-life of 2.62 years. It decays essentially by beta decay. The energy of the beta radiation is a very low 0.225 Mev. Promethium produces 0.36 watts or 1.2 Btu/hr per kilocurie. Promethium recovered from current waste contains the gamma-emitting promethium-148. Aging the promethium for two to two and one-half years allows the 42-day half-life promethium-148 to decay to innocuous levels. The low energy radiation from promethium requires only light shielding making promethium-147 a good candidate as a heat source for manned space efforts. Promethium recovered from the waste in the Waste

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Fractionization Plant is in a mixture of rare earths. The amount of promethium-147 in the rare-earth mixture will range from a fraction of 1 percent in the rare earths recovered from stored sludge waste to 3.5 percent in two-year-aged current waste. As other isotopes of promethium have short half-lives, it is possible to produce promethium-147 essentially 100 percent pure by a chromatographic ion exchange separation. The chromatographic separation of promethium is considered part of a fission product program and would not be done in the Waste Fractionization Plant.

3.5 Other Products

A number of other valuable products can be recovered during the processing of waste. Technology has been developed for the recovery of technetium-99 from stored supernatant liquid waste, and americium-241, neptunium-237, and plutonium-239 from current and stored sludge waste. Technology for the recovery of rhodium and palladium from stored supernatant liquid waste and antimony-125 from current waste is being developed for possible inclusion in the Waste Fractionization Plant or as part of a fission product program.

3.5.1 Technetium-99

Technetium-99 has a long half-life of 2.1×10^5 years and emits a weak beta radiation on decay. Technetium does not occur naturally; however, appreciable amounts are formed in nuclear fuels during irradiation. Technetium can be recovered from the same stored alkaline supernatant liquid waste from which cesium is recovered. The technetium product would be in the form of a technetium nitrate solution. Technetium has potential use as a corrosion inhibitor for steel. Technetium metal is also a superconductor of electricity at low temperatures.

3.5.2 Rhodium and Palladium

Rhodium and palladium are semi-rare metals having commercial use as industrial metals in the chemical and electrical industries. Rhodium and palladium originate from fission in nuclear fuels and are found in stored supernatant waste from which cesium is recovered. Rhodium and palladium are normally non-radioactive; however, radioactive rhodium-102 is also formed during irradiation of nuclear fuels. The amount of rhodium-102 present is not expected to constitute a radiation hazard.

3.5.3 Americium-241

Americium-241 has a half-life of 258 years. It is primarily an alpha emitter; however, several low energy gamma rays are also

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emitted. Americium-241 is formed in nuclear fuels during irradiation, and is also formed by the decay of plutonium-241. Americium is found in the current waste, and in the stored sludge waste. Americium generates 33 thermal watts or 113 Btu/hr per kilocurie when it decays. Americium can be used as a heat source for thermoelectric generators, or it can be used as target material for the production of transuranium elements.

3.5.4 Neptunium-237 and Plutonium-239

The Chemical Processing Division's chemical separation plants are designed to recover neptunium and plutonium from irradiated nuclear fuels; however, a small percentage of the neptunium and plutonium is lost in the waste streams from the separation plants. Plutonium and neptunium which was sent to the waste storage tanks has collected in the sludge layer, and can be recovered in the Waste Fractionization Plant during the processing of stored sludge waste. Neptunium and plutonium recovered in the Waste Fractionization Plant would be as nitrate solutions and could be returned to the Purex Plant for blending with Purex process streams.

3.5.5 Antimony-125

Antimony-125 has a half-life of 2.7 years. It emits a number of beta and gamma energies giving a total thermal heat output of around 3 watts per kilocurie. Antimony-125 has use as a source of X-rays, although at the present time there is no demand for the material. If a market should develop for antimony-125, technology for the recovery and purification of antimony from both current and stored waste can be developed. The isotopic purity of antimony-125 will range from 10 weight percent for well-aged sludge to 50 weight percent from current waste.

4. Waste Streams

As the primary purpose of the Waste Fractionization Plant is to prepare wastes generated by the chemical processing of nuclear fuels for permanent storage, the waste streams from the Waste Fractionization Plant can also be considered product streams. The waste generated during waste fractionization can be classified as 1) low activity waste discharged to swamps and cribs, 2) salt waste that can be solidified, and 3) salt waste that must be stored for an interim period before being solidified.

4.1 Low activity waste

The low activity wastes that can be discharged to swamps and cribs include cooling water, condensates, organic materials, etc. Any radioactivity associated with these materials are retained by the ion

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exchange capacity of the soil, or they migrate so slowly through the soil and ground water they will decay to innocuous levels by the time they reach the Columbia River or the edge of the Hanford reservation.

4.2 Solidifiable waste

Solidifiable wastes are alkaline salt wastes, primarily nitrate salts, from which a major portion of the heat-generating isotopes have been removed. The fission products remaining in the salt cake should have a heat generation rate of between 0.25 and 0.3 watts per cubic foot of salt cake. In general, solidifiable wastes generated by the Waste Fractionization Plant will come from processing stored supernatant liquid wastes for cesium removal, and stored sludge waste for strontium and rare earth removal.

4.3 Wastes requiring temporary storage

Much of the waste generated by the Waste Fractionization Plant during the processing of current wastes (PAW and ZAW) will require from three to seven years storage to allow the short-lived fission products to decay before the waste can be solidified to a salt cake. Wastes which will have to be stored temporarily include the following: Solids centrifuged from the Purex waste stream. Salt waste from the first solvent extraction column produced during the processing of current acid wastes. This salt waste, which contains cesium-137 and short-lived fission products, will be stored for three to five years to allow the short-lived fission products to decay. The cesium will be removed in the same way as when stored supernatant liquid wastes are processed. Cerium and rare earth fractions not required for beneficial use will be stored for seven to ten years for decay before being solidified to a salt cake.

D. OUTLINE OF THE WASTE MANAGEMENT PROCESS

The waste management process is designed to remove the long-lived heat producing isotopes, cesium-137 and strontium-90, from both current and stored wastes. The process is designed to make the selected isotopes cesium-137, strontium-90, cerium-144, and promethium-147, available for beneficial use. The long-lived heat producing isotopes not required for beneficial use are held in high integrity containers for long-term storage. Wastes from which the long-lived heat producing isotopes have been removed are solidified to a salt cake in steel-lined concrete tanks for permanent storage. The waste management program is composed of five interrelated processes: 1) the removal of stored wastes from underground storage, 2) an ion exchange

process to remove cesium from stored supernatant liquid wastes, 3) a precipitation process which separates desirable isotopes from associated iron and aluminum in stored sludge waste, 4) a solvent extraction process used to recover and purify desirable isotopes from both stored and current wastes, and 5) a salt solidification process. The basic principles and steps which make up these five processes are briefly explained in the following subsections. This section is intended only as an introduction to the waste management program; more complete and specific information on waste management processes is contained in other chapters.

1. Basic Principles

1.1 Precipitation Process

Stored sludge waste, which has been dissolved with nitric acid, is primarily a solution of sodium nitrate, ferric nitrate, and aluminum nitrate contaminated with small amounts of strontium and rare earths. The strontium and rare earths are concentrated and separated from the bulk of the sodium, iron, and aluminum by precipitating them as insoluble sulfates using lead as a carrier ion. The sulfate precipitates are metathesized to carbonate precipitates, then dissolved with a minimum of nitric acid. The resulting nitrate solution is adjusted as feed for solvent extraction processing. A ten-fold reduction in the volume of the solution containing the dissolved sludge is accomplished by the sulfate precipitation step. The supernatant liquid from which the insoluble sulfates have been removed is returned to underground storage where it is eventually solidified into a salt cake.

1.2 Ion Exchange Process

Ion exchange processes depend on a chemical exchange reaction between an ion in solution and an ion on the ion exchange medium. An ion exchange medium consists of a solid phase containing bound groups which carry an ionic charge in conjunction with free ions of opposite charge that can be displaced. The solid phase may be a porous inorganic material or a permeable organic resin. An ion exchange reaction may be expressed as a reversible reaction involving chemically equivalent quantities. For example, the recovery of cesium from stored waste supernates by cation exchange may be written:

where X represents the ion exchange medium. Certain ion exchange media have greater affinity for one ion over another; for example, zeolite, an alumino-silicate, will adsorb approximately 40 times more cesium than sodium. Ion exchange processes for the recovery of cesium and technetium from stored supernatant waste solutions have been developed.

1.4 Solvent Extraction Process

The solvent extraction process used in the Waste Fractionization Plant employs Di-(2-ethylhexyl)phosphoric acid (D2EHPA) in a hydrocarbon diluent. The mechanism of the solvent is discussed in detail in Chapter IV. Briefly, D2EHPA acts similar to a liquid cation exchanger, in which a hydrogen ion in the solvent is displaced with the metallic ion being extracted. The system is extremely pH-sensitive requiring a buffering agent to maintain the proper pH value. The addition of the chelating agents suppresses the extraction of various ions at certain pH values. Also, depending on the pH, certain ions are more strongly extracted than others, loading the solvent and thereby suppressing the extraction of undesirable ions. By choosing the proper pH, solvent loading, chelating agent, and residence time (kinetics), conditions can be established for the separation and purification of the desired ions.

1.4 Simplified Flowsheets

Figure I-2 is a simplified flowsheet for the fractionization of current acid waste from the Purex Plant including feed preparation, strontium removal, cerium rare-earth separation, rare-earth sulfate removal, and the solvent treatment section. Figure I-3 is a simplified flowsheet for the fractionization of stored waste which includes cesium recovery by ion exchange, removal of sludge from the underground waste tanks, feed preparation, iron and aluminum removal, strontium removal, rare-earth recovery, and solvent treatment. Figure I-4 is a simplified flowsheet for the purification of aged strontium to prepare material for use in a fission product program. Figure I-5 is a simplified flowsheet of the waste handling facilities including the high level lag storage tanks, the low level waste concentrator and neutralizer, and the in-tank solidification facility.

The flowsheets show the letters usually used to identify the various process streams in the waste management plant. A glossary of waste management terms and process streams is included in Table I-1. The code designations follow accepted solvent extraction nomenclature as much as possible with minor modifications for clarity.

FIGURE I-2
Simplified Flowsheet for
Fractionization of Current
Purex Acid Waste

FIGURE I-3
Simplified Flowsheet for Fractionization of Stored Waste

2. Removal of Wastes from Underground Storage Tanks

The purpose of the waste removal facility is to provide a way of removing high level wastes from underground storage tanks and subsequent transfer to the Waste Fractionization Plant. High activity level waste as generated by the chemical separation plants contained a high salt content and virtually all of the fission products present in irradiated nuclear fuel. The wastes were made alkaline and stored underground in steel-lined concrete tanks. Solids present in the waste settle to the bottom of the storage tank forming a sludge layer. **The sludge layer, composed of low solubility salts, contains the majority of the fission products in the waste.** The supernatant layer, composed primarily of a solution of sodium nitrate and sodium nitrite, contains cesium-137. The supernatant liquid is pumped from the underground storage tank with a deep-well turbine pump.

The sludge layer is sluice-mined by a technique similar to that used in the Uranium Recovery Process. Water heated to between 80 and 90 degrees centigrade is impinged on the sludge layer at high pressure. The slurry is pumped from the underground storage tank to a slurry receiver. This operation is continued until a slurry equivalent to about 440 tons of uranium production has accumulated. In addition to acting as the liquid vehicle for carrying the sludge, the water used to slurry the sludge also leaches the soluble salts such as sodium nitrate, nitrite, and carbonate from the sludge along with the small amount of cesium that was occluded in the sludge. In the slurry receiver tank the sludge is allowed to settle, and the water leach decanted off and combined with the original supernatant liquid. The sludge is transferred from the slurry receiver to the acidification tank, dissolved with nitric acid, and transferred to B-Plant for fractionization. Figure I-6 is a diagram of the sludge removal facility.

3. Ion Exchange Processes

Ion exchange processes are used to remove cesium from stored alkaline supernatant liquid waste. Ion exchange processes can also be used to recover technetium, rhodium, and palladium from supernatants for beneficial use, and for the longer-term storage of strontium and cesium in high integrity containers. Each of the ion exchange processes will be discussed briefly here, and in more detail in later chapters.

3.1 Cesium Recovery from Supernatants

The processing of alkaline supernates and the alkaline sludge leach supernates to remove cesium is carried out in a fixed-bed ion exchange

FIGURE I-6
Sludge Mining of Self-Boiling Wastes

unit filled with a zeolite. The zeolite used is a synthetic aluminosilicate ion exchange medium which preferentially adsorbs cesium from the high sodium supernatant solutions. After the column is loaded, the feed solution is displaced by a water wash, and sodium is selectively removed with a dilute ammonium carbonate-ammonium hydroxide wash. Cesium is eluted from the ion exchange medium with a strong solution of ammonium carbonate - ammonium hydroxide. The ammonium carbonate - ammonium hydroxide in the cesium product is recovered by distillation and re-used.

3.2 Technetium Recovery

An ion exchange process has been developed for the recovery of technetium from stored waste supernates. Technetium exists in the supernates as sodium pertechnetate which is analogous to sodium permanganate. The sodium pertechnetate is adsorbed on a strong base anion exchange medium, washed with dilute nitric acid to remove ruthenium, and eluted from the medium with strong nitric acid.

3.3 Strontium and Cesium Packaging

In the original design of the Waste Management Fractionization Plant, strontium and cesium removed from the wastes would be adsorbed on zeolite ion exchange medium in high integrity containers, dried, sealed, and stored for long-term surveillance. Technology and hardware for the packaging step were developed; however, the present plan calls for storing all of the strontium and cesium in liquid form in B-Plant, and the packaging equipment will not be used.

4. Precipitation Processes

The primary precipitation process used in the Waste Management Fractionization Plant is a sulfate precipitation based on a carrier precipitation technique. If an element in solution is not present in sufficient concentration to precipitate directly, it can be co-precipitated, or carried from solution by the formation of a precipitate of an element present in larger amounts. The most efficient carriers are those which have the same lattice type as the compound to be carried; that is, they form isomorphous crystals. In addition, the elements to be carried must form an insoluble compound with the precipitating anion. Carrying may also occur by adsorbing the trace element on the surface of the carrier, or by the trace element forming an insoluble double salt with the carrier. In the Waste Management Plant, strontium and the alkaline earths, and promethium and the rare earths are precipitated as insoluble sulfates using lead as the carrier ion. The sulfate precipitates are then metathesized to carbonate precipitates which are readily soluble in nitric acid.

Another precipitation process employs phosphotungstic acid which precipitates cesium when processing current Purex acid waste. Cesium salts of phosphotungstic acid are insoluble in an acidic system, and are removed by centrifugation. After washing, the precipitate is dissolved with caustic and the solution sent to the cesium ion exchange facility. The phosphotungstic acid process may be used as an alternate cesium separation process.

5. Solvent Extraction Processes

Solvent extraction processes are used in the Waste Fractionization Plant to remove strontium from both current and stored waste and to provide a purified strontium for beneficial use in a fission products program. Solvent extraction processes are also used to recover promethium from stored and current waste, to separate cerium from promethium, and to provide both cerium and promethium for beneficial use. The equipment used to mix the aqueous and organic phases in the solvent extraction processes are pulse columns and batch contactors. The flowsheets used for processing current waste and stored waste are briefly discussed below. A more complete discussion of flowsheets is given in Chapter IV.

5.1 Solvent Extraction of Current Acid Waste (PAW - ZAW)

In the solvent extraction process for current acid waste, the waste is clarified by centrifugation; the cesium, strontium, and rare earths are dissolved from the solids and combined with the clarified waste stream. Chelating agents are added to suppress the extraction of undesirable elements and the pH of the feed solution is adjusted with buffering agents and caustic or acid. Strontium and the rare earths are extracted into an organic phase of di-(2-ethylhexyl) phosphoric acid (D2EHPA), tributylphosphate (TBP), and hydrocarbon diluent. Cesium, short-lived fission products, and miscellaneous salts remain in the aqueous phase and are sent to underground storage for a period of two to three years, after which the cesium is recovered by ion exchange processing. The extracted strontium is separated from the rare earths by stripping the strontium in the IB column with dilute nitric acid. The strontium product is concentrated and stored in tanks in B-Plant for about one year to allow the short-lived strontium-89 to decay. Following the aging period, the strontium may be purified for beneficial use. See Section 5.3.

Cerium and the rare earths are stripped from the organic phase with strong nitric acid in the 1C column. The aqueous cerium and rare earth solution is neutralized and sent to underground waste storage for decay before being immobilized by in-tank solidification.

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If cerium or promethium is needed for beneficial use, cerium is separated from the rare earths on a continuous basis in the 1C column by oxidizing inextractable Ce(III) to extractable Ce(IV) with persulfate catalyzed with silver. Trivalent ions are not extracted by D2EHPA from 2M nitric acid, while tetravalent ions are extractable. Cerium is stripped from the organic phase on a batch basis with nitric acid containing a reducing agent. The aqueous phase from the 1C column containing the promethium and rare earth fraction contaminated with sulfate is treated further by D2EHPA solvent extraction to remove sulfate impurity.

5.2 Solvent Extraction of Stored Sludge Waste

Strontium is removed from stored sludge waste using the same solvent extraction equipment as is used for processing current wastes. Promethium for beneficial use may be recovered from the sludge waste at the same time. Solvent extraction processes have also been developed to recover neptunium and plutonium from the sludge as well; however, present plans do not include facilities to recover these two elements.

Acidified sludge waste is treated by a precipitation process to remove a major part of the iron and aluminum present. Chelating agents are added to the product solution from the precipitation step to suppress the extraction of undesirable metal ions, and the pH of the solution is adjusted with buffer solution and sodium hydroxide. As with current waste, strontium and rare earths are extracted into an organic solution of D2EHPA, TBP, and hydrocarbon diluent in the 1A Column. The extracted strontium is stripped from the organic phase in the 1B Column with dilute nitric acid. The strontium product is concentrated and stored.

The rare earths are stripped from the organic phase in the 1C Column with strong nitric acid. The rare earth solution is neutralized with sodium hydroxide and sent to underground storage for eventual solidification in an ITS facility.

If the rare earths in stored sludge are needed for beneficial use, the 1C Column is used to strip calcium from the organic phase and the promethium and rare earths are stripped from the organic phase in a batch contactor. A nitric acid solution slightly more concentrated than that used to strip strontium in the 1B Column is used to strip calcium while strong nitric acid is used to strip the rare earths in the batch contactor. The organic solvent is washed using batch contactors, and the solvent is re-used.

5.3 Strontium Purification

On demand, crude aged strontium is campaign-purified in the solvent extraction equipment to provide a purified strontium product for bene-

ficial use. A chelating agent is added to the crude feed material to suppress the extraction of undesirable metal ions, and the solution pH is adjusted with buffering agent and caustic. Strontium is extracted into an organic phase of D2EHPA, TBP, and hydrocarbon diluent in the 1A Column. Strontium is stripped from the organic phase in the 1B Column with citric acid. Citric acid permits the preferential stripping of strontium, leaving calcium in the organic phase. The citric acid in the strontium product is destroyed by a combination of chemical oxidation using hydrogen peroxide and radiolysis, as the strontium is concentrated.

6. Salt Solidification

The purpose of the salt solidification facilities is to provide a means of concentrating suitable high activity level wastes to the point of solidification within the 750,000 gallon underground storage tanks. Salt solidification is accomplished by in-tank solidification (ITS) units and by an external pot concentrator (242-T Concentrator).

In the first in-tank solidification unit, which began operation in March 1965, electrically heated air is sparged directly into the waste solution through an annulus shroud tube. The annulus shroud tube acts as a heat transfer medium and a solution circulator as well as a means of introducing air into the solution. The tank effluent gases pass through a deentrainer, condenser, and a filter before being discharged to the atmosphere. The condensed water is routed to a crib. Additional wastes are added to the tank as the concentration progresses. When the terminal volume and concentration are reached, the tank contents will be allowed to cool and solidify. Figure I-7 is a sketch of the first in-tank solidification unit. The first ITS unit was originally installed in Tank 101-BY. It was moved to 102-BY in November, 1966, after the solution in 101-BY reached terminal concentration.

The second in-tank solidification unit achieves a high boil-off rate by immersing sheathed electrical heaters directly in the waste solution. An air lift circulator is still required to mix the tank contents, but the required air volume is much less. Because of the lower air volume, the off-gas equipment is smaller also. The second ITS unit is located in 112-BY. The third unit, if needed, will be located in the 200 West Area. A sketch of the second in-tank solidification unit is shown in Figure I-8.

The 242-T concentrator is a steam-heated pot concentrator located in the TX Tank Farm. Solidifiable waste is pumped to the evaporator from underground storage tank 118-TX. In the concentrator the waste is concentrated until there are about 10 volume percent solids in the concentrator bottoms. The concentrate is dumped to underground

storage tank 116-TX where a portion of the solids settle out. The supernatant liquid is pumped to 117-TX where additional cooling and settling is achieved. Supernatant liquid is decanted from 117-TX to 118-TX, blended with fresh feed from the tank farm, and recycled to the evaporator. As with the in-tank solidification units, concentration will continue until terminal volume and concentration is reached. The tanks will then be allowed to cool and solidify. Figure I-9 is a flowsketch of the 242-TX concentrator facility.

FIGURE I-7

First In-Tank Solidification Unit

FIGURE I-8

Second In-Tank Solidification Unit

FIGURE I-9

242-T Concentrator

7. Packaging

At the time this chapter was written it was planned to store the strontium and cesium removed from wastes as nitrate solutions in tanks located in B-Plant. Eventually cesium and strontium which cannot be put to beneficial use will be "packaged" in high integrity containers for long-term storage. One approach, for which equipment has been developed but not installed, is to adsorb the cesium and strontium on synthetic aluminosilicate ion exchangers in stainless steel containers. After drying with heated air, the containers are closed and welded shut. The sealed canisters are stored under close surveillance in a water-cooled vault. Figure I-10 is a schematic flow diagram of this "packaging" process as it might be done in B-Plant.

FIGURE I-10

Strontium and Cesium Packaging

8. Alternative Processes

Alternative flowsheets have been developed as back-up for the waste fractionization processes discussed above. The purpose of alternative fractionization technology is primarily to provide attractive alternative flowsheets in the event that mainline processes are proven uneconomical, or present exceptionally difficult operating problems.

Originally the CSREX process was planned for the solvent extraction fractionization of strontium and cesium in the Waste Management Program. However, due to severe radiolysis of the CSREX solvent, the D2EHPA process was shown to be more economical and more adaptable to a fission product recovery and purification program.

8.1 CSREX Process

In the CSREX Process (Figure I-11) cesium and strontium are co-extracted in the 1A Column along with the rare earth elements. The strontium and cesium are then stripped from the solvent in the 1B Column, and the rare earths removed in the solvent treatment equipment, or if desired, in a separate contactor for rare earth recovery.

FIGURE I-11

CSREX Fractionization of Purex Acid Waste

8.2 Cesium Removal with Phosphotungstic Acid

In the event that it is desired to remove cesium from Purex Acid Waste at the same time that strontium and the rare earths are being recovered, a flowsheet has been developed to accomplish this. The cesium will be selectively precipitated as cesium phosphotungstate from the PAW with phosphotungstic acid prior to the solvent extraction processing for the recovery of strontium and rare earths. The cesium precipitate would be dissolved in sodium hydroxide and blended with stored alkaline supernates for ion exchange processing.

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E. WASTE MANAGEMENT FACILITIES

1. General Layout of Waste Management Facilities

The waste management facilities consist of the Waste Fractionization Plant, (B-Plant), in-tank solidification (ITS) units, and a waste concentrator (242-T), 149 underground waste storage tanks, a facility for the removal and handling of stored waste (244-AR vault), a storage vault (244-CR), cribs, swamps, and associated facilities. All of the facilities are located in the vicinity of Isochem's Chemical Separations Plants. The Chemical Separations Plants are in the 200 Areas, 25 to 30 miles from the city of Richland on the Atomic Energy Commission's Hanford Reservation. A layout sketch showing location of the facilities on the Hanford Reservation and a detailed description of the facilities and equipment are shown and discussed in Chapter IX.

1.1 B-Area Layout

The layout of the B-Area (Waste Fractionization Plant) is shown in Figure I-12. The arrangement within the Waste Fractionization Plant is discussed in Section 1.2 below.

FIGURE I-12

Layout of Waste Fractionization Plant Area

The function of the various facilities in the vicinity of B-Plant are as follows:

<u>Facility</u>	<u>Function</u>
221-B Waste Fractionization Plant	Processing of waste to isolate selected fission and other products.
224-B Future Products Recovery	Not used as part of initial waste management program. May be used later for the recovery of products not included in the original design.
271-B Service Building	Contains offices and aqueous make-up facilities for the Waste Fractionization Plant.
222-B Office Building	Offices for support facilities, such as Financial.
291-B Fans, Stack, and Filters	Ventilation for the process building.
282-B Raw Water Well	Emergency raw water supply.
211-B Chemical Tank Farm	Storage area for liquid chemicals used in the Waste Fractionization Plant.
217-B Water Demineralizer	Demineralized process water supply.
276-B Organic Make-up and Storage	Storage and mek-up facility for organic solvent materials.
216-B-12 Process Condensate Crib	Crib for the disposal of condensates from process concentrators.
216-B-55 Steam Condensate Crib	Crib for disposal of condensates from heating coils in process tanks.
216-B-56 Organic Crib	Crib for disposal of organic solvents.

1.2 Waste Fractionization Plant (221-B) Layout

The Waste Fractionization Plant, Building 221-B, is a multi-storied, predominantly reinforced concrete structure, approximately 810 feet in length, called a "canyon" building. Figure I-13 is a cutaway sketch of the 221-B Building.

FIGURE I-13
221-B Canyon Building

The building has two major portions: The process portion which contains the "hot" equipment and the regulated work zones, and the service portion which houses personnel and equipment necessary for remote operation of the process portion.

The canyon cells house the various pieces of process equipment used to fractionize waste. The process equipment includes solvent extraction pulse columns, precipitation vessels, centrifuges, ion exchange columns, product and waste concentrators, and associated tanks, pumps, instrumentation, etc. The function assigned to each cell is shown in Figure I-14. The paths feeds from various sources take through the plant are also shown in Figure I-14.

The regulated work zones consist of areas where limited contact of personnel with radiation and radioactive contamination is allowed under carefully prescribed and monitored conditions. The following are regulated work zones: The Canyon, the Canyon Crane Gallery, Railroad Tunnel, and the SWP lobby at the east end of the operating gallery.

The service portion of the building includes the operating, pipe, and electrical galleries. Other service areas are located adjacent to the 221-B Building in the 271-B Building.

1.3 Layout of Underground Removal Facilities

Figure I-15 is a simplified layout drawing of the 241-A and 241-AX tank farms and the 244-AR process vault. A similar process vault may be constructed in the 200 West Area at the 241-SX tank farm if it is proven feasible to recover products from the Redox sludge.

Those tanks from which the sludge is removed are equipped with a minimum of two sluice pits for high-pressure sluicing nozzles, and a pump pit for a slurry pump. The material pumped from the tanks is segregated into supernates and sludge. The supernates are pumped to the 105-C tank in the 241-C tank farm. The sludge slurry is accumulated in Tank 002 in the 244-AR vault. A high head pump in Tank 002 returns slurry to the sluicing nozzles. When a suitable amount of sludge has accumulated in Tank 002, the circulation is stopped and the sludge is transferred to Tank 004 for acidification. Dissolved sludge is transferred to CR Vault 005 Tank and then to B-Plant. See Figure I-6.

1.4 Layout of Waste Disposal Facilities

Ultimate disposal of liquid radioactive wastes or potentially radioactive liquid waste will be in the ground via cribs or swamps, or as a salt cake in underground waste tanks located in 12 existing tank farms.

FIGURE I-15

Simplified Layout of Underground Storage Tanks and
Removal Facility - 241A and 241AX Tank Farms

Reference Dwg. H-2-61916

1.4.1 Layout of Underground Waste Tank Farms

The underground waste tank farms are located within the 200 East and 200 West areas near the chemical separations plants. Each tank farm carries the number 241 followed by a letter or letters which designates the separations plant for which it was built to serve. For example, 241-A Tank Farm was built to service the Purex (A) Plant. Additional tankage built to service a plant or to replace an existing tank farm was designated with an X or a Y as 241-AX or 241-BY. The tank farms are interconnected by underground lines which makes it possible to transfer the contents of one tank farm to another. Each tank farm consists of 4 to 16 steel-lined concrete tanks. Table I-3 is a list of the tank farms showing the number and size of the tanks in each farm. The general type of waste that is stored in a particular farm is also shown in the table. Maps showing the location of the various tank farms are included in Chapter IX.

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B-Plant Cell Allocation

FIGURE I-14

ion and Fission Products Routes

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TABLE I-3UNDERGROUND WASTE TANK FARM INDEX

<u>Tank Farm</u>	<u>No. of Tanks</u>	<u>Size Gal.</u>	<u>Type of Waste</u>
241-A	6	1,000,000	Boiling high-level Purex waste to be fractionized
241-AX	4	1,000,000	Boiling high-level Purex waste to be fractionized
241-B	12	530,000	Non-boiling solidifiable wastes
	4	50,000	Non-boiling solidifiable wastes
241-BX	12	530,000	Non-boiling solidifiable wastes
	4	50,000	Non-boiling solidifiable wastes
241-BY	12	750,000	Non-boiling solidifiable wastes
241-C	12	530,000	Non-boiling solidifiable wastes
241-S	12	750,000	Non-boiling solidifiable wastes
241-SX	15	1,000,000	Boiling high-level Redox waste to be fractionized
241-T	12	530,000	Non-boiling solidifiable wastes
	4	50,000	Non-boiling solidifiable wastes
241-TX	18	750,000	Non-boiling solidifiable wastes
241-TY	6	750,000	Non-boiling solidifiable wastes
241-U	12	530,000	Non-boiling solidifiable wastes
	4	50,000	Non-boiling solidifiable wastes
Total	149		

1.4.2 In-Tank Solidification Facilities

The first in-tank solidification facility was installed in the 101-BY tank located in the 241-BY tank farm. In November, 1966, terminal concentration was reached in the 101-BY tank, and a portion of the tank contents was pumped to tank 105-BY for cooling and solidification. The In-Tank Solidification unit was moved to the adjacent 102-BY tank. Figure I-16 is a layout sketch of the facilities in the vicinity of the first In-Tank Solidification unit.

The second In-Tank Solidification unit will be installed in Tank 112-BY, and the third In-Tank Solidification unit, if needed, will be installed in a tank farm located in the 200 West Area.

FIGURE I-16
Simplified Layout
First In-Tank Solidification Unit
Reference Dwg. H-2-32263

1.4.3 Cribs and Swamps

Natural depressions where low activity liquid wastes are disposed are called swamps, and the underground caverns or chambers where intermediate activity liquid wastes are disposed are called cribs. As low and intermediate activity level liquid wastes rely on the ion exchange capacity of the soil and the time it takes for the radionuclides reaching ground water to migrate to the river, cribs and swamps are discussed together. Swamps and cribs are designated by the building number 216, followed by the area letter of the plant they serve, and a site number. For example, 216-A-1 is crib number 1 located to serve the Purex (A) area.

The status of the cribs is designated as follows:

Active	Currently receiving or ready to receive radioactive wastes.
Inactive	Cribs not presently receiving radioactive wastes, but still possess enough capacity to be used again.
Abandoned	Cribs which have reached the capacity of radioactive wastes they can handle. This capacity is indicated by the appearance of cesium-137 or strontium-90 in samples of ground water taken from beneath the crib in concentrations approaching one-tenth of the maximum permissible concentration (MCP) for drinking water.

Specific Retention Cribs used for specific retention depend solely on the physical ability of the soil to retain the liquid. The volume of waste routed to a specific retention site is limited to six percent of the soil column volume beneath the site.

Table I-4 lists the cribs and the status of the cribs for each plant area.

TABLE I-4
CRIB INDEX

Plant Area	Bldg. No.	Number of Active Cribs	Number of Inactive Cribs	Number of Abandoned Cribs	Number of Specific Retention Cribs
Purex	216-A	23	7	4	0
B-Plant	216-B	7	1	23*	25
Semiworks	216-C	5	4	1	0
200 North	216-N	0	3	4	0
Redox	216-S	8	8	6	0
T-Plant	216-T	6	3	13*	11
U-Plant	216-U	4	3	7	0
Z-Plant	216-Z	8	7	3	0

* The majority of these cribs reached their capacity between 1954 and 1957 during the ferrocyanide waste scavenging program.

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2. Special Features of the Waste Management Facilities

The high levels of radiation associated with Waste Management process solutions, the nature of the process materials, and the nature of the process itself, have necessitated the installation of many special features in the Waste Management Process. Some of these features are discussed below.

2.1 Shielding

All service portions of the Waste Management facilities must be shielded from the processing areas to prevent personnel from receiving excessive amounts of radiation. In the Waste Fractionization Plant, radiation intensities are reduced by using concrete walls. In the waste removal facilities, a combination of earth and concrete is used to reduce radiation. Other outside facilities such as the underground storage tanks, diversion boxes, transfer stations, and pipe lines are also shielded with earth and concrete. In most places, shielding reduces radiation intensities to less than 0.1 mr/hr in non-regulated service areas.

2.2 Semi-continuous Operation

Portions of the Waste Management facilities are designed to operate on a continuous basis, while other portions are operated on a batch basis. For example, a current waste will be accumulated in a storage tank in 244-AR Vault and processed through the Waste Fractionization Plant on a campaign basis. A campaign will last from two to four weeks. The solvent extraction columns will operate on a continuous basis during the campaign. The batch contactors will be operated on a batch basis.

Other facilities which operate on a continuous basis are the in-tank solidification units. Other waste facilities which are operated on a batch basis are the ion exchange facilities and the sludge removal and acidification facilities.

The diversity and types of operations used in the Waste Management facilities require the use of a variety of automatic control instruments. Instrumentation is discussed in detail in Chapter XIII.

2.3 Materials of Construction

The process equipment used in the Waste Management facilities which handles all acidic process solutions are made of stainless steel. Type 404 or 304L are commonly used. Vessels in the service areas are constructed of either stainless steel or mild steel, depending upon the nature of the solutions which they handle.

The concrete surfaces of the canyon cells are painted with a protective coating to minimize absorption of radioactive solutions.

2.4 Remote Operation

Since the process equipment is located behind massive concrete or earth and concrete shielding, all tasks are performed by remote control. The remote operational controls are similar to those employed in the Purex Plant.

Processing operations for B Plant and 244-AR Vault are controlled from operating galleries. The In-Tank Solidification units are controlled from small buildings located in the tank farms. Some of the methods and devices employed for remote operation are briefly described below.

The transfer of process solutions and slurries in the Waste Management facilities is accomplished by using jets or pumps. The ion exchange medium is removed by means of a jet also. Flow rates of pumped streams are controlled from the operating galleries by recording-controlling instruments. Automatic instruments receive signals from transmitting rotameters indicating the flow rates which, in turn, actuate air-operated valves. Agitation of process solutions is accomplished by means of electrically driven agitators. The organic-aqueous interfaces in solvent extraction columns are controlled by recorder-controller instruments which are actuated by interface floats. Weight and specific gravity of solutions are determined from differential pressure instruments actuated by air-bubbling dip tubes in the vessels. Chemical additions to the process vessels are from the service areas through seal pots and pipe lines permanently cast into the concrete shielding. Ion exchange medium is added to the ion exchange column from the service area by means of a slurry line. Solutions in process vessels are sampled via special vacuum jets which draw the solutions into shielded sample boxes at the sample stations.

2.5 Remote Maintenance

Installation and removal of process equipment and remote maintenance in the Waste Fractionization Plant and the 244-AR Vault building process areas is accomplished with the aid of cranes. The crane in the Waste Fractionization Plant canyon is operated from a shielded control cab which travels behind the concrete shielding wall of the Crane Cab Gallery (See Figure I-13). Operations are observed from the cab through periscopes mounted on the crane bridge. The crane in the 224-AR Vault building is operated by remote control from the control room. Operations are observed by periscopes and television cameras.

Maintenance in the facilities located outside of the 224-AR Vault Building and the Waste Fractionization Plant such as tank farms and diversion boxes are performed by using portable boom cranes, mirrors, periscopes, television cameras, etc.

All equipment pieces are equipped with lifting bails to facilitate moving. All equipment, including electrical and pipe jumpers, are fastened in place with enlarged nuts which may be tightened or loosened by means of a crane-operated impact wrench.

2.6 Critical Mass Control

Plutonium concentration in Waste Management facilities streams should be sufficiently low that no criticality problems are anticipated. Adequate sampling will detect any unusually high concentration of plutonium occurring in process vessels.

2.7 Process Air Ventilation

The spread of radioactive particles throughout the Waste Fractionization Plant is controlled by proper direction of air flow. Process vessels are maintained at a lower static pressure than the canyon; while the canyon, in turn, is at a lower static pressure than the pipe and operating galleries. Thus, air flow is away from operating personnel toward the process vessels. Air is exhausted from the process cells through a series of ports into the air tunnel. From the air tunnel, the air is passed through two banks of high efficiency filters and exhausted to the atmosphere through the 291-B stack.

Separate vacuum systems are used for the two vessel vent systems. One vessel vent system is used extensively for those vessels which may give off ammonia fumes. The vessel vent systems provide a minimum of four stages of filtration for the off-gas.

Off-gas from the In-Tank Solidification units passes through high efficiency filters before being discharged to the atmosphere.

2.8 Vessel Cooling System

Cooling coils or jackets are provided on all storage vessels to remove heat generated by radioactive decay. Cooling water is supplied by the 200-E area raw water supply. An emergency cooling water supply from a well located adjacent to the B-Plant area supplies cooling water by means of Diesel-driven pumps in event the primary water supply fails.

2.9 Fire and Explosion Protection

The Waste Fractionization Plant employs a flammable organic hydrocarbon as a diluent for the D2EHPA extractant. The high flash point of the diluent makes it relatively safe from a fire viewpoint.

A number of protective features for the prevention or control of fire have also been incorporated into the plant. Among these are adequate process area ventilation which prevents accumulation of explosive mixtures.

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Process tanks containing sufficient radioactivity to produce hydrogen by radiolysis are continually purged with air to dilute the hydrogen to below the lower explosive limit.

Ammonium solutions are used in the process for recovery of cesium. A separate vessel vent system is provided for those vessels where ammonium solutions are anticipated. The ammonia in this system is removed by an absorber prior to being exhausted to the atmosphere.

3. Chemical Requirements

The estimated amount of chemicals required for processing wastes in the Waste Fractionization Plant is shown in Table I-5 for current waste, and Table I-6 for stored waste. The additional amounts of chemical required to isolate fission product fractions for beneficial use are also shown in the tables.

TABLE I-5

ESTIMATED CHEMICAL REQUIREMENTS FOR
PROCESSING CURRENT ACID WASTE (PAW)
IN THE WASTE FRACTIONIZATION PLANT

I. For Waste Management

Chemical	Amt/gal. PAW	
D2EHPA	0.0323	lbs.
HEDTA	0.718	lbs.
HNO ₃	0.742	lbs.
NaOH	0.809	lbs.
Diluent	0.040	gal.
Tartaric Acid	0.372	lbs.
TBP	0.018	lbs.
Hydroxyacetic Acid	0.381	lbs.

II. To purify the rare earth fraction

Chemical	Amt/MCi Pm	
D2EHPA	180	lbs.
HNO ₃	13,000	lbs.
Diluent	230	gal.
NaOH	4,400	lbs.
NaNO ₂	100	lbs.
Na ₂ S ₂ O ₈	2,700	lbs.
AgNO ₃	190	lbs.
Sugar	650	lbs.
TBP	100	lbs.
HEDTA	1,100	lbs.

III. To purify the strontium fraction

Chemical	Amt/MCi Sr	
Acetic Acid	1,300	lbs.
Citric Acid	1,000	lbs.
D2EHPA	34	lbs.
DTPA	520	lbs.
H ₂ O ₂	580	lbs.
HNO ₃	300	lbs.
Diluent	42	gal.
NaOH	480	lbs.
TBP	18	lbs.

TABLE I-6

ESTIMATED CHEMICAL REQUIREMENTS FOR
PROCESSING STORED WASTE
IN THE WASTE FRACTIONIZATION PLANT

I. Cesium recovery by ion exchange

Material	Amt/gal. PSN	
Zeolite	0.0033	lbs.
NH ₃	0.022	lbs.
CO ₂	0.033	lbs.

II. For Waste Management

Chemical	Amt/gal. PAS	
D2EHPA	0.018	lbs.
HEDTA	0.448	lbs.
Hydroxyacetic acid	0.286	lbs.
Lead Nitrate	0.092	lbs.
HNO ₃	0.340	lbs.
Oxalic Acid	0.032	lbs.
NaHSO ₄	1.45	lbs.
Na ₂ CO ₃	0.672	lbs.
NaOH	0.295	lbs.
TBP	0.010	lbs.
Diluent	0.023	gal.

III. To purify the rare earth fraction

HNO ₃	0.237	lbs.
Sugar	0.061	lbs.

IV. To purify the strontium fraction

Acetic Acid	0.274	lbs.
Citric Acid	0.182	lbs.
DTPA	0.076	lbs.
D2EHPA	0.006	lbs.
H ₂ O ₂	0.523	lbs.
HNO ₃	0.029	lbs.
NaOH	0.088	lbs.
Diluent	0.008	gal.
TBP	0.003	lbs.

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PART II

FEED MATERIAL

CHAPTER II

NUCLEAR REACTIONS,
TRANSURANIC ELEMENTS AND FISSION PRODUCTS

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PART II: FEED MATERIALCHAPTER IINUCLEAR REACTIONS, TRANSURANIC ELEMENTS AND FISSION PRODUCTS

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A. INTRODUCTION

The separations plants are intimately associated with the production reactors. Nuclear fuel is transformed in the reactors to make plutonium and other elements heavier than uranium. Fission products are also formed in the fuel. The separations plants receive all of the irradiated fuel, recover any economically attractive components, and provide for safe disposal of other components of the spent fuel. Some understanding of what happens in the reactors will help in evaluating potential new by-products and in providing adequate waste disposal.

This chapter includes a rather elementary discussion of nuclear reactions and calculations, along with a discussion of some of their less familiar aspects. Most of the chapter does not presume much prior knowledge of radiochemistry or nuclear physics, but some parts are more detailed and specific than most introductory college level courses. Because of the inclusion of both levels of information, few readers will find use for all of the chapter, but most readers will find something of value or interest.

B. NEUTRON REACTIONS1. Capture

A neutron traveling through any matter may be captured by a target nuclide to produce a new nuclide with a mass about one unit greater than the target. As a result of this process, mass is converted into energy in accordance with Einstein's famous equation, $E = mc^2$. Each mass unit corresponds to 931 MeV when converted into energy. The total energy of a nuclide or neutron is thus the sum of the kinetic energy and the energy equivalent of the mass.

The total energy of the product nuclide is greater than the energy of the product nuclide in its lowest energy state (also called the ground state). The mass of the ground state of a product nuclide is usually between 0.994 and 1.003 units greater than the mass of the parent, while the mass of a free neutron is 1.008665 units. The mass difference is available to the product nuclide as excitation energy. The product nucleus in its highly excited state, is called a compound nucleus. The amount of energy released by neutron capture is the binding energy of a neutron in the product nuclide. This same amount of energy must be supplied to the product nuclide in its ground state in order to remove a neutron from it.

Excess energy in the compound nucleus must be lost promptly to form one or more nuclei in more stable states. Usually the transitions lead to the ground state within much less than a microsecond, but some excited states have much longer half lives, sometimes even greater than a year. Excited states of this type are called metastable states.

If the compound nucleus loses energy by emission of one or more gamma photons and no particles are emitted the reaction is called neutron capture and is referred to as a n,γ reaction. Other ways of losing energy are also possible as will be discussed later.

The production reactors at Hanford were built to take advantage of a particular neutron capture reaction. When U^{238} captures a neutron, the product after gamma emission is U^{239} . After two successive beta decays this is changed into Pu^{239} , which has been the primary product at Hanford since the reactors were built. The reactions leading to plutonium production are summarized below.

Additional neutron capture reactions are currently being investigated for possible application at Hanford, and some have been used for by-product production already. A few of these reactions are listed below.

These reactions are of no concern to Waste Management at present, but future production efforts may introduce wastes from the above or similar processes into the Waste Management system.

2. Fission

Thus far we have only considered gamma emission by the compound nucleus. Another very important manner of losing energy is by nuclear fission, in which the compound nucleus divides into two very highly excited nuclei of roughly equal size, called fission fragments. These fragments usually have excitation energy well in excess of the binding energy of a neutron, and can break up by neutron emission as well as by gamma emission. The number of neutrons produced from fission fragments depends on the fissioning nuclide and the neutron energy. On the

average each thermal fission results in the emission of 2.43 neutrons from U^{235} fission and 2.89 neutrons from Pu^{239} fissions. By some combination of neutron and gamma emission the fission products lose energy to reach a ground or metastable state. The first nuclides reached in their metastable or ground states are called primary fission products.

Primary fission products do not usually decay by neutron emission, but still contain too many neutrons to be stable (that is, the ground state of these nuclei usually contain more energy than does a nuclide of the same mass number but with one more proton and one less neutron). The unstable fission products decay by beta emission until the ground state of a stable nuclide is reached. The sequence of events in fission is summarized in the following reactions, in which parentheses are used to indicate compound or highly excited nuclei.

A rough estimate of the energy liberated in fission can be determined by adding up the masses of all of the stable products of the above reactions (i.e., Nb^{93} , Ce^{140} and three neutrons) and subtracting this from the sum of the parent mass plus one neutron mass. The difference, when converted to energy units, will represent the energy released in this particular fission reaction. The average energy released in fission of U^{235} is about 202 MeV, and is distributed as follows:

Recoil energy of fission products	166 MeV
Gammas from compound nucleus	7 MeV
Kinetic energy of neutrons	5 MeV
Neutrinos	11 MeV
Fission product decay energy	13 MeV

The neutrinos, which have no charge and essentially no mass, escape from a reactor without losing any energy, and thus carry away some fission energy. However, the extra neutrons produced in fission will be captured in the fuel or other reactor components with the release of about as much energy as is carried away by the neutrinos. The net effect is thus still about 200 MeV per fission.

Since the fission process liberates a large amount of energy, the neutrons produced in fission have a rather high average energy, about 2 MeV. The actual energies range from zero to over 15 MeV, and roughly follow the equation

$$n(E) = 0.770 \sqrt{E} e^{-0.775 E}$$

Neutrons with this energy distribution are called fission spectrum neutrons. Few have energies as great as 5 MeV or as small as 0.01 MeV.

3. Other Reactions

The compound nucleus formed by neutron capture can also break up by emission of neutrons, protons, or alpha particles provided the mass of the compound nucleus is greater than the mass of the products. Emission of a single neutron will be considered as a special case in the next section. If the energy of the incident neutron exceeds the binding energy of a neutron for the target nuclide, two neutrons may be emitted from the compound nucleus by a $n,2n$ reaction. Some of the neutrons formed in fission have this much energy. Indeed, much of the valuable Np^{237} formed in Hanford reactors results from a $n,2n$ reaction with U^{238} :

Even $n,3n$ reactions have been observed with fission-produced neutrons:

The kinetic energy of the incident neutrons must be equal to the binding energy of two neutrons in the target nuclide for $n,3n$ reactions to be possible. Since this energy is usually in excess of 12 MeV, few $n,3n$ reactions are observed.

For some nuclides, particularly the lighter ones, the compound nucleus may break up by emission of charged particles. A neutron is held in a nucleus simply by its binding energy, while charge interactions are also effective in keeping charged particles in the nucleus. The charge effect is roughly proportional to the $2/3$ power of Z , so that charged particle emission is common only among light elements. Low energy neutrons do not cause charged particle emission unless the binding energy of the charged

particle is appreciably lower than that of a neutron. Two typical charged particle emissions are as follows:

4. Scattering

When a neutron interacts with a nuclide the effect on the neutron may be more important than the effect on the nuclide. A compound nucleus may break up by neutron emission, either leaving the nuclide in its initial state (as it was before neutron capture) or in an excited state which then emits one or more gamma photons to revert to its initial state. The neutron energy is reduced by the kinetic (recoil) energy transferred to the nuclide, and in the latter case is also reduced by the energy emitted as gamma photons. The former case is equivalent to an elastic or "billiard ball" type of collision. The maximum energy transfer in an elastic collision is limited by the laws of conservation of energy and momentum to $4AE_0/(A+1)^2$ where A is the mass number of the target nuclide. For heavy targets the neutron is slowed down only very slightly, while for hydrogen atom collisions the neutron on the average loses half of its energy per collision.

A high energy neutron is slowed down largely by inelastic scattering (in which the target nuclide is left in an excited state), but as the neutron energy decreases, the probability of inelastic scattering decreases. When the neutron energy becomes less than the first excited state of the target, inelastic scattering is no longer possible. Neutrons are not reduced to thermal energies very efficiently by heavy atoms. Therefore, materials of low mass number are used to thermalize neutrons. This process is called moderation and the material is a moderator. Hanford production reactors use graphite (mass number of 12) as moderator because of its good structural properties and low neutron absorption cross section. Most power reactors use water as moderator to take advantage of the hydrogen content (mass number of 1). Some reactors such as PRTR use heavy water as moderator because of deuterium (mass number of 2) which has moderation qualities second only to hydrogen, and a vanishingly small neutron absorption cross section.

Neutrons do not continue to lose energy indefinitely, even though they may undergo a great many scatterings. When the neutron energy is less than 0.04 eV, the thermal agitation of the target nuclei may be great enough for the neutron to gain energy instead of losing energy by collision. The neutron energy is then determined by the kinetic energy distribution of the nuclei with which the neutrons collide. The energies depend on the moderator temperature and follow a Maxwellian distribution. At 20 C the most probable thermal neutron energy is

0.025 eV, which corresponds to a neutron velocity of 2200 meters per second. Neutrons which have been moderated to thermal energies are called thermal or slow neutrons.

During the moderation process the neutrons cannot be represented by either the fission spectrum or thermal distributions. In the intermediate range (about 0.2 eV to 1 MeV) the flux of neutrons at a given energy is inversely proportional to the energy. Neutrons in this range are called slowing-down neutrons, epithermal neutrons, or resonance neutrons. Neutrons with energies in excess of 1 MeV are usually called fast neutrons, although other arbitrary minimum energies for fast neutrons may also be used.

C. NEUTRON CROSS SECTIONS

1. General

The neutron cross section is a measure of the probability that a neutron will interact with a target nucleus. It is usually expressed in units of area, either square centimeters or barns. (A barn is 10^{-24} cm².) A convenient picture of the cross section may be obtained by considering it to be the area of the target nucleus as seen by the incident neutron. However, the neutron absorption cross section may be several orders of magnitude larger than the geometric area of the nucleus.

Ordinarily the cross section for a particular process is considered rather than the cross section for any interaction at all. The total cross section refers to all interactions, even elastic scattering. The absorption cross section includes all reactions except scattering. Waste Management is most concerned with cross sections for capture and for fission; and the absorption cross section is then the sum of capture and fission cross sections for the target. Capture cross sections which lead to radioactive products are also called activation cross sections.

The cross section is used in calculating the amount of product nuclide made in a nuclear reaction. Another quantity used in this calculation is the neutron flux, which is the number of neutrons passing through a sphere of unit cross sectional area per unit time. The flux is equal to the number of neutrons per unit volume times the velocity of the neutrons. The symbols ϕ and nv may be used interchangeably to denote flux, usually in units of cm⁻²sec⁻¹. The rate of a neutron reaction is proportional to the product of the cross section and the neutron flux. Thus, average cross sections for a given neutron distribution are determined with respect to neutron flux rather than number of neutrons.

2. Energy Dependence

At low energies (on the order of 1 eV) many cross sections vary inversely with the velocity of the neutron. This variation, known as

the "1/v law", is well illustrated by the n, α reaction with Boron-10, which obeys this law at least up to 10 keV.

Most nuclei exhibit absorption peaks superimposed on the 1/v variation between thermal energies and a few keV. The peak cross section may be several orders of magnitude higher than the 1/v component, and may be at sufficiently low energies to obscure the 1/v component completely in the thermal region. Peaks occur when the neutron energy is correct for formation of a compound nucleus at one of its permissible energy levels. This agreement of neutron energy with product energy level is called resonance. The height and spacing of resonances varies greatly, as shown in Figures II-1 through II-4.

The average thermal cross section for a nuclide is obtained by weighting the cross section in accordance with the Maxwellian distribution of neutron energies. As the moderator temperature increases the energy of thermal neutrons also increases. Since few cross sections are constant in the thermal region, the thermal cross section usually varies with temperature. For a 1/v absorber the thermal cross section is given as a function of temperature by

$$\sigma = \sigma_{2200}/K$$

where

$$K = \sqrt{\frac{4T}{\pi T_0}}$$

T_0 is 293.6 K (20.44 C), T is the Maxwellian temperature, and σ_{2200} is the cross section for a velocity of 2200 meters per second. Deviation from the 1/v law in the thermal region may be evaluated in terms of the parameter g , defined by the equation

$$g = \frac{K\sigma}{\sigma_{2200}}$$

The reaction rate, $\sigma\Phi$, may also be expressed as $g \sigma_{2200} \Phi/K$.

A modified or conventional thermal flux, Φ/K , is usually used instead of the true flux, along with the conventional cross section $g \sigma_{2200}$. For most nuclides g is about unity, with little temperature variation; but if resonances are involved values of g may be either higher or lower than one.

Cross sections for some reactions (e.g. $n, 2n$) are below a certain energy required by the conservation of energy. Cross sections for charged particle emission or fission may be very low below a certain energy. The limiting energy in either case is called the threshold until they reach a plateau which may contain resonance peaks.

In spite of the variation of cross sections with neutron energy, calculations are sometimes based solely on the 2200 meter per second cross sections and conventional flux. For thermal reactors such as the Hanford production reactors this gross simplification is not greatly in error for many nuclides, but for nuclides which have resonances in or near the thermal region, or which have a low thermal cross section and large resonances, the simplification may lead to errors of an order of magnitude or more.

3. Resonance Integral

In the epithermal region (between the thermal and fast regions) the cross section does not usually vary in a simple way because of resonances. The effective cross section in the epithermal region can be evaluated by integrating the product of cross section and neutron flux. The epithermal neutron flux varies inversely with energy. The integrated value (called the resonance integral, I) includes the effects of both $1/v$ and resonance contributions to the cross section. The upper limit of the integral is not critical since the $1/E$ neutron flux is very low in the MeV range. The lower limit of integration, called the cutoff energy, should be about where the upper end of the Maxwellian distribution equals the $1/E$ flux, or about 0.2 eV. The cutoff energy is proportional to neutron temperature.

The resonance integral can usually be separated into a $1/v$ component plus an excess resonance integral, which is the contribution from the resonances. A common way of doing this assumes that the 2200 meter per second cross section extends into the resonance region according to the $1/v$ law. An excess resonance integral can then be obtained from the resonance integral by subtracting a correction proportional to the thermal cross section and dependent on the cutoff energy used in obtaining the resonance integral. The excess resonance integral is only slightly dependent on temperature or cutoff energy unless resonances occur at less than 1 eV.

Westcott developed an expression for cross sections whereby the effect of both thermal and resonance neutrons may be included rather simply. The Westcott cross section is

$$\sigma_w = (g + rs) \sigma_{2200}$$

where

$$s = \frac{KI}{\sigma_{2200}} - 1.1762 g$$

I is the resonance integral, and r is the "spectral index", a measure of the epithermal flux ratio. The excess resonance integral, I' , is related to s by the equation

$$I' = s \sigma_{2200} / K$$

so that s varies with neutron temperature. The flux used with the Westcott cross section is close to the conventional flux for well-moderated reactors, but differs from it appreciably if the spectral index is high.

4. Resonance Flux Depression

In the case of an actual absorber the sample size is usually large enough so that its absorption modifies the $1/E$ neutron energy distribution appreciably. The neutron spectrum is depleted at the resonance energies and the resonance absorption integral is smaller than it would be if the spectrum were unmodified by absorption. The correct integral, or effective resonance integral, is then one in which the actual spectrum, depleted at the resonance energies, replaces the $1/E$ factor. The effect is seen most strongly with large resonance absorption peaks below 100 eV. In Hanford fuels the absorption cross section of U^{238} is greatly dependent on resonance flux depression, and the Pu^{240} cross section is affected toward the end of an irradiation as the Pu^{240} content increases. Some other cross sections are also affected, but to a lesser extent.

Because of the importance of resonance absorptions in U^{238} and the great effect of self shielding, several workers have derived empirical formulas to express the effective resonance integral. One such formula is as follows:

$$I' = 2.81 + 24.7 \sqrt{S/M}$$

where S is the effective surface area, M is the mass of uranium, and S/M is between 0.07 and 0.53. The temperature dependence is given by

$$I'_T = I'_0 [1 + 0.01(0.51 + 0.5 S/M)(\sqrt{T} - \sqrt{T_0})]$$

where the subscripts T and 0 refer to the elevated temperature and to 293°K, respectively.

For closely packed lattices the shadowing of one rod by another is important, and can reduce the effective resonance integral substantially. This can be accounted for by means of a Dancoff correction, but it is not large for the Hanford production reactors.

5. Multigroup Representation

The treatment of cross sections described above is called a two-group treatment since one cross section is used for thermal and a second for resonance reactions. Accurate evaluation of nuclear reactions might require multigroup treatment to provide for deviations from the Maxwellian thermal distribution and the simple $1/E$ approximation to the flux in the resonance region. This refinement is unnecessary for most Waste Management purposes. However, multigroup tabulations may be used to obtain resonance integral data. The sum of values in a multigroup tabulation does not usually equal the resonance integral even if the correct energy range is covered. The tabulated value is usually the partial resonance integral divided by the natural logarithm of the ratio of high to low energy. The result is an average cross section per unit logarithmic energy change, and this value must be multiplied by the logarithmic energy change for the region being integrated in order to convert to a partial resonance integral. The sum of partial resonance integrals above the cut-off energy is then equal to the total resonance integral.

D. REACTOR DESCRIPTIONS

1. General Features

As previously mentioned, each fission gives rise to more than one additional neutron. If one neutron from each fission is used to create an additional fission, a self-sustaining nuclear reaction is obtained. A nuclear reaction is a device in which a nuclear chain reaction is sustained and controlled. Fission neutrons which are not used to cause additional fissions may be used to produce desirable products, or may be lost parasitically in reactor fuels, structural materials, or reactor shielding. Most reactors are controlled by neutron-absorbing rods which may be inserted into the reactor to increase the parasitic loss of neutrons, thus decreasing the number of neutrons available to cause fissions. Adjustment of the control rods will permit operation of the reactor at the desired power level.

The number of fissions caused directly by the neutrons from a single fission is defined as the multiplication factor, k . For steady-state operation, each fission must cause exactly one additional fission, so that $k = 1.000000$. If k is less than one, the reactor power level will decrease until either fissioning essentially ceases or changes in the reactor allow the multiplication factor to increase to unity. If k is greater than one, the reactor power level will increase until k is reduced to unity or less. Ordinarily the control rods in an operating reactor are set to obtain power close to the maximum allowable operating power. If the rods were totally removed from the reactor, some of the fuel might melt and part of the water in the

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reactor might be converted into steam. These changes would reduce the multiplication factor to less than one, and under no circumstances would a thermal reactor cause a bomb-like explosion.

Fission may be caused by either fast or slow neutrons, and reactors may be designed to operate with predominantly slow neutrons (as with Hanford production reactors and most power and research reactors) or with predominantly fast neutrons (as with the Fast Flux Test Facility). A reactor which operates with slow neutrons must contain a moderator to reduce the neutron energy, while a fast reactor is built without any moderator in the reactor core.

The Hanford production reactors are all thermal reactors with graphite moderator. They are operated primarily to produce plutonium by a neutron capture reaction with U^{238} . Most of the reactor fuel is natural uranium, which contains over 99 percent U^{238} and only 0.72 percent of the fissionable isotope U^{235} . Some uranium with a slightly higher U^{235} content is also used, but all of the currently used fuels contain well over 97 percent U^{238} .

The average thermal neutron flux in all Hanford production reactors is about 3×10^{13} neutrons/cm²-sec, expressed as either a conventional or Westcott flux. The value is not constant throughout the reactor, however. The flux varies from front to back of the reactor in a cosine distribution, with a peak value about 1.4 times the average. Variation from side to side and from top to bottom is not great since reactor loadings can be varied to flatten the flux distribution in these directions. However, a few tubes near the outside of the reactor (fringe tubes) operate at lower power than the more centrally located tubes. For purposes of Waste Management the average reactor flux is usually all that needs to be considered.

The fission spectrum flux in a fuel element is roughly equal to the thermal flux at the same location. For each thermal neutron absorbed in the fuel (capture plus fission) slightly more than one fission spectrum neutron is generated. The number of fast neutrons crossing a given area of fuel per unit time will therefore be of the same order of magnitude as the number of thermal neutrons crossing the same area. At locations further removed from the fuel the fission spectrum flux is markedly lower than the thermal flux since the moderator converts fission spectrum neutrons into thermal neutrons.

2. Old Reactors

The six old reactors are designated as B, C, D, DR, F, and H. Only B and C are scheduled for continued operation at this time, with the others being held in standby condition or used for other purposes. The graphite core is 36 feet wide, 36 feet high, and 28 feet long. It

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is penetrated by 2004 process tubes, arranged on 8-3/8 inch centers in a square lattice. Most of the tubes are ribbed aluminum with 1.589" I.D., but C reactor has 1.632" aluminum and 1.681" smooth zirconium tubes. C reactor also has some tubes which are inserted into enlarged (or overbored) graphite channels. These overbore tubes are 2.147" I.D.

All of the fuel elements are tubes of uranium inside an aluminum can, with Al-Si bonding. Water flows both inside and outside of the fuel elements to obtain both internal and external cooling. Some of the fuel elements contain cross channels to permit mixing of the water between the inner and outer coolant streams. Some process tubes have been bowed by growth of the graphite moderator so that they can no longer take the normal 8" elements. Therefore, some 4" elements are also used. Most of the fuel is natural uranium with 0.72% U^{235} , but some elements contain enriched uranium with 0.947 w/o U^{235} . A summary of standard fuel elements for the old reactors and K reactor is given in Table II-1. The prefix designates the reactor type, the numeral shows the modification number, and the suffix designates the type of element (N for natural uranium, E for enriched uranium, and W for water mixing).

The old reactors have about 6.5 inches of graphite between tubes in the normal lattice, and 6.0 inches for the overbore lattice. The neutrons are very well thermalized, with a spectral index of 0.053 for normal uranium and 0.0660 for 0.947% enriched uranium. The higher spectral index for enriched uranium is caused largely by the greater depression of thermal flux in these elements. The reactors operate at total powers of between 1900 and 2300 megawatts, with an average neutron temperature of 580°K (307 C). Average power levels are 7.1 and 8.4 MW/T for natural and enriched uranium respectively, and the corresponding average goal exposures are 600 MWd/T and 850 MWd/T.

3. K Reactors

The two K reactors, KE and KW, are similar to the old reactors but the size and spacing are different. The graphite core is 41 feet wide, 41 feet high, and 33-1/2 feet long. It is penetrated by 3220 tubes arranged on 7-1/2 inch centers in a square lattice. Most of the tubes are smooth zirconium with 1.724" I.D. but a few are ribbed aluminum, 1.686" I.D. The fuel elements are similar to the ones used in the old reactors. Standard dimensions are shown in Table II-1.

The K reactors have about 5.5 inches of graphite between tubes. The spectral index is 0.0625 with normal uranium and 0.0730 with 0.947% enriched uranium. The average neutron temperature is 650°K (377 C). The reactors are operated at 4400 MW. Average power levels are 8.2 and 9.7 MW/T for natural and enriched uranium respectively, and the corresponding average goal exposures are 640 and 900 MWd/T.

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4. N Reactor

The newest Hanford production is N reactor. It is also the only reactor designed for both power generation and production of weapons grade plutonium (i.e., plutonium with a low Pu^{240} content, at present about 6%). The graphite core is 33 feet wide, 33 feet high, and 39 feet long. It is penetrated by 1004 zirconium tubes with 2.71" I.D. N reactor has a rectangular instead of a square lattice, with a spacing of 8 inches horizontally and 9 inches vertically. The graphite lattice contains rather large gas channels to permit escape of steam with minimum damage if a process tube should rupture.

The fuel elements are of a completely different design, being tube-in-tube rather than a single tube. Typical fuel element dimensions are as follows:

	<u>Inner Tube</u>		<u>Outer Tube</u>	
	<u>Cold</u>	<u>Operating</u>	<u>Cold</u>	<u>Operating</u>
Clad O. D.	1.249	1.263	2.406	2.427
Core O. D.	1.166	1.180	2.354	2.357
Core I. D.	0.492	0.495	1.819	1.829
Clad I. D.	0.438	0.441	1.764	1.774

The fuel element length is 417.6 inches cold, and 420.4 inches operating. For a normal loading, N-Reactor uses mostly 0.947% enriched uranium with a little natural uranium and some 1.25% enriched uranium for power flattening. Goal exposures for making weapons grade plutonium are about 600, 820, and 1200 MWd/T for natural uranium and 0.947% and 1.25% enriched uranium respectively. Other loadings, for making products other than plutonium, use 2.1% enriched uranium. The 2.1% enriched uranium will be exposed to about 2100 MWd/T at a power level of 17.7 MW/T, and will not yield weapons grade plutonium. Some of the 0.947% and 1.25% enriched uranium will also be exposed to 2200 MWd/T instead of the weapons-grade limits.

N-Reactor has somewhat less than 5 inches of graphite between tubes, and a spectral index of 0.105 for 0.947% enriched uranium. The reactor operates at 4000 MW with an average neutron temperature of 700°K (433 C), a fuel temperature of 380 C and a graphite temperature of 525 C.

E. TRANSURANIC ELEMENTS

1. Decay Characteristics

Elements with atomic numbers greater than that of uranium (92) are known as the transuranic elements. All transuranic nuclides are radioactive, and none of them occur in nature. Nuclear data for selected transuranics are presented in Table II-2. Past production

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activities have been concentrated on Pu-239 because of its fission characteristics which make it suitable for application in nuclear weapons. Other transuranic nuclides have desirable characteristics as radioisotope heat sources. In particular, Pu-238, Cm-242 and Cm-244 are good because of high heat output per unit weight and relatively low amount of penetrating radiations (neutrons and high energy gamma rays). Other transuranic nuclides are valuable as precursors of other products.

Five types of radioactive decay are important among the transuranics of interest at Hanford: alpha, beta, or positron emission, electron capture, and spontaneous fission. Alpha emitting nuclides are usually most important since they usually have rather long half lives and yield few high-energy gammas. Alpha emissions occur when an alpha particle (two protons and two neutrons, or a He^4 nucleus) leaves a larger nucleus. This process liberates about 5 MeV per decay, mostly as kinetic energy of the alpha particle. The daughter nuclide (nucleus after alpha emission) is usually in either the ground state or a state of very low excitation.

The next three decay types, together with neutron-induced reactions, form the desired alpha emitters. In beta decay an electron (beta particle) leaves the nucleus and a neutron is changed into a proton within the nucleus. The mass number stays the same, but the atomic number increases by one. Positron emission is similar to beta emission, but the emitted particle has a positive charge (positron) instead of a negative charge. A proton is changed into a neutron within the nucleus, and the atomic number decreases by one. Electron capture has the same general effect as positron emission, but occurs when an electron enters the nucleus. All three of these decay types are often accompanied by gamma emission. Competition among these decay types determines whether a nuclide of higher or lower atomic number is formed.

Spontaneous fission is similar to neutron-induced fission with respect to fission products and neutron emission. The rate of neutron-induced fission is dependent on the neutron flux, while the rate of spontaneous fission is solely dependent on the number of atoms of fissioning nuclide which are present. Since spontaneous fission is accompanied by both neutron and gamma radiations, it is not desirable in a heat-source nuclide.

2. Methods of Formation

The sequence of reactions and decays which form transuranics up to mass number 244 are shown in Figure II-5. Important routes to Pu-238 and Cm-242 are shown by heavy lines. It is difficult to obtain either Cm-242 or Pu-238 of high purity. In the irradiation of Np-237 to produce Pu-238, some of the Pu-238 will capture neutrons to form Pu-239. This results in a lower heat output from the plutonium. The amount of Pu-239 formed is quite dependent on irradiation time, with short irradiations yielding less Pu-239. Irradiations are therefore kept as short

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as possible within economic limits. Formation of Pu-236 by n,2n reactions on Np-237 does not affect heat generation appreciably since little Pu-236 is formed, but Pu-236 is not desired because of gamma rays which come from some rather remote daughters of Pu-236. Formation of Pu-236 is controlled by properly locating the neptunium targets within the reactors.

Curium made by irradiation of americium will have an isotopic composition dependent on initial americium composition, irradiation conditions, and decay time after irradiation. Highest Cm-242 content will be obtained if the initial americium is high in Am-241 content, and the irradiation and decay times are both short to minimize loss of Cm-242 by radioactive decay.

Another route to Pu-238 is through Cm-242. Irradiation of Am-241 followed by decay of the product Cm-242 will yield plutonium of a rather high Pu-238 content. However, Pu-242 is also formed by irradiating Am-241 and will contaminate the Pu-238 product unless it is removed prior to the Cm-242 decay. If the curium fraction from americium irradiation is separated and then allowed to decay, almost pure Pu-238 will be obtained.

Some of the transuranic nuclides have very high resonance integrals compared to their thermal cross sections. Reaction rates for these nuclides are quite sensitive to the resonance neutron flux, and resonance flux depression may be important. This is particularly important with U-238 because of its high concentration in Hanford fuels. A smaller correction is necessary with some other nuclides such as Pu-240.

3. Composition in Hanford Fuels

Empirical equations for total plutonium production, content of Pu-240 and Pu-241, and neptunium production have been developed by several workers for specific application to certain Hanford reactors and loading conditions. One such set of equations for K-Reactor are presented below.

$$\text{grams total Pu} = a M \exp (-b M + c M^2)$$

where M is the exposure in MWD/T, and for natural uranium (K5N elements) $a = 1.04068$, $b = 2.30612 \times 10^{-4}$, $c = 3.2012 \times 10^{-8}$. For enriched uranium (K5E elements) $a = 0.84995$, $b = 1.43717 \times 10^{-4}$, $c = 1.2291 \times 10^{-8}$.

$$\text{Percent Pu-240} = M / (a + b M)$$

where for K5N elements $a = 83.816$ and $b = 0.0428$. For K5E elements, $a = 123.915$, and $b = 0.03133$.

$$\text{Percent Pu-241} = a M^b$$

where for K5N elements $a = 2.4246 \times 10^{-5}$ and $b = 1.64967$. For K5E elements, $a = 7.0654 \times 10^{-6}$ and $b = 1.70693$.

Similar constants representing slightly lower plutonium production apply for the old reactors.

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Neptunium production from virgin uranium (i.e. no initial U-236) is approximately $1.24 + 0.00385 (M - 400)$ for natural uranium; $1.74 + 0.0042 (M - 500)$ for K5E elements; and $1.68 + 0.00407 (M - 500)$ for O3E elements.

Calculated amounts of certain long-lived transuranics in Hanford fuels are shown in Table II-3. Values were obtained from the above equations and from program ISOGEN computer runs. The computer runs were designed primarily for calculating fission products, and cross section and reactor flux values were not critically evaluated for effects on transuranic elements. However, the values are useful to show approximate amounts and isotopic compositions, and effects of changes in irradiation conditions.

F. FISSION PRODUCTS

1. Fission Yields

The fission process is rarely symmetrical (yielding two fission products of equal size), but ordinarily yields two products differing in mass by 30 to 50 units. The number of atoms of fission products with a given mass number produced per 100 fissions is known as the fission yield, Y, for that mass number. A fission yield curve for U-235 thermal fissions is shown in Figure II-6. This curve is typical in its general features of any fission caused by thermal or fission spectrum neutrons. The "fine structure" at masses 100 and 134 is caused by high nuclear stability for certain nuclear configurations of fission products. A high yield for a favored nuclide causes a high yield for its complement in the other mass peak. The location of the "fine structure" peaks relative to the major peaks varies with mass number of the fissioning nuclide. Fission yield values for thermal fissions of U-235 and Pu-239 and fission spectrum neutron fissions of U-238 are listed in Table II-4.

Another important distribution is superimposed on the mass distribution in fission. This is the nuclear charge distribution, which determines which element of a particular mass is formed in fission. On the average, each fission product must undergo about three beta decays to reach a stable nuclide; and nuclear charge is distributed so that the number of beta decays by the heavy and light products are about equal. Charge distribution around the average value follows a probability distribution. A primary fission product removed even four or five charge units from the average charge value might have an appreciable fission yield. The yield of a nuclide as a primary fission product is called its independent yield, and the sum of all independent yields for a given mass number is the total or chain yield. Ordinarily only chain yields need to be considered, but "shielded" nuclides such as Cs-136 are not formed from the lower atomic number chain members since the chain is terminated by a stable nuclide before reaching the "shielded" nuclide.

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2. Decay Properties

The rate of radioactive decay, dN/dt , is proportional to the amount of nuclide present, N . The constant of proportionality, λ , is called the decay constant and has units of reciprocal time.

$$\frac{dN}{dt} = -\lambda N$$

The time required for a nuclide to be reduced to one half of its initial amount is called the half life, τ . The nuclide will be reduced to one-fourth of its initial amount in two half lives, to one-eighth in three half lives, etc. The half life is related to the decay constant by the equation

$$\lambda = \ln 2 / \tau = 0.69315 / \tau$$

Most radioactive fission products and nuclides made from the fission products by neutron capture reactions decay by beta emission, but a few decay by positron emission or electron capture. Unless otherwise noted, the following discussion of beta decay applies to all three decay types. These processes were described in general terms in the preceding section on transuranic elements.

In beta decay a fixed amount of energy is liberated by one nuclide in being transformed into another nuclide. However, some of the energy is carried away by a neutrino and is not absorbed even by massive shielding. The effective energy is only that of the beta particle itself. The beta energies vary from zero to the total amount of energy available from the decay. The average beta energy is approximately one-third of the maximum energy but it varies from about 25 to 50 percent of the maximum energy. Figure II-7 shows the approximate variation of average to maximum beta energy ratio with beta energy and atomic number. Additional variation is caused by differences in nuclear transition types. However, this is beyond the scope of this manual.

Some gamma radiation accompanies most beta decays. All gamma photons are emitted with the same energy for any given transition instead of a spectrum of energies as with beta particles. The maximum gamma energy for a particular transition is thus the same as the average gamma energy. However, a single beta decay may give rise to more than one gamma transition.

Not all gamma transitions result in a gamma photon being emitted from the decaying atom. Sometimes part or all of the gamma photons are absorbed by an extra-nuclear electron of the decaying atom in a process called internal conversion. The electron is emitted from the atom with a kinetic energy equal to the gamma energy less the binding energy of the electron. When an electron drops into the site vacated in the internal conversion process an x-ray is emitted. Thus the radiation observed from gamma transitions in a given nuclide may consist partly

of monoenergetic electrons and x-rays, and fewer gamma photons than might be expected. Internal conversion is very common for gammas of less than 0.2 MeV and usually negligible for gammas above 0.7 MeV.

Some of the decay properties of fission products with half lives of over three days are shown in Table II-5. Units used to express some of the properties are more fully explained in the next section.

3. Units of Measurement

3.1 Curies

The decay rate is most commonly expressed in units of curies. Originally the curie was the disintegration rate of the radon-222 in equilibrium with one gram of radium, but it has since been standardized as 3.700×10^{10} disintegrations per second, which is the same as 2.22×10^{12} disintegrations per minute. As defined, the unit is applicable to beta and alpha radiation, but must be modified somewhat for application to gamma radiation. Two usages of the term "gamma curie" are common at Hanford. The first is based on gamma photons per second regardless of energy, while the second is based on gamma photons of some particular energy per second. For example, Ce-144 is ordinarily in equilibrium with its short-lived daughter, Pr-144, and both decay by beta emission. Ce-144 emits a low energy gamma in about 20 percent of its disintegrations, and Pr-144 emits a 2.2 MeV gamma in 0.8 percent of its disintegrations. Thus, 1000 beta curies of Ce-144, 2000 beta curies of Pr-144, 200 gamma curies of Ce-144, and 8 curies of 2.2 MeV gamma from CePr-144 are all expressions defining about the same amount of activity. Any of these units is quite acceptable provided it is adequately defined by the user.

3.2 Watts

The curie refers to the rate of disintegrations without regard to energy, while the watt refers to the energy liberated without regard to the disintegration rate. The watt is the logical unit to use if heating is being considered. Since one MeV is equal to 1.602×10^{-6} ergs, one curie of one MeV radiation emits 3.7×10^{10} MeV/sec or 5.93×10^4 ergs per second, which is equivalent to 5.93 milliwatts. Conversion from curies to watts may be accomplished if the average energy dissipated per decay is known.

$$\text{Watts} = \text{curies} \times \text{energy in MeV} \times 5.93 \times 10^{-3}$$

Particles such as alphas and betas usually lose their energy in the source itself, while gamma radiation may lose its energy at some distance from the source. Therefore, heat generation is often expressed as beta watts (including other radiations absorbed inside the source) and gamma watts (including only radiation which is often, but not necessarily, lost outside the source). The amount of gamma radiation absorbed within the source is dependent on source size and shape.

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For example, cesium-137 emits two betas. The weaker one has a maximum energy of 0.52 MeV, average energy of 0.19 MeV, and is emitted in 92 percent of the disintegrations. The stronger beta has a maximum energy of 1.18 MeV, average energy of about 0.42 MeV, and is emitted in only 8 percent of the disintegrations. The weaker beta is followed by a 0.66 MeV gamma (from Ba-137m) which is internally converted about ten percent of the time. The watts generated by 1000 curies of cesium-137 may then be calculated as follows:

$$\text{watts from 0.52 MeV beta} = 920 \times 0.19 \times 5.93 \times 10^{-3} = 1.04$$

$$\text{watts from 1.18 MeV beta} = 80 \times 0.42 \times 5.93 \times 10^{-3} = 0.20$$

$$\text{watts from gamma photons} = 828 \times 0.66 \times 5.93 \times 10^{-3} = 3.24$$

$$\text{watts from conversion electrons} = 92 \times 0.62 \times 5.93 \times 10^{-3} = 0.34$$

$$\text{watts from x-rays} = 92 \times 0.04 \times 5.93 \times 10^{-3} = 0.02$$

This is 1.58 watts of electrons (beta plus conversion electrons) 3.24 watts of gamma, and only 0.02 watt of x-rays; or 1.60 watts of soft components, and 3.24 watts of gammas.

3.3 Grams

In considering large amounts of fission products in a rather pure state it is frequently helpful to express the quantity in units of grams. Usage at Hanford has usually been to give the total grams of that particular element produced in a reactor, whether the isotopes are active or inactive. The various possible sources of error in determining the weight of a fission product element are well exemplified in the case of cesium. Three isotopes are produced in fission product chains: stable cesium-133, 2×10^6 year; cesium-135, and 30 year Cs-137. During irradiation some of the cesium-133 captures neutrons to form cesium-134 which decays with a half-life of 2.3 years. The cross section of cesium-133 is low enough that the weight change by neutron capture and the decay of cesium-134 can usually be neglected. Cesium-136 is formed in very low yield in fissions since Xenon-136 is the stable end product of the 136 chain. However, a low percentage of the fissions result in cesium-136 as a primary fission product, thus giving an additional source of cesium. The 135 chain is the most complicated. Xenon-135, which is the parent of cesium-135, has a neutron capture cross section of 3.5×10^6 barns, so that at high neutron fluxes much of this nuclide reacts by neutron capture to give stable Xenon-136 rather than cesium-135 by beta decay. A brief summary of the various cesium isotopes produced in a reactor is as follows:

- 133 - amount formed in fission less amount removed by neutron capture.
- 134 - amount formed by neutron capture by cesium-133 less radioactive decay.
- 135 - amount of 135 chain formed in fission less amount of Xenon-135 which decayed by neutron capture rather than by beta decay.
- 136 - amount formed as primary fission fragment less radioactive decay.
- 137 - amount formed in fission less radioactive decay.

All of these various possibilities should be considered when calculating the total weight of any element formed in reactors. Methods of calculating the growth and decay of the various isotopes are given in a later section of this report.

Another term which is often used along with grams of fission products is the specific activity, usually expressed in curies per gram. The activity of a radioactive nuclide is given by the product of the decay constant and the number of atoms of the nuclide. If the half-life is in days, the specific activity A in curies per gram is given by

$$A = \frac{1.30 \times 10^8}{\text{atomic weight} \times \text{half-life}} .$$

This value of specific activity must be corrected for the weight of other nuclides of the same element before being used with the total weight of an element as described above.

3.4 Tons of Uranium Equivalent

This expression is convenient in relating fission product quantities to plant production, but the term is not exact unless irradiation conditions are defined in some detail. Short-lived nuclides depend almost exclusively on the specific reactor power (MW/T) and cooling time, while long-lived nuclides depend on the integrated power (MWD/T). Amounts of fission products per ton of uranium may be calculated by the methods outlined below.

G. GENERATION AND DECAY CALCULATIONS1. Fundamentals

In a nuclear reactor some atoms of a nuclide may decay by radioactivity, while other atoms of the same nuclide may be destroyed by neutron reactions. The total rate of destruction is the sum of the rate of radioactive decay and the rate of neutron absorption. The destruction rate, dN/dt , is proportional to the number of atoms of that nuclide present, N , with the proportionality constant being the destruction constant, Λ .

$$\frac{dN}{dt} = -\Lambda N = -(\lambda + \sigma\phi)N$$

Both the radioactive decay constant, λ , and the neutron absorption constant, $\sigma\phi$ (the product of the cross section and flux), may be composed of two or more partial constants each of which yields a particular daughter nuclide. That portion of the total destruction constant which produces a particular daughter nuclide is known as the production constant, Λ^* , for that daughter from that parent. The production constant may be equal to the destruction constant if the parent has only one mode of decay, or it may be equal to a total or partial constant for either radioactive decay or neutron absorption. For example, plutonium-241 decays mostly by beta emission, but has a small alpha decay branch; and with neutrons it undergoes both fission and capture reactions. At a constant flux it has a single destruction constant, but four production constants, a different one for each mode of destruction.

Sometimes two or more decays or nuclear reactions in sequence lead from the parent to the daughter of interest. The rate equation then contains a term for production of the daughter from the parent as well as a term for destruction of the daughter:

$$\frac{dN_2}{dt} = \Lambda_1^* N_1 - \Lambda_2 N_2$$

This simply says that the rate of change of the daughter is equal to the rate of production from the parent less the rate of destruction of the daughter.

2. Bateman Equations

The rate equations are easy to work with, but must be integrated to obtain the amount of a nuclide present at a given time. The simple rate equation for a single nuclide may be easily integrated to obtain the following:

$$N_1 = N_1^0 \exp(-\Lambda_1 t)$$

where N^0 denotes the amount present initially. This equation gives the amount of parent remaining at time t . For the amount of the first daughter remaining at time t the equation is more complicated:

$$N_2 = N_1^0 \frac{\Lambda_1^*}{\Lambda_2 - \Lambda_1} [\exp(-\Lambda_1 t) - \exp(-\Lambda_2 t)]$$

For the second daughter (third chain member) the equation becomes

$$N_3 = N_1^0 \Lambda_1^* \Lambda_2^* \left[\frac{\exp(-\Lambda_1 t)}{(\Lambda_2 - \Lambda_1)(\Lambda_3 - \Lambda_1)} - \frac{\exp(-\Lambda_2 t)}{(\Lambda_2 - \Lambda_1)(\Lambda_3 - \Lambda_2)} + \frac{\exp(-\Lambda_3 t)}{(\Lambda_3 - \Lambda_1)(\Lambda_3 - \Lambda_2)} \right]$$

These equations, called the Bateman equations, express the fundamental relationships in radioactive decay or in neutron absorption at constant flux. A general form for these equations for the n th daughter, N_n , present at time t , can be conveniently considered as the product of two parts. The first part is the product of finite constants, and the second or saturation part, $S(\Lambda_i t)$, is a function of the product of total destruction constants and time. A form of the general expression is

$$N_n = N_1^0 \left[\prod_{k=1}^{n-1} (\Lambda_k^* t) \right] S(\Lambda_i t)$$

$$S(\Lambda_i t) = \sum_{j=1}^n \frac{\exp(-\Lambda_j t)}{(\Lambda_j t - \Lambda_i t)}$$

where $j \neq i$

The reactor flux to be used in evaluating the destruction constant must be derived for each desired combination of reactor type, integrated exposure (MWD/T), and exposure rate (MW/T). The ratio of integrated exposure to exposure rate defines the time in the reactor. The total number of fissions can be obtained from the integrated exposure since, at 200 MeV per fission, there are 2.70×10^{21} fissions per MWD. By trial and error the calculated number of fissions can be made equal to this derived value, and the flux required to achieve agreement is taken as the reactor flux. The number of thermal and resonance fissions may be obtained from Bateman equations for each of the fissioning nuclides, with the last chain member having a decay constant of zero and

a fission yield of one. The fissions from U-238 (due to fast neutrons) are, in Hanford production reactors, about 0.064 times the total number of fissions from thermal and resonance neutrons. These fissions must also be included in making the total number of fissions equivalent to the desired integrated exposure. As a crude approximation, the integrated conventional flux, Φt , is 1.9×10^{17} M/X where M is the integrated exposure in MWd/T and X is the percent of U-235 in the fuel.

3. Constant Fission Rate Method

Use of Bateman equations assumes the neutron flux to be constant throughout the irradiation, while another method assumes the fission rate (or specific reactor power) to be constant. Neither is exactly constant because of changes in fuel composition during irradiation and perturbations due to charge-discharge operations. However, each quantity is sufficiently constant for most fission product calculation purposes. With Bateman equations fission product generation is calculated separately for each fissioning nuclide and the results are summed. The constant fission rate method gives total fission product amounts upon evaluation of a rather simple expression in most cases. Calculation involving neutron capture reactions is possible by either method, but radioactive decay after irradiation must be handled by Bateman equations.

The number of fissions per unit time determines the heat generation rate in the reactor, or the reactor power level, P (usually expressed in MW/T). The rate of formation of a particular primary fission product is proportional to the product of power level and weighted average fission yield, $\bar{Y}$. Rate equations similar to those described above may be set up and integrated. The equation for the activity in curies of a primary fission product is as follows:

$$A = 8.45 \times 10^5 P \bar{Y} \lambda \left[\frac{1 - \exp(-\lambda t)}{\lambda} \right]$$

For the activity of the daughter of a primary fission product, the equation is:

$$A_2 = 8.45 \times 10^5 P \bar{Y} \lambda_1 \lambda_2 \left[\frac{1}{\lambda_1 \lambda_2} - \frac{\exp(-\lambda_1 t)}{\lambda_1 (\lambda_2 - \lambda_1)} + \frac{\exp(-\lambda_2 t)}{\lambda_2 (\lambda_2 - \lambda_1)} \right]$$

The quantity in brackets is identical to the saturation part of the general Bateman equation except for the "t" terms in the denominator. It includes one nuclide more than the number of members of the fission product chain, with the destruction constant for this added member being zero. A general equation could be written similar to the generalized Bateman equation.

For stable nuclides the activity is necessarily zero, but the number of atoms is a significant quantity. The number of atoms of a primary

fission product is:

$$N = 2.70 \times 10^{21} P t \bar{Y} \left[\frac{1 - \exp(-\Lambda t)}{\Lambda} \right]$$

Again a general equation similar to the Bateman equations could easily be written.

4. Average Fission Yield

The Bateman equations deal with a single fissioning nuclide at a time, and thus use only the fission yield values for that nuclide. The constant fission rate method deals with all fissions simultaneously and uses a fission yield based on a weighted average of fission yield values for all of the fissioning nuclides. For stable or long-lived fission product nuclides the weighting factor is simply the fraction of fissions from each of the fissioning nuclides:

$$\bar{Y} = 0.06Y_F + (0.94-f)Y_U + fY_{Pu}$$

where the subscripts U and Pu refer to uranium-235 and plutonium-239, respectively, F refers to fast fissions from uranium-238, and f is the fraction of total fissions from plutonium. The value of f may be determined from the Bateman equations used in determining reactor flux. Because of the small fraction of fissions from plutonium-241 it is usually not included in determining average fission yields.

The number of fissions per unit time decreases with time for uranium-235, but increases with time for plutonium-239. Therefore, the decay time in the reactor is different for the two parents. If the half-life of a primary fission product is less than the irradiation time, and the fission yields are different for uranium-235 and plutonium-239, an additional term in the weighted average yield should also be used:

$$\bar{Y} = 0.06Y_F + (0.94-f)Y_U + fY_{Pu} + (f'-f)(1-e^{-0.1\Lambda t})(Y_{Pu}-Y_U)$$

where f' is the fraction of the final fission rate which is due to plutonium, and Λ is for the primary fission product. This places additional weight on plutonium fissions since they occur at an increased rate in the latter part of the irradiation, resulting in a reduced in-reactor decay time. This equation may be used for primary fission products regardless of their destruction constants since it reduces to the proper values for both large and small values of the destruction constant.

The correction for different in-reactor decay times is more complicated for fission products after the primary one. Ordinarily sufficient accuracy is obtained if the in-reactor decay correction is ignored for such subsequent fission products.

H. COMPUTER PROGRAMS

1. Nomenclature

Several computer programs have been developed for calculating fission product generation. The data described in the next section were obtained by program ISOGEN which is accurate and flexible, but requires rather careful programming. MELEAGER provides for more automatic control of changes in reactor flux and effective cross sections with time, but works with only a few nuclides at a time and is difficult to program for a large number of fission products. RIBD calculates production of a large number of fission products with relatively simple input but does not provide the flexibility of ISOGEN or MELEAGER in calculating transuranic formation, decay by electron capture, positron emission or alpha emission, or formation of nuclides by $n,2n$ reactions. Another code, ALCHEMY, permits excellent accuracy, particularly when used in connection with good neutron diffusion codes, but requires excessive programming and computer time for application to fission product inventory calculations.

2. Tabulation of Results

Fission product data were calculated for several reactor conditions by program ISOGEN using Bateman equations, and based on one ton (2000 lbs) of uranium feed. The reactor operation was divided into three irradiation segments of approximately equal duration with constant power level for each irradiation. After the first and second irradiation steps a reactor shut-down was allowed for charge-discharge operations, so that the reactor was operating only about 85% of the time. Nuclides with a half-life of less than three days were not considered unless they are daughters of longer-lived nuclides.

Tables II-6 through II-14 show the activity as a function of decay time for the nuclides listed (not including any short-lived daughter activity). Beta watts in Tables II-15 to II-23 and gamma watts in Tables II-24 to II-32 do include contributions from both parent and short-lived daughter.

Long-lived nuclides such as strontium-90 and cesium-137 depend only on integrated exposure (MWd/T) and not on exposure rate (MW/T), while short-lived nuclides such as iodine-131 depend only on exposure rate. Long-lived nuclides such as cesium-134 which are formed from a fission product by neutron capture depend on about the square of the integrated exposure, while similar short-lived nuclides such as promethium-148m depend on the first power of the integrated exposure. Nuclides which have greatly different fission yields from uranium and plutonium do not vary in a simple manner with either integrated exposure or exposure rate. However, for most nuclides the above generalizations should permit reasonably accurate interpolation or extrapolation of the results.

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TABLE II-1
STANDARD FUEL ELEMENTS

	Fuel Element Specifications										
	Natural Uranium						0.947% Enriched Uranium				
	<u>C2N</u>	<u>C5N</u>	<u>C6N</u>	<u>K4N</u>	<u>K5N</u>	<u>O3N</u>	<u>O5N</u>	<u>C3E</u>	<u>K4E</u>	<u>K5E</u>	<u>O3E</u>
Canned Length	8.965	8.965	8.865	8.965	8.865	8.965	4.665	6.640	6.640	6.540	6.640
Core Length	8.378	8.378	8.325	8.378	8.325	8.378	4.078	6.053	6.053	6.000	6.053
Can O. D.	1.466	1.494	1.986	1.460	1.520	1.444	1.443	1.460	1.459	1.509	1.443
Core O. D.	1.370	1.406	1.883	1.370	1.431	1.356	1.356	1.370	1.370	1.419	1.356
Core I. D.	0.481	0.488	0.452	0.498	0.533	0.423	0.423	0.488	0.513	0.545	0.423
Can I. D.	0.375	0.375	0.334	0.385	0.420	0.310	0.310	0.375	0.400	0.432	0.310
Weight	7.37	7.78	14.87	7.29	7.86	7.43	3.60	5.29	5.21	5.49	5.36

Notes: Watermix elements C3W, K4W, and O3W have the same core and can dimensions as the corresponding E suffix elements, but an aluminum watermix section is added to one end.

Each type of element may also exist with spacers added to the outside in three or four radial locations. These are called bumper elements.

TABLE II-2

NUCLEAR DATA FOR SELECTED ACTINIDES

Symbol	Half Life	Decay Type	Neutron Cross Section			Heat Generation, Watts	
			Product	Thermal	Resonance	Per Kilocurie	Per Gram
U-234	2.485×10^5 y (2×10^{16} y)	Alpha Fission)	U-235	97	650	28.8	1.77×10^{-4}
U-235	7.13×10^8 y (1.9×10^{17} y)	Alpha Fission)	U-236 Fission	103 532	51.0 8.4	27.5	5.87×10^{-3}
U-236	2.39×10^7 y (2×10^{16} y)	Alpha Fission)	U-237	8	400	27.2	1.72×10^{-5}
U-237	6.75 d	Beta	U-238 Fission	150 500	225 350	2.07	169
U-238	4.51×10^9 y (8×10^{15} y)	Alpha Fission)	U-239	2.74	280	25.3	8.43×10^{-4}
U-239	23.5 m	Beta	U-240 Fission	22 15		2.90	
U-240	14.1 h	Beta				0.593	
Np-236m	22 h (43%)	Beta EC)				0.830	
Np-236	>5000 y	Beta	Fission	2500			
Np-237	2.14×10^5 y	Alpha	Np-238	170 0.02	870	29.4	2.07×10^{-6}
Np-238	2.10 d	Beta	Np-239 Fission	1600 1600		4.98	1300
Np-239	2.35 d	Beta	Np-240m Np-240	35 25	210 150	2.67	620
Np-240m	7.3 m	Beta				6.16	
Np-240	60 m	Beta				8.59	
Pu-236	2.85 y (3.5×10^9 y)	Alpha Fission)	Fission	170		34.6	18.4
Pu-238	89 y (4.9×10^{10} y)	Alpha Fission)	Pu-239 Fission	489 17	3000 16	33.1	0.559
Pu-239	24360 y (5.5×10^{15} y)	Alpha Fission)	Pu-240 Fission	657 1208	362 454	31.1	1.9×10^{-3}
Pu-240	6760 y (1.22×10^{11} y)	Alpha Fission)	Pu-241 Fission	318 0	8900 2.6	31.1	6.86×10^{-3}
Pu-241	13.0 y (0.004%)	Beta Alpha)	Pu-242 Fission	527 1400	30 80	0.030	3.38×10^{-3}
Pu-242	3.79×10^5 y (7×10^{10} y)	Alpha Fission)	Pu-243 Fission	18 0	1275 1.3	29.5	1.15×10^{-4}
Pu-243	4.98 h	Beta	Pu-244	170		1.20	
Pu-244	7.6×10^7 y (2.5×10^{16} y)	Alpha Fission)	Pu-245	1.8		27.0	5.20×10^{-7}
Pu-245	10.1 h	Beta	Pu-246 Am-242m	260 70	52		
Am-241	458 y	Alpha	Am-242 Fission	840 2.9	620 10	33.4	0.108
Am-242m	152 y (10%)	Beta EC)	Am-243 Fission	1600 6400		1.30	0.0127
Am-242	16 h (19%)	Beta EC)	Fission	3000		1.13	912
Am-243	7950 y	Alpha	Am-244m Am-244	100 2.6	1400 46	32.2	6.19×10^{-3}
Am-244m	25m (0.039%)	Beta EC)				3.20	0.0987
Am-244	10 h	Beta	Fission	2300		0.652	837
Am-245	2.07 h	Beta					
Cm-242	163 d (7.2×10^5 y)	Alpha Fission)	Cm-243	20		36.8	122
Cm-243	32 y (0.26%)	Alpha EC)	Cm-244 Fission	250 630	200 356	36.5	1.68
Cm-244	18.1 y (1.4×10^7 y)	Alpha Fission)	Cm-245	15	650	34.9	2.83
Cm-245	9320 y	Alpha	Cm-246	200		33.3	5.21×10^{-3}

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TABLE II-3
TRANSURANIC CONTENT OF SPENT FUELS

MWd/T	MW/T	U ²³⁵ , %	Grams per Ton of Uranium												235
			Pu ²³⁸	Pu ²³⁹	Pu ²⁴⁰	Pu ²⁴¹	Pu ²⁴²	Np ²³⁷	Am ²⁴¹	Am ^{242m}	Am ²⁴³	Cm ²⁴²	Cm ²⁴³	Cm ²⁴⁴	
640	8.17	Natural	0.041	542	37.3	2.70	0.066	1.99	0.056						
750	10	Natural	0.056	636	47.6	4.90	0.134	2.59	0.079	4.3 (-5)	2.5 (-6)	3.5 (-4)	2.4 (-7)	2.7 (-8)	
900	10	Natural	0.083	711	62.5	7.53	0.251	3.16	0.159	9.1 (-5)	6.3 (-6)	6.7 (-4)	6.7 (-7)	8.3 (-8)	
900	9.7	0.947	0.072	634	41.0	4.02	0.109	3.42	0.086						
1000	10	0.947	0.090	691	49.2	5.30	0.164	3.84	0.115	6.9 (-5)	4.4 (-6)	5.0 (-4)	4.4 (-7)	2.6 (-8)	
1200	10	0.947	0.133	798	67.0	8.48	0.321	4.68	0.191	1.6 (-4)	1.2 (-5)	1.2 (-3)	1.2 (-6)	1.8 (-7)	
2200	11	0.947	0.80	1336	216	33	2.40	12.3	0.87						
2200	11	1.25	0.57	1275	181	27.1	1.50	12.3	0.71						
2100	10.6	2.1	0.36	995	70.6	7.92	0.226	12.3	0.205	2.4 (-4)	1.5 (-5)	1.6 (-3)	1.5 (-6)	2.3 (-7)	

Numbers in parentheses designates a power of 10. $4.3 (-5) = 4.3 \times 10^{-5}$ or 0.000043

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TABLE II-4
CUMULATIVE FISSION YIELDS

		Fission Yield, Percent		
Nuclide		U-235	Pu-239	U-238
Zn 72		1.6×10^{-5}	1.2×10^{-4}	1.0×10^{-4}
Ge 73		1.1×10^{-4}	3.0×10^{-4}	3.0×10^{-4}
Ge 74		3.5×10^{-4}	6.0×10^{-4}	6.0×10^{-4}
As 75		8.0×10^{-4}	0.0012	0.001
Ge 76		0.0020	0.003	0.002
As 77		0.0083	0.006	0.004
Se 78		0.020	0.013	0.008
Se 79		0.056	0.03	0.017
Se 80		0.11	0.06	0.035
Br 81		0.21	0.10	0.075
Se 82		0.35	0.18	0.13
Kr 83		0.496	0.29	0.22
Kr 84		0.953	0.47	0.38
Kr 85m		1.31	0.539	0.65
Kr 86		1.84	0.76	0.95
Rb 86		2.9×10^{-5}	2.3×10^{-5}	---
Rb 87		2.50	0.92	1.5
Sr 88		3.58	1.42	2.1
Sr 89		4.73	1.71	2.5
Sr 90		5.77	2.25	2.9
Y 91		5.97	2.61	3.3
Zr 92		6.03	3.14	3.9
Zr 93		6.51	3.97	4.5
Zr 94		6.55	4.48	4.9
Zr 95		6.55	5.03	5.2
Zr 96		6.41	5.17	5.5
Mo 97		6.33	5.65	5.8
Mo 98		5.93	5.89	6.1
Mo 99		6.25	6.10	6.3
Mo 100		6.58	7.10	6.4
Ru 101		5.00	5.91	6.5
Ru 102		4.10	5.99	6.4
Ru 103		2.90	5.67	6.2
Ru 104		1.80	5.93	5.7
Rh 105		0.90	3.90	4.7
Ru 106		0.38	4.57	2.3
Pd 107		0.17	3.10	1.1
Pd 108		0.07	2.2	0.53
Ag 109		0.03	1.4	0.26
Pd 110		0.02	0.56	0.13
Ag 111		0.016	0.23	0.07
Cd 112		0.013	0.12	0.06
Cd 113		0.012	0.08	0.05
Cd 114		0.011	0.055	0.045
Cd 115m		0.0007	0.0026	0.0025
Cd 115		0.0103	0.0384	0.0375
Cd 116		0.011	0.04	0.04
Sn 117		0.011	0.04	0.035
Sn 118		0.011	0.04	0.035
Sn 119		0.011	0.04	0.035

TABLE II-4 (Continued)
Fission Yield, Percent

Nuclide		U-235	Pu-239	U-238
Sn 120		0.011	0.04	0.04
Sn 121		0.012	0.043	0.04
Sn 122		0.013	0.05	0.04
Sn 123m		0.0013	0.005	0.004
Sb 123		0.014	0.056	0.041
Sn 124		0.017	0.08	0.05
Sn 125		0.012	0.04	0.017
Sb 125		0.036	0.12	0.05
Sn 126		0.10	0.20	0.07
Sn 127		0.125	0.195	0.065
Sb 127		0.25	0.39	0.13
Te 128		0.5	0.85	0.26
Te 129m		0.36	0.54	0.19
I 129		1.0	1.5	0.53
Te 130		2.0	2.5	1.1
Te 131m		0.435	0.25	0.35
I 131		2.94	3.78	2.3
Te 132		4.22	5.26	4.7
Xe 133m		0.16	0.17	0.14
Xe 133		6.62	6.91	5.7
Xe 134		7.74	7.47	6.2
Xe 135		6.45	7.17	6.4
Xe 136		6.47	6.63	6.5
Cs 136		0.0068	0.084	0.00095
Cs 137		6.22	6.63	6.4
Ba 138		6.68	6.31	6.3
La 139		6.42	5.87	6.1
Ba 140		6.24	5.6	5.8
Ce 141		5.73	5.7	5.5
Ce 142		5.84	5.01	5.2
Ce 143		5.88	4.57	4.9
Ce 144		5.35	3.93	4.5
Nd 145		3.87	3.13	3.9
Nd 146		2.94	2.60	3.3
Pm 146		1.2×10^{-6}	1.0×10^{-6}	---
Nd 147		2.03	2.07	2.9
Nd 148		1.68	1.73	2.5
Pm 149		1.01	1.32	2.1
Nd 150		0.634	1.01	1.5
Pm 151		0.398	0.80	0.95
Sm 152		0.236	0.62	0.65
Sm 153		0.148	0.37	0.38
Sm 154		0.050	0.29	0.22
Eu 155		0.029	0.23	0.13
Eu 156		0.015	0.11	0.075
Gd 157		0.0078	0.065	0.035
Gd 158		0.0020	0.021	0.008
Gd 160		3.0×10^{-4}	0.008	0.004
Tb 161		7.6×10^{-5}	0.0039	0.0017

TABLE II-5
NUCLEAR DATA FOR SELECTED FISSION PRODUCTS

Nuclide	Half Life	Decay Energy, MeV		Cross Section, Barns		Remarks
		Beta	Gamma	Thermal	Resonance	
Se 79	7.0×10^4 y	0.06	---	---	---	
Kr 85	10.4 y	0.25	0.005	7	26	
Rb 85	Stable	---	---	1.0	1.31	
Rb 86	18.7 d	0.649	0.095	---	---	
Sr 89	50.4 d	0.58	0.0002	0.4	---	
Sr 90	28 y	0.199	---	1	1.4	
Y 90	64.2 h	0.94	---	3.5	---	
Y 91	58 d	0.62	---	1.4	---	
Zr 93	9.5×10^5	0.014	---	1.1	28	4% to Nb-93m
Nb 93m	3.7 y	0.029	---	---	---	
Zr 95	65 d	0.119	0.724	13.9	109	2% to Zr-95m
Nb 95m	90 h	0.235	---	---	---	
Nb 95	35 d	0.046	0.757	7	---	
Tc 99	2.1×10^5 y	0.084	---	22	130	
Ru 103	39.6 d	0.113	0.505	---	---	Includes Rh-103m
Rh 103	Stable	---	---	171	1110	
Rh 105	36 h	0.18	0.016	21000	165000	
Ru 106	1.0 y	1.4	0.256	0.35	2.0	Includes Rh-106
Pd 107	7.0×10^6 y	0.01	---	10	36	
Pd 108	Stable	---	---	12.2	163	
Cd 108	Stable	---	---	10	---	
Ag 109	Stable	---	---	92	1390	3 b to Ag-110m
Cd 109	1.3 y	0.088	---	---	---	
Ag 110m	260 d	0.095	2.1	80	---	
Ag 111	7.5 d	0.37	0.023	---	---	
Cd 115m	43 d	0.60	0.018	---	---	
Cd 115	2.3 d	0.30	0.56	---	---	
In 115	5.0×10^{14} y	0.2	---	203	3380	
Sb 121	Stable	---	---	6.06	200	
Sn 123m	125 d	0.54	0.022	---	---	
Sb 123	Stable	---	---	3.345	160	
Sb 124	60 d	0.37	1.9	2000	---	
Sn 125	9.4 d	0.93	0.10	---	---	
Sb 125	2.7 y	0.115	0.393	1.56	---	21% to Te-125m
Te 125m	58 d	0.145	---	---	---	
Sn 126	1.0×10^5 y	0.02	---	0.3	---	14% to Sb-126
Sb 126	12.5 d	---	---	---	---	
Sb 127	3.9 d	0.4	0.45	---	---	
Te 127m	105 d	0.09	---	---	---	2% to I-127
Te 127	9.3 h	0.23	0.004	---	---	
I 127	Stable	---	---	6.4	140	
Te 129m	33 d	0.27	---	---	---	32% to I-129
Te 129	67 m	0.48	0.43	---	---	
I 129	1.6×10^7 y	0.08	---	28	24	
I 131	8.05 d	0.34	0.38	50	---	1% to Xe-131m
Xe 131m	12 d	0.159	0.005	---	---	
Te 132	78 h	0.061	0.23	---	---	
Xe 133	5.27 d	0.15	0.03	190	---	
Cs 133	Stable	---	---	30.6	490	
Cs 134	2.1 y	0.15	1.58	136	---	
Xe 135	2.0×10^7 y	0.058	---	8.7	58	
Cs 135	9.2 h	0.30	0.26	3.22×10^6	---	
Cs 136	13 d	0.11	2.49	---	---	
Cs 137	30 y	0.26	0.56	0.11	0.26	Includes Ba-137m
Ba 140	12.8 d	0.32	0.22	12	---	
La 140	40.2 h	0.51	2.39	3.1	---	
Ce 141	32.5 d	0.18	0.07	30	---	
Pr 143	13.7 d	0.315	---	89	154	
Ce 144	285 d	1.33	0.172	1.0	2.2	Includes Pr-144
Pm 146	2020 d	0.12	0.78	8400	---	35% to Sm-146
Nd 147	11.1 d	0.28	0.22	---	---	
Pm 147	2.62 y	0.0608	---	235	3110	110 b to Pm-148m
Sm 147	1.06×10^{11} y	2.18	---	90	1300	
Pm 148m	42 d	0.26	1.98	27000	32000	8% to Pm-148
Pm 148	5.4 d	0.71	0.64	2000	44000	
Sm 148	1.2×10^{13} y	2.14	---	9	46	
Sm 149	4.0×10^{14} y	1.84	---	90100	---	
Sm 150	Stable	---	---	100	215	
Sm 151	90 y	0.02	---	9720	---	
Eu 151	Stable	---	---	6851	4700	2200 b to Eu-152m
Sm 152	Stable	---	---	210	3057	
Eu 152m	9.3 h	0.55	0.23	---	---	25% to Sm-152
Eu 152	13 y	0.13	1.16	5000	---	73% Sm-152
Eu 153	Stable	---	---	280	1020	
Eu 154	16 y	0.23	1.26	1400	---	
Eu 155	1.81 y	0.10	0.023	13000	---	
Eu 156	15 d	0.42	1.3	---	---	

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TABLE II-6
FISSION PRODUCT ACTIVITY FROM NATURAL URANIUM
640 MWd/T, 8.17 MW/T

		Activity, Curies per Ton of Uranium					
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y	
Kr 85	271.7	267.7	266.3	263.4	259.1	254.6	
Rb 86	10.01	.3561	.1171	.0127	.0005	---	
Sr 89	188900	54770	36260	15890	4607	1243	
Sr 90	1945	1934	1930	1922	1910	1898	
Y 91	222800	75990	53100	25920	8842	2832	
Zr 95	238800	91460	66420	35030	13420	4858	
Nb 95	136600	134200	108600	65190	27290	10260	
Ru 103	164600	34070	20150	7050	1459	275.4	
Ru 106	7775	6555	6192	5525	4658	3888	
Ag 110m	.3968	.3122	.2882	.2456	.1932	.1499	
Ag 111	3185	.7776	.0486	.0002	---	---	
Cd 115m	47.76	11.19	6.902	2.624	.6149	.1324	
Sn 123m	41.97	25.48	21.57	15.47	9.390	5.537	
Sn 125	1116	1.460	.1603	.0019	---	---	
Sb 125	206.6	204.0	199.8	191.5	179.8	168.1	
Te 125m	25.21	42.84	41.96	40.22	37.76	35.30	
Sb 127	18760	.0021	---	---	---	---	
Te 127m	1080	660.9	542.2	364.8	201.4	107.4	
Te 129m	20310	3067	1633	463.1	69.93	9.457	
I 131	199200	87.95	6.643	.0377	---	---	
Xe 131m	1807	31.13	5.685	.1805	.0010	---	
Te 132	303500	.0014	---	---	---	---	
Xe 133	451000	3.322	.0642	---	---	---	
Cs 134	185.6	171.1	166.5	157.7	145.4	133.4	
Cs 136	1207	9.949	2.009	.0820	.0007	---	
Cs 137	2132	2120	2116	2108	2096	2083	
Ba 140	396000	3027	596.4	23.14	.1769	.0010	
Ce 141	303200	44470	23450	6524	956.9	125.5	
Ce 144	61440	49360	45890	39660	31860	25270	
Pr 143	358900	4238	929.0	44.63	.4697	.0038	
Pm 146	.0015	.0014	.0014	.0014	.0013	.0013	
Nd 147	136200	493.7	75.83	1.789	.0065	---	
Pm 147	6125	7231	7080	6780	6352	5929	
Pm 148m	805.6	182.4	111.2	41.30	9.352	1.942	
Pm 148	4519	16.79	10.21	3.792	.8586	.1783	
Sm 151	26.45	27.60	27.58	27.55	27.49	27.44	
Eu 152	.0368	.0364	.0362	.0359	.0354	.0349	
Eu 154	3.361	3.325	3.313	3.290	3.255	3.218	
Eu 155	123.1	112.0	109.5	101.9	92.74	83.93	
Eu 156	4414	68.97	17.24	1.078	.0168	.0002	
Tb 160	.7426	.3160	.2376	.1344	.0572	.0232	
Tb 161	45.86	.0054	.0003	---	---	---	

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TABLE II-6 (Continued)

Activity, Curies per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	246.3	238.2	215.5	195.0	170.7	139.7	71.76
Rb 86	---	---	---	---	---	---	---
Sr 89	100.9	8.183	.0044	---	---	---	---
Sr 90	1874	1851	1784	1719	1636	1519	1186
Y 91	319.4	36.01	.0516	.0001	---	---	---
Zr 95	692.9	98.83	.2867	.0008	---	---	---
Nb 95	1496	214.2	.6220	.0018	---	---	---
Ru 103	11.26	.4606	---	---	---	---	---
Ru 106	2749	1944	678.2	243.0	60.74	7.593	.0074
Ag 110m	.0921	.0566	.0131	.0030	.0004	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	.0070	.0004	---	---	---	---	---
Sn 123m	2.011	.7306	.0305	.0017	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	147.9	130.1	88.50	60.22	36.03	16.68	1.280
Te 125m	31.06	27.32	18.59	12.65	7.566	3.503	0.2688
Sb 127	---	---	---	---	---	---	---
Te 127m	32.13	9.623	.2586	.0069	.0001	---	---
Te 129m	.2041	.0044	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	113.1	95.92	58.46	35.63	18.41	6.841	.2521
Cs 136	---	---	---	---	---	---	---
Cs 137	2059	2036	1966	1899	1813	1692	1343
Ba 140	---	---	---	---	---	---	---
Ce 141	2.553	.0519	---	---	---	---	---
Ce 144	16210	10400	2743	723.5	122.4	8.520	.0012
Pr 143	---	---	---	---	---	---	---
Pm 146	.0012	.0011	.0009	.0008	.0006	.0004	.0001
Nd 147	---	---	---	---	---	---	---
Pm 147	5194	4550	3060	2058	1212	548.1	38.89
Pm 148m	.0953	.0047	---	---	---	---	---
Pm 148	.0088	.0004	---	---	---	---	---
Sm 151	27.33	27.23	26.91	26.61	26.20	25.60	23.70
Eu 152	.0340	.0331	.0306	.0282	.0254	.0216	.0127
Eu 154	3.149	2.082	2.888	2.706	2.482	2.179	1.413
Eu 155	69.30	57.22	32.22	18.14	8.433	2.673	.0581
Eu 156	---	---	---	---	---	---	---
Tb 160	.0041	.0007	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-7
FISSION PRODUCT ACTIVITY FROM NATURAL URANIUM
750 MWd/T, 10 MW/T

		Activity, Curies Per Ton of Uranium				
Nuclide		Discharge	90 d	120 d	180 d	270 d
Kr	85	312.7	308.1	306.4	303.1	298.2
Rb	86	13.65	.4856	.1597	.0173	.0006
Sr	89	222800	64630	42780	18750	5437
Sr	90	2239	2225	2221	2212	2198
Y	91	262000	89370	62440	30480	10400
Zr	95	279100	106900	77640	40940	15680
Nb	95	155100	156100	126600	76070	31870
Ru	103	191900	39700	23480	8216	1700
Ru	106	8516	7179	6782	6052	5102
Ag	110m	.4920	.3870	.3573	.3045	.2395
Ag	111	3498	.8541	.0534	.0002	---
Cu	115m	54.97	12.88	7.944	3.020	.7078
Sn	123m	47.59	28.89	24.46	17.54	10.65
Sn	125	1288	1.689	.1849	.0022	---
Sb	125	232.4	229.8	225.0	215.7	202.5
Te	125m	28.35	48.26	47.25	45.30	42.52
Sb	127	21820	.0025	---	---	---
Te	127m	1244	762.0	625.1	420.7	232.2
Te	129m	23810	3596	1915	543.0	82.0
I	131	233700	103.2	7.797	.0442	---
Xe	131m	2154	36.72	6.705	.2128	.0012
Te	132	354400	.0016	---	---	---
Xe	133	528800	3.895	.0753	---	---
Cs	134	258.2	238.0	231.7	219.5	202.3
Cs	136	1349	11.11	2.245	.0916	.0008
Cs	137	2439	2425	2420	2411	2397
Ba	140	470100	3594	708.0	27.48	.2101
Ce	141	357500	52440	27650	7692	1128
Ce	144	70850	56920	52920	45730	36740
Pr	143	427400	5039	1104	53.06	.5584
Pm	146	.0017	.0016	.0016	.0016	.0015
Nd	147	161400	584.9	89.85	2.120	.0077
Pm	147	6905	8236	8065	7723	7236
Pm	148m	1001	226.7	138.2	51.34	11.63
Pm	148	6272	20.88	12.69	4.713	1.067
Sm	151	27.40	28.73	28.71	28.68	28.62
Eu	152	.0404	.0398	.0397	.0393	.0388
Eu	154	4.565	4.517	4.501	4.469	4.421
Eu	155	121.8	110.8	107.4	103.8	91.74
Eu	156	5221	81.58	20.40	1.275	.0199
Tb	160	.9845	.4189	.3150	.1782	.0758
Tb	161	49.53	.0059	.0003	---	---

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TABLE II-7 (Continued)
Activity, Curies Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	293.0	274.1	224.4	160.8	82.60
Rb 86	---	---	---	---	---
Sr 89	1467	9.656	---	---	---
Sr 90	2184	2131	1978	1748	1365
Y 91	3331	42.35	.0001	---	---
Zr 95	5678	115.5	.0010	---	---
Nb 95	11990	250.3	.0021	---	---
Ru 103	320.9	.5368	---	---	---
Ru 106	4258	2129	266.1	8.316	.0081
Ag 110m	.1858	.0702	.0038	---	---
Ag 111	---	---	---	---	---
Cd 115m	.1524	.0004	---	---	---
Sn 123m	6.279	.8284	.0019	---	---
Sn 125	---	---	---	---	---
Sb 125	189.4	146.5	67.81	18.79	1.442
Te 125m	39.77	30.76	14.24	3.946	.3028
Sb 127	---	---	---	---	---
Te 127m	123.8	11.10	.0080	---	---
Te 129m	11.09	.0052	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	185.6	133.4	49.57	9.517	.3508
Cs 136	---	---	---	---	---
Cs 137	2383	2328	2173	1935	1536
Ba 140	.0012	---	---	---	---
Ce 141	147.9	.0612	---	---	---
Ce 144	29140	11990	834.3	9.825	.0014
Pr 143	.0045	---	---	---	---
Pm 146	.0015	.0013	.0009	.0005	.0001
Nd 147	---	---	---	---	---
Pm 147	6753	5183	2344	624.4	44.31
Pm 148m	2.414	.0058	---	---	---
Pm 148	.2216	.0005	---	---	---
Sm 151	28.57	28.35	27.70	26.65	24.68
Eu 152	.0383	.0363	.0309	.0237	.0139
Eu 154	4.372	4.186	3.676	2.960	1.919
Eu 155	83.02	56.61	17.94	2.645	.0574
Eu 156	.0002	---	---	---	---
Tb 160	.0307	.0010	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-8
FISSION PRODUCT ACTIVITY FROM NATURAL URANIUM

900 MWd/T, 10 MW/T

Activity, Curies Per Ton of Uranium					
Nuclide	Discharge	90 d	120 d	180 d	270 d
Kr 85	370.2	364.7	362.7	358.8	352.9
Rb 86	16.85	.5994	.1971	.0213	.0008
Sr 89	242100	70210	46470	20360	5906
Sr 90	2652	2636	2631	2620	2604
Y 91	287600	98100	68540	33460	11410
Zr 95	310200	118800	86280	45500	17430
Nb 95	192200	176800	142500	85100	35510
Ru 103	210600	43580	25780	9019	1866
Ru 106	10730	9047	8546	7626	6429
Ag 110m	.7705	.6061	.5595	.4768	.3751
Ag 111	3893	.9505	.0594	.0002	---
Cd 115m	61.79	14.48	8.930	3.395	.7957
Sn 123m	56.37	34.22	28.98	20.78	12.61
Sn 125	1345	1.764	.1931	.0023	---
Sb 125	285.0	279.7	273.9	262.6	246.5
Te 125m	39.90	58.74	57.52	55.15	51.76
Sb 127	21990	.0025	---	---	---
Te 127m	1451	877.0	719.4	484.1	267.3
Te 129m	25650	3874	2063	585.0	88.35
I 131	236500	104.4	7.884	.0045	---
Xe 131m	2230	37.42	6.831	.2168	.0012
Te 132	354500	.0016	---	---	---
Xe 133	529500	3.898	.0076	---	---
Cs 134	375.9	346.6	337.3	319.5	294.6
Cs 136	1556	12.82	2.589	.1056	.0009
Cs 137	2915	2898	2893	2882	2865
Ba 140	475600	3636	716.2	27.79	.2125
Ce 141	381300	55920	29490	8203	1203
Ce 144	82860	66570	61890	53480	42970
Pr 143	433100	5093	1116	53.63	.5644
Pm 146	.0020	.0019	.0019	.0018	.0018
Nd 147	163200	591.3	90.83	2.143	.0078
Pm 147	8439	9693	9490	9088	8514
Pm 148m	1264	286.2	174.4	64.80	14.67
Pm 148	7796	26.35	16.01	5.949	1.347
Sm 151	29.72	31.56	31.04	31.00	30.95
Eu 152	.0573	.0566	.0563	.0558	.0551
Eu 154	6.640	6.570	6.547	6.500	6.431
Eu 155	136.2	124.1	120.2	112.9	102.7
Eu 156	5967	93.24	23.31	1.457	.0228
Tb 160	1.445	.6146	.4623	.2615	.1113
Tb 161	56.55	.0067	.0003	---	---

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TABLE II-8 (Continued)
Activity, Curies Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	346.8	324.5	265.7	190.4	97.75
Rb 86	---	---	---	---	---
Sr 89	1593	10.49	---	---	---
Sr 90	2578	2524	2343	2071	1617
Y 91	3656	46.48	.0001	---	---
Zr 95	6311	128.4	.0011	---	---
Nb 95	13340	278.2	.0023	---	---
Ru 103	352.3	.5892	---	---	---
Ru 106	5366	2683	335.4	10.48	.0102
Ag 110m	.2910	.1099	.0059	---	---
Ag 111	---	---	---	---	---
Cd 115m	.1714	.0005	---	---	---
Sn 123m	7.438	.9814	.0023	---	---
Sn 125	---	---	---	---	---
Sb 125	230.5	178.3	82.55	22.87	1.755
Te 125m	48.40	37.44	17.34	4.803	.3686
Sb 127	---	---	---	---	---
Te 127m	142.5	12.77	.0092	---	---
Te 129m	11.95	.0094	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	270.3	194.3	72.17	13.86	.5107
Cs 136	---	---	---	---	---
Cs 137	2848	2783	2597	2313	1836
Ba 140	.0012	---	---	---	---
Ce 141	157.8	.0653	---	---	---
Ce 144	34080	14020	975.8	11.49	.0016
Pr 143	.0046	---	---	---	---
Pm 146	.0017	.0015	.0010	.0006	.0002
Nd 147	---	---	---	---	---
Pm 147	7947	6099	2758	734.7	52.14
Pm 148m	3.046	.0073	---	---	---
Pm 148	.2797	.0007	---	---	---
Sm 151	30.88	30.65	29.95	28.81	26.68
Eu 152	.0543	.0515	.0439	.0336	.0197
Eu 154	6.359	6.089	5.347	4.306	2.792
Eu 155	92.97	63.39	20.09	2.961	.0643
Eu 156	.0003	---	---	---	---
Tb 160	.0450	.0014	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-9
FISSION PRODUCT ACTIVITY FROM 0.947% ENRICHED URANIUM
900 MWd/T, 9.7 MW/T

		Activity, Curies Per Ton of Uranium					
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y	
Kr 85	384.0	378.3	376.2	372.1	366.0	359.7	
Rb 86	13.78	.4903	.1612	.0174	.0006	---	
Sr 89	245600	71240	47160	20660	5993	1617	
Sr 90	2752	2735	2730	2719	2702	2685	
Y 91	292000	99590	69580	33970	11590	3712	
Zr 95	313800	120200	87280	46030	17630	6383	
Nb 95	198400	179600	144500	86200	35940	13500	
Ru 103	207700	42980	25420	8895	1841	347.4	
Ru 106	10180	8586	8111	7238	6101	5092	
Ag 110m	.5532	.4352	.4018	.3424	.2693	.2089	
Ag 111	3525	.8607	.0538	.0002	---	---	
Cd 115m	59.97	14.06	8.667	3.295	.7722	.1663	
Sn 123m	55.47	33.68	28.51	20.44	12.41	7.319	
Sn 125	1304	1.711	.1873	.0022	---	---	
Sb 125	285.0	279.3	273.5	262.2	246.1	230.2	
Te 125m	42.75	58.65	57.44	55.06	51.68	48.34	
Sb 127	22060	.0025	---	---	---	---	
Te 127m	1460	881.7	723.3	486.8	268.7	143.3	
Te 129m	25390	3834	2042	579.0	87.43	11.82	
I 131	237100	104.7	7.909	.0449	---	---	
Xe 131m	2186	37.25	6.802	.2159	.0012	---	
Te 132	358200	.0017	---	---	---	---	
Xe 133	536800	3.954	.0764	---	---	---	
Cs 134	293.6	270.7	263.4	249.5	230.0	211.1	
Cs 136	1413	11.64	2.352	.0960	.0008	---	
Cs 137	2993	2976	2971	2960	2943	2925	
Ba 140	477100	3647	718.5	27.88	.2132	.0012	
Ce 141	380600	55830	29440	8188	1201	157.2	
Ce 144	85040	68320	63510	54890	44100	34980	
Pr 143	434700	5122	1123	53.94	.5676	.0046	
Pm 146	.0020	.0020	.0020	.0019	.0018	.0018	
Nd 147	163600	593.0	91.09	2.149	.0078	---	
Pm 147	8825	10060	9850	9432	8837	8248	
Pm 148m	1173	266.5	162.4	60.34	13.66	2.837	
Pm 148	6270	24.52	14.91	5.540	1.254	.2604	
Sm 151	34.88	36.21	36.19	36.14	36.07	36.00	
Eu 152	.0624	.0616	.0614	.0608	.0600	.0592	
Eu 154	5.211	5.156	5.138	5.101	5.047	4.990	
Eu 155	153.3	139.5	135.2	126.9	115.5	104.5	
Eu 156	5317	83.08	20.77	1.298	.0203	.0002	
Tb 160	1.041	.4430	.3332	.1885	.0802	.0325	
Tb 161	49.75	.0059	.0003	---	---	---	

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TABLE II-9 (Continued)
Activity, Curies Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	348.0	336.5	304.5	275.6	241.2	197.5	101.4
Rb 86	---	---	---	---	---	---	---
Sr 89	131.2	10.64	.0057	---	---	---	---
Sr 90	2652	2619	2524	2432	2314	2148	1677
Y 91	418.5	47.19	.0674	.0001	---	---	---
Zr 95	910.5	129.9	.3768	.0011	---	---	---
Nb 95	1966	281.4	.817?	.0024	---	---	---
Ru 103	14.21	.5811	---	---	---	---	---
Ru 106	3601	2546	900.2	318.3	79.57	9.946	.0097
Ag 110m	.1284	.0789	.0183	.0042	.0006	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	.0088	.0005	---	---	---	---	---
Sn 123m	2.658	.9656	.0463	.0022	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	202.4	178.0	121.1	82.42	49.33	22.83	1.753
Te 125m	42.50	37.38	25.43	17.31	10.36	4.794	.3681
Sb 127	---	---	---	---	---	---	---
Te 127m	42.87	12.84	.3450	.0093	.0001	---	---
Te 129m	.2551	.0055	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	179.0	151.7	92.48	56.37	29.13	10.82	.3988
Cs 136	---	---	---	---	---	---	---
Cs 137	2892	2858	2761	2667	2546	2376	1886
Ba 140	---	---	---	---	---	---	---
Ce 141	3.204	.0652	---	---	---	---	---
Ce 144	22430	14390	3796	1001	169.4	11.79	.0016
Pr 143	---	---	---	---	---	---	---
Pm 146	.0017	.0016	.0013	.0011	.0008	.0006	.0002
Nd 147	---	---	---	---	---	---	---
Pm 147	7226	6330	4257	2862	1683	762.5	54.11
Pm 148m	.1393	.0068	---	---	---	---	---
Pm 148	.0128	.0006	---	---	---	---	---
Sm 151	35.86	35.73	35.31	34.91	34.38	33.59	31.10
Eu 152	.0576	.0561	.0518	.0478	.0430	.0366	.0215
Eu 154	4.883	4.779	4.478	4.196	3.848	3.379	2.191
Eu 155	86.31	71.27	40.12	22.59	10.50	3.329	.0723
Eu 156	---	---	---	---	---	---	---
Tb 160	.0057	.0010	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-10
FISSION PRODUCT ACTIVITY FROM 0.947% ENRICHED URANIUM
1000 MWd/T, 10 MW/T

Nuclide	Discharge	Activity, Curies Per Ton of Uranium			
		90 d	120 d	180 d	270 d
Kr 85	427.2	420.7	418.4	413.9	407.1
Rb 86	16.50	.5870	.1931	.0209	.0007
Sr 89	266800	77380	51220	22440	6509
Sr 90	3061	3042	3036	3024	3005
Y 91	318200	108500	75830	37020	12630
Zr 95	342800	131300	95340	50280	19260
Nb 95	222700	197100	158400	94330	39290
Ru 103	224600	46480	27490	9618	1990
Ru 106	11560	9745	9206	8215	6925
Ag 110m	.7322	.5760	.5317	.4531	.3565
Ag 111	3931	.9598	.0600	.0002	---
Cd 115m	64.72	15.17	9.352	3.550	.8333
Sn 123m	61.29	37.21	31.51	22.59	13.71
Sn 125	1398	1.834	.2007	.0024	---
Sb 125	322.0	314.8	308.3	295.6	277.4
Te 125m	45.08	66.11	64.74	62.08	58.25
Sb 127	22950	.0026	---	---	---
Te 127m	1619	972.9	798.1	537.1	296.5
Te 129m	27480	4150	2210	626.8	94.65
I 131	249600	110.2	8.322	.0472	---
Xe 131m	2372	39.60	7.227	.2294	.0013
Te 132	370800	.0017	---	---	---
Xe 133	557200	4.104	.0794	---	---
Cs 134	385.8	355.7	346.2	328.0	302.3
Cs 136	1642	13.53	2.732	.1115	.0009
Cs 137	3329	3310	3304	3292	3273
Ba 140	503400	3849	758.2	29.42	.2249
Ce 141	410900	60270	31780	8840	1297
Ce 144	94070	75580	70260	60720	48780
Pr 143	460400	5409	1185	56.95	.5994
Pm 146	.0022	.0022	.0021	.0021	.0020
Nd 147	171300	620.9	95.37	2.250	.0082
Pm 147	9776	11040	10840	10350	9693
Pm 148m	1393	315.2	192.1	71.38	16.16
Pm 148	7557	29.01	17.64	6.553	1.484
Sm 151	36.07	37.44	37.42	37.37	37.30
Eu 152	.0713	.0703	.0700	.0694	.0685
Eu 154	6.620	6.550	6.526	6.480	6.411
Eu 155	162.0	147.4	142.8	134.1	122.0
Eu 156	5930	92.66	23.17	1.488	.0226
Tb 160	1.358	.5780	.4347	.2459	.1046
Tb 161	55.68	.0066	.0004	---	---

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TABLE II-10 (Continued)
Activity, Curies Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	400.1	374.0	306.5	219.6	112.8
Rb 86	---	---	---	---	---
Sr 89	1756	11.56	---	---	---
Sr 90	2986	2913	2705	2390	1866
Y 91	4045	51.42	.0001	---	---
Zr 95	6973	141.9	.0012	---	---
Nb 95	14750	307.5	.0026	---	---
Ru 103	375.7	.6284	---	---	---
Ru 106	5780	2890	361.2	11.29	.0110
Ag 110m	.2765	.1044	.0056	---	---
Ag 111	---	---	---	---	---
Cd 115m	.1795	.0005	---	---	---
Sn 123m	8.087	1.067	.0025	---	---
Sn 125	---	---	---	---	---
Sb 125	259.5	200.7	92.92	25.74	1.976
Te 125m	54.50	42.15	19.51	5.405	.4150
Sb 127	---	---	---	---	---
Te 127m	158.1	14.17	.0102	---	---
Te 129m	12.80	.0060	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	277.4	199.4	74.08	14.22	.5242
Cs 136	---	---	---	---	---
Cs 137	3253	3179	2966	2642	2097
Ba 140	.0013	---	---	---	---
Ce 141	170.0	.0704	---	---	---
Ce 144	38690	15920	1108	13.04	.0018
Pr 143	.0048	---	---	---	---
Pm 146	.0020	.0017	.0012	.0006	.0002
Nd 147	---	---	---	---	---
Pm 147	9046	6943	3140	836.4	59.35
Pm 148m	3.356	.0081	---	---	---
Pm 148	.3081	.0007	---	---	---
Sm 151	37.23	36.94	36.10	34.73	32.16
Eu 152	.0676	.0640	.0546	.0418	.0245
Eu 154	6.339	6.070	5.331	4.292	2.783
Eu 155	110.4	75.30	23.87	3.518	.0764
Eu 156	.0003	---	---	---	---
Tb 160	.0424	.0013	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-11
FISSION PRODUCT ACTIVITY FROM 0.947% ENRICHED URANIUM
1200 MWd/T, 10 MW/T

		Activity, Curies Per Ton of Uranium				
Nuclide		Discharge	90 d	120 d	180 d	270 d
Kr	85	507.4	499.5	496.8	491.4	483.4
Rb	86	20.22	.7195	.2366	.0256	.0009
Sr	89	284700	82580	54660	23950	6946
Sr	90	3638	3616	3608	3594	3572
Y	91	343600	117200	81890	39980	13640
Zr	95	375600	143900	104500	55090	21100
Nb	95	268600	220200	175900	104100	43170
Ru	103	243100	50310	29760	10410	2154
Ru	106	14670	12360	11680	10420	8787
Ag	110m	1.160	.9123	.8422	.7177	.5646
Ag	111	4385	1.071	.0669	.0003	---
Cd	115m	71.99	16.87	10.40	3.955	.9270
Sn	123m	72.41	43.96	37.22	26.69	16.20
Sn	125	1461	1.917	.2098	.0025	---
Sb	125	396.3	385.2	377.2	361.6	339.4
Te	125m	73.98	80.89	79.21	75.94	71.27
Sb	127	23240	.0027	---	---	---
Te	127m	1868	1111	911.5	613.4	338.6
Te	129m	29160	4404	2345	665.0	100.4
I	131	252500	111.4	8.414	.0478	---
Xe	131m	2429	40.21	7.338	.2329	.0013
Te	132	372800	.0017	---	---	---
Xe	133	558600	4.114	.0796	---	---
Cs	134	562.2	518.3	504.5	477.9	440.5
Cs	136	1891	15.58	3.147	.1284	.0011
Cs	137	3997	3974	3966	3951	3929
Ba	140	506600	3873	763.0	29.61	.2264
Ce	141	430900	63200	33330	9271	1360
Ce	144	109800	88230	82020	70890	56950
Pr	143	462900	5432	1191	57.20	.6020
Pm	146	.0026	.0025	.0025	.0025	.0024
Nd	147	172700	625.8	96.12	2.268	.0082
Pm	147	11860	13010	12730	12190	11420
Pm	148m	1739	393.8	240.0	89.17	20.19
Pm	148	9307	36.24	22.04	8.186	1.854
Sm	151	39.11	40.51	40.48	40.43	40.35
Eu	152	.1011	.0998	.0993	.0985	.0972
Eu	154	9.700	9.597	9.563	9.495	9.394
Eu	155	182.3	165.9	160.8	151.0	137.4
Eu	156	6751	105.5	26.37	1.648	.0258
Tb	160	2.005	.8530	.6416	.3629	.1544
Tb	161	63.76	.0076	.0004	---	---

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TABLE II-11 (Continued)
Activity, Curies Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	475.1	444.4	363.9	260.7	133.9
Rb 86	---	---	---	---	---
Sr 89	1874	12.34	---	---	---
Sr 90	3549	3462	3214	2840	2217
Y 91	4368	55.53	.0001	---	---
Zr 95	7641	155.4	.0013	---	---
Nb 95	16180	336.9	.0028	---	---
Ru 103	406.6	.6801	---	---	---
Ru 106	7334	3667	458.2	14.32	.0140
Ag 110m	.4380	.1654	.0089	.0001	---
Ag 111	---	---	---	---	---
Cd 115m	.1996	.0006	---	---	---
Sn 123m	9.553	1.260	.0029	---	---
Sn 125	---	---	---	---	---
Sb 125	317.5	245.6	113.7	31.50	2.417
Te 125m	66.68	51.58	23.88	6.615	.5076
Sb 127	---	---	---	---	---
Te 127m	180.6	16.18	.0117	---	---
Te 129m	13.58	.0063	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	404.2	290.6	107.9	20.72	.7638
Cs 136	---	---	---	---	---
Cs 137	3905	3816	3561	3172	2518
Ba 140	.0013	---	---	---	---
Ce 141	178.3	.0738	---	---	---
Ce 144	45170	18580	1293	15.23	.0021
Pr 143	.0049	---	---	---	---
Pm 146	.0023	.0020	.0014	.0008	.0002
Nd 147	---	---	---	---	---
Pm 147	10660	8183	3700	985.7	69.95
Pm 148m	4.192	.0101	---	---	---
Pm 148	.3849	.0009	---	---	---
Sm 151	40.27	39.96	39.05	37.57	34.79
Eu 152	.0958	.0909	.0774	.0593	.0348
Eu 154	9.289	8.895	7.811	6.290	4.078
Eu 155	124.3	84.76	26.87	3.960	.0860
Eu 156	.0003	---	---	---	---
Tb 160	.0625	.0019	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-12
FISSION PRODUCT ACTIVITY FROM 0.947% ENRICHED URANIUM
2200 MWd/T, 11MW/T

		Activity, Curies Per Ton of Uranium				
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	869.3	856.2	851.3	842.1	828.5	812.8
Rb 86	41.31	1.470	.4834	.0523	.0019	.0001
Sr 89	320300	92910	61500	26950	7815	2109
Sr 90	6264	6226	6213	6188	6150	6111
Y 91	403200	137500	96090	46910	16000	5126
Zr 95	472800	181100	131500	69340	26560	9617
Nb 95	413000	289700	228300	133100	54700	20420
Ru 103	319600	66150	39120	13690	2833	534.7
Ru 106	35680	30080	28410	25350	21370	17840
Ag 110m	5.607	4.411	4.072	3.470	2.730	2.118
Ag 111	7429	1.814	.1133	.0004	---	---
Cd 115m	107.8	25.27	15.58	5.922	1.388	.2989
Sn 123m	130.4	79.14	67.01	48.04	29.17	17.20
Sn 125	1946	2.553	.2794	.0033	---	---
Sb 125	822.1	789.3	772.8	740.9	695.5	650.5
Te 125m	172.6	165.8	162.3	155.6	146.1	136.6
Sb 127	27290	.0031	---	---	---	---
Te 127m	2870	1678	1377	926.4	511.4	272.7
Te 129m	35690	5389	2870	813.8	122.9	16.62
I 131	289500	127.4	9.623	.0546	---	---
Xe 131m	2807	46.15	8.421	.2673	.0015	---
Te 132	423500	.0020	---	---	---	---
Xe 133	619100	4.560	.0882	---	---	---
Cs 134	2511	2315	2253	2134	1968	1805
Cs 136	3598	29.65	5.989	.2443	.0020	---
Cs 137	7349	7307	7293	7265	7224	7181
Ba 140	554700	4241	835.4	32.42	.2478	.0014
Ce 141	495200	72630	38310	10650	1563	204.9
Ce 144	176600	141800	131900	114000	91560	72620
Pr 143	498100	5840	1280	61.50	.6472	.0052
Pm 146	.0043	.0042	.0041	.0040	.0039	.0038
Nd 147	193400	700.9	107.7	2.540	.0092	---
Pm 147	20470	21290	20840	19960	18700	17450
Pm 148m	4110	930.7	567.3	210.7	47.72	9.907
Pm 148	22070	85.65	52.08	19.35	4.381	.9095
Sm 151	53.73	55.43	55.40	55.32	55.22	55.11
Eu 152	.2768	.2732	.2720	.2697	.2661	.2625
Eu 154	42.52	42.07	41.92	41.62	41.18	40.72
Eu 155	309.1	281.2	272.5	255.9	232.9	210.7
Eu 156	11780	184.1	46.02	2.877	.0449	.0006
Tb 160	9.898	4.211	3.167	1.792	.7623	.3086
Tb 161	118.0	.0140	.0007	---	---	---

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TABLE II-12 (Continued)
Activity, Curies Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	787.4	761.7	689.2	623.3	545.3	446.8	229.4
Rb 86	---	---	---	---	---	---	---
Sr 89	171.1	13.88	.0074	---	---	---	---
Sr 90	6035	5961	5744	5535	5267	4890	3818
Y 91	577.9	65.17	.0934	.0001	---	---	---
Zr 95	1372	195.6	.5677	.0016	---	---	---
Nb 95	2964	424.1	1.231	.0036	---	---	---
Ru 103	21.87	.8943	.0001	---	---	---	---
Ru 106	12610	8919	3153	1115	278.7	34.84	.0340
Ag 110m	1.301	.7998	.1856	.0431	.0061	.0003	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	.0157	.0008	---	---	---	---	---
Sn 123m	6.247	2.259	.1088	.0052	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	572.1	503.2	342.4	232.9	139.4	64.53	4.953
Te 125m	120.1	105.7	71.90	48.91	29.27	13.55	1.040
Sb 127	---	---	---	---	---	---	---
Te 127m	81.63	24.45	.6569	.0176	.0001	---	---
Te 129m	.3586	.0077	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	1531	1298	791.0	482.1	249.2	92.56	3.411
Cs 136	---	---	---	---	---	---	---
Cs 137	7098	7017	6778	6547	6251	5833	4629
Ba 140	---	---	---	---	---	---	---
Ce 141	4.169	.0848	---	---	---	---	---
Ce 144	46580	29870	7881	2079	351.8	24.48	.0034
Pr 143	---	---	---	---	---	---	---
Pm 146	.0036	.0033	.0028	.0023	.0018	.0012	.0004
Nd 147	---	---	---	---	---	---	---
Pm 147	15290	13390	9007	6057	3568	1613	1145
Pm 148m	.4864	.0239	---	---	---	---	---
Pm 148	.0446	.0022	---	---	---	---	---
Sm 151	54.90	54.69	54.06	53.44	52.62	51.42	47.61
Eu 152	.2556	.2488	.2297	.2121	.1906	.1624	.0953
Eu 154	39.84	38.99	36.54	34.24	31.40	27.57	17.38
Eu 155	174.0	143.7	80.90	45.55	21.18	6.713	.1458
Eu 156	---	---	---	---	---	---	---
Tb 160	.0545	.0096	.0001	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-13
FISSION PRODUCT ACTIVITY FROM 1.25% ENRICHED URANIUM
2200 MWd/T, 11 MW/T

		Activity, Curies Per Ton of Uranium					
Nuclide		Discharge	90 d	120 d	180 d	270 d	1 y
Kr	85	904.7	890.5	885.5	876.2	861.9	847.0
Rb	86	34.73	1.236	.4064	.0440	.0016	---
Sr	89	339100	98340	65100	28520	8272	2232
Sr	90	6523	6484	6470	6444	6405	6364
Y	81	422900	144300	100800	49210	16780	5377
Zr	95	481400	184400	133900	70610	27040	9397
Nb	95	419600	294800	232400	135500	55690	20790
Ru	103	300400	62160	36770	12860	2662	502.5
Ru	106	28120	23710	22390	19980	16850	14060
Ag	110m	3.185	2.505	2.313	1.971	1.550	1.203
Ag	111	5577	1.362	.0851	.0004	---	---
Cd	115m	95.08	22.28	13.74	5.223	1.224	.2637
Sn	123m	115.3	70.00	59.27	42.50	25.80	15.21
Sn	125	1711	2.245	.2457	.0029	---	---
Sb	125	742.5	712.4	697.5	668.7	627.8	587.1
Te	125m	148.5	149.6	146.5	140.4	131.8	123.3
Sb	127	25950	.0030	---	---	---	---
Te	127m	2770	1619	1328	893.6	493.3	263.1
Te	129m	34340	5183	2761	783.0	118.2	15.99
I	131	280800	123.8	9.348	.0531	---	---
Xe	131m	2733	44.86	8.186	.2598	.0014	---
Te	132	412200	.0019	---	---	---	---
Xe	133	614000	4.522	.0874	---	---	---
Cs	134	2009	1852	1802	1707	1574	1444
Cs	136	2903	23.92	4.831	.1971	.0016	---
Cs	137	7320	7278	7264	7237	7196	7152
Ba	140	558330	4268	840.8	32.63	.2494	.0014
Ce	141	494800	72570	38270	10650	1561	204.8
Ce	144	179600	144300	134200	116000	93160	73890
Pr	143	507800	5953	1305	62.67	.6596	.0053
Pm	146	.0044	.0043	.0042	.0042	.0040	.0039
Nd	147	192500	697.5	107.1	2.528	.0092	---
Pm	147	21110	21890	21420	20510	19220	17940
Pm	148m	4024	911.2	555.3	206.3	46.71	9.699
Pm	148	18890	83.82	50.98	18.94	4.288	.8904
Sm	151	60.24	61.79	61.75	61.68	61.56	61.44
Eu	152	.3142	.3101 m	.3088	.3061	.3021	.2979
Eu	154	31.73	31.40	31.28	31.06	30.73	30.39
Eu	155	291.6	265.4	257.2	241.5	219.7	198.9
Eu	156	9153	143.0	35.75	2.234	.0349	.0004
Tb	160	6.119	2.603	1.958	1.108	.4713	.1908
Tb	161	84.50	.0100	.0005	---	---	---

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TABLE II-13 (Continued)

Activity, Curies Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	818.8	792.3	717.0	648.3	567.8	464.9	238.7
Rb 86	---	---	---	---	---	---	---
Sr 89	181.1	14.69	.0078	---	---	---	---
Sr 90	6285	6208	5982	5764	5485	5093	3976
Y 91	606.3	68.36	.0980	.0001	---	---	---
Zr 95	1397	199.2	.5780	.0017	---	---	---
Nb 95	3018	431.8	1.254	.0036	---	---	---
Ru 103	20.55	.8404	.0001	---	---	---	---
Ru 106	9943	7030	2486	878.8	219.7	27.46	.0268
Ag 110m	.7391	.4542	.1054	.0245	.0035	.0002	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	.0139	.0007	---	---	---	---	---
Sn 123m	5.526	2.007	.0962	.0046	.0001	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	516.4	454.2	309.0	210.3	125.8	58.25	4.470
Te 125m	108.4	95.38	64.89	44.16	26.42	12.23	.9387
Sb 127	---	---	---	---	---	---	---
Te 127m	78.74	23.58	.6336	.0170	.0001	---	---
Te 129m	.3451	.0074	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	1224	1038	632.7	385.7	199.3	74.04	2.729
Cs 136	---	---	---	---	---	---	---
Cs 137	7070	6989	6751	6521	6227	5810	4611
Ba 140	---	---	---	---	---	---	---
Ce 141	4.165	.0847	---	---	---	---	---
Ce 144	47390	30400	8019	2115	357.9	24.91	.0035
Pr 143	---	---	---	---	---	---	---
Pm 146	.0037	.0034	.0029	.0024	.0018	.0013	.0004
Nd 147	---	---	---	---	---	---	---
Pm 147	15720	13770	9258	6226	3668	1658	117.7
Pm 148m	.4762	.0234	---	---	---	---	---
Pm 148	.0437	.0021	---	---	---	---	---
Sm 151	61.20	60.96	60.26	59.57	58.66	57.32	53.07
Eu 152	.2901	.2824	.2607	.2407	.2163	.1844	.1082
Eu 154	29.74	29.10	27.27	25.55	23.43	20.58	13.34
Eu 155	164.2	135.6	76.34	42.98	19.98	6.334	.1376
Eu 156	---	---	---	---	---	---	---
Tb 160	.0337	.0059	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-14
FISSION PRODUCT ACTIVITY FROM 2.1% ENRICHED URANIUM
2100 MWd/T, 10.6 MW/T

		Activity, Curies Per Ton of Uranium					
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y	
Kr 85	900.0	886.1	880.8	871.7	857.6	842.6	
Rb 86	21.48	.7641	.2513	.0272	.0001	---	
Sr 89	347300	100700	66670	29210	8472	2286	
Sr 90	6494	6454	6441	6415	6376	6335	
Y 91	428700	146200	102200	49880	17020	5451	
Zr 95	472400	180900	131400	69290	26540	9610	
Nb 95	409300	288900	227900	132900	54640	20400	
Ru 103	267100	55280	32690	11440	2367	446.8	
Ru 106	18710	15780	14900	13300	11210	9357	
Ag 110m	1.011	.795	.7339	.6254	.492	.3817	
Ag 111	3188	.7784	.0486	.0002	---	---	
Cd 115m	77.03	18.05	11.13	4.232	.9919	.2136	
Sn 123m	93.96	57.04	48.3	34.63	21.02	12.4	
Sn 125	1373	1.801	.1971	.0024	---	---	
Sb 125	622.8	597	384.6	560.4	526.1	492	
Te 125m	93.42	125.4	122.8	117.7	110.5	103.3	
Sb 127	23460	.0027	---	---	---	---	
Te 127m	2546	1486	1219	820.5	452.9	241.5	
Te 129m	31510	4758	2534	718.6	108.5	14.67	
I 131	260600	115.1	8.693	.0493	---	---	
Xe 131m	2547	41.75	7.617	.2417	.0013	---	
Te 132	384700	.0018	---	---	---	---	
Xe 133	586600	4.32	.0835	---	---	---	
Cs 134	1141	1052	1023	969.4	893.7	820	
Cs 136	1882	15.5	3.132	.1278	.001	---	
Cs 137	6946	6906	6893	6867	6828	6787	
Ba 140	542400	4147	816.9	31.7	.2423	.0014	
Ce 141	476000	69820	36820	10240	1502	197	
Ce 144	175000	140600	130700	113000	90760	71990	
Pr 143	500800	5869	1286	61.8	.6504	.0053	
Pm 146	.0044	.0043	.0042	.0041	.0040	.0039	
Nd 147	184400	668.4	102.7	2.422	.0088	---	
Pm 147	21170	21850	21390	20480	19190	17910	
Pm 148m	3408	771.7	470.4	174.7	39.57	8.215	
Pm 148	12060	70.96	43.18	16.04	3.632	.7541	
Sm 151	76.90	78.21	78.16	78.06	77.91	77.76	
Eu 152	.3296	.3253	.3239	.321	.3168	.3125	
Eu 154	16.53	16.36	16.3	16.18	16.01	15.83	
Eu 155	287.1	261.3	253.2	237.8	216.4	195.8	
Eu 156	5749	89.83	22.46	1.404	.0219	.0003	
Tb 160	2.364	1.006	.7566	.428	.1821	.0737	
Tb 161	42.05	.005	.0003	---	---	---	

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TABLE II-14 (Continued)
Activity, Curies Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	815.0	788.5	713.3	645.3	564.9	462.6	237.5
Rb 86	---	---	---	---	---	---	---
Sr 89	185.5	15.05	.008	---	---	---	---
Sr 90	6257	6180	5955	5738	5461	5070	3958
Y 91	614.6	69.30	.0993	.0001	---	---	---
Zr 95	1371	195.5	.5672	.0016	---	---	---
Nb 95	2961	423.8	1.23	.0036	---	---	---
Ru 103	18.27	.7473	.0001	---	---	---	---
Ru 106	6616	4678	1654	584.8	146.2	18.27	.0178
Ag 110m	.2346	.1441	.0334	.0078	.0011	.0001	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	.0112	.0006	---	---	---	---	---
Sn 123m	4.503	1.636	.0784	.0038	.0001	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	432.7	380.6	259	176.2	105.4	48.81	3.746
Te 125m	90.87	79.93	54.39	37.00	22.13	10.25	.7867
Sb 127	---	---	---	---	---	---	---
Te 127m	72.29	21.65	.5817	.0156	.0001	---	---
Te 129m	.3167	.0068	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	695.2	589.5	359.3	219	113.2	42.04	1.550
Cs 136	---	---	---	---	---	---	---
Cs 137	6709	6632	6406	6188	5909	5513	4376
Ba 140	---	---	---	---	---	---	---
Ce 141	4.007	.0815	---	---	---	---	---
Ce 144	46170	29610	7812	2061	348.7	24.27	.0034
Pr 143	---	---	---	---	---	---	---
Pm 146	.0036	.0034	.0029	.0024	.0018	.0013	.0004
Nd 147	---	---	---	---	---	---	---
Pm 147	15690	13740	9242	6215	3661	1655	117.5
Pm 148m	.4033	.0198	---	---	---	---	---
Pm 148	.037	.0018	---	---	---	---	---
Sm 151	77.46	77.16	76.27	75.4	74.25	72.55	67.17
Eu 152	.3042	.2962	.2735	.2524	.2269	.1934	.1135
Eu 154	15.49	15.16	14.21	13.31	12.21	10.72	6.951
Eu 155	161.7	133.5	75.16	42.32	19.67	6.237	.1355
Eu 156	---	---	---	---	---	---	---
Tb 160	.013	.0023	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-15
FISSION PRODUCT BETA HEAT FROM NATURAL URANIUM
640 MWd/T, 8.17 MW/T

Beta Heat, Watts Per Ton of Uranium						
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	.4027	.3968	.3946	.3903	.3840	.3773
Rb 86	.0385	.0014	.0005	---	---	---
Sr 89	649.3	188.3	124.7	54.62	15.84	4.274
Sr 90	12.78	13.06	13.03	12.98	12.90	12.82
Y 91	818.8	279.3	195.1	95.26	32.49	10.41
Zr 95	174.8	68.22	48.81	25.75	9.860	3.571
Nb 95	37.24	36.60	29.63	17.78	7.440	2.799
Ru 103	110.2	22.83	13.50	4.724	.9776	.1846
Ru 106	64.53	54.40	51.38	45.85	38.66	32.26
Ag 110m	.0002	.0002	.0002	.0001	.0001	.0001
Ag 111	6.986	.0017	.0001	---	---	---
Cd 115m	.1699	.0398	.0246	.0093	.0022	.0005
Sn 123m	.1341	.0816	.0690	.0495	.0301	.0177
Sn 125	6.154	.0081	.0009	---	---	---
Sb 125	.1408	.1391	.1362	.1306	.1226	.1146
Te 125m	.0217	.0368	.0361	.0346	.0325	.0303
Sb 127	67.36	---	---	---	---	---
Te 127m	2.025	1.239	1.016	.6839	.3776	.2013
Te 129m	71.79	10.85	5.778	1.638	.1474	.0334
I 131	401.4	.1773	.0140	.0001	---	---
Xe 131m	1.703	.0293	.0054	.0002	---	---
Te 132	919.9	---	---	---	---	---
Xe 133	401.0	.0030	.0001	---	---	---
Cs 134	.1650	.1521	.1481	.1403	.1293	.1186
Cs 136	.7872	.0065	.0013	.0001	---	---
Cs 137	3.286	3.267	3.261	3.248	3.230	3.211
Ba 140	1937	16.27	3.205	.1244	.0009	---
Ce 141	323.5	47.45	25.03	6.961	1.021	.1339
Ce 144	495.5	388.6	361.3	312.2	250.8	199.0
Pr 143	670.2	7.914	1.735	.0833	.0009	---
Pm 146	---	---	---	---	---	---
Nd 147	226.1	.8194	.1259	.0030	---	---
Pm 147	2.208	2.606	2.552	2.444	2.289	2.137
Pm 148m	1.242	.2811	.1714	.0637	.0144	.0030
Pm 148	19.02	.0707	.0430	.0160	.0036	.0008
Sm 151	.0031	.0033	.0033	.0033	.0033	.0033
Eu 152	---	---	---	---	---	---
Eu 154	.0046	.0045	.0045	.0045	.0044	.0044
Eu 155	.0730	.0664	.0643	.0604	.0550	.0498
Eu 156	10.99	.1717	.0429	.0027	---	---
Tb 160	.0013	.0005	.0004	.0002	.0001	---
Tb 161	.0625	---	---	---	---	---

TABLE II-15 (Continued)
Beta Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	.3650	.3530	.3194	.2890	.2530	.2071	.1063
Rb 86	---	---	---	---	---	---	---
Sr 89	.3468	.0281	---	---	---	---	---
Sr 90	12.66	12.50	12.04	11.61	11.05	10.26	8.008
Y 91	1.174	.1323	.0002	---	---	---	---
Zr 95	.5092	.0726	.0002	---	---	---	---
Nb 95	.4078	.0584	.0002	---	---	---	---
Ru 103	.0075	.0003	---	---	---	---	---
Ru 106	22.81	16.13	5.703	2.016	.5041	.0630	.0001
Ag 110m	.0001	---	---	---	---	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0064	.0023	.0001	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	.1008	.0887	.0603	.0410	.0246	.0114	.0009
Te 125m	.0267	.0235	.0160	.0109	.0065	.0030	.0002
Sb 127	---	---	---	---	---	---	---
Te 127m	.0602	.0180	.0005	---	---	---	---
Te 129m	.0007	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	.1006	.0853	.0520	.0317	.0164	.0061	.0002
Cs 136	---	---	---	---	---	---	---
Cs 137	3.174	3.137	3.030	2.927	2.795	2.608	2.070
Ba 140	---	---	---	---	---	---	---
Ce 141	.0027	.0001	---	---	---	---	---
Ce 144	127.6	84.84	21.59	5.695	.9637	.0671	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	1.872	1.640	1.103	.7416	.4369	.1975	.0140
Pm 148m	.0001	---	---	---	---	---	---
Pm 148	---	---	---	---	---	---	---
Sm 151	.0032	.0032	.0032	.0032	.0031	.0030	.0028
Eu 152	---	---	---	---	---	---	---
Eu 154	.0043	.0042	.0039	.0037	.0034	.0030	.0019
Eu 155	.0411	.0339	.0191	.0108	.0050	.0016	---
Eu 156	---	---	---	---	---	---	---
Tb 160	---	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-16
FISSION PRODUCT BETA HEAT FROM NATURAL URANIUM
750 MWd/T, 10 MW/T

		Beta Heat, Watts Per Ton of Uranium				
Nuclide		Discharge	90 d	120 d	180 d	270 d
Kr 85		.4634	.4566	.4541	.4492	.4419
Rb 86		.0525	.0019	.0006	.0001	---
Sr 89		766.2	222.2	147.1	64.45	18.69
Sr 90		14.71	15.02	15.00	14.94	14.83
Y 91		962.9	328.4	229.5	112.0	38.21
Zr 95		204.3	78.57	57.06	30.09	11.52
Nb 95		42.28	42.57	34.51	20.74	8.691
Ru 103		128.5	26.60	15.73	5.505	1.139
Ru 106		70.67	59.58	56.28	50.22	42.34
Ag 110m		.0003	.0002	.0002	.0002	.0001
Ag 111		7.673	.0019	.0001	---	---
Cd 115m		.1955	.0458	.0282	.0107	.0025
Sn 123m		.1523	.0925	.0783	.0561	.0341
Sn 125		7.099	.0093	.0010	---	---
Sb 125		.1584	.1566	.1534	.1470	.1380
Te 125m		.0024	.0041	.0040	.0039	.0036
Sb 127		78.35	---	---	---	---
Te 127m		2.333	1.428	1.172	.7885	.4351
Te 129m		84.19	12.72	6.775	1.921	.2901
I 131		471.1	.2080	.0157	.0001	---
Xe 131m		2.030	.0346	.0063	.0002	---
Te 132		1074	---	---	---	---
Xe 133		470.2	.0035	.0001	---	---
Cs 134		0.2296	.2117	.2060	.1951	.1799
Cs 136		0.8794	.0073	.0015	.0001	---
Cs 137		3.758	3.737	3.730	3.716	3.695
Ba 140		2304	19.32	3.806	.1477	.0011
Ce 141		381.4	55.95	29.51	8.207	1.204
Ce 144		575.1	448.1	416.5	360.1	289.2
Pr 143		798.0	9.409	2.062	.0991	.0010
Pm 146		---	---	---	---	---
Nd 147		267.9	.9708	.1491	.0035	---
Pm 147		2.488	2.968	2.907	2.783	2.608
Pm 148m		1.543	.3495	.2130	.0791	.0179
Pm 148		26.40	.0879	.0534	.0198	.0045
Sm 151		.0033	.0034	.0034	.0034	.0034
Eu 152		---	---	---	---	---
Eu 154		.0062	.0062	.0061	.0061	.0060
Eu 155		.0722	.0657	.0636	.0598	.0544
Eu 156		13.00	0.2031	.0508	.0032	---
Tb 160		.0016	.0007	.0005	.0003	.0001
Tb 161		.0675	---	---	---	---

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TABLE II-16 (Continued)
Beta Heat, Watts Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	.4343	.4063	.3326	.2384	.1224
Rb 86	---	---	---	---	---
Sr 89	5.043	.0332	---	---	---
Sr 90	14.75	14.39	13.36	11.80	9.216
Y 91	12.24	.1556	---	---	---
Zr 95	4.174	.0849	---	---	---
Nb 95	3.270	.0683	---	---	---
Ru 103	.2151	.0004	---	---	---
Ru 106	35.34	17.67	2.208	.0690	.0001
Ag 110m	.0001	---	---	---	---
Ag 111	---	---	---	---	---
Cd 115m	.0005	---	---	---	---
Sn 123m	.0201	.0027	---	---	---
Sn 125	---	---	---	---	---
Sb 125	.1291	.0998	.0463	.0128	.0010
Te 125m	.0034	.0026	.0012	.0003	---
Sb 127	---	---	---	---	---
Te 127m	.2322	.0208	---	---	---
Te 129m	.0392	---	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	.1650	.1186	.0441	.0085	.0003
Cs 136	---	---	---	---	---
Cs 137	3.673	3.589	3.348	2.983	2.368
Ba 140	---	---	---	---	---
Ce 141	.1579	.0001	---	---	---
Ce 144	229.4	94.37	6.569	.0773	---
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	---	---	---	---	---
Pm 147	2.434	1.868	.8447	.2250	.0160
Pm 148m	.0037	---	---	---	---
Pm 148	.0009	---	---	---	---
Sm 151	.0034	.0034	.0033	.0032	.0029
Eu 152	---	---	---	---	---
Eu 154	.0060	.0057	.0050	.0040	.0026
Eu 155	.0492	.0336	.0106	.0016	---
Eu 156	---	---	---	---	---
Tb 160	---	---	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-17
FISSION PRODUCT BETA HEAT FROM NATURAL URANIUM
900 MWd/T, 10 MW/T

		Beta Heat, Watts Per Ton of Uranium				
Nuclide		Discharge	90 d	120 d	180 d	270 d
Kr	85	.5487	.5407	.5377	.5313	.5234
Rb	86	.0648	.0023	.0008	.0001	---
Sr	89	832.3	241.4	159.8	70.01	20.30
Sr	90	17.58	17.80	17.76	17.69	17.58
Y	91	1057	360.5	251.9	123.0	41.95
Zr	95	227.1	87.32	60.86	33.44	12.81
Nb	95	52.40	48.22	38.86	23.20	9.684
Ru	103	141.1	29.20	17.28	6.044	1.251
Ru	106	89.06	75.08	70.92	63.29	53.35
Ag	110m	.0004	.0003	.0003	.0003	.0002
Ag	111	8.539	.0021	.0001	---	---
Cd	115m	.2198	.0515	.0318	.0121	.0028
Sn	123m	.1805	.1096	.0928	.0665	.0404
Sn	125	7.413	.0097	.0011	---	---
Sb	125	.1943	.1907	.1867	.1790	.1680
Te	125m	.0034	.0050	.0049	.0047	.0044
Sb	127	79.25	---	---	---	---
Te	127m	2.721	1.644	1.349	.9076	.5010
Te	129m	90.71	13.71	7.299	2.070	.3126
I	131	476.7	.2104	.0159	.0001	---
Xe	131m	2.102	.0353	.0064	.0002	---
Te	132	1075	---	---	---	---
Xe	133	470.6	.0035	.0001	---	---
Cs	134	.3342	.3082	.2999	.2841	.2619
Cs	136	1.014	.0084	.0017	.0001	---
Cs	137	4.492	4.467	4.458	4.441	4.416
Ba	140	2335	19.55	3.850	.1494	.0011
Ce	141	406.8	59.67	31.47	8.753	1.284
Ce	144	669.7	524.2	487.2	421.1	338.3
Pr	143	808.7	9.510	2.084	.1001	.0011
Pm	146	---	---	---	---	---
Nd	147	270.8	.9814	.1508	.0036	---
Pm	147	3.041	3.493	3.420	3.275	3.069
Pm	148m	1.948	.4411	.2688	.0999	.0226
Pm	148	32.81	.1109	.0674	.0250	.0057
Sm	151	.0035	.0037	.0037	.0037	.0037
Eu	152	---	---	---	---	---
Eu	154	.0091	.0090	.0089	.0089	.0088
Eu	155	.0808	.0735	.0713	.0669	.0609
Eu	156	14.86	.2321	.0580	.0036	.0001
Tb	160	.0023	.0010	.0007	.0004	.0002
Tb	161	.0771	---	---	---	---

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TABLE II-17 (Continued)
Beta Heat, Watts Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	.5140	.4809	.3937	.2821	.1449
Rb 86	---	---	---	---	---
Sr 89	5.478	.0361	---	---	---
Sr 90	17.47	17.05	15.82	13.98	10.92
Y 91	13.44	.1708	---	---	---
Zr 95	4.638	.0943	---	---	---
Nb 95	3.638	.0759	---	---	---
Ru 103	.2360	.0004	---	---	---
Ru 106	44.53	22.26	2.783	0.0870	.0001
Ag 110m	.0002	.0001	---	---	---
Ag 111	---	---	---	---	---
Cd 115m	.0006	---	---	---	---
Sn 123m	.0238	.0031	---	---	---
Sn 125	---	---	---	---	---
Sb 125	.1571	.1216	.0563	.0156	.0012
Te 125m	.0042	.0032	.0015	.0004	---
Sb 127	---	---	---	---	---
Te 127m	.2671	.0239	---	---	---
Te 129m	.0423	---	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	.2403	.1727	.0642	.0123	.0005
Cs 136	---	---	---	---	---
Cs 137	4.390	4.289	4.002	3.565	2.830
Ba 140	---	---	---	---	---
Ce 141	.1684	.0001	---	---	---
Ce 144	268.3	183.6	7.682	.0905	---
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	---	---	---	---	---
Pm 147	2.864	2.198	.9940	.2648	.0188
Pm 148m	.0047	---	---	---	---
Pm 148	.0012	---	---	---	---
Sm 151	.0037	.0036	.0036	.0034	.0032
Eu 152	---	---	---	---	---
Eu 154	.0087	.0083	.0073	.0059	.0038
Eu 155	.0551	.0376	.0191	.0018	---
Eu 156	---	---	---	---	---
Tb 160	.0001	---	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-18
FISSION PRODUCT BETA HEAT FROM 0.947% ENRICHED URANIUM
900 MWd/T, 9.7 MW/T

		Beta Heat, Watts Per Ton of Uranium					
Nuclide		Discharge	90 d	120 d	180 d	270 d	1 y
Kr	85	.5690	.5606	.5576	.5513	.5425	.5328
Rb	86	.0530	.0019	.0006	.0001	---	---
Sr	89	844.5	244.9	162.1	71.04	20.60	5.559
Sr	90	18.19	18.47	18.43	18.36	18.25	18.13
Y	91	1073	366.0	255.7	124.8	42.59	13.64
Zr	95	229.7	88.32	64.14	33.83	12.95	4.692
Nb	95	54.10	48.96	39.41	23.50	9.801	3.681
Ru	103	139.1	28.80	17.03	5.960	1.233	.2328
Ru	106	84.52	71.25	67.31	60.06	50.63	42.26
Ag	110m	.0003	.0002	.0002	.0002	.0002	.0001
Ag	111	7.732	.0019	.0001	---	---	---
Cd	115m	.2133	.0500	.0308	.0117	.0027	.0006
Sn	123m	.1776	.1078	.0913	.0654	.0397	.0234
Sn	125	7.191	.0094	.0010	---	---	---
Sb	125	.1943	.1904	.1864	.1787	.1678	.1569
Te	125m	.0367	.0504	.0494	.0473	.0444	.0415
Sb	127	79.49	---	---	---	---	---
Te	127m	2.737	1.652	1.356	.9125	.5038	.2686
Te	129m	89.77	13.56	7.224	2.049	.3093	.0418
I	131	477.8	.2110	.0159	.0001	---	---
Xe	131m	2.060	.0351	.0064	.0002	---	---
Te	132	1086	---	---	---	---	---
Xe	133	477.3	.0035	.0001	---	---	---
Cs	134	.2610	.2407	.2342	.2219	.2045	.1877
Cs	136	.9214	.0076	.0015	.0001	---	---
Cs	137	4.614	4.587	4.579	4.561	4.535	4.508
Ba	140	2338	19.61	3.862	.1499	.0011	---
Ce	141	406.1	59.56	31.41	8.737	1.282	.1681
Ce	144	682.9	537.8	500.0	432.1	347.1	275.3
Pr	143	811.7	9.564	2.096	.1007	.0011	---
Pm	146	---	---	---	---	---	---
Nd	147	271.6	.9843	.1512	.0036	---	---
Pm	147	3.181	3.626	3.550	3.399	3.185	2.972
Pm	148m	1.814	.4107	.2503	.0930	.0211	.0044
Pm	148	26.39	.1032	.0628	.0233	.0053	.0011
Sm	151	.0041	.0043	.0043	.0043	.0043	.0043
Eu	152	---	---	---	---	---	---
Eu	154	.0071	.0070	.0070	.0070	.0069	.0068
Eu	155	.0909	.0827	.0801	.0752	.0685	.0620
Eu	156	13.24	.2068	.0517	.0032	.0001	---
Tb	160	.0017	.0007	.0005	.0003	.0001	.0001
Tb	161	.0678	---	---	---	---	---

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TABLE II-18 (Continued)
Beta Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	.5153	.4987	.4513	.4084	.3574	.2926	.1503
Rb 86	---	---	---	---	---	---	---
Sr 89	.4510	.0366	---	---	---	---	---
Sr 90	17.91	17.69	17.05	16.42	15.63	14.50	11.33
Y 91	1.538	.1734	.0003	---	---	---	---
Zr 95	.6691	.0954	.0003	---	---	---	---
Nb 95	.5360	.0767	.0002	---	---	---	---
Ru 103	.0095	.0004	---	---	---	---	---
Ru 106	29.88	21.13	7.471	2.641	.6603	.0825	.0001
Ag 110m	.0001	---	---	---	---	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0085	.0031	.0001	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	.1380	.1214	.0826	.0562	.0336	.0156	.0012
Te 125m	.0365	.0321	.0219	.0149	.0089	.0041	.0003
Sb 127	---	---	---	---	---	---	---
Te 127m	.0804	.0241	.0006	---	---	---	---
Te 129m	.0009	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	.1591	.1349	.0822	.0501	.0259	.0096	.0004
Cs 136	---	---	---	---	---	---	---
Cs 137	4.456	4.405	4.255	4.110	3.925	3.662	2.906
Ba 140	---	---	---	---	---	---	---
Ce 141	.0034	.0001	---	---	---	---	---
Ce 144	176.6	113.3	29.88	7.884	1.333	.0928	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	2.604	2.282	1.534	1.032	.6078	.2748	.0195
Pm 148m	.0002	---	---	---	---	---	---
Pm 148	.0001	---	---	---	---	---	---
Sm 151	.0043	.0042	.0042	.0041	.0041	.0040	.0037
Eu 152	---	---	---	---	---	---	---
Eu 154	.0067	.0065	.0061	.0057	.0052	.0046	.0030
Eu 155	.0512	.0422	.0238	.0134	.0062	.0020	---
Eu 156	---	---	---	---	---	---	---
Tb 160	---	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-19
FISSION PRODUCT BETA HEAT FROM 0.947% ENRICHED URANIUM
1000 MWd/T, 10 MW/T

		Beta Heat, Watts Per Ton of Uranium				
Nuclide		Discharge	90 d	120 d	180 d	270 d
Kr 85		.6338	.6233	.6203	.6133	.6033
Rb 86		.0635	.0023	.0007	.0001	---
Sr 89	917.3		266.1	176.1	77.16	22.38
Sr 90	20.30		20.55	20.50	20.42	20.30
Y 91	1169		398.8	278.7	136.0	46.40
Zr 95	251.0		96.49	70.07	36.96	14.15
Nb 95	60.72		53.76	43.20	25.12	10.71
Ru 103	150.4		31.14	18.42	6.445	1.334
Ru 106	95.93		80.87	76.40	68.17	57.47
Ag 110m	.0004		.0003	.0003	.0003	.0002
Ag 111	8.622		.0021	.0001	---	---
Cd 115m	.2302		.0540	.0333	.0126	.0030
Sn 123m	.1962		.1191	.1009	.0723	.0439
Sn 125	7.708		.0101	.0011	---	---
Sb 125	.2195		.2146	.2102	.2015	.1891
Te 125m	.0387		.0568	.0556	.0534	.0501
Sb 127	82.83		---	---	---	---
Te 127m	3.035		1.824	1.496	1.007	.5558
Te 129m	97.18		14.68	7.819	2.217	.3349
I 131	503.1		.2220	.0168	.0001	---
Xe 131m	2.235		.0373	.0068	.0002	---
Te 132	1124		---	---	---	---
Xe 133	495.4		.0036	.0001	---	---
Cs 134	.3431		.3163	.3079	.2916	.2688
Cs 136	1.070		.0088	.0018	.0001	---
Cs 137	5.131		5.102	5.092	5.073	5.044
Ba 140	2473		20.69	4.075	.1581	.0012
Ce 141	438.4		64.30	33.91	9.432	1.384
Ce 144	755.4		595.0	553.1	477.0	384.0
Pr 143	859.6		10.10	2.214	.1063	.0011
Pm 146	---		---	---	---	---
Nd 147	284.4		1.031	.1583	.0037	---
Pm 147	3.523		3.977	3.894	3.729	3.493
Pm 148m	2.146		.4859	.2961	.1100	.0249
Pm 148	31.80		.1221	.0742	.0276	.0062
Sm 151	.0043		.0044	.0044	.0044	.0044
Eu 152	.0001		.0001	.0001	.0001	.0001
Eu 154	.0090		.0089	.0089	.0088	.0087
Eu 155	.0960		.0874	.0847	.0795	.0723
Eu 156	14.76		.2307	.0577	.0036	.0001
Tb 160	.0022		.0009	.0007	.0004	.0002
Tb 161	.0759		---	---	---	---

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TABLE II-19 (Continued)

Beta Heat, Watts Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	.5928	.5552	.4542	.3255	.1671
Rb 86	---	---	---	---	---
Sr 89	6.038	.0398	---	---	---
Sr 90	20.16	19.68	18.26	16.14	12.60
Y 91	14.87	.1890	---	---	---
Zr 95	5.125	.1043	---	---	---
Nb 95	4.022	.0838	---	---	---
Ru 103	.2518	.0004	---	---	---
Ru 106	47.97	23.98	2.998	.0937	.0001
Ag 110m	.0002	.0001	---	---	---
Ag 111	---	---	---	---	---
Cd 115m	.0006	---	---	---	---
Sn 123m	.0259	.0034	---	---	---
Sn 125	---	---	---	---	---
Sb 125	.1769	.1368	.0633	.0176	.0013
Te 125m	.0468	.0362	.0168	.0046	.0004
Sb 127	---	---	---	---	---
Te 127m	.2963	.0266	---	---	---
Te 129m	.0453	---	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	.2467	.1773	.0659	.0126	.0005
Cs 136	---	---	---	---	---
Cs 137	5.014	4.899	4.571	4.073	3.232
Ba 140	---	---	---	---	---
Ce 141	.1814	.0001	---	---	---
Ce 144	304.6	125.3	8.720	.1027	---
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	---	---	---	---	---
Pm 147	3.260	2.502	1.132	.3014	.0214
Pm 148m	.0052	---	---	---	---
Pm 148	.0013	---	---	---	---
Sm 151	.0044	.0044	.0043	.0041	.0038
Eu 152	.0001	---	---	---	---
Eu 154	.0086	.0083	.0073	.0058	.0038
Eu 155	.0655	.0446	.0142	.0021	---
Eu 156	---	---	---	---	---
Tb 160	.0001	---	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-20
FISSION PRODUCT BETA HEAT FROM 0.947% ENRICHED URANIUM
1200 MWd/T, 10 MW/T

		Beta Heat, Watts Per Ton of Uranium				
Nuclide		Discharge	90 d	120 d	180 d	270 d
Kr 85		.7522	.7406	.7365	.7278	.7166
Rb 86		.0778	.0028	.0009	.0001	---
Sr 89		978.9	283.9	187.9	82.34	23.88
Sr 90		24.30	24.42	24.37	24.27	24.12
Y 91		1263	430.7	300.9	146.9	50.11
Zr 95		275.1	105.8	76.78	40.49	15.50
Nb 95		73.23	60.03	47.96	28.37	11.77
Ru 103		162.8	33.71	19.94	6.976	1.444
Ru 106		121.7	102.6	96.93	86.50	72.92
Ag 110m		.0007	.0005	.0005	.0004	.0003
Ag 111		9.618	.0023	.0001	---	---
Cd 115m		.2560	.0600	.0370	.0140	.0033
Sn 123m		.2318	.1407	.1191	.0854	.0519
Sn 125		8.056	.0106	.0012	---	---
Sb 125		.2702	.2626	.2571	.2465	.2314
Te 125m		.0636	.0695	.0681	.0653	.0613
Sb 127		84.20	---	---	---	---
Te 127m		3.502	2.083	1.708	1.150	.6348
Te 129m		103.1	15.58	8.297	2.352	.3553
I 131		509.0	.2245	.0170	.0001	---
Xe 131m		2.289	.0379	.0069	.0002	---
Te 132		1130	---	---	---	---
Xe 133		496.7	.0037	.0001	---	---
Cs 134		.4999	.4609	.4486	.4249	.3917
Cs 136		1.233	.0102	.0021	.0001	---
Cs 137		6.159	6.125	6.113	6.090	6.055
Ba 140		2492	20.82	4.101	.1592	.0012
Ce 141		459.7	67.44	35.56	9.892	1.451
Ce 144		879.5	694.6	645.8	558.1	448.3
Pr 143		864.3	10.14	2.223	.1068	.0011
Pm 146		---	---	---	---	---
Nd 147		286.6	1.039	.1595	.0038	---
Pm 147		4.276	4.688	4.589	4.394	4.117
Pm 148m		2.681	.6070	.3699	.1374	.0311
Pm 148		39.17	.1525	.0928	.0344	.0078
Sm 151		.0046	.0048	.0048	.0048	.0048
Eu 152		.0001	.0001	.0001	.0001	.0001
Eu 154		.0132	.0131	.0130	.0130	.0128
Eu 155		.1082	.0983	.0953	.0895	.0814
Eu 156		16.81	.2626	.0656	.0041	.0001
Tb 160		.0032	.0014	.0010	.0006	.0002
Tb 161		.0869	---	---	---	---

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TABLE II-20 (Continued)
Beta Heat, Watts Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	.7041	.6585	.5397	.3864	.1984
Rb 86	---	---	---	---	---
Sr 89	6.444	.0424	---	---	---
Sr 90	23.97	23.38	21.71	19.18	14.98
Y 91	16.05	.2041	---	---	---
Zr 95	5.616	.1142	---	---	---
Nb 95	4.412	.0919	---	---	---
Ru 103	.2725	.0005	---	---	---
Ru 106	60.86	30.43	3.804	.1189	.0001
Ag 110m	.0002	.0001	---	---	---
Ag 111	---	---	---	---	---
Cd 115m	.0007	---	---	---	---
Sn 123m	.0306	.0040	---	---	---
Sn 125	---	---	---	---	---
Sb 125	.2164	.1674	.0775	.0215	.0016
Te 125m	.0573	.0443	.0205	.0057	.0004
Sb 127	---	---	---	---	---
Te 127m	.3384	.0303	---	---	---
Te 129m	.0480	---	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	.3594	.2584	.0960	.0184	.0007
Cs 136	---	---	---	---	---
Cs 137	6.019	5.881	5.487	4.889	3.880
Ba 140	---	---	---	---	---
Ce 141	.1903	.0001	---	---	---
Ce 144	355.6	146.3	10.18	.1198	---
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	---	---	---	---	---
Pm 147	3.843	2.949	1.334	.3553	.0252
Pm 148m	.0065	---	---	---	---
Pm 148	.0016	---	---	---	---
Sm 151	.0048	.0047	.0046	.0045	.0041
Eu 152	.0001	.0001	.0001	---	---
Eu 154	.0127	.0121	.0106	.0086	.0056
Eu 155	.0737	.0502	.0159	.0023	.0001
Eu 156	---	---	---	---	---
Tb 160	.0001	---	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-21
FISSION PRODUCT BETA HEAT FROM 0.847% ENRICHED URANIUM
2200 MWd/T, 11 MW/T

		Beta Heat, Watts Per Ton of Uranium				
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	1.289	1.268	1.261	1.248	1.227	1.206
Rb 86	.1589	.0057	.0019	.0002	---	---
Sr 89	1101	319.4	211.4	92.64	26.87	7.250
Sr 90	42.53	42.04	41.96	41.79	41.54	41.27
Y 91	1482	505.4	353.2	172.4	58.81	18.84
Zr 95	346.5	133.1	96.64	50.97	19.52	7.068
Nb 95	112.6	78.99	62.26	36.29	14.91	5.568
Ru 103	214.1	44.32	26.22	9.172	1.898	.3581
Ru 106	296.1	249.6	235.8	210.4	177.4	148.0
Ag 110m	.0032	.0025	.0023	.0020	.0015	.0012
Ag 111	16.29	.0040	.0002	---	---	---
Cd 115m	.3834	.0899	.0554	.0211	.0049	.0011
Sn 123m	.4173	.2533	.2145	.1538	.0934	.0550
Sn 125	10.73	.0141	.0015	---	---	---
Sb 125	.5604	.5380	.5268	.5051	.4741	.4434
Te 125m	.1483	.1425	.1395	.1337	.1256	.1174
Sb 127	99.71	---	---	---	---	---
Te 127m	5.381	3.146	2.580	1.736	.9587	.5112
Te 129m	126.3	19.06	10.15	2.879	.4348	.0588
I 131	583.4	.2568	.0194	.0001	---	---
Xe 131m	2.645	.0435	.0079	.0003	---	---
Te 132	1283	---	---	---	---	---
Xe 133	530.5	.0041	.0001	---	---	---
Cs 134	2.233	2.059	2.003	1.898	1.750	1.605
Cs 136	2.346	.0193	.0039	.0002	---	---
Cs 137	11.33	11.26	11.24	11.20	11.13	11.07
Ba 140	2934	22.79	4.491	.1743	.0013	---
Ce 141	528.3	77.50	40.87	11.37	1.667	.2186
Ce 144	1409	1116	1038	897.1	720.8	571.7
Pr 143	930.0	10.90	2.390	.1148	.0012	---
Pm 145	---	---	---	---	---	---
Nd 147	321.0	1.163	.1787	.0042	---	---
Pm 147	7.376	7.674	7.512	7.193	6.739	6.290
Pm 148m	6.335	1.434	.8743	.3248	.0735	.0153
Pm 148	92.89	.3605	.2192	.0814	.0184	.0038
Sm 151	.0064	.0066	.0066	.0066	.0065	.0065
Eu 152	.0002	.0002	.0002	.0002	.0002	.0002
Eu 154	.0580	.0574	.0572	.0567	.0561	.0555
Eu 155	.1832	.1667	.1616	.1517	.1380	.1249
Eu 156	29.33	.4583	.1146	.0072	.0001	---
Tb 160	.0158	.0067	.0051	.0029	.0012	.0005
Tb 161	.1609	---	---	---	---	---

TABLE II-21 (Continued)
Beta Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	1.167	1.128	1.021	.9241	0.8090	.6119	.3400
Rb 86	---	---	---	---	---	---	---
Sr 89	.5882	.0477	---	---	---	---	---
Sr 90	40.76	40.25	38.79	37.38	35.57	33.03	25.78
Y 91	2.124	.2395	.0003	---	---	---	---
Zr 95	1.008	.1438	.0004	---	---	---	---
Nb 95	.8081	.1156	.0003	---	---	---	---
Ru 103	.0147	.0006	---	---	---	---	---
Ru 106	104.7	74.02	26.17	9.252	2.313	.2891	.0003
Ag 110m	.0007	.0005	.0001	---	---	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	.0001	---	---	---	---	---	---
Sn 123m	.0200	.0073	.0003	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	.3900	.3430	.2334	.1588	.0950	.0440	.0034
Te 125m	.1032	.0908	.0618	.0420	.0252	.0116	.0009
Sb 127	---	---	---	---	---	---	---
Te 127m	.1530	.0458	.0012	---	---	---	---
Te 129m	.0012	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	1.361	1.154	.7033	.4287	.2215	.0823	.0030
Cs 136	---	---	---	---	---	---	---
Cs 137	10.94	10.81	10.45	10.09	9.635	8.989	7.135
Ba 140	---	---	---	---	---	---	---
Ce 141	.0044	.0001	---	---	---	---	---
Ce 144	366.7	235.2	62.04	16.37	2.769	.1927	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	5.510	4.827	3.246	2.183	1.286	.5815	.0413
Pm 148m	.0007	---	---	---	---	---	---
Pm 148	.0002	---	---	---	---	---	---
Sm 151	.0065	.0065	.0064	.0063	.0062	.0061	.0056
Eu 152	.0002	.0002	.0002	.0002	.0001	.0001	.0001
Eu 154	.0543	.0532	.0498	.0467	.0428	.0376	.0244
Eu 155	.1032	.0852	.0480	.0270	.0126	.0040	.0001
Eu 156	---	---	---	---	---	---	---
Tb 160	.0001	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-22
FISSION PRODUCT BETA HEAT FROM 1.25% ENRICHED URANIUM
2200 MWd/T, 11 MW/T

Nuclide	Discharge	Beta Heat, Watts Per Ton of Uranium				
		90 d	120 d	180 d	270 d	1 y
Kr 85	1.341	1.320	1.312	1.298	1.277	1.255
Rb 86	.1336	.0048	.0016	.0002	---	---
Sr 89	1166	338.1	223.8	98.06	28.44	7.674
Sr 90	44.10	43.79	43.69	43.52	43.26	42.98
Y 91	1554	530.2	370.4	180.8	61.69	19.76
Zr 95	352.9	135.6	98.41	51.90	19.88	7.198
Nb 95	114.4	80.40	63.38	36.95	15.19	5.670
Ru 103	201.2	41.65	24.64	8.619	1.784	.3467
Ru 106	233.4	196.7	185.9	165.8	139.8	116.7
Ag 110m	.0018	.0014	.0013	.0011	.0009	.0007
Ag 111	12.23	.0030	.0002	---	---	---
Cd 115m	.3382	.0793	.0489	.0186	.0044	.0009
Sn 123m	.3691	.2241	.1897	.1360	.0826	.0487
Sn 125	9.434	.0124	.0014	---	---	---
Sb 125	.5061	.4856	.4755	.4559	.4279	.4002
Te 125m	.1276	.1286	.1259	.1207	.1133	.1060
Sb 127	95.00	---	---	---	---	---
Te 127m	5.193	3.035	2.489	1.675	.9248	.4931
Te 129m	121.5	18.35	9.769	2.770	.4183	.0566
I 131	565.9	.2494	.0188	.0001	---	---
Xe 131m	2.575	.0423	.0077	.0002	---	---
Te 132	1249	---	---	---	---	---
Xe 133	545.9	.0040	.0001	---	---	---
Cs 134	1.786	1.647	1.603	1.518	1.399	1.284
Cs 136	1.893	.0156	.0032	.0001	---	---
Cs 137	11.28	11.22	11.20	11.15	11.09	11.02
Ba 140	2731	22.95	4.519	.1754	.0013	---
Ce 141	527.9	77.44	40.84	11.36	1.666	.2185
Ce 144	1429	1136	1056	912.9	733.4	581.7
Pr 143	948.1	11.11	2.436	.1170	.0012	---
Pm 146	---	---	---	---	---	---
Nd 147	319.4	1.158	.1778	.0042	---	---
Pm 147	7.609	7.888	7.721	7.393	6.927	6.465
Pm 148m	6.202	1.404	.8559	.3180	.0720	.0150
Pm 148	79.52	.3528	.2146	.0797	.0180	.0037
Sm 151	.0071	.0073	.0073	.0073	.0073	.0073
Eu 152	.0002	.0002	.0002	.0002	.0002	.0002
Eu 154	.0433	.0428	.0426	.0424	.0419	.0414
Eu 155	.1729	.1573	.1524	.1431	.1303	.1179
Eu 156	22.79	.3560	.0890	.0056	.0001	---
Tb 160	.0098	.0042	.0031	.0018	.0007	.0003
Tb 161	.1152	---	---	---	---	---

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TABLE II-22 (Continued)
Beta Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	1.214	1.174	1.062	.9616	.8416	.6891	.3537
Rb 86	---	---	---	---	---	---	---
Sr 89	.6226	.0505	---	---	---	---	---
Sr 90	42.44	41.92	40.40	38.92	37.04	34.39	26.85
Y 91	2.228	.2512	.0004	---	---	---	---
Zr 95	1.027	.1464	.0004	---	---	---	---
Nb 95	.8229	.1177	.0003	---	---	---	---
Ru 103	.0138	.0006	---	---	---	---	---
Ru 106	82.51	58.34	20.63	7.293	1.823	.2279	.0002
Ag 110m	.0004	.0003	.0001	---	---	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0177	.0064	.0003	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	.3520	.3096	.2107	.1433	.0858	.0397	.0030
Te 125m	.0932	.0820	.0558	.0380	.0227	.0105	.0008
Sb 127	---	---	---	---	---	---	---
Te 127m	.1476	.0442	.0012	---	---	---	---
Te 129m	.0012	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	1.089	.9231	.5626	.3429	.1772	.0658	.0024
Cs 136	---	---	---	---	---	---	---
Cs 137	10.90	10.77	10.40	10.05	9.596	8.954	7.107
Ba 140	---	---	---	---	---	---	---
Ce 141	.0044	.0001	---	---	---	---	---
Ce 144	373.1	239.3	63.13	16.65	2.818	.1961	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	5.664	4.962	3.337	2.244	1.322	.5977	.0424
Pm 148m	.0007	---	---	---	---	---	---
Pm 148	.0002	---	---	---	---	---	---
Sm 151	.0073	.0072	.0071	.0071	.0070	.0068	.0063
Eu 152	.0002	.0002	.0002	.0002	.0002	.0001	.0001
Eu 154	.0405	.0397	.0372	.0348	.0320	.0280	.0182
Eu 155	.0973	.0804	.0452	.0255	.0118	.0038	.0001
Eu 156	---	---	---	---	---	---	---
Tb 160	.0001	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-23
FISSION PRODUCT BETA HEAT FROM 2.1% ENRICHED URANIUM
2100 MWd/T, 10.6 MW/T

		Beta Heat, Watts Per Ton of Uranium				
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	1.334	1.313	1.306	1.291	1.270	1.248
Rb 86	.0826	.0029	.0010	.0001	---	---
Sr 89	1194	346.3	229.2	100.4	29.13	7.859
Sr 90	43.58	43.58	43.49	43.31	43.06	42.78
Y 91	1576	537.5	375.5	183.3	62.53	20.03
Zr 95	346.2	132.9	96.56	50.93	19.50	7.063
Nb 95	111.6	78.78	67.13	36.24	14.9	5.563
Ru 103	178.9	37.04	21.91	7.665	1.585	.2993
Ru 106	155.3	130.9	123.7	110.4	93.03	77.65
Ag 110m	.0006	.0004	.0004	.0004	.0003	.0002
Ag 111	6.993	.0017	.0001	---	---	---
Cd 115m	.274	.0642	.0396	.0150	.0035	.0008
Sn 123m	.3008	.1826	.1546	.1108	.0673	.0397
Sn 125	7.57	.0099	.0011	---	---	---
Sb 125	.4246	.407	.3985	.382	.3586	.3354
Te 125m	.0803	.1078	.1055	.1012	.0950	.0888
Sb 127	55.63	---	---	---	---	---
Te 127m	4.773	2.785	2.285	1.538	.849	.4527
Te 129m	111.4	16.84	8.966	2.542	.3839	.0518
I 131	525.2	.232	.0175	.0001	---	---
Xe 131m	2.4	.0393	.0072	.0002	---	---
Te 132	1165	---	---	---	---	---
Xe 133	521.6	.0038	.0001	---	---	---
Cs 134	1.014	.935	.9100	.862	.7946	.7291
Cs 136	1.227	.0101	.002	.0001	---	---
Cs 137	10.70	10.64	10.62	10.58	10.52	10.46
Ba 140	2670	22.28	4.39	.1704	.0013	---
Ce 141	507.9	74.50	39.29	10.93	1.603	.2102
Ce 144	1387	1107	1029	889.3	714.4	566.7
Pr 143	935.1	10.96	2.402	.1154	.0012	---
Pm 146	---	---	---	---	---	---
Nd 147	306.1	1.109	.1704	.004	---	---
Pm 147	7.628	7.875	7.708	7.380	6.915	6.454
Pm 148m	5.253	1.189	.7249	.2693	.061	.0127
Pm 148	50.75	.2986	.1817	.0675	.0153	.0032
Sm 151	.0091	.0093	.0093	.0092	.0092	.0092
Eu 152	.0002	.0002	.0102	.0002	.0002	.0002
Eu 154	.0225	.0223	.0222	.022	.0218	.0216
Eu 155	.1702	.1549	.1501	.1409	.1282	.1161
Eu 156	14.31	.2236	.0559	.0035	---	---
Tb 160	.0038	.0016	.0012	.0007	.0002	.0001
Tb 161	.0573	---	---	---	---	---

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TABLE II-23 (Continued)

Beta Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	1.208	1.168	1.057	.9564	0.8368	.6857	.3520
Rb 86	---	---	---	---	---	---	---
Sr 89	.6376	.0517	---	---	---	---	---
Sr 90	42.25	41.74	40.21	38.74	36.87	34.24	26.73
Y 91	2.259	.2547	.0004	---	---	---	---
Zr 95	1.0073	.1437	.0004	---	---	---	---
Nb 95	.8075	.1155	.0003	---	---	---	---
Ru 103	.0122	.0005	---	---	---	---	---
Ru 106	54.91	38.82	13.73	4.853	1.213	.1517	.0001
Ag 110m	.0001	.0001	---	---	---	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0144	.0052	.0002	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	.295	.2595	.1765	.1201	.0719	.0333	.0026
Te 125m	.0781	.0687	.0467	.0318	.0190	.0088	.0007
Sb 127	---	---	---	---	---	---	---
Te 127m	.1355	.0406	.0011	---	---	---	---
Te 129m	.0011	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	.6182	.5241	.3195	.1947	.1006	.0374	.0014
Cs 136	---	---	---	---	---	---	---
Cs 137	10.34	10.22	9.873	9.537	9.106	8.496	6.744
Ba 140	---	---	---	---	---	---	---
Ce 141	.0043	.0001	---	---	---	---	---
Ce 144	363.4	233.1	61.49	16.23	2.746	.1911	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	5.654	4.953	3.331	2.240	1.320	.5966	.0423
Pm 148m	.0006	---	---	---	---	---	---
Pm 148	.0002	---	---	---	---	---	---
Sm 151	.0092	.0091	.009	.0089	.0088	.0086	.0080
Eu 152	.0002	.0002	.0002	.0002	.0002	.0001	.0001
Eu 154	.0211	.0207	.0194	.0182	.0166	.0146	.0095
Eu 155	.0958	.0791	.0446	.025	.0117	.0037	.0001
Eu 156	---	---	---	---	---	---	---
Tb 160	---	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-24
FISSION PRODUCT GAMMA HEAT FROM NATURAL URANIUM
640 MWd/T, 8.17 MW/T

		Gamma Heat, Watts Per Ton of Uranium				
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	.0081	.0079	.0079	.0078	.0077	.0075
Rb 86	.0056	.0002	.0001	---	---	---
Sr 89	.2239	.0649	.0430	.0188	.0055	.0015
Sr 90	---	---	---	---	---	---
Y 91	---	---	---	---	---	---
Zr 95	1025	392.5	285.1	150.3	57.58	20.85
Nb 95	612.8	602.3	487.5	292.5	122.4	46.05
Ru 103	492.9	102.0	60.33	21.10	4.368	.8245
Ru 106	11.80	9.947	9.396	8.385	7.068	5.900
Ag 110m	.0064	.0050	.0046	.0039	.0031	.0024
Ag 111	.4343	.0001	---	---	---	---
Cd 115m	.0051	.0012	.0007	.0003	.0001	---
Sn 123m	.0055	.0033	.0028	.0020	.0012	.0007
Sn 125	.6617	.0009	.0001	---	---	---
Sb 125	.4813	.4753	.4654	.4462	.4188	.3917
Te 125m	---	---	---	---	---	---
Sb 127	50.44	---	---	---	---	---
Te 127m	.0252	.0154	.0126	.0085	.0047	.0025
Te 129m	35.19	5.323	2.834	.8038	.1214	.0164
I 131	448.6	.1981	.0150	.0001	---	---
Xe 131m	.0536	.0009	.0002	---	---	---
Te 132	4662	---	---	---	---	---
Xe 133	80.20	.0006	---	---	---	---
Cs 134	1.738	1.603	1.560	1.477	1.362	1.250
Cs 136	17.82	.1468	.0297	.0012	---	---
Cs 137	7.077	7.036	7.023	6.996	6.957	6.915
Ba 140	6075	53.30	10.50	.4074	.0031	---
Ce 141	125.8	18.45	9.732	2.707	.3970	.0521
Ce 144	62.95	50.32	46.78	41.43	32.48	25.76
Pr 143	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---
Nd 147	177.7	.6438	.0989	.0023	---	---
Pm 147	---	---	---	---	---	---
Pm 148m	9.455	2.141	1.305	.4848	.1098	.0228
Pm 148	17.14	.0637	.0387	.0144	.0033	.0007
Sm 151	---	---	---	---	---	---
Eu 152	.0003	.0002	.0002	.0002	.0002	.0002
Eu 154	.0251	.0248	.0248	.0246	.0243	.0240
Eu 155	.0168	.0153	.0148	.0139	.0126	.0114
Eu 156	34.01	.5315	.1329	.0083	.0001	---
Tb 160	.0052	.0022	.0017	.0009	.0004	.0002
Tb 161	.0001	---	---	---	---	---

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TABLE II-24 (Continued)
Gamma Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	.0073	.0071	.0064	.0058	.0051	.0041	.0021
Rb 86	---	---	---	---	---	---	---
Sr 89	.0001	---	---	---	---	---	---
Sr 90	---	---	---	---	---	---	---
Y 91	---	---	---	---	---	---	---
Zr 95	2.974	.4241	.0012	---	---	---	---
Nb 95	6.711	.9611	.0028	---	---	---	---
Ru 103	.0337	.0014	---	---	---	---	---
Ru 106	4.172	2.950	1.043	.3687	.0922	.0115	---
Ag 110m	.0015	.0009	.0002	---	---	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0003	.0001	---	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	.3445	.3030	.2062	.1403	.0840	.0389	.0030
Te 125m	---	---	---	---	---	---	---
Sb 127	---	---	---	---	---	---	---
Te 127m	.0007	.0002	---	---	---	---	---
Te 129m	.0004	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	1.060	.8984	.5476	.3337	.1725	.0641	.0024
Cs 136	---	---	---	---	---	---	---
Cs 137	6.835	6.757	6.527	6.305	6.020	5.617	4.458
Ba 140	---	---	---	---	---	---	---
Ce 141	.0011	---	---	---	---	---	---
Ce 144	16.52	10.60	2.796	.7376	.1248	.0087	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	---	---	---	---	---	---	---
Pm 148m	.0011	.0001	---	---	---	---	---
Pm 148	---	---	---	---	---	---	---
Sm 151	---	---	---	---	---	---	---
Eu 152	.0002	.0002	.0002	.0002	.0002	.0001	.0001
Eu 154	.0235	.0230	.0216	.0202	.0185	.0163	.0106
Eu 155	.0094	.0078	.0044	.0025	.0012	.0004	---
Eu 156	---	---	---	---	---	---	---
Tb 160	---	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-25
FISSION PRODUCT GAMMA HEAT FROM NATURAL URANIUM

750 MWd/T, 10 MW/T

		Gamma Heat, Watts Per Ton of Uranium				
Nuclide		Discharge	90 d	120 d	180 d	270 d
Kr 85		.0092	.0091	.0091	.0090	.0088
Rb 86		.0077	.0003	.0001	---	---
Sr 89		.2642	.0766	.0507	.0222	.0064
Sr 90		---	---	---	---	---
Y 91		---	---	---	---	---
Zr 95	1198		458.8	333.2	175.7	67.30
Nb 95	695.9		700.5	568.0	341.3	143.0
Ru 103	57.54		119.0	70.44	24.59	5.090
Ru 106	12.92		10.89	10.29	9.184	7.742
Ag 110m		.0079	.0062	.0057	.0049	.0038
Ag 111		.4770	.0001	---	---	---
Cd 115m		.0059	.0014	.0008	.0003	.0001
Sn 123m		.0062	.0038	.0032	.0023	.0014
Sn 125		.7633	.0010	.0001	---	---
Sb 125		.5414	.5352	.5241	.5025	.4717
Te 125m	---	---	---	---	---	---
Sb 127	58.66		---	---	---	---
Te 127m		.0290	.0178	.0146	.0098	.0054
Te 129m	41.28		6.241	3.324	.9425	.1423
I 131	526.5		.2325	.0176	.0001	---
Xe 131m	0.0638		.0011	.0002	---	---
Te 132	5445		---	---	---	---
Xe 133	94.03		.0007	---	---	---
Cs 134	2.418		2.229	2.170	2.055	1.895
Cs 136	19.91		.1640	.0331	.0014	---
Cs 137	8.095		8.049	8.034	8.003	7.958
Ba 140	7229		63.27	12.46	.4837	.0037
Ce 141	148.3		21.76	11.47	3.192	.4681
Ce 144	72.69		58.04	53.95	46.62	37.46
Pr 143	---		---	---	---	---
Pm 146	---		---	---	---	---
Nd 147	210.5		.7628	.1172	.0028	---
Pm 147	---		---	---	---	---
Pm 148m	11.75		2.661	1.622	.6026	.1364
Pm 148	23.80		.0792	.0481	.0179	.0040
Sm 151	---		---	---	---	---
Eu 152		.0003	.0003	.0003	.0003	.0003
Eu 154		.0341	.0337	.0336	.0334	.0330
Eu 155		.0166	.0151	.0146	.0138	.0125
Eu 156	40.24		.6287	.1572	.0098	.0002
Tb 160		.0069	.0030	.0022	.0013	.0005
Tb 161		.0001	---	---	---	---

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TABLE II-25 (Continued)

Gamma Heat, Watts Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	.0087	.0081	.0066	.0047	.0024
Rb 86	---	---	---	---	---
Sr 89	.0017	---	---	---	---
Sr 90	---	---	---	---	---
Y 91	---	---	---	---	---
Zr 95	24.37	.4958	---	---	---
Nb 95	53.82	1.123	---	---	---
Ru 103	.9609	.0016	---	---	---
Ru 106	6.461	3.231	.4038	.0126	---
Ag 110m	.0030	.0011	.0001	---	---
Ag 111	---	---	---	---	---
Cd 115m	---	---	---	---	---
Sn 123m	.0008	.0001	---	---	---
Sn 125	---	---	---	---	---
Sb 125	.4411	.3412	.1580	.0438	.0034
Te 125m	---	---	---	---	---
Sb 127	---	---	---	---	---
Te 127m	.0029	.0003	---	---	---
Te 129m	.0192	---	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	1.739	1.250	.4643	.0891	.0033
Cs 136	---	---	---	---	---
Cs 137	7.910	7.729	7.212	6.425	5.099
Ba 140	---	---	---	---	---
Ce 141	.0614	---	---	---	---
Ce 144	29.72	12.23	.8507	.0100	---
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	---	---	---	---	---
Pm 147	---	---	---	---	---
Pm 148m	.0283	.0001	---	---	---
Pm 148	.0008	---	---	---	---
Sm 151	---	---	---	---	---
Eu 152	.0003	.0002	.0002	.0002	.0001
Eu 154	.0326	.0313	.0275	.0221	.0143
Eu 155	.0113	.0077	.0024	.0004	---
Eu 156	---	---	---	---	---
Tb 160	.0002	---	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-26
FISSION PRODUCT GAMMA HEAT FROM NATURAL URANIUM
900 MWd/T, 10 MW/T

Gamma Heat, Watts Per Ton of Uranium					
Nuclide	Discharge	90 d	120 d	180 d	270 d
Kr 85	.0110	.0108	.0107	.0106	.0104
Rb 86	.0095	.0003	.0001	---	---
Sr 89	.2870	.0832	.0551	.0241	.0070
Sr 90	---	---	---	---	---
Y 91	---	---	---	---	---
Zr 95	1331	509.9	370.3	195.3	74.79
Nb 95	862.3	793.5	639.5	381.9	159.4
Ru 103	630.6	130.5	77.19	27.01	5.588
Ru 106	16.29	13.73	12.97	11.57	9.756
Ag 110m	.0124	.0097	.0090	.0077	.0060
Ag 111	.5308	.0001	---	---	---
Cd 115m	.0066	.0015	.0010	.0004	.0001
Sn 123m	.0074	.0045	.0038	.0027	.0016
Sn 125	.7971	.0010	.0001	---	---
Sb 125	.6640	.6516	.6380	.6117	.5742
Te 125m	---	---	---	---	---
Sb 127	59.14	---	---	---	---
Te 127m	.0338	.0204	.0168	.0113	.0062
Te 129m	44.48	6.724	3.581	1.015	.1533
I 131	532.8	.2351	.0178	.0001	---
Xe 131m	.0661	.0011	.0002	---	---
Te 132	5447	---	---	---	---
Xe 133	94.11	.0007	---	---	---
Cs 134	3.521	3.246	3.159	2.992	2.759
Cs 136	22.96	.1892	.0382	.0016	---
Cs 137	9.675	9.621	9.602	9.566	9.512
Ba 140	7319	64.00	12.60	.4892	.0037
Ce 141	158.2	23.21	12.24	3.404	.4993
Ce 144	84.94	67.88	63.10	54.54	43.81
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	212.8	.7711	.1184	.0028	---
Pm 147	---	---	---	---	---
Pm 148m	14.83	3.359	2.047	.7606	.1722
Pm 148	29.58	.1000	.0608	.0226	.0051
Sm 151	---	---	---	---	---
Eu 152	.0004	.0004	.0004	.0004	.0004
Eu 154	.0496	.0491	.0489	.0486	.0480
Eu 155	.0186	.0169	.0164	.0154	.0140
Eu 156	45.98	.7185	.1796	.0112	.0002
Tb 160	.0102	.0043	.0033	.0018	.0008
Tb 161	.0001	---	---	---	---

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TABLE II-26 (Continued)
Gamma Heat, Watts Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	.0103	.0096	.0079	.0056	.0029
Rb 86	---	---	---	---	---
Sr 89	.0019	---	---	---	---
Sr 90	---	---	---	---	---
Y 91	---	---	---	---	---
Zr 95	27.08	.5509	---	---	---
Nb 95	59.87	1.248	---	---	---
Ru 103	1.055	.0018	---	---	---
Ru 106	8.143	4.071	.5089	.0159	---
Ag 110m	.0047	.0018	.0001	---	---
Ag 111	---	---	---	---	---
Cd 115m	---	---	---	---	---
Sn 123m	.0010	.0001	---	---	---
Sn 125	---	---	---	---	---
Sb 125	.5370	.4154	.1923	.0533	.0041
Te 125m	---	---	---	---	---
Sb 127	---	---	---	---	---
Te 127m	.0033	.0003	---	---	---
Te 129m	.0207	---	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	2.531	1.820	.6760	.1298	.0048
Cs 136	---	---	---	---	---
Cs 137	9.454	9.239	8.620	7.679	6.095
Ba 140	---	---	---	---	---
Ce 141	.0655	---	---	---	---
Ce 144	34.76	14.30	.9949	.0117	---
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	---	---	---	---	---
Pm 147	---	---	---	---	---
Pm 148m	.0358	.0001	---	---	---
Pm 148	.0011	---	---	---	---
Sm 151	---	---	---	---	---
Eu 152	.0004	.0004	.0003	.0002	.0001
Eu 154	.0475	.0455	.0399	.0322	.0208
Eu 155	.0127	.0086	.0027	.0004	---
Eu 156	---	---	---	---	---
Tb 160	.0003	---	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-27
FISSION PRODUCT GAMMA HEAT FROM 0.947% ENRICHED URANIUM
900 MWd/T, 9.7 MW/T

Gamma Heat, Watts Per Ton of Uranium						
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	.0114	.0112	.0112	.0111	.0108	.0107
Rb 86	.0078	.0003	.0001	---	---	---
Sr 89	.2912	.0845	.0559	.0245	.0071	.0019
Sr 90	---	---	---	---	---	---
Y 90	---	---	---	---	---	---
Zr 95	1347	515.8	374.6	197.5	75.65	27.40
Nb 95	890.3	805.7	648.5	386.8	161.3	60.58
Ru 103	621.9	128.7	76.13	26.64	5.511	1.042
Ru 106	15.46	13.03	12.31	10.98	9.259	7.728
Ag 110m	.0089	.0070	.0065	.0055	.0043	.0034
Ag 111	.4807	.0001	---	---	---	---
Cd 115m	.0064	.0015	.0009	.0004	.0001	---
Sn 123m	.0072	.0044	.0037	.0027	.0016	.0010
Sn 125	.7732	.0010	.0001	---	---	---
Sb 125	.6639	.6506	.6370	.6107	.5733	.5362
Te 125m	---	---	---	---	---	---
Sb 127	59.32	---	---	---	---	---
Te 127m	.0340	.0206	.0169	.0114	.0063	.0033
Te 129m	44.01	6.655	3.544	1.005	.1518	.0205
I 131	534.1	.2358	.0178	.0001	---	---
Xe 131m	.0648	.0007	.0002	---	---	---
Te 132	5502	---	---	---	---	---
Xe 133	95.46	.0011	---	---	---	---
Cs 134	2.749	2.535	2.467	2.337	2.154	1.977
Cs 136	20.86	.1719	.0347	.0014	---	---
Cs 137	9.937	9.881	9.862	9.824	9.769	9.710
Ba 140	7339	64.21	12.65	.4909	.0037	---
Ce 141	157.9	23.16	12.22	3.398	.4984	.0654
Ce 144	87.05	69.66	64.76	55.96	42.97	35.66
Pr 143	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---
Nd 147	213.4	.7734	.1188	.0028	---	---
Pm 147	---	---	---	---	---	---
Pm 14 m	13.81	3.128	1.906	.7082	.1604	.0330
Pm 148	23.79	.0930	.0566	.0210	.0048	.0010
Sm 151	---	---	---	---	---	---
Eu 152	.0004	.0004	.0004	.0004	.0004	.0004
Eu 154	.0389	.0385	.0384	.0381	.0377	.0373
Eu 155	.0209	.0190	.0184	.0173	.0158	.0142
Eu 156	40.98	.6402	.1601	.0100	.0002	---
Tb 160	.0073	.0031	.0024	.0013	.0006	.0002
Tb 161	.0001	---	---	---	---	---

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TABLE II-27 (Continued)
Gamma Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	.0103	.0100	.0090	.0082	.0071	.0059	.0030
Rb 86	---	---	---	---	---	---	---
Sr 89	.0002	---	---	---	---	---	---
Sr 90	---	---	---	---	---	---	---
Y 91	---	---	---	---	---	---	---
Zr 95	3.907	.5573	.0016	---	---	---	---
Nb 95	8.821	1.263	.0037	---	---	---	---
Ru 103	.0425	.0017	---	---	---	---	---
Ru 106	5.464	3.864	1.366	.4830	.1207	.0151	---
Ag 110m	.0021	.0013	.0003	.0001	---	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0003	.0001	---	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	.4716	.4148	.2822	.1920	.1149	.0532	.0041
Te 125m	---	---	---	---	---	---	---
Sb 127	---	---	---	---	---	---	---
Te 127m	.0010	.0003	---	---	---	---	---
Te 129m	.0004	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	1.676	1.421	.8661	.5279	.2728	.1013	.0037
Cs 136	---	---	---	---	---	---	---
Cs 137	9.598	9.488	9.165	8.853	8.453	7.887	6.260
Ba 140	---	---	---	---	---	---	---
Ce 141	.0013	---	---	---	---	---	---
Ce 144	22.88	14.67	3.870	1.021	.1727	.0120	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	---	---	---	---	---	---	---
Pm 148m	.0016	.0001	---	---	---	---	---
Pm 148	---	---	---	---	---	---	---
Sm 151	---	---	---	---	---	---	---
Eu 152	.0004	.0004	.0004	.0003	.0003	.0003	.0001
Eu 154	.0365	.0357	.0334	.0313	.0287	.0252	.0164
Eu 155	.0118	.0097	.0055	.0031	.0014	.0005	---
Eu 156	---	---	---	---	---	---	---
Tb 160	---	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-28

FISSION PRODUCT GAMMA HEAT FROM 0.947% ENRICHED URANIUM

1000 MWd/T, 10 MW/T

Gamma Heat, Watts Per Ton of Uranium

Nuclide	Discharge	90 d	120 d	180 d	270 d
Kr 85	.0127	.0125	.0124	.0123	.0121
Rb 86	.0093	.0003	.0001	---	---
Sr 89	.3163	.0917	.0607	.0266	.0077
Sr 90	---	---	---	---	---
Y 91	---	---	---	---	---
Zr 95	1471	563.4	409.2	215.8	82.65
Nb 95	999.2	884.6	710.9	423.3	176.3
Ru 103	672.5	139.4	82.32	29.36	5.959
Ru 106	17.54	14.79	13.97	12.47	10.51
Ag 110m	.0118	.0093	.0085	.0073	.0057
Ag 111	.5360	.0001	---	---	---
Cd 115m	.0069	.0016	.0010	.0004	.0001
Sn 123m	.0080	.0049	.0041	.0029	.0018
Sn 125	.8288	.0011	.0001	---	---
Sb 125	.7500	.7314	.7182	.6885	.6463
Te 125m	---	---	---	---	---
Sb 127	61.70	---	---	---	---
Te 127m	.0378	.0227	.0186	.0125	.0069
Te 128m	47.65	7.204	3.836	1.088	1.643
I 131	562.3	.2482	.0188	.0001	---
Xe 131m	.0703	.0012	.0002	---	---
Te 132	5696	---	---	---	---
Xe 133	99.09	.0007	---	---	---
Cs 134	3.614	3.332	3.243	3.072	2.832
Cs 136	24.23	.1997	.0403	.0016	---
Cs 137	11.05	10.99	10.97	10.93	10.86
Ba 140	7772	67.75	13.35	.5180	.0040
Ce 141	170.5	25.01	13.19	3.668	.5380
Ce 144	96.30	77.06	71.64	61.91	49.73
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	223.4	.8097	.1244	.0029	---
Pm 147	---	---	---	---	---
Pm 148m	16.34	3.700	2.255	.8378	.1897
Pm 148	28.67	.1101	.0669	.0249	.0056
Sm 151	---	---	---	---	---
Eu 152	.0005	.0005	.0005	.0005	.0005
Eu 154	.0494	.0489	.0487	.0484	.0479
Eu 155	.0221	.0201	.0195	.0183	.0166
Eu 156	45.70	.7141	.1785	.0112	.0002
Tb 160	.0096	.0041	.0031	.0017	.0007
Tb 161	.0001	---	---	---	---

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TABLE II-28 (Continued)

Gamma Heat, Watts Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	.0119	.0111	.0091	.0065	.0033
Rb 86	---	---	---	---	---
Sr 89	.0021	---	---	---	---
Sr 90	---	---	---	---	---
Y 91	---	---	---	---	---
Zr 95	29.93	.6088	---	---	---
Nb 95	66.19	1.380	---	---	---
Ru 103	1.127	.0019	---	---	---
Ru 106	8.771	4.386	.5482	.0171	---
Ag 110m	.0044	.0017	.0001	---	---
Ag 111	---	---	---	---	---
Cd 115m	---	---	---	---	---
Sn 123m	.0011	.0001	---	---	---
Sn 125	---	---	---	---	---
Sb 125	.6045	.4676	.2165	.0600	.0046
Te 125m	---	---	---	---	---
Sb 127	---	---	---	---	---
Te 127m	.0037	.0003	---	---	---
Te 129m	.0222	---	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	2.598	1.868	.6938	.1332	.0049
Cs 136	---	---	---	---	---
Cs 137	10.80	10.55	9.846	8.772	6.962
Ba 140	---	---	---	---	---
Ce 141	.0706	---	---	---	---
Ce 144	39.45	16.24	1.129	.0133	---
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	---	---	---	---	---
Pm 147	---	---	---	---	---
Pm 148m	.0394	.0001	---	---	---
Pm 148	.0012	---	---	---	---
Sm 151	---	---	---	---	---
Eu 152	.0005	.0004	.0004	.0003	.0002
Eu 154	.0464	.0453	.0398	.0321	.0208
Eu 155	.0151	.0103	.0033	.0005	---
Eu 156	---	---	---	---	---
Tb 160	.0003	---	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-29
FISSION PRODUCT GAMMA HEAT FROM 0.947% ENRICHED URANIUM
1200 MWd/T, 10 MW/T

		Gamma Heat, Watts Per Ton of Uranium				
Nuclide		Discharge	90 d	120 d	180 d	270 d
Kr	85	.0150	.0148	.0147	.0146	.0143
Rb	86	.0114	.0004	.0001	---	---
Sr	89	.3376	.0979	.0648	.0284	.0082
Sr	90	---	---	---	---	---
Y	91	---	---	---	---	---
Zr	95	1612	617.4	448.3	236.4	90.56
Nb	95	1205	987.9	789.2	466.9	193.7
Ru	103	727.8	150.6	89.09	31.17	6.450
Ru	106	22.26	18.76	17.73	15.82	13.33
Ag	110m	.0186	.0147	.0135	.0115	.0091
Ag	111	.5979	.0001	---	---	---
Cd	115m	.0077	.0018	.0011	.0004	.0001
Sn	123m	.0094	.0057	.0049	.0035	.0021
Sn	125	.8663	.0011	.0001	---	---
Sb	125	.9233	.8974	.8787	.8424	.7908
Te	125m	---	---	---	---	---
Sb	127	62.50	---	---	---	---
Te	127m	.0436	.0259	.0213	.0143	.0079
Te	129m	50.56	7.643	4.070	1.154	.1743
I	131	568.9	.2509	.0190	.0001	---
Xe	131m	.0720	.0012	.0002	---	---
Te	132	5728	---	---	---	---
Xe	133	99.34	.0007	---	---	---
Cs	134	5.266	4.855	4.725	4.476	4.126
Cs	136	27.91	.2299	.0464	.0019	---
Cs	137	13.27	13.19	13.17	13.12	13.04
Ba	140	7836	68.18	13.44	.5213	.0040
Ce	141	178.8	26.23	13.83	3.847	.5643
Ce	144	112.4	89.96	83.63	72.28	58.06
Pr	143	---	---	---	---	---
Pm	146	---	---	---	---	---
Nd	147	225.2	.8161	.1254	.0030	---
Pm	147	---	---	---	---	---
Pm	148m	20.41	4.622	2.817	1.047	.2370
Pm	148	35.31	.1375	.0836	.0311	.0070
Sm	151	---	---	---	---	---
Eu	152	.0007	.0007	.0007	.0007	.0007
Eu	154	.0724	.0717	.0714	.0709	.0702
Eu	155	.0249	.0226	.0219	.0206	.0187
Eu	156	52.02	.8128	.2032	.0127	.0002
Tb	160	.0141	.0060	.0045	.0026	.0011
Tb	161	.0002	---	---	---	---

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TABLE II-29 (Continued)
Gamma Heat, Watts Per Ton of Uranium

Nuclide	1 y	2 y	5 y	10 y	20 y
Kr 85	.0141	.0132	.0108	.0077	.0040
Rb 86	---	---	---	---	---
Sr 89	.0022	---	---	---	---
Sr 90	---	---	---	---	---
Y 91	---	---	---	---	---
Zr 95	32.79	.6671	---	---	---
Nb 95	72.61	1.512	---	---	---
Ru 103	1.217	.0020	---	---	---
Ru 106	11.13	5.564	.6956	.0217	---
Ag 110m	.0070	.0027	.0001	---	---
Ag 111	---	---	---	---	---
Cd 115m	---	---	---	---	---
Sn 123m	.0012	.0002	---	---	---
Sn 125	---	---	---	---	---
Sb 125	.7396	.5721	.2649	.0734	.0056
Te 125m	---	---	---	---	---
Sb 127	---	---	---	---	---
Te 127m	.0042	.0004	---	---	---
Te 129m	.0236	---	---	---	---
I 131	---	---	---	---	---
Xe 131m	---	---	---	---	---
Te 132	---	---	---	---	---
Xe 133	---	---	---	---	---
Cs 134	3.786	2.721	1.011	.1941	.0072
Cs 136	---	---	---	---	---
Cs 137	12.96	12.67	11.82	10.53	8.357
Ba 140	---	---	---	---	---
Ce 141	.0740	---	---	---	---
Ce 144	46.06	18.94	1.318	.0155	---
Pr 143	---	---	---	---	---
Pm 146	---	---	---	---	---
Nd 147	---	---	---	---	---
Pm 147	---	---	---	---	---
Pm 148m	.0492	.0001	---	---	---
Pm 148	.0015	---	---	---	---
Sm 151	---	---	---	---	---
Eu 152	.0007	.0006	.0005	.0004	.0002
Eu 154	.0694	.0664	.0583	.0470	.0305
Eu 155	.0170	.0116	.0037	.0005	---
Eu 156	---	---	---	---	---
Tb 160	.0004	---	---	---	---
Tb 161	---	---	---	---	---

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TABLE II-30
FISSION PRODUCT GAMMA HEAT FROM 0.947% ENRICHED URANIUM
2200 MWd/T, 11 MW/T

		Gamma Heat, Watts Per Ton of Uranium				
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	.0258	.0254	.0252	.0250	.0246	.0241
Rb 86	.0233	.0008	.0002	---	---	---
Sr 89	.3798	.1101	.0729	.0320	.0093	.0025
Sr 90	---	---	---	---	---	---
Y 91	---	---	---	---	---	---
Zr 95	2029	777.1	564.3	297.6	114.0	41.27
Nb 95	1853	1300	1025	597.2	245.4	91.63
Ru 103	957.1	198.0	117.1	40.99	8.481	1.603
Ru 106	54.14	45.64	43.11	38.47	32.43	27.07
Ag 110m	.0901	.0709	.0654	.0557	.0438	.0340
Ag 111	1.013	.0002	---	---	---	---
Cd 115m	.0115	.0027	.0017	.0006	.0001	---
Sn 123m	.0170	.0103	.0087	.0063	.0038	.0022
Sn 125	1.154	.0015	.0002	---	---	---
Sb 125	1.915	1.839	1.800	1.726	1.620	1.515
Te 125m	---	---	---	---	---	---
Sb 127	73.41	---	---	---	---	---
Te 127m	.0669	.0391	.0321	.0216	.0119	.0064
Te 129m	61.95	9.353	4.981	1.412	.2133	.0288
I 131	652.0	.2870	.0217	.0001	---	---
Xe 131m	.0832	.0014	.0002	---	---	---
Te 132	6502	---	---	---	---	---
Xe 133	110.1	.0008	---	---	---	---
Cs 134	23.52	21.68	21.10	19.99	18.43	16.91
Cs 136	53.11	.4376	.0884	.0036	---	---
Cs 137	24.39	24.26	24.21	24.12	23.98	23.84
Ba 140	8605	74.65	14.71	.5708	.0043	---
Ce 141	205.5	30.14	15.89	4.421	.6484	.0850
Ce 144	180.5	144.6	134.4	116.2	93.35	74.05
Pr 143	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---
Nd 147	252.2	.9140	.1404	.0033	---	---
Pm 147	---	---	---	---	---	---
Pm 148m	48.24	10.92	6.658	2.473	.5600	.1163
Pm 148	83.73	.3249	.1976	.0734	.0166	.0034
Sm 151	---	---	---	---	---	---
Eu 152	.0019	.0019	.0019	.0019	.0018	.0018
Eu 154	.3176	.3142	.3131	.3109	.3076	.3041
Eu 155	.0421	.0383	.0372	.0349	.0318	.0287
Eu 156	90.80	1.419	.3547	.0222	.0003	---
Tb 160	.0698	.0297	.0223	.0126	.0054	.0022
Tb 161	.0003	---	---	---	---	---

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TABLE II-30 (Continued)

Gamma Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	.0233	.0226	.0204	.0185	0.0162	.0132	.0068
Rb 86	---	---	---	---	---	---	---
Sr 89	.0002	---	---	---	---	---	---
Sr 90	---	---	---	---	---	---	---
Y 91	---	---	---	---	---	---	---
Zr 95	5.887	.8396	.0024	---	---	---	---
Nb 95	13.30	1.903	.0055	---	---	---	---
Ru 103	.0655	.0027	---	---	---	---	---
Ru 106	19.14	13.53	4.785	1.692	.4230	.0529	.0001
Ag 110m	.0209	.0128	.0030	.0007	.0001	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0008	.0003	---	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sn 125	1.333	1.172	.7976	.5427	.3247	.1503	.0115
Te 125m	---	---	---	---	---	---	---
Sb 127	---	---	---	---	---	---	---
Te 127m	.0019	.0006	---	---	---	---	---
Te 129m	.0006	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	14.34	12.15	7.408	4.515	2.333	0.8669	.0320
Cs 136	---	---	---	---	---	---	---
Cs 137	23.56	23.29	22.50	21.73	20.75	19.36	15.37
Ba 140	---	---	---	---	---	---	---
Ce 141	.0017	---	---	---	---	---	---
Ce 144	47.49	30.46	8.035	2.119	.3586	.0249	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	---	---	---	---	---	---	---
Pm 148m	.0057	.0003	---	---	---	---	---
Pm 148	.0002	---	---	---	---	---	---
Sm 151	---	---	---	---	---	---	---
Eu 152	.0018	.0017	.0016	.0015	.0013	.0011	.0007
Fu 154	.2976	.2912	.2729	.2557	.2345	.2059	.1335
Eu 155	.0237	.0196	.0110	.0062	.0029	.0009	---
Eu 156	---	---	---	---	---	---	---
Tb 160	.0004	.0001	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-31
FISSION PRODUCT GAMMA HEAT FROM 1.25% ENRICHED URANIUM
2200 MWd/T, 11 MW/T

		Gamma Heat, Watts Per Ton of Uranium				
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	.0268	.0264	.0262	.0260	.0255	.0251
Rb 86	.0196	.0007	.0002	---	---	---
Sr 89	.4020	.1166	.0772	.0338	.0098	.0026
Sr 90	---	---	---	---	---	---
Y 91	---	---	---	---	---	---
Zr 95	2066	791.3	574.6	303.0	116.1	43.03
Nb 95	1883	1323	1043	608.0	249.9	93.30
Ru 103	899.4	186.1	110.1	38.52	7.971	1.504
Ru 106	42.68	35.98	33.98	30.33	25.57	21.34
Ag 110m	.0512	.0402	.0372	.0317	.0249	.0193
Ag 111	.7604	.0002	---	---	---	---
Cd 115m	.0101	.0024	.0015	.0006	.0001	---
Sn 123m	.0150	.0091	.0077	.0055	.0034	.0020
Sn 125	1.014	.0013	.0001	---	---	---
Sb 125	1.730	1.660	1.625	1.558	1.462	1.368
Te 125m	---	---	---	---	---	---
Sb 127	69.81	---	---	---	---	---
Te 127m	.0646	.0378	.0310	.0208	.0115	.0061
Te 129m	59.59	9.000	4.793	1.359	.2052	.0278
I 131	632.4	.2788	.0211	.0001	---	---
Xe 131m	.0810	.0013	.0002	---	---	---
Te 132	6331	---	---	---	---	---
Xe 133	109.2	.0008	---	---	---	---
Cs 134	18.81	17.34	16.88	15.99	14.74	13.53
Cs 136	42.85	.3531	.0713	.0029	---	---
Cs 137	24.30	24.16	24.11	24.02	23.89	23.74
Ba 140	865.6	75.14	14.80	.5744	.0044	---
Ce 141	205.3	30.11	15.88	4.417	.6479	.0850
Ce 144	183.6	147.2	136.8	118.2	94.98	75.34
Pr 143	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---
Nd 147	251.0	.9096	.1397	.0033	---	---
Pm 147	---	---	---	---	---	---
Pm 148m	47.23	10.69	6.518	2.421	.5483	.1138
Pm 148	71.68	.3180	.1934	.0718	.0163	.0034
Sm 151	---	---	---	---	---	---
Eu 152	.0002	.0021	.0021	.0021	.0021	.0020
Eu 154	.2370	.2345	.2337	.2320	.2295	.2270
Eu 155	.0398	.0362	.0351	.0329	.0300	.0271
Eu 156	70.53	1.102	.2755	.0172	.0003	---
Tb 160	.0432	.0184	.0138	.0078	.0033	.0013
Tb 161	.0002	---	---	---	---	---

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TABLE II-31 (Continued)
Gamma Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	.0243	.0235	.0212	.0192	.0168	.0138	.0072
Rb 86	---	---	---	---	---	---	---
Sr 89	.0002	---	---	---	---	---	---
Sr 90	---	---	---	---	---	---	---
Y 91	---	---	---	---	---	---	---
Zr 95	5.994	.8550	.0025	---	---	---	---
Nb 95	13.54	1.938	.0056	---	---	---	---
Ru 103	.0615	.0025	---	---	---	---	---
Ru 106	15.09	10.67	3.772	1.334	.333 ^d	.0417	---
Ag 110m	.0119	.0073	.0017	.0004	.0001	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0007	.0003	---	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	1.203	1.058	.7199	.4898	.2931	.1357	.0104
Te 125m	---	---	---	---	---	---	---
Sb 127	---	---	---	---	---	---	---
Te 127m	.0018	.0006	---	---	---	---	---
Te 129m	.0006	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	11.47	9.723	5.926	3.612	1.867	.6934	.0256
Cs 136	---	---	---	---	---	---	---
Cs 137	23.47	23.20	22.41	21.65	20.67	19.29	15.31
Ba 140	---	---	---	---	---	---	---
Ce 141	.0017	---	---	---	---	---	---
Ce 144	48.32	30.99	8.176	2.157	.3649	.0254	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	---	---	---	---	---	---	---
Pm 148m	.0056	.0003	---	---	---	---	---
Pm 148	.0002	---	---	---	---	---	---
Sm 151	---	---	---	---	---	---	---
Fu 152	.0020	.0019	.0018	.0017	.0015	.0013	.0007
Fu 154	.2221	.2173	.2037	.1909	.1750	.1537	.0996
Fu 155	.0224	.0185	.0104	.0059	.0027	.0009	---
Fu 156	---	---	---	---	---	---	---
Tb 160	.0002	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-32
FISSION PRODUCT GAMMA HEAT FROM 2.1% ENRICHED URANIUM
2100 MWd/T, 10.6 MW/T

		Gamma Heat, Watts Per Ton of Uranium				
Nuclide	Discharge	90 d	120 d	180 d	270 d	1 y
Kr 85	.0267	.0262	.0261	.0258	.0254	.0250
Rb 86	.0120	.0004	.0001	---	---	---
Sr 89	.4117	.1194	.079	.0346	.01	.0027
Sr 90	---	---	---	---	---	---
Y 91	---	---	---	---	---	---
Zr 95	2027	776.5	563.9	297.4	113.9	41.24
Nb 95	1837	1296	1022	596.3	245.2	91.55
Ru 103	799.8	165.5	97.89	34.24	7.086	1.337
Ru 106	28.4	23.94	22.61	20.18	17.01	14.2
Ag 110m	.0162	.0128	.0118	.01	.0079	.0061
Ag 111	.4347	.0001	---	---	---	---
Cd 115m	.0082	.0019	.0012	.0005	.0001	---
Sn 123m	.0122	.0074	.0063	.0045	.0027	.0016
Sn 125	.8139	.0011	.0001	---	---	---
Sb 125	1.451	1.391	1.362	1.306	1.226	1.146
Te 125m	---	---	---	---	---	---
Sb 127	62.58	---	---	---	---	---
Te 127m	.0594	.0347	.0284	.0192	.0106	.0056
Te 129m	54.65	8.259	4.398	1.247	.1883	.0254
I 131	587	.2592	.0196	.0001	---	---
Xe 131m	.0755	.0012	.0002	---	---	---
Te 132	5907	---	---	---	---	---
Xe 133	104.3	.0008	---	---	---	---
Cs 134	10.68	9.849	9.585	9.080	8.370	7.68
Cs 136	27.77	.2288	.0462	.0019	---	---
Cs 137	23.06	22.93	22.88	22.8	22.67	22.53
Ba 140	8397	72.99	14.38	.5580	.0042	---
Ce 141	197.5	28.97	15.28	4.25	.6234	.0817
Ce 144	178.6	143.3	133.3	115.18	92.54	73.40
Pr 143	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---
Nd 147	240.5	.8716	.1339	.0032	---	---
Pm 147	---	---	---	---	---	---
Pm 148m	40	9.057	5.521	2.051	.4644	.0964
Pm 148	45.74	.2692	.1638	.0609	.0138	.0029
Sm 151	---	---	---	---	---	---
Eu 152	.0023	.0022	.0022	.0022	.0022	.0021
Eu 154	.1235	.1222	.1217	.1209	.1196	.1182
Eu 155	.0392	.0356	.0345	.0324	.0295	.0267
Eu 156	44.30	.6922	.1731	.0108	.0002	---
Tb 160	.0167	.007	.0053	.003	.0013	.0005
Tb 161	.0001	---	---	---	---	---

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TABLE II-32 (Continued)

Gamma Heat, Watts Per Ton of Uranium

Nuclide	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Kr 85	.0241	.0233	.0211	.0191	.0167	.0137	.0070
Rb 86	---	---	---	---	---	---	---
Sr 89	.0002	---	---	---	---	---	---
Sr 90	---	---	---	---	---	---	---
Y 91	---	---	---	---	---	---	---
Zr 95	5.882	.8390	.0024	---	---	---	---
Nb 95	13.29	1.901	.0055	---	---	---	---
Ru 103	.0547	.0022	---	---	---	---	---
Ru 106	10.04	7.099	2.51	.8874	.2219	.0277	---
Ag 110m	.0038	.0023	.0005	.0001	---	---	---
Ag 111	---	---	---	---	---	---	---
Cd 115m	---	---	---	---	---	---	---
Sn 123m	.0006	.0002	---	---	---	---	---
Sn 125	---	---	---	---	---	---	---
Sb 125	1.008	.8867	.6033	.4105	.2456	.1137	.0087
Te 125m	---	---	---	---	---	---	---
Sb 127	---	---	---	---	---	---	---
Te 127m	.0017	.0005	---	---	---	---	---
Te 129m	.0005	---	---	---	---	---	---
I 131	---	---	---	---	---	---	---
Xe 131m	---	---	---	---	---	---	---
Te 132	---	---	---	---	---	---	---
Xe 133	---	---	---	---	---	---	---
Cs 134	6.512	5.521	3.365	2.051	1.060	.3938	.0145
Cs 136	---	---	---	---	---	---	---
Cs 137	22.27	22.02	21.27	20.54	19.61	18.30	14.52
Ba 140	---	---	---	---	---	---	---
Ce 141	.0017	---	---	---	---	---	---
Ce 144	47.08	30.18	7.965	2.101	.3556	.0247	---
Pr 143	---	---	---	---	---	---	---
Pm 146	---	---	---	---	---	---	---
Nd 147	---	---	---	---	---	---	---
Pm 147	---	---	---	---	---	---	---
Pm 148m	.0047	.0002	---	---	---	---	---
Pm 148	.0001	---	---	---	---	---	---
Sm 151	---	---	---	---	---	---	---
Eu 152	.0021	.0020	.0019	.0017	.0016	.0013	.0008
Eu 154	.1157	.1132	.1061	.0994	.0912	.0801	.0519
Eu 155	.0220	.0182	.0102	.0058	.0027	.0009	---
Eu 156	---	---	---	---	---	---	---
Tb 160	.0001	---	---	---	---	---	---
Tb 161	---	---	---	---	---	---	---

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TABLE II-33
COMPOSITION OF IRRADIATED NATURAL URANIUM
640 MWd/T, 8.17 MW/T

Element	Discharge	Weight, Grams Per Ton of Uranium				
		90 d	120 d	180 d	270 d	1 y
Ge	.0057	.0057	.0057	.0057	.0057	.0057
As	.0023	.0018	.0018	.0018	.0018	.0018
Se	1.172	1.172	1.172	1.172	1.172	1.172
Br	.4494	.4494	.4494	.4494	.4494	.4494
Kr	8.115	8.085	8.078	8.064	8.043	8.021
Rb	8.061	8.090	8.097	8.112	8.133	8.155
Sr	28.59	23.90	23.24	22.48	22.01	21.81
Y	13.66	12.33	12.04	11.64	11.34	11.21
Zr	82.51	81.56	81.33	81.00	80.75	80.68
Nb	3.490	3.423	2.770	1.662	.3955	.2616
Mo	56.34	62.47	64.31	66.90	68.89	69.73
Tc	16.75	17.65	17.65	17.65	17.65	17.65
Ru	42.16	37.72	37.18	36.57	36.14	35.88
Rh	4.639	8.591	9.025	9.435	9.609	9.646
Pd	6.570	7.058	7.165	7.363	7.620	7.849
Ag	.4802	.4598	.4598	.4598	.4598	.4598
Cd	.3475	.3642	.3640	.3639	.3638	.3638
In	.0447	.0483	.0485	.0487	.0487	.0488
Sn	.7464	.7323	.7319	.7311	.7304	.7300
Sb	.3845	.3142	.3106	.3036	.2932	.2827
Te	11.44	9.806	9.751	9.703	9.684	9.684
I	5.629	4.670	4.733	4.790	4.819	4.831
Xe	101.71	101.89	101.90	101.90	101.90	101.90
Cs	52.56	54.88	54.83	54.73	54.58	54.43
Ba	31.75	26.52	26.54	26.63	26.78	26.93
La	26.00	25.30	25.30	25.30	25.30	25.30
Ce	72.51	65.14	63.35	60.80	58.16	56.06
Pr	17.78	21.54	22.23	22.81	23.00	23.03
Nd	59.78	67.79	68.92	70.89	73.34	75.42
Pm	6.914	7.798	7.632	7.306	6.843	6.387
Sm	8.404	9.176	9.346	9.673	10.13	10.59
Eu	1.006	.9586	.9555	.9512	.9457	.9407
Gd	.2574	.3442	.3479	.3536	.3611	.3682
Tb	.0142	.0138	.0138	.0138	.0138	.0138
Dy	.0017	.0021	.0021	.0021	.0021	.0021
RE	192.67	198.06	198.10	198.10	198.10	198.10
Np	28.47	2.164	2.164	2.164	2.164	2.164
Am	.0087	.0446	.0564	.0800	.1149	.1513

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TABLE II-33 (Continued)

Weight, Grams Per Ton of Uranium

Element	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Ge	.0057	.0057	.0057	.0057	.0057	.0057	.0057
As	.0018	.0018	.0018	.0018	.0018	.0018	.0018
Se	1.172	1.172	1.172	1.172	1.172	1.172	1.172
Br	.4494	.4494	.4494	.4494	.4495	.4495	.4495
Kr	7.979	7.939	7.827	7.726	7.606	7.453	7.116
Rb	8.196	8.236	8.348	8.450	8.570	8.723	9.059
Sr	21.61	21.44	20.96	20.51	19.92	19.10	16.75
Y	11.15	11.14	11.14	11.14	11.14	11.14	11.14
Zr	80.74	80.89	81.36	81.82	82.41	83.23	85.58
Nb	.0381	.0055	.0001	.0001	.0001	.0001	.0002
Mo	70.15	70.21	70.22	70.22	70.22	70.22	70.22
Tc	17.65	17.65	17.65	17.65	17.65	17.65	17.65
Ru	35.53	35.29	34.92	34.79	34.73	34.72	34.72
Rh	9.654	9.655	9.655	9.655	9.655	9.655	9.655
Pd	8.186	8.425	8.797	8.929	8.983	8.999	9.001
Ag	.4598	.4598	.4598	.4598	.4598	.4598	.4598
Cd	.3638	.3638	.3638	.3638	.3638	.3638	.3638
In	.0488	.0488	.0488	.0488	.0488	.0488	.0488
Sn	.7295	.7294	.7293	.7293	.7293	.7293	.7293
Sb	.2640	.2473	.2081	.1814	.1586	.1403	.1258
Te	9.694	9.709	9.747	9.774	9.793	9.815	9.830
I	4.839	4.841	4.842	4.842	4.842	4.842	4.842
Xe	101.90	101.90	101.90	101.90	101.90	101.90	101.90
Cs	54.14	53.86	53.03	52.24	51.24	49.84	45.82
Ba	27.22	27.51	28.34	29.12	30.12	31.53	35.55
La	25.30	25.30	25.30	25.30	25.30	25.30	25.30
Ce	53.21	51.38	48.97	48.34	48.15	48.11	48.11
Pr	23.04	23.04	23.04	23.04	23.03	23.03	23.03
Nd	78.26	80.09	82.50	83.13	83.32	83.36	83.36
Pm	5.595	4.902	3.296	2.216	1.306	5904	.0419
Sm	11.37	12.06	13.66	14.73	15.62	16.31	16.79
Eu	.9327	.9268	.9177	.9171	.9234	.9395	1.004
Gd	.3802	.3901	.4111	.4234	.4326	.4392	.4465
Tb	.0137	.0137	.0137	.0137	.0137	.0137	.0137
Dy	.0022	.0022	.0022	.0022	.0022	.0022	.0022
RE	198.10	198.10	198.10	198.10	198.10	198.10	198.10
Np	2.164	2.164	2.164	2.166	2.168	2.174	2.195
Am	.2197	.2863	.4754	.6495	.8602	1.135	1.180

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TABLE II-34

COMPOSITION OF IRRADIATED NATURAL URANIUM

750 MWd/T, 10 MW/T

Weight, Grams Per Ton of Uranium

Element	Discharge	90 d	120 d	180 d	270 d
Ge	.0065	.0065	.0065	.0065	.0065
As	.0027	.0021	.0021	.0021	.0021
Se	1.346	1.347	1.347	1.347	1.347
Br	.5166	.5166	.5166	.5166	.5166
Kr	9.332	9.299	9.291	9.274	9.250
Rb	9.277	9.311	9.319	9.336	9.360
Sr	33.09	27.56	26.78	25.98	25.34
Y	15.76	14.22	13.88	13.42	13.06
Zr	94.74	93.67	93.40	93.02	92.74
Nb	3.963	3.981	3.227	1.939	.8124
Mo	64.28	71.36	73.49	76.52	78.84
Tc	19.14	20.19	20.19	20.19	20.19
Ru	48.06	42.92	42.29	41.60	41.11
Rh	5.109	9.719	10.23	10.70	10.91
Pd	7.257	7.795	7.913	8.130	8.411
Ag	.5026	.4803	.4803	.4803	.4803
Cd	.3847	.4028	.4026	.4024	.4023
In	.0497	.0539	.0541	.0543	.0544
Sn	.8435	.8272	.8267	.8259	.8251
Sb	.4351	.3536	.3496	.3416	.3300
Te	13.10	11.19	11.13	11.08	11.05
I	6.453	5.331	5.399	5.465	5.499
Xe	117.2	117.4	117.4	117.4	117.4
Cs	59.16	61.88	61.82	61.70	61.53
Ba	36.57	30.36	30.38	30.49	30.66
La	29.81	28.98	28.97	28.97	28.97
Ce	83.34	74.80	72.72	69.77	66.71
Pr	20.22	24.59	25.40	26.08	26.31
Nd	68.19	77.59	78.90	81.17	84.00
Pm	7.818	8.883	8.695	8.322	7.795
Sm	9.580	10.48	10.67	11.04	11.57
Eu	1.153	1.099	1.096	1.092	1.086
Gd	.2897	.3907	.3946	.4003	.4078
Tb	.0153	.0148	.0148	.0148	.0148
Dy	.0018	.0023	.0023	.0023	.0023
RE	220.5	226.8	226.9	226.9	226.9
Np	35.29	2.588	2.588	2.588	2.588
Am	.0143	.0791	.1005	.1430	.2061
Cm*	.4798	.3482	.3067	.2377	.1622

*Curium values are in milligrams

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TABLE II-34 (Continued)

Weight, Grams Per Ton of Uranium

Element	1 y	2 y	5 y	10 y	20 y
Ge	.0065	.0065	.0065	.0065	.0065
As	.0021	.0021	.0021	.0021	.0021
Se	1.347	1.347	1.347	1.347	1.347
Br	.5166	.5166	.5166	.5166	.5166
Kr	9.224	9.131	8.885	8.570	8.183
Rb	9.385	9.479	9.725	10.04	10.43
Sr	25.10	24.68	23.60	21.98	19.28
Y	12.91	12.83	12.83	12.83	12.83
Zr	92.65	92.89	93.97	95.59	98.29
Nb	.3057	.0064	.0001	.0001	.0003
Mo	79.82	80.38	80.39	80.39	80.39
Tc	20.19	20.19	20.19	20.19	20.19
Ru	40.82	40.18	39.63	39.55	39.55
Rh	10.95	10.96	10.96	10.96	10.96
Pd	8.661	9.293	9.845	9.921	9.924
Ag	.4803	.4802	.4802	.4802	.4802
Cd	.4023	.4024	.4024	.4024	.4024
In	.0544	.0544	.0544	.0544	.0544
Sn	.8246	.8239	.8238	.8238	.8238
Sb	.3181	.2783	.2041	.1578	.1414
Te	11.05	11.18	11.15	11.20	11.21
I	5.513	5.524	5.525	5.525	5.525
Xe	117.4	117.4	117.4	117.4	117.4
Cs	61.35	60.69	58.83	56.07	51.47
Ba	30.84	31.50	33.36	36.12	40.72
La	28.97	28.97	28.97	28.97	28.97
Ce	64.29	58.90	55.39	55.13	55.13
Pr	26.35	26.35	26.35	26.35	26.35
Nd	86.39	91.78	95.28	95.54	95.55
Pm	7.275	5.584	2.525	.6726	.0477
Sm	12.09	13.77	16.80	18.61	19.16
Eu	1.081	1.068	1.058	1.081	1.147
Gd	.4150	.4370	.4709	.4878	.4970
Tb	.0148	.0148	.0148	.0148	.0148
Dy	.0023	.0023	.0023	.0023	.0023
RE	226.9	226.9	226.9	226.9	226.9
Np	2.588	2.588	2.588	2.588	2.588
Am	.2720	.5158	1.172	2.050	3.214
Cm*	.1083	.0232	.0006	.0003	.0003

*Curium values are in milligrams

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TABLE II-35
COMPOSITION OF IRRADIATED NATURAL URANIUM
900 MWd/T, 10 MW/T

Weight, Grams Per Ton of Uranium					
Element	Discharge	90 d	120 d	180 d	270 d
Ge	.0078	.0078	.0078	.0078	.0078
As	.0031	.0025	.0025	.0025	.0025
Se	1.599	1.599	1.599	1.599	1.599
Br	.6128	.6128	.6128	.6128	.6128
Kr	11.06	11.03	11.02	11.00	10.97
Rb	11.00	11.04	11.05	11.07	11.09
Sr	38.46	32.44	31.59	30.61	30.00
Y	18.50	16.75	16.37	15.85	15.45
Zr	12.60	111.32	111.01	110.58	110.25
Nb	4.909	4.509	3.634	2.169	.9053
Mo	77.44	85.84	88.26	91.65	94.24
Tc	23.05	24.10	24.10	24.10	24.10
Ru	57.37	51.60	50.95	50.16	49.58
Rh	6.757	11.83	12.38	12.91	13.13
Pd	9.234	9.881	10.03	10.30	10.66
Ag	.6676	.6427	.6427	.6427	.6427
Cd	.4897	.5100	.5098	.5096	.5096
In	.0609	.0654	.0656	.0658	.0659
Sn	1.025	1.008	1.007	1.006	1.005
Sb	.5159	.4316	.4267	.4170	.4028
Te	15.38	13.41	13.34	13.28	13.26
I	7.507	6.423	6.497	6.570	.608
Xe	140.19	140.44	140.44	140.44	140.44
Cs	71.30	73.97	73.90	73.76	73.56
Ba	42.52	36.28	36.31	36.44	36.65
La	35.42	34.58	34.57	34.57	34.57
Ce	98.51	88.61	86.25	82.88	79.33
Pr	24.59	29.59	30.46	31.19	31.43
Nd	82.75	92.94	94.47	97.12	100.42
Pm	9.497	10.46	10.23	9.793	9.173
Sm	11.72	12.74	12.97	13.41	14.03
Eu	1.424	1.360	1.356	1.351	1.345
Gd	.3897	.5051	.5095	.5160	.5245
Tb	.0198	.0192	.0192	.0192	.0192
Dy	.0024	.0030	.0030	.0030	.0030
RE	264.32	270.81	270.84	270.85	270.84
Np	34.58	3.165	3.165	3.165	3.165
Am	.0265	.1264	.1594	.2251	.3223
Cm*	1.066	.7663	.6746	.5230	.3570

*Curium values are in milligrams

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TABLE II-35 (Continued)

Weight, Grams Per Ton of Uranium

Element	1 y	2 y	5 y	10 y	20 y
Ge	.0078	.0078	.0078	.0078	.0078
As	.0025	.0025	.0025	.0025	.0025
Se	1.599	1.599	1.599	1.599	1.599
Br	.6128	.6128	.6129	.6129	.6129
Kr	10.94	10.83	10.54	10.16	9.709
Rb	11.12	11.24	11.53	11.90	12.36
Sr	29.74	29.24	27.96	26.04	22.84
Y	15.29	15.20	15.20	15.20	15.20
Zr	110.15	110.46	111.73	113.65	116.85
Nb	.3401	.0071	.0001	.0002	.0003
Mo	95.33	95.96	95.97	95.97	95.97
Tc	24.10	24.10	24.10	24.10	24.10
Ru	49.22	48.41	47.71	47.62	47.61
Rh	13.18	13.19	13.19	13.19	13.19
Pd	10.97	11.77	12.46	12.56	12.56
Ag	.6427	.6426	.6426	.6426	.6426
Cd	.5095	.5096	.5096	.5096	.5096
In	.0660	.0660	.0660	.0660	.0660
Sn	1.005	1.004	1.004	1.004	1.004
Sb	.3883	.3398	.2495	.1932	.1732
Te	13.27	13.30	13.39	13.44	13.46
I	6.623	6.637	6.638	6.638	6.638
Xe	140.44	140.44	140.44	140.44	140.44
Cs	73.34	72.53	70.29	66.99	61.49
Ba	36.86	37.67	39.91	43.21	48.71
La	34.57	34.57	34.57	34.57	34.57
Ce	76.50	70.19	66.09	65.79	65.78
Pr	31.47	31.47	31.47	31.47	31.47
Nd	103.22	109.52	113.62	113.92	113.93
Pm	8.561	6.571	2.971	.7914	.0562
Sm	14.64	16.62	20.19	22.33	22.98
Eu	1.339	1.323	1.311	1.333	1.401
Gd	.5326	.5577	.5968	.6174	.6302
Tb	.0192	.0192	.0192	.0192	.0192
Dy	.0030	.0030	.0030	.0030	.0030
RE	270.85	270.84	270.84	270.84	270.84
Np	3.165	3.165	3.171	3.191	3.253
Am	.4238	.8001	1.812	3.167	4.962
Cm*	.2384	.0512	.0014	.0008	.0007

*Curium values are in milligrams

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TABLE II-36
COMPOSITION OF IRRADIATED 0.947% ENRICHED URANIUM
900 MWd/T, 9.7 MW/T

Element	Discharge	Weight, Grams Per Ton of Uranium				
		90 d	120 d	180 d	270 d	1 y
Ge	.0079	.0079	.0079	.0079	.0079	.0079
As	.0031	.0026	.0025	.0025	.0025	.0025
Se	1.655	1.656	1.656	1.656	1.655	1.656
Br	.6353	.6353	.6353	.6353	.6353	.6353
Kr	11.47	11.43	11.42	11.40	11.37	11.34
Rb	11.42	11.46	11.47	11.49	11.52	11.55
Sr	39.71	33.60	32.74	31.75	31.13	30.86
Y	19.14	17.36	16.97	16.44	16.04	15.87
Zr	116.31	115.04	114.74	114.30	113.99	113.89
Nb	5.068	4.579	3.685	2.197	.9162	.3441
Mo	79.94	88.52	90.97	94.41	97.03	98.13
Tc	23.75	24.81	24.81	24.81	24.81	24.81
Ru	58.04	52.42	51.73	50.95	50.40	50.05
Rh	7.091	12.09	12.64	13.16	13.38	13.42
Pd	8.940	9.558	9.699	9.958	10.29	10.59
Ag	.6017	.5792	.5792	.5792	.5792	.5792
Cd	.4713	.4894	.4892	.4890	.4890	.4890
In	.0620	.0664	.0666	.0668	.0669	.0069
Sn	1.029	1.013	1.012	1.011	1.010	1.010
Sb	.5161	.4312	.4263	.4166	.4024	.3879
Te	15.69	13.72	13.65	13.59	13.56	13.57
I	7.652	6.556	6.630	6.702	6.740	6.756
Xe	142.43	142.64	142.64	142.64	142.64	142.64
Cs	74.79	77.52	77.45	77.31	77.10	76.88
Ba	43.58	37.32	37.35	37.48	37.69	37.91
La	36.45	35.60	35.60	35.60	35.60	35.60
Ce	101.12	91.10	88.71	85.27	81.63	78.73
Pr	25.55	30.50	31.37	32.10	32.34	32.38
Nd	85.52	95.88	97.45	100.16	103.56	106.43
Pm	9.896	10.85	10.62	10.16	9.520	8.885
Sm	11.89	12.93	13.17	13.62	14.26	14.89
Eu	1.392	1.334	1.330	1.325	1.318	1.312
Gd	.3676	.4726	.4772	.4843	.4936	.5027
Tb	.0184	.0180	.0180	.0179	.0179	.0179
Dy	.0022	.0027	.0027	.0027	.0027	.0028
RE	272.21	278.69	278.75	278.75	278.75	278.75
Np	30.01	3.420	3.420	3.420	3.420	3.420
Am	.0153	.0686	.0863	.1213	.1732	.2273

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PART II, Continued

FEED MATERIAL

CHAPTER III

SOURCES OF FEED MATERIAL

By

D. E. Larson

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PART III

PROCESS

CHAPTER IV

PROCESS CHEMISTRY AND ENGINEERING

By

G. L. Richardson

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PACIFIC NORTHWEST LABORATORY

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PART III: PROCESS

CHAPTER IV: PROCESS CHEMISTRY AND ENGINEERING

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CHAPTER IV: PROCESS CHEMISTRY AND ENGINEERING

A. SCOPE AND ARRANGEMENT OF CHAPTER

This chapter describes and discusses the process chemistry and engineering of those waste management precipitation, solvent extraction, and ion exchange processes performed in the B-Plant proper. Because of the broad spectrum of subjects treated, this chapter is a very lengthy one. It is appropriate, therefore, to sketch for the reader in a general fashion what is covered in each of the sections of this chapter.

Section B describes head-end processes for preparing suitable feedstocks for subsequent solvent extraction operations. Specifically discussed are removal and leaching of solids from Purex Acid Waste and lead sulfate carrier precipitation of a strontium-rare earth fraction from Purex Acid Sludge solution.

Section C treats in detail the theory and application of D2EHPA solvent extraction processes to the recovery and purification of strontium, rare earths, and americium from the various waste solutions.

Engineering concepts of solvent extraction and solvent extraction equipment are discussed in Section D. Pulse column demonstration runs of several of the B-Plant solvent extraction processes are also described in this section.

Purex Acid Sludge solutions contain considerable quantities of neptunium and plutonium. A batch D2EHPA extraction process suitable for recovery of these actinides has been developed and is discussed in Section E.

Ion exchange processes for recovery of Cs-137 and Tc-99 from alkaline waste supernate solutions form the subject matter for Section F. The theory of zeolite exchange systems and their application in storing purified Sr-90 and Cs-137 fractions is also covered in this section.

Two alternate precipitation schemes for recovering Cs-137 from various waste solutions - the cesium phosphotungstate and the cesium nickel ferrocyanide processes - are discussed in Section G.

Finally, in Section H are tabulated and discussed selected chemical and physical properties of many of the chemicals used in the waste management solvent extraction processes.

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B. HEAD-END PROCESSES1. Clarification of PAW Solution1.1 Source and Characterization of Solids

Purex Acid Waste (PAW) solution is made by sugar denitration of Purex LWV solution⁽⁴⁾. Purex LWV solution is known to contain at least 4 vol % solids. The most significant and comprehensive examination of the LWV solids is that of Van Tuyl⁽¹³⁾. His data indicate the solids are largely $Zr_3(PO_4)_4 \cdot xH_2O$ (30 vol %) and $SiO_2 \cdot xH_2O$ (60 vol %); metal silicates, $BaSO_4$, and $PbSO_4$ account for the other 10 vol %. Van Tuyl found the solids to be gelatinous but readily centrifugable. No single chemical reagent tested completely dissolved the solids, but successive leaches with 7M HNO_3 , 0.5M oxalic acid, 1-2M NaOH, and 0.5M sodium tartrate in 1M NaOH dissolved the major portion. These leaching experiments indicated that as much as 75% of the zirconium and 90% of the niobium in the LWV solution are probably adsorbed on these solids. Much smaller amounts of other nuclides (Ce-144, Sr-90, etc) appear to be present on these solids.

Laboratory and Purex plant tests in progress as this manual was written demonstrate additional solids can precipitate, depending on conditions, during sugar denitration of LWV solution. For example, in laboratory experiments with plant LWV solution (concentrated to a volume equivalent to 50 gal of waste per ton of uranium processed), dense, black, crystalline solids precipitated when sugar was added to adjust the acidity to about 1M⁽¹⁰⁾. X-ray diffraction analyses tentatively identify them as sulfates. Limited Purex plant experience with centrifugation of denitrated LWV solution appears to be in agreement with the laboratory work⁽⁸⁾. The plant experience indicates denitrated LWV contains 10 to 20 vol % solids. Also, plant results indicate about 60% of the Sr-90, about 70% of the Ce-144, about 50% of the Sb-125, and 90-100% of the ZrNb-95 activity in the LWV are associated with these solids.

A significant laboratory observation is that little or no sulfate solids precipitate when 75 gal/ton LWV is denitrated to about 1M acid. Obviously, if further laboratory and plant tests confirm that sulfate solids do not precipitate at 75 gal/ton, dilution to this volume before denitration would appear to be a highly efficient way of avoiding, or at least minimizing, a difficult problem.

1.2 Leaching Procedures

As this manual was written only one Purex plant test of leaching of solids produced during denitration of LWV solution had been conducted with inconclusive results⁽⁸⁾. In this test, solids from 1750 gal of denitrated LWV were leached at 80 C successively with about 400 gal of 4 M HNO_3 and 400 gal of 2M NaOH-0.1M tartrate. The HNO_3 leach removed about 25% of the Sr-90 and about 50% of the Ce-144. The efficiency of the NaOH-tartrate leach could not be established because of analytical difficulties.

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1.3 Chemical Flowsheet

A chemical flowsheet for the centrifugation and leaching of Purex Acid Waste solids is given in Figure IV-1⁽¹¹⁾. In view of the present (mid-1966) inadequate knowledge of the formation, composition, and leach properties of PAW solids, the flowsheet should be regarded as conceptual only.

2. Lead Sulfate Carrier Precipitation Process

2.1 Introduction

A lead sulfate carrier precipitation process was developed in 1960 for recovering Sr-90 from Purex high level waste (LHW)^(2,6,7,14). The process, shown in Figure IV-2, has the following steps:

1. Add hydroxyacetic acid (originally tartaric acid) to complex iron.
2. Adjust the sulfate concentration to about 1M by the addition of Na_2SO_4 .
3. Neutralize the solution to pH 0.7 to 2 with NaOH.
4. Heat to 90 C and digest 30 min to precipitate the double salt $\text{Na}_2\text{SO}_4 \cdot \text{RE}_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$ ⁽¹⁵⁾.
5. Add $\text{Pb}(\text{NO}_3)_2$ to 0.02M to co-precipitate lead and strontium sulfates.
6. Digest the precipitate about 30 min at 90 C.
7. Centrifuge and wash the precipitate cake with 1M Na_2SO_4 (pH 1). Most of the undesired components (iron, sodium, aluminum, magnesium, manganese, chromium, nickel, calcium, zirconium-niobium, ruthenium, and cesium) are discarded in this step.
8. Metathesize the precipitate in the centrifuge with a mixture of NaOH and Na_2CO_3 to convert the sulfate cake to a carbonate cake.
9. Wash the sulfate from the cake with dilute Na_2CO_3 .
10. Dissolve the carbonate precipitate in HNO_3 .

The strontium and rare earths are further separated by selective precipitation of the rare earth oxalates (not shown). Over 90% recovery of strontium and rare earths have been demonstrated with this process in the Purex plant and in B-Plant Phase I operations.

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Fig. IV-1 CENTRIFUGATION AND LEACHING OF PUREX ACID
WASTE SOLIDS - CONCEPTUAL FLOWSHEET

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Fig. IV-2 LEAD-CARRIER SULFATE PRECIPITATION PROCESS
PAW FEED

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A modification of this procedure has been developed for removing strontium and rare earths from the stored alkaline waste sludge (5,14). The process is similar to the LW process except that it uses a weaker base, Na_2CO_3 , for pH adjustment rather than NaOH and thus obviates the need for a complexant to prevent ferric hydroxide precipitation. A flowsheet based on the dissolved Purex sludge, described in Chapter III, is presented in Figure IV-3.

The variables affecting the performance of the two processes are discussed in the following sections. Most of the laboratory studies were made with the Purex LW and dissolved sludge compositions shown in Table IV-1. These solutions were diluted about two-fold, typically, during the precipitation procedure. With the exception of iron, variations in the concentrations of the cationic constituents over the range studied did not appear to affect the performance of the process. Although solutions derived from Redox sludge (RAS) were not tested, the results are expected to be similar.

TABLE IV-1
TYPICAL PUREX WASTE COMPOSITIONS USED IN LABORATORY
AND PILOT PLANT STRONTIUM PRECIPITATION STUDIES
(Source of Data: HW-69534, HW-79286, BNWL-4)

Constituent	Concentration, M ^(a)		
	Purex LW	Purex Dissolved Sludge	
		#1	#2
Na	0.6	0.5	1.4
H	4.0	1.0	0.7
Fe(III)	0.5	0.1	0.3 - 0.7
Al	0.1	0.29	0.20
Cr	0.01	0.02	0.014
Ni	0.01	0.02	0.014
U(VI)	0.01	----	----
Sr	0.002	0.0008	0.0008
RE	0.01	0.004	0.004
Ca	----	0.014	0.01
Mg	----	0.004	0.0028
Mn	----	0.02	0.014
$\text{SO}_4^{=}$	1.0	0.044	1.4
$\text{PO}_4^{=}$	0.01	----	0.02
NO_3^{-}	4.5	2.8	2.1

(a) Initial composition. Final solution was usually diluted about two-fold by addition of complexant, sulfate, and pH adjustment solutions.

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Procedure

- Adjust PAC to 1M SO_4 and pH 1 with NaHSO_4 and Na_2CO_3 .
- Heat to 80 C, add $\text{Pb}(\text{NO}_3)_2$ and digest for 30 minutes.
- Allow slurry to settle and cool (1 hr), then decant through centrifuge.
- Repeat Steps 1, 2, and 3 two more times.
- Wash accumulated ppt. 3 times with hot water; settle and decant each wash through centrifuge.
- Slurry precipitates from precipitator and centrifuge to metathesis tank.
- Add sufficient metathesis solution to give 20 moles OH^- mole Pb. Digest 30 min. at 80 C. Decant through centrifuge.
- Wash ppt. with hot Na_2CO_3 solution; decant through centrifuge.
- Dissolve ppt. with HNO_3 (routed first through centrifuge).

Fig. IV-3 LEAD-CARRIER SULFATE PRECIPITATION

PROCESS - PAS FEED: Conceptual Flowsheet

(Based on data from BNWL-4)

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2.2 Strontium and Rare Earth Precipitation

2.2.1 Effect of Sulfate Concentration

Sulfate alone precipitated much of the strontium from synthetic Purex 1MW, as shown in Figure IV-4⁽⁷⁾. The strontium recovery reached a maximum of 80% at 3M sulfate.

Copious amounts of iron also precipitated when the sulfate concentrations exceeded 1M at pH 1. Iron precipitation could be prevented without affecting strontium recovery by adding about one mole of tartrate per mole of iron, and most of the laboratory and Purex plant data were obtained with tartrate present. More recently, iron precipitation in Purex plant runs has been prevented by the addition of less expensive hydroxyacetic acid at the rate of two moles per mole of iron.

2.2.2 Effect of Carriers

The use of carrier precipitates gave improved strontium recovery at relatively low sulfate concentrations. Several carrier ions were tested, with the results shown in Figure IV-5⁽⁷⁾. Of the ions tested, lead was chosen for Purex plant use because of ease of subsequent removal.

The precipitation was found to be an adsorption or carrier-type reaction and not simply a solubility-product precipitation of SrSO_4 . The fraction of strontium precipitated decreased with increasing strontium concentration, implying saturation of specific adsorption sites.

2.2.3 Effect of Sulfate and Lead Carrier Concentration

The effect of lead carrier concentration on strontium recovery at various sulfate concentrations is shown in Figure IV-6⁽⁷⁾. The results show that near quantitative strontium recovery can be obtained at pH 0.4 upon the addition of 0.02 to 0.03M $\text{Pb}(\text{NO}_3)_2$ to feed adjusted to $\geq 1\text{M}$ sulfate.

Cerium losses (not shown) were not affected by the addition of lead. Cerium losses were generally less than 4% except at 0.5M sulfate where the losses increased to 14 to 37%.

2.2.4 Effect of pH and Tartrate

The effect of pH on strontium precipitation is shown in Figure IV-7 at several levels of lead and sulfate concentrations⁽⁷⁾. Strontium recovery was near optimum at a pH of 1 to 2 (with 1.7 to 2 moles of tartrate present per mole of iron). The losses tended to increase gradually as the pH increased beyond 2, possibly through tartrate complexing. In another series of experiments with about 50% more tartrate present (2.5 moles

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FIGURE IV-4

Recovery of Strontium From Synthetic Purex Waste as a Function of the Sulfate Concentration
(Source of Data: HW-69534)

FIGURE IV-5

Recovery of Strontium From Synthetic Purex Waste as a Function of the Carrier Concentration
(Source of Data: HW-69534)

FIGURE IV-6

EFFECT OF LEAD CARRIER AND SULFATE CONCENTRATION ON STRONTIUM RECOVERY
(Source of Data: HW-69534)

FIGURE IV-7

EFFECT OF pH ON STRONTIUM RECOVERY
(Source of Data: HW69534, HW79286)

tartrate/mole iron), the strontium losses rose sharply from 6.4% at pH 2.5 to 65% at pH 3.6⁽⁷⁾. Cerium losses increased even more sharply with increasing pH and tartrate concentration, and a pH of 2 would be the maximum pH recommended for recovering strontium and rare earths with a tartrate-complexed flowsheet.

2.2.5 Effect of Temperature

Both strontium and cerium losses were substantially lowered by digestion at elevated temperatures, as shown in Figure IV-8^(5,7). Pilot plant studies indicated that the effect was irreversible; after digestion at 80 C, precipitate slurries were cooled and held overnight without significant increases in the concentrations of either strontium or cerium in the supernate⁽¹²⁾.

2.2.6 Effect of Digestion Time

Strontium recovery was improved by digesting the feed at 80 C several minutes prior to lead addition, as shown in Table IV-2⁽⁵⁾.

TABLE IV-2
EFFECT OF DIGESTION TIME ON STRONTIUM LOSSES
(Source of Data: HW-79286)

Synthetic Purex LW

1.1M $\text{SO}_4^{=}$

0.02M Pb

pH 1.0

Digested at 80 C for
indicated time before lead
addition and centrifugation

<u>Digestion Time, Min</u>	<u>% Sr Remaining in Supernate</u>
1	19.0
15	4.1
30	5.0
45	2.4
60	4.8

Strontium losses in pilot plant runs were not affected by the rate of lead addition, by the degree of agitation during addition, or by the time of addition after reaching the digestion temperature, provided that at least 15 min of digestion were provided⁽¹²⁾. In other experiments, losses increased significantly when the lead was added before the pH adjustment step⁽⁷⁾.

The digestion period was not required in the absence of rare earths⁽⁵⁾. This suggests that the formation of the sodium-rare earth sulfates, known to be

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FIGURE IV-8

EFFECT OF DIGESTION TEMPERATURE ON
STRONTIUM AND CERIUM RECOVERY

(Source of Data: HW-69534, HW-79286)

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temperature dependent and slow^(6,15), has an initially adverse effect on strontium recovery.

Lead sulfate precipitate from a previous strontium precipitation strike will scavenge strontium from fresh feed solution (after sulfate addition and pH adjustment). Equilibrium removal in pilot plant runs was reached within about 40 minutes after reaching the 80 C digestion temperature⁽¹²⁾.

2.2.7 Effect of Iron Concentration

Iron proved to be the most troublesome impurity in the feed. Its presence in Purex feed required the addition of tartaric or hydroxyacetic acid to prevent its precipitation during the NaOH pH adjustment step. In several Purex plant runs, higher-than-normal iron concentrations (ca 0.7M) also limited the maximum pH to about 1.5 through precipitation of an iron-tartrate complex that solubilized the cake during subsequent metathesis operations.

In the absence of complexing agents, the pH can be adjusted to at least pH 2 without precipitating iron by using a weak base such as sodium carbonate to neutralize the excess acid⁽⁵⁾. Further safe "neutralization" can be obtained by adding the required sulfate as Na_2SO_4 , which reduces the free hydrogen ion concentration through formation of the bisulfate ion (HSO_4^-). Very little foaming was observed during neutralization of sludge feed #1 (Table IV-1) when carbonate was added after the sulfate concentration had been adjusted to 1M by the addition of 2M Na_2SO_4 ⁽¹²⁾.

Without complexants, the iron solubility in synthetic sludge feeds was limited to about 0.2M at 1M sulfate (pH 1.2)⁽¹²⁾. The precipitate obtained with higher iron concentrations was apparently ferric sulfate. High strontium losses (6 to 28%) in several pilot plant runs with 0.35M iron initially present in the adjusted feed were attributed to sulfate depletion due to iron complexing and precipitation⁽¹²⁾.

2.3 Sulfate Cake Washing

The supernate must be removed from the lead sulfate cake to prevent precipitation of sulfate-soluble impurities (iron, magnesium, manganese, etc.) during the alkaline metathesis step. Commonly, 1M Na_2SO_4 at pH 1 has been used for this purpose, with the sulfate added to prevent dissolution of the cake. Laboratory and pilot plant studies have since shown that the cake was equally insoluble in water and 0.05M HNO_3 at temperatures ranging from 30 to 80 C^(3,12). Cerium and strontium losses, however, were excessive in 0.1M HNO_3 washes⁽¹²⁾. Typical solubility losses obtained during pilot plant washing studies are shown in Table IV-3. The use of a dilute acid or salt wash solution may be preferred over water to prevent possible peptization of the precipitate, though this was not observed in laboratory water washing tests.

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TABLE IV-3
STRONTIUM AND CERIUM LOSSES
OBTAINED DURING SULFATE CAKE WASHING STUDIES
(Source of Data: BNWL-4)

Conditions: Precipitate stirred with wash solutions for
5 to 20 min. at indicated temperatures.

Wash Composition <u>M HNO₃</u>	Vol. per Wash, <u>L./Mole Pb</u>	No. of Washes	Temp <u>°C</u>	Total % <u>Dissolved</u>	
				<u>Sr</u>	<u>Ce</u>
0	3	1	30	< 2	--
0.05	1.5	3	40	1.3	--
0.05	{ 2.8 7.3	2	50	2.3	--
		1(a)	80	0.7	--
0.1	2.5	2	80	3.1	--
0.1	8.8	2	80	18(b)	63(b)

(a) The third of three successive washes.

(b) Approximately 5% loss in the first wash.

2.4 Metathesis and Cake Dissolution

Although various leaching techniques have been tested for dissolving the lead sulfate cake⁽⁷⁾, the most effective cake dissolution method has involved carbonate metathesis: The cake is digested with a sodium carbonate solution to convert the sulfate precipitates to the less soluble carbonates; the sulfate supernate is washed from the converted carbonate cake; and the precipitate is dissolved in nitric acid. Sodium hydroxide is usually added to the metathesis solution to partially or completely dissolve the lead and to accelerate the metathesis reaction.

Lead sulfate forms hydrated lead oxide with NaOH and is soluble in an excess of the reagent, forming the plumbite ion:

Typical data for the solubility of lead in NaOH are shown in Figure IV-9^(1,9,12). The data show that the lead solubility in saturated solutions is greatly lowered by aging, attributed to the conversion of the more soluble hydrated lead oxide to the less soluble but more stable yellow and red lead oxides⁽¹⁾.

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FIGURE IV-9

LEAD SOLUBILITY IN SODIUM HYDROXIDE

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Lead, strontium, and cerium losses to some of the carbonate-hydroxide metathesis solutions used in laboratory and pilot plant tests are shown in Table IV-4. Strontium and cerium losses were quite low under all conditions shown. As little as 0.1M carbonate was sufficient to prevent strontium dissolution⁽³⁾. In the absence of carbonate, however, about 20 to 50% of the strontium was dissolved along with 85% of the lead⁽⁷⁾.

TABLE IV-4
LEAD, STRONTIUM, AND CERIUM DISSOLUTION
DURING METATHESIS OF LEAD SULFATE CAKE
WITH CARBONATE-HYDROXIDE MIXTURES

(Source of Data: HW-69534, HW-81201, BNWL-4)

Conditions: Lead sulfate cake from LW or dissolved sludge precipitations was washed 2 or 3 times to remove supernatant waste, then contacted 10 to 30 min with leach solutions, using the conditions shown.

Leach Composition, M		Vol per Leach L/Mole Pb	Number of Leaches	NaOH/Pb (a)	Temp °C	Total % Dissolved			Ref.
Na ₂ CO ₃	NaOH					Pb	Sr	Ce	
1	5	1.3	2	13	60	41	2.2	<0.4	(7)
1	5	1.3	3	20	60	33	1.0	<0.3	(7)
1	5	2.0	3	30	60	70	1.2	---	(7)
1	5	1.3	6	40	60	57	<1.0	<0.5	(7)
1	5	2.7	4	53	60	95	1.3	<1.0	(7)
1	5	8.0	3	120	60	81	0.7	---	(7)
1	1	~2.5	1	~2.5	80	--	≤1.2	---	(3)
0.5	2	7.3	1	15	80	66	0.8	---	(12)
0.5	1	3.1	2	6.9	80	--	1.2	---	(12)
0.2	2	8.3	1	17	80	87	1.5	0.4	(12)
0.1	6	~2.5	1	15	80	--	≤2.0	---	(3)
0.1	6	~2.5	3	45	80	--	≤2.0	---	(3)

(a) Cumulative mole ratio for the complete series of leaches.

Lead solubility increased both with increasing temperature and cumulative NaOH addition. In all cases, however, the total lead dissolved was less than predicted from the solubility data shown in Figure IV-9. This may be partially due to sulfate and carbonate competition, but it may also be caused by the intermediate conversion of the lead sulfate to less soluble lead oxide crystalline forms or inadequate digestion times.

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The solubility of the metathesized precipitate in HNO_3 is dependent on both the completion of the metathesis and the elimination of the displaced sulfate ions. With good agitation, the metathesis reaction was essentially complete within 5 min at 80°C ⁽³⁾; but with inadequate agitation (slow-speed stirring or air sparging), strontium conversion was incomplete even after digesting 40 min at 80°C ⁽¹²⁾.

The free sulfate can be washed from the cake with water or dilute Na_2CO_3 . Product losses in pilot plant wash solutions were low in either case, as shown in Table IV-5. The effectiveness of the wash in removing sulfate is dependent on the wash volume and the degree of agitation and phase separation. These factors have not been extensively investigated, but 6 to 9 liters of wash solution per mole of lead in the initial cake proved adequate in pilot plant runs to permit quantitative strontium dissolution in nitric acid.

TABLE IV-5
STRONTIUM AND CERIUM LOSSES
OBTAINED DURING METATHESIZED-CAKE WASHING
(Source of Data: BNWL-4)

Conditions: Metathesized (carbonate) precipitates were stirred with wash solutions for 15 to 40 min at the indicated temperature.

Wash Composition <u>M Na_2CO_3</u>	Wash Vol L/Mole Pb ^(a)	Temp., <u>$^\circ\text{C}$</u>	<u>% in Supernate</u>	
			<u>Sr</u>	<u>Ce</u>
0	2.5	50	1.5	--
0.1	2.8	25	0.6	--
0.1	0.8	40	0.2	--
0.1	2.3	40	1.3	--
0.1	2.8	80	0.2	--
0.1	8.3	80	1.5	0.3

(a) Based on lead content of original sulfate cake.

2.5 Precipitate - Supernate Separation Methods

2.5.1 Centrifugation

Centrifugation has been satisfactorily used as the conventional plant method for removing the supernate from the lead sulfate and metathesized carbonate slurries. Table IV-6 illustrates the effect of centrifuge operating variables on pilot plant strontium losses when removing the supernate

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from the lead sulfate cake⁽¹²⁾. The results were obtained with a 26-in. solid-bowl centrifuge. The data indicate that adequate separation can be obtained over at least a two-fold range of flow rates and operating speeds. The centrifuge cake volume averaged about 0.5 liter per mole of lead added. The lead sulfate cake had a pasty, clay-like consistency and was very difficult to slurry and wash in the pilot-plant centrifuge.

TABLE IV-6
EFFECT OF HOLD-UP TIME AND CENTRIFUGAL FORCE
ON CENTRIFUGATION OF LEAD-SULFATE STRONTIUM-
SULFATE SLURRIES

(Source of Data: BNWL-4)

Conditions: Strontium precipitated with 0.02M Pb, digested 30 min at 80 C before pumping to centrifuge.
(Run 12 had an additional decantation step preceding the centrifuge that removed 80 to 95% of the strontium.)

<u>Run No.</u>	<u>Hold-up Time, Min.</u>	<u>Centrifuge Speed, RPM</u>	<u>Centrifugal Force, Gravities</u>	<u>% Sr in Supernate</u>
10	3.8	1860	1280	5.3
10	5.1	1860	1280	4.7
10	5.7	1860	1280	3.6
10	7.1	1860	1280	3.2
<hr/>				
12	4.6	930	320	2.4
12	4.6	1860	1280	1.9

2.5.2 Settling and Decantation

Settling rates for pilot plant lead sulfate and carbonate precipitates are shown in Table IV-7 as a function of supernatant solutions and temperature⁽¹²⁾. In all cases, the settling rate was greatest at elevated temperature and in low-salt wash solutions. The settling studies showed that effective particle sizes were at least 10 microns, much greater than the sub-micron sizes found by microscopic analysis, indicating that coagulation occurred during settling.

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TABLE IV-7
SETTLING RATES FOR LEAD SULFATE
AND CARBONATE PRECIPITATES

(Source of Data: BNWL-4)

Conditions: Slurry at indicated temperatures allowed to settle in a tall, graduated cylinder over distances of 4 and 8 inches.

<u>Supernatant Solution</u>	<u>Temp, °C</u>	<u>Settling Rate, in/min</u>	
		<u>4</u>	<u>8</u>
Sulfate waste supernate (a)	30	1.1	---
Sulfate waste supernate (a)	40	0.9	0.7
Sulfate waste supernate (a)	50	1.7	---
Sulfate waste supernate (a)	80	2.2 (b)	2.5 (c)
0.1M HNO ₃ (sulfate cake wash)	80	5.3, 6.0	---
2M NaOH, 0.2M Na ₂ CO ₃	20	0.5	---
2M NaOH, 0.2M Na ₂ CO ₃	50	1.0	1.1
2M NaOH, 0.2M Na ₂ CO ₃	80	2.8	2.3
0.1M Na ₂ CO ₃ (carbonate cake wash)	80	6.0	5.6

(a) Supernate from lead sulfate precipitation of synthetic sludge wastes

(b) Average of 8 determinations, ranging from 1.6 to 3.1 in/min

(c) Average of 5 determinations, ranging from 1.3 to 3.8 in/min

Pilot plant decantation studies, made in a 55 gal drum with a central bottom outlet, demonstrated excellent separation performance⁽¹²⁾. The precipitates were allowed to settle 10 to 75 min at 80 C (liquid depths of 15 to 24 in) before the supernate was pumped from the bottom of the first drum to a second drum where the procedure was repeated - this time pumping to waste. The complete process, including dissolution of the metathesized cake, was demonstrated in this fashion. Supernate samples accounted for 98% of the strontium in the system, showing that very little settled precipitate was lost - even without a backup centrifuge.

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Settling and decantation through a backup centrifuge would afford the greatest flexibility for B-Plant. For example, several batches of feed can be precipitated in the precipitation tank without removing the lead sulfate cake. The cake can be washed, metathesized, and dissolved in the same vessel or transferred to a smaller tank for metathesis and dissolution. The centrifuge load should be less than 5% of the precipitate.

Multiple lead sulfate strikes were made in pilot plant precipitators without removing the lead sulfate cake between strikes to demonstrate this concept⁽¹²⁾. This method of operation actually reduced lead consumption. Although 0.02M lead was required on the first strike, the remaining strikes required as little as 0.010 to 0.0125M added lead to reduce the strontium losses to 5% or less. As discussed in Section 2.2.6, a 40 min digestion period was required to obtain the optimum benefit with this scavenging technique.

3. References

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C. STRONTIUM AND RARE EARTH SOLVENT EXTRACTION PROCESSES:
PROCESS CHEMISTRY

1. General Principles of Solvent Extraction

If an aqueous solution of $\text{Sr}(\text{NO}_3)_2$ is placed in a beaker and a layer of di(2-ethylhexyl)phosphoric acid (D2EHPA) diluted with kerosene is added and stirred with the aqueous layer for a few minutes, it may be shown by chemical analysis of the resulting aqueous and organic phases that some of the strontium transferred from the aqueous to the organic phase. The operation is referred to as solvent extraction. Further, if the organic layer is removed from the above-mentioned system and placed in contact with a dilute solution of acid in water, some of the strontium transfers back to the aqueous phase. These two steps, extraction and stripping, operated in sequence and under optimized conditions, are the basic elements of a solvent extraction process for recovering and purifying a desired constituent from an aqueous feed containing one or more impurities.

In either of the above two-phase systems, if mixing is continued long enough, the strontium concentration in each phase becomes constant, although usually not the same in each phase. When constant concentrations have been attained, a dynamic equilibrium has become established, with the amount of strontium leaving the aqueous phase equal to the amount returning in a given time. The process is referred to as equilibration of the phases.

The ratio between the concentrations of a given solute in each of two liquid phases in contact equilibrium is variously referred to as the distribution ratio, distribution coefficient, or partition coefficient. It is designated in this manual by the letter E to which a subscript and superscript are appended to indicate which phase is the reference phase. Thus, E_{a}^{o} indicates the ratio of the solute concentration in the organic phase to the concentration in the aqueous phase. The term "distribution ratio" is used in the sense of this organic-to-aqueous distribution ratio throughout this manual, although E_{o}^{a} , the reciprocal of E_{a}^{o} , is sometimes used elsewhere in project literature. Other symbols (e.g. D, K_{d} , etc.) are also employed in solvent extraction literature.

The distribution ratio is the ratio of solute concentrations regardless of the relative volumes of the two liquid phases. It is apparent, however, that the amount of strontium extracted from the aqueous solutions by a D2EHPA solution, for example, is dependent upon the relative volume of D2EHPA phase as well as on the strontium distribution ratio.

The equilibrium distribution of a solute in liquid-liquid extraction systems ordinarily depends on many factors. For instance, in the example cited above, the distribution of strontium between aqueous and D2EHPA phases depends on the aqueous phase acidity, temperature, presence of complexing agents in the aqueous phase, and concentration of D2EHPA in the organic phase, as well as on several other factors. D2EHPA is also

an excellent solvent for extracting many other metal ions, but it is possible by careful control of these variables to improve greatly the selectivity of the solvent for a desired cation. A comprehensive account of the theory and operation of D2EHPA extraction processes is given in the ensuing parts of this section.

2. Theory of D2EHPA Solvent Extraction Systems

2.1 Historical Introduction

Active interest in D2EHPA as an extractant in solvent extraction separations began about 10 years ago. In 1955, K. B. Brown and associates at Oak Ridge National Laboratory (ORNL) developed the Dapex process^(7,8,9,34) for the D2EHPA extraction recovery of uranium from uranium ore sulfate leach liquors. Since that time numerous applications have been made in chemical separations processes, especially in the nuclear field. Processes have been developed both at Hanford and at ORNL for recovering Sr-90^(46,76,81), mixed fission product rare earths⁽⁴¹⁾, ZrNb-95⁽²⁶⁾, and Np-237 from reactor fuel process waste liquors. An important milestone has been operation of a D2EHPA extraction process in the Hanford Strontium Semiworks to recover and purify more than 10 megacuries of Sr-90^(5,33,76).

Extensive physicochemical studies of the theory and mechanisms involved in D2EHPA extraction systems have progressed concurrently with the process studies. Especially significant contributions have been made at Argonne National Laboratory by Peppard, et. al.^(15,48-58); at ORNL by Baes, McDowell, Coleman et. al.^(1-3,45); in Sweden by Dyrssen⁽³⁶⁾; and in Japan by Sato⁽⁶⁶⁻⁶⁹⁾. Pertinent aspects of the current (1966) theory of D2EHPA extraction systems are reviewed in the sections immediately following. More detailed reviews are to be found in recent papers by Baes⁽²⁾ and Peppard, et. al.⁽⁵⁸⁾.

2.2 Reactor Mechanisms

2.2.1 Trace Solvent Loading

D2EHPA exists as a hydrogen-bonded dimer in the non-polar diluents n-hexane, cyclohexane, benzene, and CCl₄⁽³⁷⁾. Presumably the same is true in the non-polar, commercially available hydrocarbon solutions used as diluents for D2EHPA in B-Plant operations.

The general extraction of tracer-level concentrations of a metal ion M^{+b} may be represented as

where R represents the di(2-ethylhexyl)phosphate anion, (HR)₂ represents

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dimerized D2EHPA, and the subscripts aq and org refer to aqueous and organic phases, respectively. In general, extraction of a bth-valent metal ion requires b dimer molecules and releases b hydrogen ions to the aqueous phase.

Expression (1) is applicable, for example, to the D2EHPA extraction of tracer level U(VI) existing as $UO_2^{++(1)}$. Further, Peppard and co-workers^(48,50,52-56) in a long series of investigations have established that D2EHPA in non-polar diluents extracts tracer-level lanthanide(III) and actinide(III) elements according to the reaction:

Peppard notes that Reaction (2) is in accord with observed solvent dependencies but that dependency data do not distinguish between $M(HR_2)_3$, $MR_3(HR)_3$, $MR_2(HR_2)(HR)_2$, etc. Peppard chooses the $M(HR_2)_3$ formulation because it represents extraction by a mono-ionized dimer, but no proof that this is correct has been given.

Recent tracer-level studies have indicated D2EHPA extraction mechanisms other than that given in Reaction (1). Cases are now known where the extractant dependency for M^{+b} is either greater or less than bth power. For example, a third power extractant dependency has been found for Ca(II) [Peppard and Mason⁽⁵⁷⁾] and for Sr(II) [McDowell and Coleman⁽⁴⁵⁾]. Peppard suggests the "third power extractant dependency" systems might be expressed as:

with the reservation that the formulation of the extracted species is consistent with the stoichiometric data but is not necessarily structurally correct. Along these same lines McDowell and Coleman⁽⁴⁵⁾ also report that the stoichiometry for tracer sodium extraction by dimerized D2EHPA is:

In contra-distinction to calcium, strontium, and sodium which exhibit an extractant dependency greater than the charge of the cation, thorium exhibits an extractant dependency smaller than the charge of the cation. Thus, third-power dependency was observed when tracer thorium was extracted from a nitrate media into toluene-D2EHPA solutions⁽⁵⁶⁾. Also in

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this system, the presence of nitrate in the organic phase was proved. Consequently, Peppard represents the extraction as:

Similarly, in the D2EHPA (toluene) vs. (perchlorate + nitrate) system, the neptunium(IV) extracted species has been shown to contain one nitrate group and the mechanism to correspond to Equation (5) (58). No corresponding study of Pu(IV) is known.

2.2.2 High Solvent Loading

Although extraction of tracer-level U(VI) may be represented by the expression:

this expression is only valid if a reasonably large portion of the D2EHPA is free, i.e., not found in the extracted species. As the relative UO_2^{++} content of the organic is increased (high solvent loading), a point is reached at which the solution becomes quite viscous, and finally a gel-like solid is found. This solid has the empirical composition UO_2R_2 and appears to exist in solution as a chain polymer (1).

Similarly, trivalent lanthanides at saturation in D2EHPA form a gel-like solid of empirical composition MR_3 which is assumed to be formed through three dimensional polymerization (38). The phenomenon appears general. Peppard and co-workers have prepared, for example, solids having the composition KR , LiR , NaR , ScR_3 , ThR_4 and HfR_4 . McDowell and Coleman (45) have also reported that ultimate loading of a D2EHPA solution with sodium or strontium leads to the salts NaR and SrR_2 , respectively.

According to Peppard the simplest interpretation of these observations is as follows: "In the region far below saturation, the M^{+b} cation is complexed by a mono-ionized dimer forming $\text{M}(\text{HR}_2)_b$, the HR_2^{-} being capable of chelation to form an eight-membered ring with the M atom as a member. However, as saturation is approached, the proton of the extracted species may be replaced by an M atom. This replacement results, ultimately, in the formation of a three-dimensional polymer of empirical formula MR_b ."

2.3 Effects of pH and Ion Charge and Size

For the generalized reaction

the equilibrium constant can be written as

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$$k_{eq} = \frac{[M(HR_2)_b] [H^+]^b}{[(HR)_2]^b [N^{+b}]} \quad (7)$$

Defining $[M(HR_2)_b] / [M^{+b}]$ as the distribution ratio, D_M (using concentrations rather than activities), Equation (7) can be rearranged to

$$D_M = \frac{k_{eq} [(HR)_2]^b}{[H^+]^b} \quad (8)$$

Equation (8) illustrates a general principle in D2EHPA extraction systems, namely that the distribution ratio for a M^{+b} metal ion is inversely proportional to the bth power of the equilibrium aqueous phase hydrogen ion concentration. Proper control of aqueous phase acidity (pH) is thus essential in D2EHPA systems to extract desired metals and to separate them from impurities. To achieve such pH control it is customary, as discussed more fully later, to add organic acids as buffering agents to aqueous streams.

Lewis at ORNL, among others, has made detailed studies of the variation of the distribution ratio of various metal ions (at tracer level concentration) into 1M D2EHPA as a function of aqueous phase pH⁽⁴⁴⁾. Selected data from Lewis' work are shown in Figure IV-10.

In general, the larger the charge on the metal cation the greater the magnitude of the equilibrium constant as expressed by Equation (1). That is to say, quadrivalent ions are extracted more strongly than divalent ions, etc. A partial list of the affinity of metal ions for D2EHPA is $Zr(IV) \simeq Ce(IV) \simeq Pu(IV) > Np(IV) > Y(III) > Eu(III) > Fe(III) > Pm(III) > Ce(III) > La(III) > Ca(II) > Ru(III) > Sr(II) > Ba(II) > Na(I) > Cs(I)$ ⁽³⁹⁾.

Dyrssen⁽³⁶⁾ has pointed out that for the trivalent lanthanide and actinide ions $\log k_{eq}$ appears to vary inversely with ion radius. A similar correlation has been found for the alkali and the alkaline earth ions⁽²⁾. In all of these groups, the smaller the metal ion the more strongly it is extracted.

The oxocations UO_2^{++} , PuO_2^{++} , and NpO_2^{++} are by far more strongly extracted than other divalent cations⁽²⁾. These cations appear to hold a unique position in the affinity series.

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2.4 Effects of Aqueous Phase Complexants

Strontium, fission product rare earths, and americium in PAS and PAW solutions are associated with various inert (e.g., iron, chromium, nickel, etc) and radioactive (e.g., Ru-106, ZrNb-95, etc.) contaminants. Chemical flowsheets used in the B-Plant for D2EHPA extraction recovery of Sr-90, Am-241, and rare earths specify, as discussed more fully later, preparation of extraction column feed solutions having a pH in the range 3 to 5. It is customary to add to these feed solutions water soluble organic reagents to form soluble coordination compounds with many of the polyvalent inert and radioactive contaminants. Addition of these complexing agents serves the primary purpose of preventing or suppressing coextraction of contaminants and of preventing their precipitation as hydroxides or basic salts in feed solutions adjusted to pH's above 3. Added benefits accrue with certain of the complexing agents from the pH control afforded during the D2EHPA extraction step by the formation or dissociation of protonated forms of the complexing agent.

The complexing agents (ligands) most intensively studied in connection with suppressing extraction of undesirable elements in B-Plant D2EHPA processes are HEDTA (N-hydroxyethylethylenediaminetriacetic acid), EDTA (ethylenediaminetetraacetic acid), DTPA (diethylenetriaminepentaacetic acid), citric acid, tartaric acid, and oxalic acid. The reagents acetic acid and hydroxyacetic acid are also used in B-Plant D2EHPA processes. These latter reagents, although added generally for pH control, also form weak complexes with various di- and trivalent metal ions.

The general reaction of a metal ion M^{+b} and an unprotonated ligand L^{-a} which react stepwise to form the coordination complex ML_n can be represented as (omitting charges for simplicity)

The thermodynamic stability constants for each step are given by an expression of the form

$$K_n = \frac{[ML_n]}{[ML_{n-1}][L]} \quad (10)$$

Generally n is greater than 1; in certain important instances, however, (e.g., EDTA, HEDTA, DTPA), 1:1 complexes are the only significant ones found. Extensive tabulations of K_n values for various metal ions and ligands have been prepared⁽⁶⁾; K_n values of interest to B-Plant separations are listed in Table IV-67.

The complexing agents useful in B-Plant separations are all weak organic acids and thus, depending on aqueous phase acidity (pH), can

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be present as various protonated species. For example, EDTA(H_4L) can be present as H_4L , H_3L^{-1} , H_2L^{-2} , HL^{-3} , and L^{-4} . The relative proportions of the various protonated forms can be calculated from the appropriate acid dissociation constants tabulated in Table IV-66 and more extensively in Reference 6.

The protonated ligands can also react with metal ions to form complexes. Thus, omitting charges, the general reaction is

with the stability constant defined as

$$K_{MH_pL}^M = \frac{[MH_pL]}{[M][H_pL]} \quad (12)$$

Normally $K_{MH_pL}^M$ values are considerably less than K_n values for the same

ligand and can be ignored except at low pH's where the proportion of protonated ligands greatly exceeds the fully dissociated ligands. Selected $K_{MH_pL}^M$ values are listed in Table IV-67.

Since the relative proportions of free ligand and protonated ligands are a function of the hydrogen ion concentration, a conditional stability constant can be defined at any given pH by

$$K' = \frac{(ML')}{(M^{+b})(L')} \quad (13)$$

where (L') is the total concentration of uncomplexed ligand species (H_nL , $H_{n-1}L^{-}$, $H_{n-2}L^{-}$... L^{-n}) and (ML') is the total concentration of complexed metal species. This equation can be rearranged to

$$(ML') = K'(M^{+b})(L') \quad (14)$$

The distribution ratio for M can be written as

$$E_{aM}^O = \frac{M_{org}}{M_{aq}} = \frac{\text{Concentration of all species of M in organic phase}}{\text{Concentration of all species of M in aqueous phase}} \quad (15)$$

In the presence of a complexing agent L in the aqueous phase, the metal M exists in the aqueous phase both in complexed and uncomplexed forms. Hence, the distribution ratio can be written as

$$E_{aM}^O = \frac{[M_{org}]}{[M^{+b}] + [ML']} \quad (16)$$

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Substituting (14) into (16) yields

$$E_{aM}^O = \frac{[M_{org}]}{(M^{+b}) [1 + K'(L')]} \quad (17)$$

If there is only species of M in the organic phase, the previously defined D_M (the distribution ratio for M in the absence of a complexing agent - see Sect. 2.3) can be substituted for $\frac{[M_{org}]}{[M^{+b}]_{aq}}$ and (17) can be written as

$$E_{aM}^O = \frac{D_M}{1 + K'(L')} \quad (18)$$

The importance of selecting and controlling aqueous phase pH in B-Plant D2EHPA processes cannot be over-emphasized. The distribution ratio for an M^{+b} metal ion, as noted earlier (Sec. 2.3) is inversely proportional to the bth power of the equilibrium aqueous phase hydrogen ion concentration irrespective of the presence or absence of a complexing agent. With a complexing agent present, the aqueous phase pH, as just noted, also determines the relative proportions of protonated ligands and hence the extent of complexing of metal ions. A pH must be specified, therefore, which permits quantitative recovery of desired constituents with maximum complexing of unwanted impurities.

2.5 Calculation Procedures for Estimating Strontium Distribution Ratios

In D2EHPA solvent extraction processes for recovering and purifying Sr-90, it is obviously desirable to be able to predict quantitatively the effect of flowsheet variables on strontium distribution ratios. As discussed above, there are three principal factors which affect the strontium E_a^O : (a) the pH of the aqueous feed; (b) the presence in the aqueous feed of other extractable metal ions which compete with strontium for the solvent; and (c) the presence in the aqueous phase of ligands such as acetate, EDTA, etc which can form in-extractable complexes with strontium.

A procedure for estimating the strontium E_a^O which takes into account the three factors mentioned above is outlined in the following sections (33a). As will become apparent, certain assumptions (particularly about solvent extraction mechanisms) and approximations have been made in developing this calculation procedure. These approximations reflect the present inadequate knowledge of D2EHPA extraction chemistry as applied to other than extraction of metals at tracer concentrations. Nevertheless, the calculation procedure shown is the best currently available and, as will be shown, can be used to predict strontium distribution ratios.

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2.5.1 Estimation of Strontium E_a^0 in Absence of Complexants

A procedure for estimating the Sr E_a^0 will be considered first for a D2EHPA-TBP-hydrocarbon diluent solution in contact with an aqueous solution containing small concentrations of strontium and other divalent and trivalent ions and up to 1.5M Na^+ . Subsequently, the effects of aqueous phase complexing agents which lower the Sr E_a^0 will be considered.

In treating this system, any effects of TBP (Section 2.6.2) and of the hydrocarbon diluent on the extraction reactions are neglected. Further, it is assumed that Sr^{++} , Ca^{++} , Am^{+++} , and the trivalent rare earths are extracted according to the mechanism shown in Equation (1), Section 2.2.1, that is, as the species $M(HR_2)_2$. Because of its high concentration in extraction feeds of interest, Na^+ may be extracted as $(NaR)_x$ as well as $NaHR_2$. For the purposes of this calculation procedure, it was assumed that $x = 2$.

The equilibrium constants for the reactions of interest, expressed in molar concentrations, are

$$Sr \ k_{eq} = \frac{[Sr(HR_2)_2] [H^+]^2}{[Sr^{++}] [(HR)_2]^2} \quad , \quad (19)$$

$$Na \ k_1 = \frac{[NaHR_2] [H^+]}{[Na^+] [(HR)_2]} \quad , \quad (20)$$

$$\text{and} \quad Na \ k_2 = \frac{[(NaR)_2] [H^+]^2}{[Na^+]^2 [(HR)_2]} \quad . \quad (21)$$

Using the definition of D_M from Section 2.4, Equation (19) can be rearranged to

$$D_{Sr} = \frac{Sr \ k_{eq} [(HR)_2]^2}{[H^+]^2} \quad . \quad (22)$$

The extent to which the solvent is loaded with other extractable ions must be considered in determining the value of $[(HR)_2]$ to be used in Equation (22). Since extraction of rare earth and alkaline earth ions has been assumed to occur by the mechanism shown in Equation (1), it follows that a suitable solvent loading correction for such ions in the solvent is given by $\underline{M}$ "free D2EHP" = $2 [(HR)_2] + 2 [(NaHR_2)] + 2 [(NaR)_2] =$

$$R-4 (\sum \underline{M}^{+2})_{org} - 6 (\sum \underline{M}^{+3})_{org} \quad (23)$$

where R represents the initial D2EHPA molarity (formula weights of D2EHPA/liter).

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Equation (23) defines the free D2EHP as that amount of solvent not associated with multivalent ions. (Iron and aluminum are often present in fission product feeds and can extract under certain conditions but their effect on solvent loading is relatively minor. Data obtained by Bray⁽¹⁷⁾ on the inhibiting effect of iron and aluminum on the strontium E_a^0 suggests that only about 1.8 to 2.6 moles of D2EHPA are tied up by the extraction of a mole of combined iron and aluminum.)

To obtain a suitable correction for sodium loading, Equation (20) and (21) are rearranged to give

$$[\text{NaHR}_2] = \frac{\text{Na } k_1 [(\text{HR})_2] [\text{Na}^+]}{[\text{H}^+]} \quad (24)$$

and

$$[(\text{NaR})_2] = \frac{\text{Na } k_2 [(\text{HR})_2] [\text{Na}^+]^2}{[\text{H}^+]^2} \quad (25)$$

Substitution of these values of $[\text{NaHR}_2]$ and $[(\text{NaR})_2]$ in Equation (23) and rearranging slightly leads to

$$2 [(\text{HR})_2] \left[1 + \text{Na } k_1 \frac{[\text{Na}^+]}{[\text{H}^+]} + \text{Na } k_2 \frac{[\text{Na}^+]^2}{[\text{H}^+]^2} \right] = \underline{M} \text{ free D2EHP.} \quad (26)$$

Hence,

$$[(\text{HR})_2] = \frac{\underline{M} \text{ free D2EHP}}{2 \left[1 + \text{Na } k_1 \frac{[\text{Na}^+]}{[\text{H}^+]} + \text{Na } k_2 \frac{[\text{Na}^+]^2}{[\text{H}^+]^2} \right]} \quad (27)$$

Finally, substituting this value of $[(\text{HR})_2]$ into Equation (22), the expression for D_{Sr} is

$$D_{\text{Sr}} = \frac{\text{Sr } k_{\text{eq}}}{[\text{H}^+]^2} \cdot \frac{[\underline{M} \text{ free D2EHP}]^2}{4 \left[1 + \text{Na } k_1 \frac{[\text{Na}^+]}{[\text{H}^+]} + \text{Na } k_2 \frac{[\text{Na}^+]^2}{[\text{H}^+]^2} \right]^2} \quad (28)$$

The value of D_{Sr} is thus shown to be a function of $[\text{Na}^+] / [\text{H}^+]$.

Experimentally obtained values of $\frac{(D_{\text{Sr}}) [\text{H}^+]^2}{[\underline{M} \text{ free D2EHP}]^2}$ are plotted versus

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the ratio $[Na^+]/[H^+]$ in Figure IV-11. Similarly, experimental values of

$\frac{(D_{Na}) [H^+]}{M \text{ free D2EHP}}$ versus the ratio $[Na^+]/[H^+]$ are plotted in Figure IV-12.

Until the chemistry of D2EHPA extraction systems is better understood, caution should be exercised in extrapolating the curves in Figures IV-11 and IV-12 to conditions far removed from those used in their derivation.

2.5.2 Estimation of $Sr E_a^O$ in Presence of Complexants

As discussed in Section 2.4, ligands such as acetate, HEDTA, EDTA, etc. which are added to the aqueous phase to control pH or to suppress extraction of undesirable inert and fission product ions form complexes with strontium which lower the strontium distribution ratio. A method of correcting the $Sr E_a^O$ for the effect of such complexing agents is considered below.

The essential points in the derivation of the correction factor are:

- (1) Consider a system which contains the ligands, L_a , L_b , and L_c in the aqueous phase which form with Sr^{++} only inextractable 1:1 complexes of the type SrL_a' , SrL_b' , and SrL_c' . Assume, for the time being, that there are no other metal ions present which will form complexes with these ligands; the effect of the presence of these metal ions will be considered later.

- (2) From Equations (15) and (16)

$$Sr E_a^O = \frac{\text{Concentration of all Sr species in organic phase}}{\text{Concentration of all Sr species in aqueous phase}}$$

$$= \frac{[Sr]_{org}}{[Sr^{++}] + [SrL_a'] + [SrL_b'] + [SrL_c']}. \quad (29)$$

- (3) At any given pH the conditional stability constant (Equation 13) for ligand L_a can be written as

$$K_a' = \frac{[SrL_a']}{[Sr^{++}] [L_a']}. \quad (30)$$

Thus,

$$[SrL_a'] = K_a' [Sr^{++}] [L_a']. \quad (31)$$

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FIGURE IV-11

Preliminary Correlation of D2EHPA-Strontium Extraction Data
 (Source of Data: HW-72666)

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FIGURE IV-12

Preliminary Correlation of D2EHPA - Sodium Extraction Data
(Source of Data: HW-72666)

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- (4) Substitution of this value of $[SrL'_a]$ and the analogous values of SrL'_b and SrL'_c into Equation (29) gives

$$Sr E_a^O = \frac{[Sr]_{org}}{[Sr^{++}] + K'_a [L'_a] [Sr^{++}] + K'_b [L'_b] [Sr^{++}] + K'_c [L'_c] [Sr^{++}]} \quad (32)$$

- (5) If, as has been assumed earlier, the only species of strontium in the organic phase is the complex $Sr(HR_2)_2$, then by Equation (18),

$$Sr E_a^O = \frac{D_{Sr}}{1 + K'_a [L'_a] + K'_b [L'_b] + K'_c [L'_c]} \quad (33)$$

Equation (33) is the relationship desired to permit calculation of the strontium extraction coefficient in the presence of aqueous phase complexing agents. Application requires a knowledge of the values of the various K' and $[L']$ terms and the value of D_{Sr} , which can be obtained from Figure IV-11.

Conditional stability constants for the various ligands studied in this program are presented in Figure IV-13. The values for acetate, hydroxyacetate, and tartrate were calculated from the published dissociation constants of the acids and corresponding strontium complexes (See Tables IV-66 and IV-67). The K' values for citrate, HEDTA, EDTA, and DTPA were calculated from the experimental effect of these complexants on strontium E_a^O 's^(33a). Experimental values of K' are preferred when available because of the complexity of systems containing multibasic acids.

Estimation of the $[L']$ values to use in Equation (33) requires a knowledge of the metal ions other than strontium ion which are present in the aqueous phase and the extent and manner in which these other metal ions react with the various complexing ligands. The sample flowsheet calculation shown below illustrates how $[L']$ values are calculated.

2.5.3 Sample Calculation of Strontium E_a^O

With the above correlation for estimating strontium distribution ratios, it is now possible to determine the feasibility of a given flowsheet to quantitatively extract strontium. The following steps can be used for this purpose:

- (1) Determine the feed composition, including the concentration of both the extractable ions (strontium, calcium, sodium, etc) and those ions which will be essentially completely complexed

FIGURE IV-13

Effect of pH on Conditional Strontium Stability Constants
(Source of Data: HW-72666)

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by ligands (iron, lead, etc.). If a scrub stream is used, assume that it is stoichiometrically combined with the feed to establish the total concentration of ligands and metal ions entering the extraction section at the feed point.

- (2) Select a feed pH. This will normally be in the range of pH 3.5 to 5, high enough to prevent extraction of undesired, complexed metals (such as iron) but not high enough for sodium extraction to depress strontium extraction. If the system is adequately buffered, the equilibrium pH will be essentially the same as the feed (or combined feed plus scrub) pH.
- (3) Select a solvent concentration and a solvent-to-feed flow ratio. Assume that the more extractable ions, and only these ions (such as calcium, strontium, and the rare earths), are completely extracted. Calculate their concentrations in the product solvent and use the values to determine the free D2EHP concentration in the product (Equation 23). This will be the minimum value of free D2EHP in the system.
- (4) Assume that the equilibrium sodium concentration in the aqueous phase at the feed point is the same as the stoichiometric sodium concentration in the combined feed plus scrub. This will be approximately true if sodium extraction is minimized by selection of a low feed pH, a low solvent-to-feed flow ratio, or the use of a scrub stream which returns extracted sodium to the extraction section.
- (5) Calculate D_{Sr} using Figure IV-11 and the values of (free D2EHP), pH, and (Na^+) determined above.
- (6) Establish the ligand concentrations in the feed and scrub according to the requirements of the process. Calculate the concentrations of uncomplexed ligands in the combined feed-plus-scrub. If only 1:1 complexes are formed, this will be equal to the total ligand concentration minus the total molarity of metal ions complexed by that ligand. (In a mixture of metal ions and ligands, the complexes with the greatest stability constants would preferentially be formed. Thus in a mixture of ferric and lead ions and EDTA and citrate ligands, the ferric-EDTA complex would form first; any excess EDTA would then complex the lead. Citrate would form complexes only if there were insufficient EDTA to complex all of the iron and lead.) Assume that only negligible quantities of the extracting ions (strontium, calcium, etc.) are complexed (this will be true if the concentrations of extractable components are small and if the distribution ratios are relatively high).
- (7) Determine the ligand-complexing correction factor $[1 + K'_a(L'_a) + K'_b(L'_b) \dots + K'_c(L'_c)]$, from Figure IV-13, using the above values of free ligand concentrations and the feed pH to determine individual $K'(L')$ values.

- (8) Calculate the actual strontium E_a by dividing the D_{Sr} , determined in Step 5, by the ligand-complexing correction factor (see Equation (33)).

To insure adequate strontium extraction, the calculated distribution ratio should be at least twice the assumed aqueous-to-organic flow ratio. If not, a new flow ratio or a more favorable pH should be assumed and the calculation repeated. A safety margin of $\pm 50\%$ should be applied to the results to compensate for the simplifications inherent in the derivation. The use of the procedure is more clearly illustrated in the following example (33a).

1. Initial Aqueous Phase Composition:

	<u>Feed</u>	<u>Scrub</u>	<u>Combined Feed and Scrub</u>
$\underline{M}$ Sr	0.0016	0	0.0015
$\underline{M}$ Ca	0.004	0	0.0038
$\underline{M}$ Na	1.1	0.3	1.06*
$\underline{M}$ Fe + Pb	0.033	0	0.031
$\underline{M}$ Acetate	0.46	0	0.435
$\underline{M}$ EDTA	0.09	0	0.085
$\underline{M}$ Citrate	0	0.6	0.033
pH	4.7	2.9	(4.7)*
Relative Flow	130	7.5	137.5

*Assumed equilibrium values

2. Solvent Composition: 0.4M D2EHPA; 0.2M TBP; Relative Flow = 30.

3. Free D2EHP: (Assume only strontium and calcium extract and that their extraction is quantitative.)

$$\underline{M} (\text{Sr} + \text{Ca})_{aq} = 0.0053$$

$$\underline{M} (\text{Sr} + \text{Ca})_{org} = \frac{(0.0053)(137.5)}{30} = 0.0243$$

$$\underline{M} \text{ free D2EHP} = 0.4 - 4(0.0243) = 0.303$$

4. Strontium Distribution Ratio, D_{Sr} :

$$\text{For } \text{Na}^+ = 1.06 \text{ and } \text{pH} = 4.7 \log \frac{(\text{Na}^+)}{(\text{H}^+)} = 4.72$$

$$\text{From Figure IV-11, } \frac{D_{Sr} (\text{H}^+)^2}{(\text{free D2EHP})^2} = 8 \times 10^{-7}$$

$$\text{Then } D_{Sr} = \frac{(8 \times 10^{-7})(0.303)^2}{(2 \times 10^{-5})^2} = 184$$

5. "Free" Ligand Concentration, [L] :
(Assume all iron and lead are complexed by EDTA)

$$\text{Free EDTA} = 0.085 - 0.031 = 0.054\text{M}$$

$$\text{Free Citrate} = 0.033\text{M} = \text{total citrate}$$

$$\text{Free Acetate} = 0.435\text{M} = \text{total acetate}$$

6. Correction Factor for Ligand Complexing:

From Figure IV-13, using the feed pH of 4.7,

$$K'_{\text{EDTA}} = 60 \quad \text{and} \quad (K'L')_{\text{EDTA}} = (60)(0.054) = 3.2$$

$$K'_{\text{Citrate}} = 100 \quad \text{and} \quad (K'L')_{\text{Citrate}} = (100)(0.033) = 3.3$$

$$K'_{\text{Acetate}} = 1.5 \quad \text{and} \quad (K'L')_{\text{Acetate}} = (1.5)(0.435) = 0.7$$

$$\therefore 1 + \sum(K'L') = 8.2$$

7. Corrected Strontium E_a^0 :

$$\begin{aligned} \text{Sr } E_a^0 &= \frac{D_{\text{Sr}}}{1 + \sum(K'L')} \\ &= \frac{184}{8.2} = 22. \end{aligned}$$

Applying the recommended $\pm 50\%$ safety margin, the minimum E_a^0 would be about 11.

2.6 Diluent and Solvent Modifier Effects

2.6.1 Third Phase Formation

Alkaline (Na_2CO_3 or NaOH) wash solutions are commonly used to remove yttrium and other contaminants from recycled D2EHPA extractants. Treatment of the extractant with such solutions converts D2EHPA to its sodium salt, NaD2EHP. This salt is soluble in water but only sparingly soluble in aqueous solutions which contain sodium ion. The solubility of NaD2EHP in Na_2CO_3 solutions, for example, decreases from 325 mg/l at 0.38M Na^+ to 7 mg/l at 2.8M Na^+ (23).

The sodium salt also has limited solubility in common kerosene-type diluents (e.g., Soltrol-170 or NPH). Under certain conditions a NaD2EHP-rich phase can form when kerosene solutions containing D2EHPA are contacted with alkaline wash solutions. This NaD2EHP-rich phase lies between the kerosene diluent and the alkaline aqueous phase. To prevent

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formation of this third liquid phase, it is customary to add to the D2EHPA extractant a modifier such as tributylphosphate (TBP). ORNL workers have shown⁽⁸⁾ that the solubility of NaD2EHP in kerosene diluents is greatly increased by addition of neutral organic phosphorous compounds such as TBP, tributyl phosphine oxide, dibutyl-butylphosphonate, etc. TBP is the preferred modifier at Hanford because of its low cost and availability.

An empirical expression:

$$\underline{M} \text{ TBP} = 0.063 + 0.2 (\underline{M} \text{ D2EHPA}) \quad (34)$$

defining the concentration of TBP necessary to prevent third phase formation was derived at ORNL^(8,9). This expression was derived for a specific diluent (Amsco 125-82) from data obtained with an aqueous phase initially 10% Na₂CO₃ and, according to recent Hanford work⁽⁵⁹⁾, is not valid for systems in which the aqueous sodium concentration is less than about 0.6M. TBP requirements at aqueous phase sodium concentrations lower than 0.6M have been determined by Mendel⁽⁷²⁾ for the system NaOH-TBP-D2EHP-Soltrol-170-H₂O. Mendel's data, plotted in Figure IV-14, have been correlated by the equation:⁽⁵⁹⁾

$$\underline{M} \text{ TBP} = 0.156 - 0.093 (\underline{M} \text{ Na}_{\text{aq}}^{+}) + 0.2 (\underline{M} \text{ Na.D2EHP}_{\text{org}}) \quad (35)$$

for (Na⁺)_{aq} concentrations above 0.2M.

The nature of the diluent is believed to affect the constants in the above equation, and suitable correction factors should be obtained for other candidate diluents.

2.6.2 Synergistic Effects

A strong enhancement of U(VI) extraction was first observed at ORNL⁽⁹⁾ when mixtures of dialkylphosphoric acids and neutral organophosphorus compounds were used as solvents, the extraction power of the mixture being greater than the sum of the extraction powers of the separate reagents. The term synergistic extraction was applied to the effect by Coleman.

Recent studies at Hanford have also shown that D2EHPA extraction of strontium from various aqueous solutions is slightly enhanced when TBP is present in the extractant⁽⁷²⁾. McDowell, Coleman, and Case at ORNL⁽²⁹⁾ have confirmed the synergistic effect of TBP on the D2EHPA extraction of strontium when an aliphatic hydrocarbon is used as the diluent (Figure IV 15). Almost complete lack of synergism was noted when benzene was used as a diluent for D2EHPA.

A general review of synergistic effects in extraction systems involving D2EHPA (HR) and neutral organophosphorus reagents (B) has been given by Baes⁽³⁾. According to Baes the effect may be attributed to the formation of a mixed complex - either a substitution product or an addition product - resulting from the reaction of B with the extraction complex normally formed with HR alone. Available extraction data appear more consistent with the addition product model.

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FIGURE IV-14

Third Phase Formation in System:
NaOH-H₂O-TBP-D2EHPA-Soltrol-170
(Source of Data: HW-79762PT1)

FIGURE IV-15

Strontium Extraction by 0.10 M D2EHPA in *n*-Nonane as a
Function of Added Tri-*n*-butyl Phosphate Molarity
(Source of Data: ORNL 3492)

2.6.3 CSREX Process

A most unusual synergistic effect, discovered by L. A. Bray⁽¹⁰⁾, occurs when 4-sec-butyl-2(6-methylbenzyl)phenol (BMBP) is added to D2EHPA in a kerosene carrier solvent. In the pH range 4 to 5, as noted above, D2EHPA extracts strontium and rare earths very efficiently but cesium hardly at all. Conversely, BMBP is a highly specific solvent for cesium at pH's above 12⁽¹⁵⁾ and does not extract strontium and rare earths. However when BMBP is added to D2EHPA, the combined solvent exhibits maximum cesium extraction at a pH of 4 to 5, the aforementioned optimum pH range for extraction of strontium and rare earths.

From this unusual phenomenon evolved the CSREX process for co-extraction of cesium, strontium and rare earths from various waste solutions. (The name CSREX is an acronym for Cesium, Strontium, and Rare Earth Extraction.) The CSREX process has been thoroughly explored on both laboratory and pilot plant scale^(12,60). In many ways it parallels the D2EHPA process for extraction of strontium and rare earths described later (Section C-3) in this chapter. Thus, strontium, cesium, and rare earths are coextracted from a tartrate-complexed feed in the extraction column, along with calcium and about 10 to 20% of the sodium. The sodium is removed from the solvent in the scrub column and the strontium and cesium, along with calcium and residual sodium, are stripped in the partition column with very dilute acid. Finally, cerium and other rare earths are stripped from the solvent with stronger acid in the strip column.

The major limitation to the use of the CSREX process at the present time is the unusually high susceptibility of the solvent to radiation and nitrous acid degradation^(47,65). Sulfamic acid and hydrazine have been successfully used in nonradioactive solutions to inhibit nitrous acid formation and solvent degradation, but their performance in preventing degradation in a radiation field has not yet been satisfactorily demonstrated.

2.7 Kinetic Effects

No systematic study of the rate of extraction of metal ions from aqueous phases into D2EHPA-containing organic solutions has been made. Results obtained at both Hanford and ORNL indicate the reaction between strontium and D2EHPA is complete within about a minute at either 25 or 60 C. Recent work at Hanford and ORNL also has shown that rare earth (III) ions extract considerably more slowly than strontium ions at 25 C and that an increase of temperature to 50 or 60 C markedly increases the rate of extraction of the rare earth ions. Kinetics of extraction of strontium and rare earth ions are more fully discussed later (Section 3.2.3).

Extraction of Fe(III), Zr(IV), and Al(III) is especially slow at 25 C, requiring up to several hours to attain equilibrium^(7,24,25,26). The back-extraction of these ions with HNO₃ is also slow. Effective removal of iron and aluminum from a D2EHPA extractant within a practical time at 25 C requires the use of alkaline wash solutions or aqueous solutions containing complexing agents.

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3. Extraction of Strontium, Rare Earths, and Americium

3.1 Process Concept

The D2EHPA continuous countercurrent extraction process for recovery of strontium, americium, and fission product rare earths from clarified PAW and PAS solutions can be readily visualized with the aid of the accompanying schematic (Figure IV-16). The processing sequence for PAS solution also includes PbSO_4 carrier precipitation of strontium, americium, and rare earths (Section B-2) prior to the D2EHPA extraction process discussed in this section.

FIGURE IV-16

Schematic of D2EHPA Extraction Process

Extraction column feedstock is prepared from the PAW or PAS solution by addition of a suitable complexant, a buffer reagent (hydroxyacetic acid is currently favored) for pH control, and NaOH to adjust the pH to 4. This feed solution is contacted countercurrently with a D2EHPA-TBP diluent extractant in the IA Column to extract strontium, americium, and rare earths. The bulk of the contaminants, both inert and radioactive, including Cs-137 from the PAW solution, are rejected to the aqueous raffinate; however, essentially all of the calcium and magnesium in the feed solutions are also extracted.

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Further purification of the extracted strontium, americium, and rare earths is achieved in the 1S Column. Here a small flow of hydroxyacetic acid solution partially neutralized with NaOH is used to scrub out sodium and other weakly coextracted impurities. The pH is carefully controlled to retain most of the strontium, americium, and rare earths in the organic phase. The aqueous stream from the scrub column is routed back to the extraction column to re-extract the small amounts of strontium, americium, and rare earths present.

In the 1B Column, strontium is partitioned from americium, rare earths, and from most of the calcium by stripping with a dilute HNO_3 solution. The pH of the aqueous phase in the column is controlled at approximately 2 to allow stripping of strontium but to retain americium, rare earths, and calcium in the organic phase. Sodium, magnesium, nickel, and some manganese - if present - follow the strontium.

Cerium is separated from the other rare earths, americium, and calcium in the 1C Column. This is done by oxidizing Ce(III) to the much more extractable Ce(IV) with a HNO_3 solution containing peroxydisulfate (persulfate) and silver ions. The other rare earths, including Pm-147, are not oxidized and they, along with americium and residual calcium, transfer to the aqueous phase. A D2EHPA scrub stream is employed to assure maximum decontamination from cerium.

Finally cerium is batch stripped with a HNO_3 solution containing NaNO_2 to reduce Ce(IV) to Ce(III). The D2EHPA extractant is then washed with various reagents to remove impurities and recycled to the extraction column. With PAW feeds where the Ce-144 content is negligible, the silver peroxydisulfate are omitted, and the cerium is stripped along with the other rare earths.

The remaining parts of this section discuss this process in detail.

3.2 1A Column

3.2.1 Function

The Function of the 1A Column is to provide for essentially complete extraction of strontium, americium, and rare earths, including Pm-147, while rejecting the bulk of the inert and radioactive contaminants to the aqueous raffinate. This is accomplished by proper choice of complexant and control of aqueous phase pH, temperature, D2EHPA, concentration, and flowrates.

3.2.2 Complexant - Choice and Effects

Proper selection of the complexant(s) to add to the extraction column feed to prevent extraction of unwanted impurities and yet permit extraction of strontium, americium, and rare earths is critical to

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satisfactory operation of the 1A Column. Choice of this complexant is influenced by economic as well as chemical factors. Among the latter are the nature and concentration of the contaminants to be complexed in the various waste solutions, and the relative strengths (stability constants) of the complexes formed at a particular pH with these contaminants and with strontium, rare earths, and americium.

A large amount of laboratory work with synthetic waste solutions has been done to furnish an empirical basis for selecting complexants for PAW and ZAW feeds (17,18,72). The most promising candidates as this manual was written were HEDTA, citric acid, and tartaric acid. Gluconic acid has been eliminated from consideration because of the weak complexes it forms with iron and aluminum (17). EDTA and DTPA are unacceptable in this application because of the strong complexes they form with rare earths and americium (Figure IV-17 and Section C-4). Laboratory tests of nitrilotriacetic acid were in progress as this manual was written; published formation constants (Table IV-67) indicate this complexant may compare favorably to HEDTA and citric and tartaric acids.

As this manual was written, the final choice of complexant for PAW and ZAW feeds had not been made. Tests in the Semiworks with radioactive feeds were being made to evaluate the performance of the various complexants under B-Plant flowsheet conditions. Only HEDTA of the complexants studied adequately prevented lead extraction (see below), and it is specified as the complexant for lead-containing PAS solutions.

Compositions of synthetic wastes used in the laboratory studies are presented in Table IV-8. The PAW compositions are representative of Purex acid waste derived from processing of aluminum-clad uranium fuels. The ZAW (Zirflex Acid Waste) is that expected from Purex Plant processing of zircaloy-clad N-reactor fuel. It contains a relatively large amount of aluminum added to complex fluoride carried over into the waste from the Zirflex decladding process.

Feeds were normally aged several hours to assure chromium complexing. Digestion for 3 to 5 hours at room temperature or 30 min at 60 C resulted in a 10-fold decrease in the chromium distribution ratio compared with that after aging only one hour (72). The distribution ratios of other components were unaffected by digestion. As discussed in Section D, feed aging or digestion generally improved the stability of the 1A Column. Solvents used in most of the studies were either 0.37 - 0.4M D2EHPA - 0.2M TBP in Shell Spray Base, Soltrol-170, or NPH diluents or 0.2M D2EHPA - 0.1M TBP in Soltrol-170. Feed solutions were contacted 10 min at room temperature with an equal volume of extractant unless otherwise noted.

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TABLE IV-8
APPROXIMATE SYNTHETIC WASTE COMPOSITIONS USED IN LABORATORY STUDIES

Source of Data: ORNL-3204 (ORNL PAW)
HW-79762 PT1 (PAW-A and B)
BNWL-CC-595 (PAW-C, ZAW)

Constituent	PAW				ZAW
	ORNL	A	B	C	
Na	2.7	0.8	1.2	1.5	1.5
Fe	0.15	0.037	0.075	0.038	0.17
Al	0.033	0.0185	0.0375	0.034	0.34
Cr	0.0033	0.0074	0.015	0.013	0.007
Ni	0.0033	0.0037	0.0075	0.007	0.004
Sr	0.00065	0.00033	0.00068	0.00056	0.00056
RE	0.0030	0.0020	0.0041	0.0028	0.0028
F ⁻	0	0.0007	0.0015	0	0.15
SO ₄ ⁼	0.33	0.019	0.038	0.104	0.052
PO ₄ ⁼	0.003	0.0019	0.0038	0	0
HEDTA	0	(a)	(b)	(d)	(e)
Citrate	0	(a)	(b)	(d)	0
Tartrate	0.33	(a)	(b)	(d)	(e)
Acetate	0	0.35	0 (c)	0	0
Hydroxy-acetate	0	0	0	0.25	0.25

(a) 0.12M complexant; either HEDTA, citrate, or tartrate.

(b) Either 0.19M HEDTA, 0.19M citrate or 0.25M tartrate.

(c) The HEDTA feed also contained 0.35M acetate.

(d) 0.17M complexant (HEDTA, citrate, or tartrate) plus an additional 0.0125M tartrate.

(e) Either 0.5M HEDTA plus 0.0125M tartrate or 0.6125M tartrate.

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Effect of Complexant Type and pH

Data obtained to compare the effects of the complexants on distribution ratios of various constituents of PAW and ZAW at several pH's are presented in Tables IV-9⁽¹⁷⁾ and IV-10⁽⁷²⁾. The data in Table IV-10 are also presented graphically in Figures IV-17 through IV-23. Data for tracer americium extraction from a 1M NaNO₃ solution is presented in Figure IV-24⁽¹⁸⁾. With the exception of the ZAW data in Table IV-9, all systems contained 0.05M free complexant (above that required to form 1:1 complexes).

TABLE IV-9
DISTRIBUTION RATIOS AS A FUNCTION OF COMPLEXING AGENTS

(Data from BNWL-CC-595)

Contact Time: 2 minutes

Temperature: 35 C

O/A: 1

Extractant: 0.4M D2EHPA-0.2M TBP-NPH

Feed: (see Table IV-8)

	Distribution Ratio, E_a^0					
	HEDTA		Tartaric Acid		Citric Acid	
	pH3	pH4	pH3	pH4	pH3	pH4
PAW-C						
Strontium	2	17	0.85	10	1.4	13
Cerium	460	48	800	200	700	40
Promethium	32	3.6	700	150	370	16
Lead	0.006	0.0009	4.5	9	4.5	2
Iron	0.0006	0.0006	0.45	0.75	0.08	0.016
Aluminum	0.07	0.07	0.15	0.28	0.52	0.026
ZAW						
Strontium	0.8	7	0.65	6		
Cerium	1000	600	170	160		
Promethium	440	210	70	63		
Lead	0.007	0.002	2.7	4.5		
Iron	0.0003	0.0003	0.1	0.025		
Aluminum	0.12	0.09	0.03	0.13		

Significant conclusions derived from these data are:

- Iron, aluminum, and lead are complexed much more effectively by HEDTA than by either citrate or tartrate. In turn citrate is more effective than tartrate in complexing iron, and tartrate is more effective than citrate in complexing aluminum. (The apparent superiority of tartrate over HEDTA for complexing aluminum in ZAW feed is probably due to the greater excess of complexant with the tartrate feed.)

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TABLE IV-10
EFFECT OF COMPLEXANT TYPE AND pH ON DISTRIBUTION RATIOS, 25 C

Data from: HW-79762PT1

Conditions: PAW-A feed solutions (Table IV-8) were spiked with various radioisotopes and allowed to stand at least 16 hr at 25 C. Solutions then contacted 10 min at 25 C with an equal volume of 0.37M D2EHPA-0.2MTBP - SSB.

Final Aqueous pH	Distribution Ratios							
	Sr-85	Ce-144	Fe-59	Cr-51	Eu-152	ZrNb-95	Ru-106	Pm-147
<u>0.12 M Citrate</u>								
3.1	3.1	77.8	0.22		30.0	0.021	0.0046	34.7
3.6	26.1	35.7	0.050		20.4	0.0086	0.0032	21.4
4.15	78.8	55.4	0.017		20.1	0.0093	0.0036	20.9
4.5	76.7	23.2	0.013		3.34	0.0086	0.0045	3.71
4.85	29.2	7.22	0.032		4.92	0.017	0.020	3.98
<u>0.12M Tartrate</u>								
3.65	19.8	81.6	0.29		30.0	0.20	0.0035	20.8
4.2	50.8	35.5	0.19		17.5	0.13	0.0045	16.9
4.6	59.6	18.2	0.29		8.22	0.13	0.0074	9.37
4.85	41.6	8.99	0.71		2.63	0.17	0.023	4.07
<u>0.12M HEDTA</u>								
3.5	20.8	509	0.0017	0.0018	10.3			15.6
4.0	62.8	867	0.0010	0.0029	7.0			4.48
4.5	88.6	137	0.00024	0.0006	1.9			3.1

- Tartrate and citrate are about equally effective in suppressing ruthenium extraction; however citrate is more effective than tartrate in suppressing ZrNb-95 extraction.
- Citrate and HEDTA have about the same effect on strontium extraction. Below pH 4.7, strontium extracts better from citrate or HEDTA-complexed feeds than from tartrate complexed feeds.
- The relative effects of the complexants on rare earth extraction in the two studies are anomalous. Apparently extraction kinetics, discussed in Section C 3.2.3, were overriding factors.
- An aqueous phase pH of about 4 appears optimum for satisfactory extraction of strontium, rare earths, and americium. Strontium extraction is depressed at lower pH's, and rare earth extraction (and extraction kinetics) are decreased at higher pH's. A pH of 4 also provides near minimum distribution ratios for many of the impurities, including iron and aluminum.

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FIGURE IV-17

Variation of Strontium Extraction with Complexant Type and pH at 25 C
(Source of Data: HW-79762PT1)

FIGURE IV-18

Variation of Cerium Extraction with Complexant Type and pH at 25 C
(Source of Data: HW-79762PT1)

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FIGURE IV -19

Variation of Promethium Extraction with Complexant Type and pH at 25 C
(Source of Data: HW-79672PT1)

FIGURE IV -20

Variation of Europium Extraction with Complexant Type and pH at 25 C
(Source of Data: HW-79672PT1)

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FIGURE IV-21

Variation of Iron Extraction with Complexant Type and pH at 25 C
(Source of Data: HW-79726PT1)

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FIGURE IV-22

Variation of Zr-Nb Extraction with Complexant Type and pH at 25 C
(Source of Data: HW-79762PT1)

FIGURE IV-23

Variation of Ruthenium Extraction with Complexant Type and pH at 25 C
(Source of Data: HW-79762PT1)

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FIGURE IV-24

Effect of Complexants on Extraction of Americium
(Source of Data: ISO-95)

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Effect of Temperature and D2EHPA Concentration

Additional data to compare the tartrate and citrate systems at 25 and 60 C are presented in Table IV-11 and Figure IV-25(72). The extractant for these tests contained 50% less D2EHPA and TBP than the solvent in the preceding studies. The data show the expected 4-fold decrease in strontium distribution ratios because of the lower solvent concentration. Kinetic effects evidently obscured the solvent dependency effect for other constituents.

TABLE IV-11
EFFECT OF COMPLEXANT TYPE AND pH ON DISTRIBUTION RATIOS

(Data from HW-79762PT1)

		Contact Time: 10 min.							
		Temperature: 25 C and 60 C							
		O/A: 1							
		Extractant: 0.2M D2EHPA, 0.1M TBP, Soltrol-170							
		Feed: PAW-B (Table IV-8)							
		0.25M Tartrate System				0.19M Citrate System			
		25 C		60 C		25 C		60 C	
Element	pH	E_a^0	pH	E_a^0	pH	E_a^0	pH	E_a^0	
Strontium	3.3	1.3	3.3	0.071	3.1	0.845	3.2	0.0971	
	3.9	2.3	3.7	0.19	3.5	6.43	3.7	1.29	
	4.0	3.5	4.0	0.40	4.0	24.2	4.1	12.1	
	4.4	8.0	4.4	2.6	4.4	28.2	4.6	16.9	
	4.9	10	4.9	12	5.0	16.2	5.1	13.6	
Iron	3.3	0.34	3.3	0.96	3.05	0.085	3.18	0.27	
	3.85	0.27	3.7	0.65	3.5	0.031	3.65	0.16	
	4.0	0.37	4.0	0.95	4.0	0.012	4.10	0.066	
	4.3	0.40	4.3	0.86	4.42	0.008	4.55	0.035	
	4.9	0.29	4.9	1.47	5.0	0.010	5.05	0.027	
Chromium	3.3	0.0037	3.3	0.0080	3.05	0.0070	3.18	0.0012	
	3.85	0.0034	3.7	0.0072	3.50	0.00030	3.65	0.0026	
	4.0	0.0027	4.0	0.0079	4.0	0.00093	4.10	0.00013	
	4.4	0.0020	4.4	0.0025	4.42	0.00082	4.55	0.00017	
	4.9	0.013	4.9	0.019	5.0	0.0067	5.05	0.0071	
Aluminum	3.3	0.26	3.3	0.39					
	3.85	0.29	3.7	0.39					
	4.0	-	4.0	0.53					
	4.9	0.40	4.9	0.77					
Europium	3.3	2.51	3.3	32.6					
	3.85	8.19	3.7	155					
	4.0	9.11	4.0	85.9					
	4.4	4.75	4.3	64.1					
	4.9	2.41	4.9	40.1					

In both systems, an increase in temperature decreased the strontium distribution ratios while extraction of all other major constituents, including rare earths, increased with temperature. The adverse effect of increased temperature on strontium extraction may be attributed to the greater loading of the solvent with trivalent ions, although there may also be an enthalpy effect.

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FIGURE IV-25

Variation of Sr Extraction with Complexant Type and pH at 25 and 60 C
(Source of Data: HW-79762PT1)

Effect of Complexant Concentration

The complexant concentration used in most laboratory studies and specified in chemical flowsheets was based on the assumption of the formation of 1:1 complexes with iron, aluminum, chromium, nickel, and other polyvalent impurities. An excess of 0.05M complexant was usually supplied to simulate an assumed 20 to 30% Plant safety margin. Higher concentrations are uneconomical and, in HEDTA systems, lead to decreased distribution ratios for strontium and rare earths as shown in Table IV-12⁽⁷²⁾. In citric-acid complexed feeds, however, an increase in unused complexant concentration of 0.05 to 0.1M resulted in improved rare earth extraction, as shown in Table IV-13⁽⁷²⁾. This unusual effect was less pronounced at elevated temperatures and may reflect a change in extraction kinetics.

Effect of Radiolysis

B-Plant complexants, particularly in PAW and ZAW solutions, are subject to radiolytic destruction. Calculations based on data published by Van Tuyl⁽⁷⁸⁾ indicate the exposure level in feed solutions prepared from PAW will be about 2×10^6 rad/hr. At this exposure level, about 10 hours will be required to attain a total exposure of 2×10^7 rad. Limited results indicate that both HEDTA and citrate are sufficiently stable at this exposure to permit their use as complexants⁽⁷²⁾.

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TABLE IV-12
EFFECT OF FEED HEDTA CONCENTRATION
ON DISTRIBUTION RATIOS
 (Data from HW-79762PT1)

Contact Time: 10 min.
 Temperature: 25 C
 O/A: 1
 Extractant: 0.37M D2EHPA, 0.2MTBP, SSB
 Feed: PAW-A (Table IV-8) except variable HEDTA concentration.

HEDTA M	Distribution Ratios			
	Sr	Ce	Pm	Eu
0.10	67.9	-	18.0	-
0.12	63.3	572	19.0	4.22
0.20	38.7	303	-	4.22
0.30	22.9	179	9.0	1.49

(a) Final aqueous pH was 4.0

TABLE IV-13
EFFECT OF FEED CITRATE CONCENTRATION ON DISTRIBUTION RATIOS
 (Data from HW-79762PT1)

Contact Time: 10 min.
 Temperature: 25 C
 O/A: 1
 Extractant: 0.2M D2EHPA, 0.1M TBP, Soltrol-170
 Feed: PAW-B (Table IV-8) except variable citrate concentration.

Citrate M	Temperature C	Aqueous pH	Distribution Ratios				
			Ce	Eu	Sr	Fe	Cr
0.19	25	4.0	14.7	1.72	20.3	0.013	0.00058
0.25	25	4.0	35.3	16.7	18.4	0.013	0.00017
0.30	25	4.1	29.3	20.6	8.77	0.017	0.00015
0.35	25	4.1	15.7	18.6	7.36	0.017	0.000011
0.19	60	4.2	89.1	107.0	7.10	0.057	0.00094
0.25	60	4.2	104.0	145.0	-	0.059	0.00011
0.30	60	4.0	86.2	131.0	3.74	0.11	0.00020
0.35	60	3.9	47.0	133.0	2.55	0.11	0.000064

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3.2.3 Extraction Kinetics

Kinetics of D2EHPA extraction of various elements from complexed feed solutions have been studied at Hanford(17,72) and ORNL(27). Data illustrating the variation of distribution ratios with contact time at both 25 and 60 C for PAW feeds containing either citrate or tartrate are presented in Table IV-14 and Figures IV-26 through 29(72). The results of studies at 35 C with HEDTA, citrate, and/or tartrate-complexed PAW and ZAW feeds are presented in Figures IV-30 through 34(17).

TABLE IV-14
EXTRACTION KINETICS: CITRATE AND TARTRATE FEEDS
(Data from HW-79762PT1)

Contact Time: Variable				
Temperature: 25 and 60 C				
O/A: 1				
Extractant: 0.2M D2EHPA, 0.1M TBP, Soltrol-170				
Feed: PAW-B (Table IV-8)				
Contact Time min.	Distribution Ratios			
	0.25M Tartrate System			0.19M Citrate System
	Cr	Ru	ZrNb	Cr
25 C ^(a)				
1	0.00054	0.0012	0.017	0.00088
3	0.0018	0.0019	0.035	0.00079
5	0.0020	0.0015	0.028	0.00067
10	0.0020	0.0017	0.039	0.00058
30	0.0021	0.0024	0.066	0.00044
60	0.0015	0.0018	0.075	0.00085
60 C ^(b)				
1	0.00063	--	0.018	0.00071
3	--	0.0017	0.050	0.00061
5	--	0.0015	0.069	0.00049
10	0.0025	0.0028	0.067	0.00094
30	0.0029	0.0028	0.11	0.00049
60	0.0049	0.0028	0.098	0.0014

(a) Final aqueous pH was 4.0 for citrate feeds and 4.2 to 4.4 for tartrate feeds.

(b) Final aqueous pH was 4.15 for citrate feeds and 4.1 to 4.5 for tartrate feeds.

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FIGURE IV-26

Kinetics of Extraction of Cerium
(Source of Data: HW-79762PT1)

FIGURE IV-27

Kinetics of Extraction of Europium
(Source of Data: HW-79762PT1)

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FIGURE IV-28

Kinetics of Extraction of Strontium
(Source of Data: HW-79762PT1)

FIGURE IV-29

Kinetics of Extraction of Iron
(Source of Data: HW-79762PT1)

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FIGURE IV-30

Distribution Ratio as a Function of Contact Time-PAW
(HEDTA Complexed)
(Source of Data: BNWL-CC-595)

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FIGURE IV-31

Distribution Ratio as a Function of Contact Time-PAW
(Citric Acid Complexed)
(Source of Data: BNWL-CC-595)

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FIGURE IV-32

Distribution Ratio as a Function of Contact Time-PAW
 (Tartrate Complexed)
 (Source of Data: BNWL-CC-595)

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FIGURE IV-33

Distribution Ratio as a Function of Contact Time - ZAW
(HEDTA Complexed)
(Source of Data: BNWL-CC-595)

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FIGURE IV-34

Distribution Ratio as a Function of Contact Time - ZAW
 (Tartrate Complexed)
 (Source of Data: BNWL-CC-595)

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Generally, four classes of extraction performance were observed, irrespective of either the feed type or complexant. Strontium and lead were representative of the first class: Equilibrium was reached within one minute, and the distribution ratios began to fall with increased contact time as the solvent became loaded with the slower extracting components. The rare earths represented the second class: Extraction was appreciably slower than with strontium, and several minutes were usually required for the distribution ratio to reach a maximum before decreasing from increased solvent loading. In the third class were iron, aluminum, and ZrNb-95 which extracted very slowly and continued to extract throughout the 60 min equilibrations. Finally, ruthenium and chromium extraction appeared to be unaffected by contact time.

The decrease in strontium extraction can be accounted for by the continually increasing concentrations of iron and aluminum in the solvent. For example, the observed decrease in strontium E_d^0 from 14 to 3.1 (pH 4) over the 60 min experiment shown in Figure IV-32 was accompanied by an increase from 0.025M to 0.090M (Fe + Al) in the solvent. If the strontium extraction obeyed a squared free solvent concentration dependency as expected (Section C.2), the change in the strontium E_d^0 implies that 2.5 to 2.6 moles of D2EHPA were tied up for each mole of iron plus aluminum extracting. For comparison, trivalent lanthanides are reported to complex six moles (formula weights) of D2EHPA per mole of lanthanide at low solvent loading⁽⁴⁸⁾.

Increased temperature greatly speeds up the rate of extraction of rare earths from citrate and tartrate-complexed feeds (and presumably also from HEDTA-complexed feeds), as shown in Figures IV-26 and IV-27. For example, in a 3-minute contact with a citrate-complexed feed, distribution ratios at 60 C for cerium and europium were 22 and 81 times higher, respectively, than they were at 25 C. A disadvantage of increased temperature, however, is that strontium extraction decreases while extraction of iron increases, (Figures IV-28 and IV-29).

The extent of complexing by ligands is less at lower pH's, and the rates of rare earth extraction are markedly improved by reducing the pH, as shown in Figures IV-30 through 34.

Almost without exception, the rates of rare earth extraction decreased with increasing atomic number (Ce Pm Eu). The effect was less pronounced with tartrate feeds (Figures IV-32 and IV-34); and in an ORNL study, the cerium-promethium order was reversed⁽²⁷⁾.

Evidence has been obtained which suggests the kinetics of rare earth extraction from HEDTA-complexed PAW are noticeably improved when the feed also contains 0.01 to 0.03M tartrate⁽¹⁸⁾. For example, the cerium and promethium E_d^0 's were 7 and 0.6, respectively, when PAW containing 0.17M HEDTA at pH was contacted 3 min with an equal volume of 0.4M D2EHPA-0.2M TBP-NPH. The distribution ratios were about 10-fold higher

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for the same extraction conditions when the feed also contained 0.125M tartrate (Figure IV-30). By comparison of these data and those in Table IV-9, the relative promethium extraction rates at 35 C are seen to decrease with complexants in the order tartrate citrate (+0.0125M tartrate) HEDTA (+0.0125M tartrate) HEDTA.

Detailed studies with citrate-complexed feeds have shown that the presence of several of the major cations in the feed have a pronounced inhibiting effect on the rate of cerium extraction^(59,72). The largest effect was found with chromium ion and attributed to the formation of a stable complex, identified as $\text{CeCr}(\text{citrate})_2$,⁽⁷⁵⁾ which dissociates very slowly under extraction conditions. The results of a series of 10 min equilibrations, in which several PAW components were added separately to simplified feeds containing 0.05M excess citrate, are shown in Table IV-15⁽⁷²⁾. Data from pilot plant runs with similar feeds⁽⁵⁹⁾ indicated that the equilibrium cerium E_a^O exceeds 100 in all cases. Similar kinetic effects have been noted at ORNL with tartrate-complexed feeds⁽³⁵⁾.

TABLE IV-15
EFFECT OF FEED IMPURITIES ON THE EXTRACTION OF STRONTIUM
AND CERIUM FROM CITRATE-COMPLEXED FEEDS

(Data from HW-79762PT1)

Conditions: Feed solutions containing 1.4M NaNO_3 , 0.001M Sr, 0.038M rare earths and indicated impurity and citrate concentrations contacted 10 min. at 25 C with an equal volume of 0.2M D2EHPA, 0.2M TBP, Soltrol-170.

<u>M Fe</u>	<u>M Cr</u>	<u>M Ni</u>	<u>M Al</u>	<u>M Citrate</u>	Equil. pH	<u>E_a^O</u>	
						Ce	Sr
0	0	0	0	0.05	4.05	2740.	28
0.075	0	0	0	0.125	4.2	54.	24
0	0.015	0	0	0.065	4.1	1.9	27
0	0	0.0075	0	0.0575	4.05	384.	29
0	0	0	0.0375	0.0875	4.0	95.	28
0.075	0.015	0.0075	0.0375	0.185	4.1	3.4	21

Laboratory kinetic data can be used to estimate (very approximately) the extraction performance of a pulse column when the extraction rate is limited by reaction kinetics in the raffinate (feed) phase. Under these conditions, particularly when the time required for the desired solute in the feed to reach equilibrium with the solvent exceeds the feed residence time in the column, the performance of the column will approach that of a single stage batch contactor. The percent of the solute extracted will be given approximately by the material balance equation.

$$\% \text{ extracted} = \frac{100 E_a^O}{E_a^O + (A/O)} \quad (36)$$

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where E_a^0 is the laboratory distribution ratio for a contact time corresponding to the feed residence time in the column and A/O is the aqueous to organic volumetric flow ratio. From this equation and the data in Figure IV-30, 31 and 32, the estimated residence times to achieve 95% promethium extraction from HEDTA, citrate, and tartrate-complexed PAW feeds (pH 4) are 6, 2, and 1 min, respectively, at an A/O of 1.

3.2.4 Extraction of Miscellaneous Feed Impurities

The extraction of major inert and radioactive impurities has been extensively covered in preceding sections. Considerably less work has been done to determine the extraction behavior of minor inert impurities such as nickel, calcium, barium, etc, under B-Plant flowsheet conditions. Highlights of some of the most applicable data are presented below.

Uranium. Uranium will quantitatively extract from a tartrate-complexed feed. A distribution ratio of 150 was measured at pH 4.5 with the ORNL PAW recipe shown in Table IV-8 and a solvent containing 0.3M D2EHPA-0.15M TBP-Amsco 125-82 diluent(28).

Calcium. Calcium distribution ratios are generally about 30 to 50-fold higher than strontium distribution ratios under all flowsheet conditions. A calcium distribution ratio of 490 was measured under the tartrate flowsheet conditions described above(81).

Barium. Barium distribution ratios of 0.03 and 0.1 were measured in batch counter-current contacts with the ORNL tartrate-complexed PAW (pH 4 to 5)(81). Barium distribution ratios as high as 3 (compared with 19 for strontium) have been measured under somewhat similar conditions but with sulfate absent(30). Sulfate addition to a simplified strontium-sodium nitrate system has essentially no effect on strontium extraction(81), and deliberate sulfate addition to sulfate-deficient feeds would appear warranted to improve the barium decontamination.

Molybdenum. Molybdenum E_a^0 's into 0.4M D2EHPA - 0.2M TBP - NPH were less than 0.01 at pH's from 4 to 5. The aqueous phase contained 1M NaNO_3 , 0.01M Mo, and 0.05M of either citrate, tartrate, or HEDTA(18).

Nickel. The nickel distribution ratio from the ORNL tartrate-complexed PAW was about 0.7 at pH 4.6(28). The addition of 0.02M EDTA to a feed containing 0.017M Ni, 0.001M Sr, 1.7M NaNO_3 and 0.004M tartrate decreased the nickel E_a^0 from 8.4 to 0.006 at pH 4.2(28). From the stability constants (Table IV-67), HEDTA should be just about as effective as EDTA in suppressing nickel extraction.

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Magnesium. Magnesium and strontium distribution ratios were found to be identical for 0.4M D2EHPA-0.2M TBP-Soltrol-170 and were unaffected by the addition of complexing agents⁽¹⁶⁾.

Manganese. Manganese distribution ratios of 0.8 to 1.2 have been measured between a rare earth crude feed complexed with 0.15M HEDTA and 0.4M D2EHPA-0.2M TBP-NPH over the pH range 2.2 to 3.8⁽²²⁾. In the absence of complexants, manganese distribution ratios fall midway between those of calcium and strontium (Figure IV-10).

Cesium. Cesium distribution ratios were 0.0068, 0.038, 0.054 and 0.067 at equilibrium pH's of 3.2, 4.1, 4.4, and 4.7, respectively, between 0.37M D2EHPA-0.2M TBP-Shell Spray Base and PAW-B (See Table IV-8 for composition)⁽⁷⁰⁾.

3.2.5 pH Control

As discussed earlier, an aqueous phase pH of about 4 is optimum of coextraction of strontium and rare earths. The complexant and the hydrolytic impurities iron and aluminum provide some hydrogen ion buffer capacity, but additional buffering is usually required to assure a smooth titration to the desired feed pH and to prevent an excessive pH change during extraction. Reagents satisfactory for this purpose are acetic and hydroxyacetic acids. The latter is preferred since its dissociation constant (Table IV-66) provides more buffer capacity at pH 4 than that of acetic acid. The curve shown in Figure IV-116 can be used to estimate feed neutralization requirements. Unfortunately, at this time there is no good procedure to compensate for the base used up in titrating iron and aluminum and their respective complexes. Additional pH control can be provided in batch and column extractions by partially pre-neutralizing the solvent with NaOH. In this way, sodium ions rather than hydrogen ions are exchanged for part of the extracted strontium, americium, and rare earths.

3.3 1S Column

3.3.1 Function

The 1S Column is used primarily to reduce the concentration of sodium in the solvent to a level that will not interfere with the performance of the 1B Column. Secondary benefits will be gained by elimination of feed entrainment from the 1A Column and from scrubbing the more weakly extracted cations from the 1A product stream. Hydrogen-ion control is achieved at the desired pH range of 2.4 to 4 by buffering the scrub stream with any of several suitable organic acids. Hydroxyacetic is the current choice but formic acid and citric acid have also been used successfully.

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3.3.2 Calculated Sodium Equilibrium

The sodium distribution between the solvent and scrub solutions is highly dependent on the buffer used and its concentration. The overall reaction for sodium exchange between the solvent and a weak buffer acid, HA, can be expressed by

which is equivalent to the neutralization reaction for the weak acid:

The pH varies during the exchange reaction because of the dissociation of the buffer acid. For a monobasic acid, the dissociation constant is given by

$$K_{\text{dis}} = \frac{(\text{H}^+) (\text{A}^-)}{(\text{HA})}. \quad (39)$$

Since $(\text{Na}^+) = (\text{A}^-)$ and $(\text{HA}) + (\text{A}^-) = (\text{total A})$, Equation (39) can be rearranged to give

$$(\text{H}^+) = \frac{K_{\text{dis}} [(\text{total A}) - (\text{Na}^+)]}{(\text{Na}^+)} \quad (40)$$

Values of (H^+) determined in this way were used in the empirical sodium equilibrium correlation presented in Figure IV-14 Section 2.5.1 to calculate the sodium equilibrium curves shown in Figure IV-35. These curves were developed specifically for hydroxyacetate buffer solutions but should be valid, within the accuracy of the correlation, for formic acid buffer solutions also. (The dissociation constants for hydroxyacetic acid and formic acid are 1.52×10^{-4} and 1.77×10^{-4} respectively.)

The amount of sodium in the solvent entering the 1S Column can be estimated from Figure IV-36. The equilibrium data shown in this figure was calculated in the same method as the scrub data with the exception that sufficient buffering is usually provided in the 1A Column so that the pH is essentially constant throughout the column.

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FIGURE IV-35

1S Column Sodium Equilibrium Data
(Calculated from data given in Figure IV-10)

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FIGURE IV-36

1A Column Sodium Equilibrium Data
(Calculated from data given in Figure IV-10)

3.3.3 Selection of Scrub Compositions

The optimum scrub composition for a given aqueous/organic flow ratio (ISS/ISF) is one that will provide a sodium distribution ratio less than the flow ratio over the entire range of sodium concentrations in the aqueous phase. This can most conveniently be determined by constructing a sodium operating diagram as described in Section D. The minimum allowable pH of the scrub will be about 2.4. Below this pH, the strontium distribution ratio becomes low enough for significant strontium reflux to occur.

3.4 1B Column

3.4.1 Function

The purpose of the 1B (partition column) is to remove strontium to an aqueous phase while retaining, as completely as possible, americium, fission product rare earths, and calcium in the organic phase. Successful partitioning depends on maintaining the aqueous phase pH in the range 1.5 to 2.2. The pH is dependent on the quantity of ions exchanged between the solvent and strip solution. In the chemical flow-sheets specified for B-Plant use (Section C 3.6), the hydrogen ion exchange is minimized by removing sodium, the macro exchangeable cation,

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from the organic phase in the scrub column, and by extracting strontium to a low concentration in the solvent. These provisions make it relatively easy to control pH in the partition column, even when a small flow of dilute HNO_3 is used as the partitioning agent.

3.4.2 Partitioning of Strontium with Dilute Nitric Acid

The efficiency of dilute (0.02 to 0.03M HNO_3) in partition column operations has been amply demonstrated in cold pilot plant pulse column studies. Results of these studies are discussed in detail elsewhere in this manual (Section D). They show that, when the sodium concentration in the D2EHPA phase is controlled by proper scrub column operation, a small flow of 0.02 to 0.03M HNO_3 strips over 99% of the strontium with minimal contamination from rare earths and calcium.

The effect of pH on strontium and cerium distribution ratios under conditions approximating those of the LB Column is shown in Figure IV-37⁽¹³⁾. Complexant concentrations up to 0.05M had little or no effect on strontium and cerium E_d^0 below pH's of 3 and 2, respectively. Calcium distribution ratios have not been determined for this system but should be about 30 to 50-fold greater than corresponding strontium distribution ratios. These data indicate that the optimum decontamination performance will be obtained by operating the LB Column at the highest pH compatible with strontium recovery. The maximum allowable pH for quantitative strontium recovery, using the data shown in Figure IV-37, is about 2.1 at an A/O of 0.2. Higher pH's are allowable at lower solvent concentrations or at higher A/O ratios.

Results plotted in Figure IV-38 demonstrate that 0.03M HNO_3 strips strontium from a 0.2M D2EHPA solution very rapidly at both 25 and 60 C. The equilibrium distribution ratio, although lower at 60 C than at 25 C, was attained at both temperatures in about three minutes.

3.4.3 Partitioning of Strontium with Organic Acids

Aqueous solutions of di- and tricarboxylic acids, such as tartaric and citric acids, can also be used as strontium partitioning agents in LB Column operation. Such solutions have the advantage over HNO_3 solutions of providing more hydrogen ion buffer capacity to offset possible off-standard extraction or scrub column operation.

Dilute citric acid solutions, in particular, have been examined as candidate partitioning agents. Such solutions readily strip strontium from the organic D2EHPA phase, as is evident from the data in Table IV-16 but at the expense, compared to HNO_3 solutions, of decreased decontamination from cerium. The higher cost of citric acid over HNO_3 is also a disadvantage. Problems arising from the radiolytic decomposition of

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FIGURE IV-37

Strontium and Cerium Distribution as a
Function of pH and Complexing Ion
(Source of Data: HW-80595)

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FIGURE IV-38

Kinetics of Strontium Stripping
(Source of Data: HW-79762PT1)

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citrate solutions containing high concentrations of Sr-90 (see Section 4.3.5) constitute, perhaps, the greatest objection to partitioning with citric acid solutions.

TABLE IV-16
EFFECT OF CITRATE CONCENTRATION ON
PARTITION COLUMN DISTRIBUTION RATIOS

(Source of Data: HW-79762PT1)

Conditions: Synthetic 1SP (0.2M D2EHPA, 0.2M TBP, Soltrol-170) contacted 10 min. at 25 C with one-fourth volume of aqueous phase.

Citric Acid, <u>M</u>	Cerium Final Aqueous		Strontium Final Aqueous	
	pH	E_a^O	pH	E_a^O
0.0*	1.70	48.3	--	--
0.1	1.70	28.5	1.78	0.0133
0.2	1.76	18.1	1.72	0.0124
0.3	1.70	10.6	1.72	0.0127
0.4	1.72	8.1	1.72	0.0127
0.5	1.75	6.5	1.80	0.0145

*Initially 0.035M HNO_3

3.5 1C Column

3.5.1 Function

When processing feeds prepared from PAW solution the 1C Column has two functions: to provide for oxidation of Ce(III) to Ce(IV) so so that Ce-144 is retained in the D2EHPA phase and to strip americium and trivalent lanthanides, including Pm-147, to an aqueous HNO_3 solution. Both purposes are accomplished in a single step by using, as aqueous phase in the 1C Column, a HNO_3 solution containing the strong oxidant, peroxydisulfate (persulfate), plus silver ion as a catalyst. Retention of cerium in the organic phase is neither desirable nor necessary when processing feeds derived from PAS, and in this case peroxydisulfate and silver are not added to the HNO_3 solution.

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3.5.2 Nitric Acid Stripping of Americium and Trivalent Rare Earths

As noted earlier, the extraction of trivalent rare earths, and presumably americium as well, into D2EHPA solutions can be represented by the reaction

By Le Chatelier's principle, increase of aqueous phase acidity shifts this equilibrium to the left; thus HNO_3 solutions can be used to strip americium and trivalent rare earths from D2EHPA extractants. Typical distribution coefficient data for rare earths under strip column conditions are shown in Figure IV-39^(20,27). The distribution ratios obey the expected $(M HNO_3)^{-3}$ dependency at low acidities, but above $1M HNO_3$ the acid dependency falls off to about the -1.4 power. Comparable data for americium are not available, but an americium distribution ratio of about 0.1 has been reported at $1M HNO_3$ for a system containing $0.3M$ D2EHPA in N-dodecane⁽⁷⁹⁾. Also, comparison of the americium and cerium distribution ratio data in Figures IV-24 and IV-37 indicates that americium behaves much like cerium at low pH's; thus americium should follow the trivalent rare earths in the 1C Column.

FIGURE IV-39

Distribution of Rare Earths as a Function of Acid Concentration
(Source of Data: ORNL-TM-265 and HW-78987REV)

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Nitric acid stripping of cerium is only slightly faster at 60 C than at 25 C as shown in Figure IV-40⁽⁷²⁾. Kinetics of cerium stripping thus parallel those of strontium shown in Figure IV-38.

FIGURE IV-40

Kinetics of Cerium Stripping
(Source of Data: HW-79762PT1)

Calcium, iron, and aluminum will be major impurities in the LCF. Calcium will quantitatively be stripped with the rare earths, iron will remain in the solvent, and aluminum will tend to follow the rare earths.

Iron distribution ratios of 21 to 28 have been obtained when a synthetic LCF (obtained during the demonstration of a citrate-complexed PAW flow-sheet) was stripped with one-tenth volumes of 1 to 3M HNO₃⁽⁷²⁾. The solvent was 0.2M D2EHPA-0.2M TBP-Soltrol-170.

Aluminum distribution ratios under stripping conditions have been obtained for a solvent system containing about 0.23M aluminum in 0.55M D2EHPA-0.25M TBP-Soltrol-170⁽⁷¹⁾. Distribution ratios measured after 30 min equal-volume equilibrations at 60 C were 0.06, 0.04, and 0.01 at equilibrium nitric acid concentrations of 1.4, 2.1, and 4.2M, respectively. Aluminum stripping was quite slow, even at 60 C; and the distribution ratios (obtained in a similar system but at double the solvent concentration) continued to decrease after 30 min of contact. Except for the kinetic factor, aluminum should strip as readily as the rare earths.

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3.5.3 Silver-Catalyzed Persulfate Oxidation of Cerium(III)

Factors affecting the oxidation of Ce(III) to Ce(IV) by silver-catalyzed persulfate have been extensively investigated by Bray and Roberts(20,21,22) and Richardson(61). Persulfate has a sufficiently high oxidation potential to oxidize cerium quantitatively, but the reaction rate at room temperature is so slow that oxidation does not occur. The addition of silver ion markedly increases the rate. The rates of reaction catalyzed by silver are, without exception, independent of the reductant concentration but depend on the first power of the persulfate and catalyst concentrations⁽⁴²⁾; that is,

$$\frac{-d(S_2O_8^{2-})}{dt} = k(S_2O_8^{2-})(Ag^+) \quad (41)$$

The following rate controlling reaction has been proposed by several investigators⁽⁴²⁾:

where the sulfate radical ion, $\cdot SO_4^-$, and the Ag^{++} are the active oxidants:

Since the silver ion concentration for a given composition remains constant while the persulfate is used up, the rate law in effect corresponds to a first order reaction in which the half-life of the persulfate is inversely proportional to the silver ion concentration:

$$t_{1/2} = \frac{0.693}{k(Ag^+)} \quad (44)$$

When used to oxidize cerium in a solvent extraction process, much of the persulfate will be destroyed by radiolysis and in side reactions with water and solvent. Hence it is important to use low silver concentrations to increase the persulfate life and to maintain the desired reaction rate by starting with high persulfate concentrations.

Hot cell batch contacts were made to demonstrate the effects of composition variables on the rate of extraction and the life of the persulfate⁽²⁰⁾. The solvent feed for these tests was prepared by quantitative extraction of rare earths from one liter of Purex Plant rare earth concentrate containing 800 Ci Ce-144/l and 100 Ci Pm-147/l into 2.2 liters of 0.4M D2EHPA-0.2M TBP-Soltrol-170 diluent.

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Portions of the loaded solvent were then contacted with equal volumes of aqueous solutions containing Ag^+ , $\text{S}_2\text{O}_8^{=}$, and HNO_3 . Samples were taken at intervals and analyzed to determine the cerium distribution ratio. Results of the tests, all carried out at about 35 C, are shown in Figures IV-41, IV-42 and IV-43. The following observations can be made from these results:

1. Cerium initially transfers to the aqueous phase, and five minutes or more are required to quantitatively oxidize it to solvent-favoring Ce(IV) .
2. The initial rates of oxidation are improved by increasing either the silver or persulfate ion concentrations.
3. The life of the persulfate is greatly reduced by silver concentrations above 0.02M and HNO_3 concentrations above 2M.
4. The persulfate concentrations should be greater than 0.1M to assure quantitative cerium extraction.

The adverse effect of high radiation fields on cerium separation is shown in Figure IV-44 where the results of tracer experiments are compared with those of full-level runs⁽²⁰⁾.

The effect of temperature in a tracer system is shown in Figure IV-45⁽²⁰⁾. The initial rate of oxidation is greatly accelerated at elevated temperature, but the effect is balanced by the reduced life of the persulfate. Comparable data with full level cerium are not available.

The effect of solvent radiolysis on cerium separation was determined by measuring the cerium behavior in the persulfate system with fresh solvent and with solvent that had been in contact with an aqueous phase containing 300 curies Ce-144/1 in 2M HNO_3 for over 100 hours^(21,22). Two diluents were used: Soltrol-170 and South Hampton NPH (Normal Paraffin Hydrocarbon). The results, presented in Figure IV-46, show that prolonged radiation seriously affects the Ce(IV) distribution ratio and that the NPH diluent is definitely superior to Soltrol-170 in resisting the adverse effect of radiation.

3.5.4 Alternate Oxidants for Cerium(III)

Potassium permanganate has been used satisfactorily to oxidize cerium in batch D2EHPA extraction processes^(32,33). Cerium distribution ratios in excess of 100 have been measured when feeds containing 0.05M KMnO_4 and 0.033M Ce in 1M HNO_3 were contacted with an equal quantity of 0.4M D2EHPA-0.2M TBP-Shell Spray Base^(33b). The permanganate life is quite short in radiation fields, and permanganate must continually be

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added to maintain the oxidation potential⁽³²⁾. Phase separation is complicated by the formation of interface-seeking MnO_2 precipitate. The MnO_2 can be further reduced to Mn^{++} , however, by adding citric acid before allowing the phases to settle. Although used routinely at ORNL to extract Ce-144, the process has been tested with only mixed success at the Semiworks^(33,43).

An electrolytic oxidation procedure for oxidizing cerium has also been developed at ORNL⁽⁴⁰⁾. The aqueous feed is adjusted to 2M HNO_3 - $2\text{M H}_2\text{SO}_4$ and pumped through an electrolytic cell where a portion of the cerium is oxidized to Ce(IV). The feed then overflows into a vessel where it is intimately contacted with a continuously introduced stream of 0.5M D2EHPA . The two phases are pumped together to a settling chamber where the solvent containing the Ce(IV) is withdrawn and the aqueous phase is returned to the electrolytic cell. The process proceeds until the cerium content of the feed is reduced to the desired level. Under optimum conditions, about 12% of the cerium was removed per cycle through the laboratory apparatus.

3.5.5 Stripping of Cerium(IV)

Extracted Ce(IV) is slowly reduced to Ce(III) by the solvent. In one experiment, over 95% of the Ce(IV) in a solvent loaded to about 300 Ci Ce-144/l was reduced and transferred to an aqueous phase containing 2M HNO_3 after 4 hours of contact (Figure IV-47)⁽⁴⁵⁾.

Rapid, quantitative reduction of Ce(IV) can be obtained by adding H_2O_2 or NaNO_2 to the HNO_3 strip. The effect of NaNO_2 concentration is shown in Figure IV-47. The reaction is complete within 25 minutes with 0.005M NaNO_2 and within 5 minutes with 0.05M NaNO_2 ⁽²²⁾. The reaction with $0.3\text{M H}_2\text{O}_2$ in 1 to 5 M HNO_3 was complete within 10 minutes^(33b).

3.5.6 Disposition of Cerium Product

Cerium-144 production is expected to exceed the market requirements. The excess cerium product will be neutralized and sent to a single underground storage tank for aging⁽⁴⁾. Eventually the aged cerium product will be combined with other high-level wastes for in-tank solidification.

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FIGURE IV-41

Cerium Distribution as a Function
of Time and Silver Concentration
(Source of Data: HW-78987)

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PART III, Cont.

PROCESS

CHAPTER V

PROCEDURES AND FLOW DIAGRAMS

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Waste Management Process Engineering

PART III: PROCESS, Con't.CHAPTER VPROCEDURES AND FLOW DIAGRAMS

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PART III: PROCESS, Cont.CHAPTER VPROCEDURES AND FLOW DIAGRAMS

In this chapter, flow diagrams and outlines of the operating procedures for the following B-Plant processing operations are presented:

1. Stored waste feed preparation
2. Current acid waste feed preparation
3. Solvent extraction battery operations for strontium-rare earth separation, strontium purification, and cerium-promethium separation
4. Ion exchange recovery of cesium from stored supernates

The main emphasis is on the normal procedures for steady-state operation, startups, and shutdowns. Off-standard conditions and methods of their detection and remedy are presented. The reader should refer to the Standard Operating Procedures for detailed processing procedures.

A. FLOW DIAGRAMS

The Waste Management Fractionization Plant (B-Plant) is capable of processing current Purex Acid Waste (PAW and ZAW), stored Purex supernatant liquid waste (PSN and PSS), stored Purex sludge waste (PAS), and stored Redox supernatant liquid waste (RSN, RSXN and RSS). Sources of feed are discussed in detail in Chapter III of this manual.

The equipment is sized to permit simultaneous processing of the stored high-level and current waste so as to work off the stored waste inventory within five to seven years. Instantaneous processing rates which formed the original basis for design are based on the Waste Management Program Process Flowsheets^(1,2) and are presented in Table V-1⁽³⁾. Current capacities based on the B-Plant Phase III Flowsheets⁽⁴⁾ which will be used at startup are presented in Table V-2.

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TABLE V-1
WAFRAX DESIGN CAPACITY

<u>Stream</u>	<u>Process</u>	<u>Instantaneous Rate Gallons/Day*</u>
PAW	CSREX	3,000
PAW	D2EHPA	3,300
PAS	Head End	4,000
PAS	CSREX	12,000
PAS	D2EHPA	13,200
PSN	Ion Exchange	46,450
RSXN**	Ion Exchange	46,450
RSN***	Ion Exchange	46,450

*Based on as-received volumes before head-end treatment

**Aged supernatant from 241-SX Farm

***Aged supernatant from 241-S Farm

TABLE V-2
B-PLANT PROCESSING CAPACITIES

<u>Process</u>	<u>Stream Basis</u>	<u>Gallons/Day*</u>
1) PAW Solids Treatment	PAW	4,600
2) PAW Solvent Extraction	PAW (1AF)	4,600 (6,900)
3) ZAW Solids Treatment	ZAW	3,900
4) ZAW Solvent Extraction	ZAW (1AF)	3,900 9,200
5) PAS Sludge Preparation	PAS (TU)	4,200 (88 TU)
6) PAS Metallic Ion Removal	PAS	3,600
7) PAS Solvent Extraction	PAS (1AF)	19,000 (4,800)
8) PSN Ion Exchange	PSN	30,000
9) PSS Ion Exchange	PSS	35,000

*Based on full operating capacity at 100% over-all operating efficiency

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A basic flow sketch of the operations performed within the B-Plant is presented in Figure V-1. Flow diagrams of various segments of the operation schematically showing the process streams and equipment are presented as follows:

<u>Figure</u>	<u>Function</u>
V-2	Feed Preparation - Current Acid Waste
V-3	Feed Preparation - Acid Sludge Waste
V-4	Extraction - 1A and 1S Columns
V-5	Partition and Strip - 1B and 1C Columns
V-6	Strontium Product Concentration and Storage
V-7	Organic Treatment
V-8	Cesium Ion Exchange
V-9	Cesium Product Concentration and Storage

Tank volumes as shown are the approximate volumes to overflow; consequently, the maximum working volumes are about 80% of the volumes given. The reader should refer to Part V, Chapters IX through XII (Plant and Equipment) and Chapter XIII (Instrumentation) for the mechanical and physical details of the facilities.

B. NORMAL PROCEDURES

1. Feed Preparation Procedures

Prior to solvent extraction processing, both current acid waste and sludge waste are given a feed preparation "head-end" treatment. For current acid waste the feed preparation process removes solids present in the waste and recovers greater than 95 percent of the strontium and rare earths associated with the solids. For sludge waste the feed preparation process removes a large portion of the iron, aluminum and magnesium present while concentrating the strontium and rare earths by means of a sulfate precipitation step. The procedures for feed preparation are discussed below.

1.1 Current Acid Wastes (PAW, ZAW)

The PAW and ZAW solutions received from the Purex plant via lag storage in the 244-AR Vault, are the concentrated and denitrated high level wastes from solvent extraction processing of irradiated aluminum-clad, (PAW) and zircaloy-clad, (ZAW) reactor fuels. The solutions contain a large amount of fission-product decay heat and inert salts. The solutions as received also contain 1-10 percent solids by volume (primarily phosphates, sulfates and silicates). Roughly 55 percent of the strontium and 70 percent of the rare earths are associated with these solids. A carbonate metathesis process is used to recover greater than 95 percent of the strontium and rare earths from these solids.

1.1.1 Carbonate Metathesis of PAW and ZAW

The carbonate metathesis process consists basically of the following steps. (Refer to Figure V-2).

1. PAW (or ZAW) is pumped from TK-001 in the 244-AR Vault to TK-11-2 in B-Plant. TK-11-2 is a precipitation tank with 3400 gallons working volume which has been specially modified by the addition of a large, low-level coil and extra temperature elements for this service. The PAW solids are allowed to settle in TK-11-2 for a period of approximately two hours.
2. After the solids have settled, the supernatant liquid is decanted from TK-11-2 (using a special jet to minimize solids transfer) through centrifuge G-12-2 to receiver tank TK-12-1 and then stored in TK-9-2.
3. Metathesis solution ($0.5M$ NaOH- $1M$ Na_2CO_3) from scale tank TK-12-2B is used to slurry any solids from G-12-2 back to TK-11-2 via TK-11-1. Concurrently, hot metathesis solution is added to TK-11-2 from scale tank TK-11-2C. The solids and solution in TK-11-2 are digested at $75^\circ C$ for one hour which converts the fission products associated with the solids (primarily sulfates) to a carbonate-hydroxide precipitate. The precipitate is then allowed to settle for two hours.
4. At the completion of the metathesis settling step, the waste metathesis solution is decanted through the centrifuge to TK-12-1 and sampled. This waste solution is then discarded to high-level waste tank TK-25-2 via TK-11-1 after centrifuge clean-out, Step 5, is completed.
5. Carbonate cake wash solution ($0.1M$ Na_2CO_3) is used to slurry any solids from G-12-2 back to TK-11-2 via TK-11-1. Additional cake wash solution is concurrently added to TK-11-2 and the solution agitated to remove residual sulfates. The solids are then allowed to settle for approximately one-half hour. The supernate is then decanted through G-12-2 to TK-12-1, sampled, and discarded to waste via TK-11-1 as in Step 4.
6. A nitric acid solution ($1.5M$) is used to remove the solids from G-12-2 back to TK-11-2 via TK-11-1 and is concurrently added to TK-11-2 to dissolve the carbonate-hydroxide cake remaining in TK-11-2. When TK-12-1 and TK-31-2 are available, this solution is slurried (using a minimum heel jet) to TK-12-1 via G-12-2 and immediately transferred to TK-31-2 for storage since the TK-12-1 cooling coil is inadequate for this small volume.

7. Any undissolved solids (primarily siliceous in nature) remaining in TK-11-2 and G-12-2 are slurried to TK-11-1, sampled and discarded to high-level waste.

The over-all time cycle for this process is approximately 15.5 hours, however it should be possible to trim to 13.5 to 14.5 hours as experience is gained during operation.

The process is basically quite simple, but the high-heating solids present major problems. The solids cake, if allowed to dry out in a vessel, would quickly reach temperatures high enough to partially volatilize some of the fission products such as ruthenium and cesium and also create a severe corrosion problem in the vessel. The same problems would arise in the centrifuge if large quantities of the cake were present or if the cake is not quickly removed. The centrifuge is susceptible to mechanical failure much more quickly with large quantities of high-heating cake. Therefore, the operating procedures are designed to minimize the cake volume transferred to the centrifuge and to minimize the periods during which the solids cake cannot be adequately cooled. Special equipment and instrumentation, such as the two jets and additional temperature elements on TK-11-2, have been provided to help control these problems. The radiation detection elements in the cells are also used to indicate the volumes of solids present in, and transferred between vessels. A special safety circuit is provided on scale tank TK-11-1E to automatically dump the TK-11-1E contents (approximately 70 gallons of water) to TK-11-2 if excessive cake temperatures are encountered. If for some reason processing is interrupted, it may be necessary to add water or process solution to the vessels via the chemical add scale tanks to maintain adequate cooling capability.

1.1.2 PAW, ZAW Solids Leaching

The original process planned for PAW, ZAW solids treatment in Cells 11 and 12 was a leach process. This process used the same equipment and the same general type of operations. The PAW was settled, decanted through the centrifuge and the centrifuge washed back to the settling tank (TK-11-2). Successive leaches of 5M HNO_3 and 2M NaOH - 0.1M sodium tartrate were then performed on the solids in much the same manner as the carbonate metathesis of 1.1.1 above.

Strontium recovery from solids with the leaching process was low, approximately 25 percent, with the added disadvantage that excessive amounts of ZrNb-95 were recovered which produced problems in solvent extraction. The poor performance of the leaching process led to the development of the carbonate metathesis process.

1.1.3 Waste Handling

The three waste streams from the PAW and ZAW solids treatment process, the metathesis waste, carbonate cake wash and the final solids slurry waste are all high-level waste. Therefore, these wastes are jetted directly to the high-level waste tank, TK-25-2, after sampling without waiting for results. Initially the solutions may be held for sample results to confirm that strontium waste losses are low. If necessary, the solutions can be routed back to TK-11-2 from TK-11-1 for rework.

1.2 Purex Acid Sludge (PAS)

The PAS feed received in B-Plant for feed preparation is quite different from the current acid waste feeds. The solution is not nearly as radioactive as PAW or ZAW since cesium is not present and the short-lived fission products have decayed to low levels. However, the PAS contains high concentrations of metallic ions, primarily iron and aluminum, which would make solvent extraction more expensive if a feed pretreatment step were not used. Therefore, the objective of the PAS feed treatment process is to remove these undesirable metallic ions while still maximizing the recovery of strontium and long-lived rare earths. A sulfate precipitation-carbonate metathesis process is used to obtain this objective, and in addition, a concentration factor of approximately 10 is obtained. The over-all strontium and rare earth losses for the combined process are estimated to be 7.5 and 5 percent, respectively.

1.2.1 Sulfate Precipitation of PAS

The sulfate precipitation for metallic ion removal consists of the following steps (refer to Figure V-3).

1. The PAS batches (approximately 1400 gallons) are transferred from the CR-Vault lag storage tank TK-003 to the B-Plant sulfate precipitation tank TK-31-3. Sufficient 6M NaHSO_4 is added to make the final solution 1M in sulfate ion. A solution of 1.8M Na_2CO_3 is used to neutralize the solution to a pH of approximately 1.0 (both the bisulfate and carbonate solutions are added through scale tank TK-31-3A). The solution pH is critical, so a pH cell is installed in the TK-31-3 sampler with a readout in the operating gallery. The solution is heated to a temperature of 80 C after neutralization.
2. After an initial digestion of one hour, 1M $\text{Pb}(\text{NO}_3)_2$ solution is added from scale tank TK-31-3E to make a final lead concentration of 0.02M. This provides a PbSO_4 carrier precipitate for the strontium sulfate. Digestion is continued for an additional hour.

3. The digested slurry is allowed to settle and then the supernatant, using a special high temperature jet, is decanted through centrifuge G-32-2 to waste receiver tank, TK-32-1. The waste is sampled in TK-32-1 and transferred to TK-24-1 for concentration in the Cell 23 Concentrator and ultimate disposal to an In-Tank Solidification facility.
4. This procedure is repeated twice more for a total of three sulfate strikes. The $\text{Pb}(\text{NO}_3)_2$ addition may be reduced on the second and third strikes since PbSO_4 is already present in the solution. The sulfate cake in TK-31-3 is washed with a small volume of water from TK-31-3A, which is decanted through the centrifuge and combined with the waste in TK-32-1.
5. The cake in TK-31-3 and centrifuge G-32-2 is slurried directly to the metathesis tank TK-31-1 with water. Tank 31-3 is then ready to begin a new series of sulfate strikes.

The estimated time cycle for each sulfate strike is approximately 8 hours; the over-all time cycle for a three-strike process is 28 hours.

1.2.2 Carbonate Metathesis of PAS

The PAS carbonate metathesis process is similar to the one used for metathesis of the PAW solids. (See section B. 1.1.1)

1. The water slurried sulfate cake in TK-31-1 is butted with an approximately equal volume of metathesis solution ($5\text{M NaOH} - 0.5\text{M Na}_2\text{CO}_3$) from scale tank TK-31-1F. The solution is heated to 80°C and digested for one-half hour. The sulfate precipitate is converted during the digestion to a carbonate-hydroxide precipitate.
2. The slurry is then allowed to settle and cool and the metathesis supernatant is decanted to TK-32-1 via centrifuge G-32-2.
3. The cake is washed twice with $0.1\text{M Na}_2\text{CO}_3$ solutions to remove residual sulfate. The cake washes are decanted through G-32-2 and combined with the metathesis waste in TK-32-1. Tank 32-1 is then sampled and routed to the Cell 23 Concentrator.
4. The cake in TK-31-1 is dissolved with a 1.2M nitric acid solution. The acid solution is added to TK-31-1 via TK-32-2C and centrifuge G-32-2 thereby recovering any carbonate cake in the centrifuge.

5. The dissolved carbonate cake product is decanted to the PAS feed storage tank, TK-33-1. A small water flush is added to TK-31-1 via G-32-2 and likewise decanted to TK-33-1. Batches of treated PAS are jetted from TK-33-1 to TK-29-2 for feed make-up during PAS solvent extraction campaigns.

The metathesis time cycle is approximately 10 hours. It should be possible to carry on the metathesis process concurrently with the sulfate precipitation strikes with a minimum amount of conflict for centrifuge time.

1.2.3 Waste Handling

The wastes from the sulfate precipitation and carbonate metathesis of PAS are relatively low-level wastes. Therefore, after sampling in TK-32-1, the wastes are routed to the Cell 23 Concentrator via TK-24-1. If necessary, the sulfate strike waste solutions will be neutralized in TK-32-1 before transfer to TK-24-1. The Cell 23 Concentrator effluent is routed to an ITS unit in the tank farm for ultimate disposal. Routes are available from TK-32-1 for rework if sample results show this to be necessary.

2. Solvent Extraction Procedures

Upon completion of appropriate head-end treatments, PAW, ZAW, and PAS aqueous wastes are processed by solvent extraction to separate the strontium and rare earths from the balance of metallic and fission product impurities.

The crude head-end product is chemically adjusted to make suitable feed for the solvent extraction battery. Complexant is added to aid in obtaining the desired metallic ion distribution ratios in the 1A Column. A ten to twenty percent excess of complexant is generally added to the feed to ensure adequate complexing and provide contingency for feed composition variations. A buffering agent is added to provide pH control since the metallic ion distribution ratios are sensitive to pH fluctuations. A small amount of tartaric acid is also added to the feed to improve the extraction kinetics in the 1A Column. The pH is adjusted with sodium hydroxide or nitric acid as necessary.

The separation is effected in a battery of four piston-pulsed columns - 1A, 1S, 1B, and 1C. The strontium and rare earths are extracted into the organic phase [di(2-ethylhexyl)phosphoric acid with tributyl phosphate modifier and normal paraffin hydrocarbon diluent] in the 1A Column. Cesium, other fission products, and the majority of the metallic impurities remain in the aqueous phase and are removed as waste. Additional decontamination of impurities, particularly sodium, is obtained in the 1S scrub column.

Strontium and the rare earths are partitioned in the 1B Column with the strontium being stripped into the aqueous stream and the rare earths and americium remaining in the organic stream. The rare earths and americium are stripped from the organic in the 1C Column. Strict pH control is essential throughout the extraction battery to ensure the proper separation of metallic ion and fission product impurities from the strontium and rare earth product streams.

Operating conditions are similar for processing PAW, ZAW, and PAW with the main difference being in the complexant used and the flow rates of the aqueous and organic streams.

Modifications of the flowsheet for specific product recovery and purification are discussed in Section C of this chapter.

2.1 Feed Makeup

2.1.1 Current Acid Waste (PAW and ZAW)

Feed for the solvent extraction system is made up in the 1AF Make-up Tank (TK-29-2). Current acid waste supernatant from the feed preparation step is jetted from the storage tank, TK-9-2, to TK-29-2. For PAW makeup, the premixed crude feed butt consisting of metallic ion complexant, buffering agent, and tartaric acid is gravity fed to TK-29-2 from the operating gallery scale tank, TK-29-2A. Because of the large volume of chemicals required for ZAW makeup, the complexant is added to TK-29-2 prior to the balance of the premixed butt.

The pH of the butted feed is initially adjusted to approximately 6.0 with sodium hydroxide from TK-29-2B. Dissolved carbonate cake solution from the feed preparation step is then jetted from TK-31-2 to TK-29-2 causing the pH to drop. Alternating additions of sodium hydroxide and dissolved cake solution are made in such a manner as to maintain the pH in the range of 3.0 to 6.0 which prevents precipitation of iron hydroxide at high pH or cerium, strontium, and rare earth sulfates at low pH. Final adjustment of the pH to flowsheet conditions is made with sodium hydroxide or nitric acid. When the feed has been adjusted to the desired pH, it is jetted to the 1AF Feed Tank (TK-29-3).

2.1.2 Acid Sludge Waste (PAS)

Feed for the solvent extraction system is made up in the 1AF Make-up Tank (TK-29-2). Treated acid sludge waste is jetted from the storage tank, TK-33-1, to TK-29-2. The premixed feed butt consisting of metallic ion complexant, buffering agent, and tartaric acid is gravity fed to TK-29-2 from TK-29-2A. Dilution water required to establish satisfactory aqueous to organic flow rates in the columns and to extend the run time to

reduce fission product losses during startup and shutdown of the solvent extraction battery is added to TK-29-2 from TK-29-2A. The pH of the butted feed is initially adjusted with sodium hydroxide from TK-29-2B. Final adjustment is made with sodium hydroxide or nitric acid. When the feed has been adjusted to the desired pH, it is jetted to the LAF Pump Tank (TK-29-3).

2.2 LA and LS Columns

2.2.1 Current Acid Waste (PAW)

The LA (T-30-1) and LS (T-29-1) columns form an extraction and scrub system. The feed (LAF) to the LA Column is pumped from TK-29-3 to the top of the column where it joins with the sodium scrub stream (LSR) from the LS Column. The aqueous streams form the dispersed phase and flow down through the organic extractant (LAX) to the bottom disengagement section, where the aqueous-organic interface is located and separation of the phases is effected.

The organic extractant (LAX) is pumped from the LAX Pump Tank (TK-30-3) to the bottom of the LA Column. The organic flowing up the column forms the continuous phase. When the column is operated at flowsheet conditions, essentially all of the strontium, rare earths, calcium, manganese, magnesium, uranium and yttrium are extracted. Small amounts of the iron, aluminum, and zirconium-niobium are also extracted. The organic phase (LAP), now the product-bearing stream, overflows from the upper disengagement section and is gravity fed to the bottom of the LS Column where it forms the continuous phase.

The aqueous stream (LAW) leaving the LA Column, bearing the bulk of the Cs-134, Cs-137, Sb-125, ZrNb-95, Ru-106, other fission products, radioactively inert salts, and approximately 1% of the Sr and RE, flows by gravity from the lower disengagement section to the LAW Receiver Tank (TK-30-2). (See Section B. 2.7.1 for further routing.)

In the LS Column, the organic is contacted with an aqueous scrub stream (LSS) for reduction of the sodium concentration to approximately 0.001M. The scrub solution is composed of buffering agent for pH control and a small concentration of complexing agent to remove trace amounts of undesired metallic impurities carried over from the LA Column. The LSS butt is pumped from TK-29-1F to an in-line blending tee for mixing with water to provide the desired concentration and flow rate as the LSS stream to the top of LS Column. After passing through the organic continuous LS Column the aqueous stream enters the bottom disengagement section where the aqueous-organic interface is located and separation of the phases is effected. The aqueous waste scrub stream (LSR) is then jetted to the upper part of LA Column. The organic (LSP) overflows from the top of the column to the LBF Feed Pump Tank (TK-28-4).

2.2.2 Current Acid Waste (ZAW)

The 1A and 1S Column operation is similar to that for PAW (Section 2.2.1). Recoveries of Sr and rare earths (RE) are slightly less than for PAW processing. Approximately 2% of the Sr and 10% of the RE are not extracted and remain in the aqueous waste stream (1AW) leaving the 1A Column. It is expected that RE recovery can be significantly improved with minor flowsheet development.

2.2.3 Acid Sludge Waste (PAS)

The 1A and 1S Column operation is similar to that for PAW (Section 2.2.1), although the various stream flowrates are different in order to provide pH control and an acceptable solvent loading. When the columns are operated at flowsheet conditions, essentially all of the strontium, rare earths, calcium, magnesium, manganese, uranium, and yttrium are extracted along with small amounts of iron, aluminum, and lead. Since many of the short-lived fission products present in PAW and ZAW are not present in PAS, the radioactivity level of the 1AW is significantly lower than for current acid wastes. The 1AW stream contains small amounts of Sr-90, Ce-144, Pm-147, and Sm-151.

2.3 1B Column

2.3.1 Current Acid Waste (PAW)

The LBF Feed Pump Tank (TK-28-4) continuously receives the LSP (organic overflow from the 1S Column) and pumps it to the bottom feed point of the 1B partition column (T-28-1) where it becomes the continuous phase. Strontium is stripped from the organic phase with dilute nitric acid (1BX). The 1BX nitric acid butt is pumped from TK-28-1F to an in-line blending tee for mixing with water to provide the desired concentration and flow rate to the top of the 1B Column. The interface in the organic-continuous column is located in the bottom disengagement section. The exiting aqueous phase (1BP), bearing about 98 percent of the strontium entering the column, 0.3 percent of the rare earths, the sodium not removed in the 1S Column, some calcium and trace amounts of other metallic impurities such as aluminum, iron, and zirconium-niobium flows by gravity to the 1BP Product Receiver (TK-28-2). The organic stream containing the rare earths overflows from the top of the column to the 1CF Pump Tank (TK-27-4).

2.3.2 Current Acid Waste (ZAW)

The 1B Column operation is similar to that for PAW (Section 2.3.1). Strontium recovery (~97%) is expected to be slightly less than that accomplished during PAW processing.

2.3.3 Acid Sludge Waste (PAS)

The 1B Column operation is similar to that for PAW (Section 2.3.1), although the various stream flow rates are different in order to provide pH control.

2.4 1C Column (PAW, ZAW, PAS)

The 1CF Pump Tank (TK-27-4) continuously receives the organic overflow from the 1B Column and pumps it to the bottom feed point of the 1C Column (T-27-1) where it becomes the dispersed phase since the 1C Column is operated aqueous continuous with a top interface. Rare earths, the balance of the calcium, and trace amounts of other metallic impurities and fission products are removed by stripping with strong nitric acid (1CX). The 1CX butt (concentrated nitric acid) is gravity fed from the 2718 HDR to an in-line blending tee for mixing with demineralized water to the desired acid concentration and flow rate as the 1CX stream to the top of the 1C Column where it becomes the continuous phase. The aqueous stream leaving the 1C Column (1CP), bearing 90-99 percent of the rare earths entering the column, flows by gravity from the lower disengagement section to the 1CP Receiver Tank (TK-27-2). The stripped organic stream (1CW) overflows from the top of the column to the 1CW Receiver (TK-26-3).

2.5 Solvent Treatment (PAW, ZAW, PAS)

The solvent received in TK-26-3 from the 1C Column is pumped batchwise to TK-27-3 where it is contacted with a sodium hydroxide - sodium tartrate wash solution (1OS) for removal of yttrium, cerium, zirconium-niobium, ruthenium, uranium, nitric acid, iron, and small amounts of other metallic impurities. The primary D2EHPA degradation product mono(2-ethylhexyl)phosphoric acid is also removed. The wash solution is gravity fed to TK-27-3 from AMU TK H-321 (via the 2707 HDR). After each contact of organic and wash solution, an appropriate settling time is allowed for separation of the phases. The organic is then decanted to TK-26-1. The present flowsheet does not specify that any organic washing be done in TK-26-1 but the tank can be used for that purpose if necessary. After an appropriate settling time to allow separation of the phases, the organic is pumped to the 1AX Makeup Tank (TK-28-3).

In TK-28-3 the washed organic is butted with 12.2M nitric acid (100 butt) gravity fed from TK-28-3C to obtain the desired acid to salt ratio of the D2EHPA for pH control in the 1A Column. TK-28-3C is flushed with a small volume of water to reduce the residual acid holdup and minimize tank corrosion. The flush water is also added to TK-28-3. Periodically, the aqueous heel in TK-28-3 is jetted to the Low-level Waste Receiver (TK-24-1). The butted organic is pumped to the 1AX Pump Tank (TK-30-3) for reuse in the columns.

The aqueous wash solution from TK-27-3 is jetted to a Waste Receiver for disposal after each contact. Any aqueous heel in TK-26-1 is periodically jetted to a Waste Receiver. (See Section B.2.7 for further routing of both solutions.)

2.6 Strontium Product Concentration and Storage

The strontium product solution (LBP) is pumped on a semi-continuous basis from the LBP Product Receiver (TK-28-2) to the Cell 5 Concentrator (E-5-2) where it is concentrated. The degree of concentration is limited by the heat removal capacities of the strontium product storage tanks. The concentrator is operated on either a batch basis or an intermittent overflow basis due to the large concentration factor and small concentrated product flow. When the desired concentration is attained during batch operation, the concentrator is shut down and the concentrated solution is cooled before being jetted to the Concentrate Receiver (TK-5-1) for sampling. When the desired concentration is attained during intermittent overflow operation, the diaphragm-operated valve between E-5-2 and TK-5-1 is opened to permit a small batch gravity transfer of solution to TK-5-1 where cooling takes place. This mode of operation reduces thermal shock on the E-5-2 tube bundle due to less frequent cooling. Concentrated strontium product is jetted from TK-5-1 to TK-6-2 or TK-8-1 for segregation into two systems as desired. One system is composed of TK's 6-2, 6-1, 7-1, and 7-2; and the other is composed of TK's 8-1 and 8-2. Transfers are made between the two systems by a jet from TK-7-2 to TK-8-1. Out-of-specification strontium product requiring rework is jetted from TK-5-1 to TK-29-2.

2.7 Waste Handling

2.7.1 Current Acid Waste (PAW and ZAW)

Aqueous wastes generated from PAW and ZAW processing operations are considered to be high-level wastes. These streams are the 1A Column wastes (LAW), 1C Column aqueous rare-earth fraction, and the organic wash wastes from TK-27-3 and TK-26-1 (if necessary).

The LAW is collected batchwise in the LAW Receiver Tank (TK-30-2) and jetted to the Waste Receiver (TK-9-1) for interim storage and sampling, if necessary. It is then jetted to the High-level Waste Receiver (TK-25-2) for neutralization and disposal or to the PAW Supernatant Receiver (TK-9-2) for rework through the 1A Column via TK-29-2 and TK-29-3.

The 1C Column aqueous stream is collected batchwise in TK-27-2 and jetted to TK-26-2 for sampling to confirm that it meets disposal specifications. The contents of TK-26-2 are then jetted to the High-level Waste Receiver (TK-25-1) for neutralization or for eventual rework through the 1A Column via TK-29-2.

The organic wash wastes from TK-27-3 are jetted to TK-25-1 for disposal. Wastes from TK-26-1 are jetted to TK-25-2 for disposal.

Degraded organic which is unsuitable for further processing activities is disposed of by burning. Facilities for this operation are in the conceptual stage at the time this section of the manual is being written.

Further handling of waste solutions is discussed in Chapter VIII.

2.7.2 Acid Sludge Waste (PAS)

Aqueous wastes generated from PAS processing operations are low-heating, high-level wastes. These streams are the 1A Column wastes (1AW), 1C Column aqueous rare-earth fraction, and the organic wash waste from TK-27-3. These wastes are all transferred to the Low-level Waste Receiver (TK-24-1) or reworked via appropriate routings.

3. Ion Exchange Procedures

An ion exchange process is used in B-Plant to remove the heat generating radioactive cesium from stored alkaline wastes. The majority of the radioactive cesium is associated with the supernatant liquid waste. The supernatant is passed downflow through a bed of ion exchange material which selectively adsorbs the cesium. Cesium can be removed from both Purex and Redox wastes by an ion exchange process. Technology has been developed for the long term storage of radioactive cesium and radioactive strontium adsorbed on synthetic zeolites in high integrity containers. However, at the time this section of the manual was written, an ion exchange process was used only to remove cesium from stored Purex alkaline supernatant liquid waste. The procedures used to remove the cesium from the waste are discussed below.

3.1 Loading Cycle

Feed for the ion exchange column is pumped to the Cesium Supernatant Receiver (TK-17-2) in the B-Plant from Tank-105-C, a 500,000 gallon Waste Storage Tank in C-Farm used for lag storage. Feed samples are taken from the lag storage tank periodically and analyzed for sodium, cesium, aluminum, and pH. Adjustments are made to the sodium/cesium ratio as required by blending in out-of-specification product material. From TK-17-2, the feed is pumped to the LXF Pump Tank (TK-18-3) and from there to the top of the LX Column (T-18-2) for downflow operation. The column will initially contain 1550 gallons (about 8,970 pounds) of a synthetic zeolite ion exchanger, AW-500*, which adsorbs cesium and sodium during the loading cycle. The ion exchange bed is loaded to an instantaneous breakthrough of 7 percent maximum as observed by the radiation monitor in the effluent waste line. Following the loading cycle, demineralized water is added to TK-18-3 and pumped through T-18-2 to remove the residual feed solution from the bed. Both the waste effluent and the wash stream are routed to the LXW Receiver (TK-18-1).

* Trademark of the Linde Division, Union Carbide Corporation.

3.2 Sodium Removal Cycle

The sodium ion is removed from the zeolite ion exchanger by a 0.2 molar ammonium carbonate scrub solution which is added to TK-18-3 from the 173 header. Seven column volumes of scrub remove greater than 99 percent of the adsorbed sodium. Demineralized water is used to flush the ion exchange bed following the sodium removal cycle. The waste effluent and the wash stream are both routed to TK-18-1.

3.3 Cesium Elution Cycle

The cesium ion is removed by pumping a 3M $(\text{NH}_4)_2\text{CO}_3$ - 2M NH_4OH solution downflow through the bed from TK-18-3. Twelve column volumes of eluent remove greater than 99 percent of the cesium loaded on the bed. During this process, the zeolite exchanger is converted to the ammonium form, readying it for the next loading cycle. From T-18-2, the eluent flows to the LXP Receiver (TK-19-1).

3.4 Cesium Product Concentration and Eluent Regeneration

The LXP Receiver (TK-19-1) is also the feed tank for LXP Concentrator (E-20-2). The dilute cesium product is concentrated to a maximum of 5000 curies of cesium-137 per gallon in the concentrator. The concentrated product is jetted to the LXP Concentrate Receiver (TK-20-1) from when it is jetted to one of the Cesium Storage Tanks, TK-14-2 or TK-17-1. The overheads from E-20-2 are condensed in the E-20-3 condenser and collected in the Cesium Eluent Storage Tank TK-21-1. The non-condensables from E-20-3 are vented to an ammonium carbonate absorber T-21-2 which is positioned on top of TK-21-1. A small recycle stream is admitted to the top of the absorber from TK-21-1 to recover additional NH_3 and CO_2 before they are vented to the NH_3 scrubber (T-22-2) situated on top of the condensate Receiver Tank TK-22-1. According to laboratory data, approximately 2 percent of the ammonia and 7.5 percent of the carbon dioxide are lost in this process. To make up for these losses, ammonia and carbon dioxide are sparged into the solution in TK-21-1 from their respective headers. The regenerated eluent is then recycled to TK-18-3 during the cesium elution cycle.

3.5 Recycle of Product

The concentrated cesium product is sampled in TK-20-1 and, if the product does not meet specifications, it can be blended with incoming feed in TK-17-2. The concentrated product can be recycled from TK-17-1 and TK-14-2 to TK-17-2 if the need arises.

3.6 Waste Handling

All waste streams which originate within the ion exchange system are collected in TK-18-1. These streams include the loading cycle waste effluent, column washes, and the sodium scrub waste. From TK-18-1 the wastes are pumped to the Low-Level Waste Receiver (TK-24-1) and concentrated in

the Low-Level Waste Concentrator (E-23-3). The wastes can also be pumped directly to an ITS unit in the event the low-level waste evaporator is shut down or if TK-24-1 cannot accept additional waste volumes.

3.7 Bed Makeup and Removal

The zeolite ion exchange is hydrated on the third floor AMU area in Tank H-317 and slurried into TK-18-2 by gravity. Due to the exothermic reaction which results when water is added to the zeolite, it is necessary to fill H-317 with water and slowly add the zeolite. In this manner the volume of water is large compared to the volume of zeolite being added and the heat produced is quickly dissipated preventing degradation of the zeolite. The zeolite is removed from TK-18-2 by installing an alternate jumper on the ion exchange column which allows fluidization of the bed when pumping demineralized water from TK-18-3 upflow through the column. Fluidizing the bed facilitates jetting the zeolite to TK-18-1. From TK-18-1 the zeolite water slurry is pumped to an ITS unit via diversion box 241-BX-154.

C. SPECIAL PROCEDURES

1. Solvent Extraction Purification of Strontium

The concentrated strontium product resulting from normal operation of the solvent extraction system may contain amounts of calcium, sodium, rare earths, and Ce-144 in excess of those desired by some future customer. Purification of the product solutions stored in Cells 6, 7 and 8 is accomplished in the solvent extraction system on a campaign basis in conjunction with current acid waste and acid sludge waste processing. The complexant and buffering agent used are different than for the initial separation operations.

1.1 Feed Makeup

Feed for the solvent extraction system is made up in the LAF Makeup Tank (TK-29-2). Crude strontium solution is jetted from the storage tanks TK-6-1, TK-6-2, TK-7-1, TK-7-2, TK-8-1 and TK-8-2 via appropriate routing to TK-9-2 and then to TK-29-2. The premixed feed butt consisting of the complexing agent [pentasodium diethylenetriaminepentaacetate (Na_5DTPA)] and the buffering agent [acetic acid] is gravity fed to TK-29-2 from TK-29-2A. The pH of the butted feed is initially adjusted with sodium hydroxide from TK-29-2B. Final adjustment is made with sodium hydroxide or nitric acid. When the feed has been adjusted to the desired pH, it is jetted to the LAF Pump Tank (TK-29-3).

1. 1A and 1S Columns

The 1A (T-30-1) and 1S (T-29-1) Columns form an extraction and scrub system. The feed (LAF) to the 1A Column is pumped from TK-29-3 to the top of the column where it joins with the sodium scrub stream (1SR) from the 1S

Column. The aqueous streams form the dispersed phase and flow down through the organic extractant (LAX) to the bottom disengagement section, where the aqueous-organic interface is located and separation of the phases is effected.

The organic extractant (LAX) is pumped from the LAX Pump Tank (TK-30-3) to the bottom of the 1A Column. The organic flowing up the column forms the continuous phase. When the column is operated at flowsheet conditions, essentially all of the strontium and calcium are extracted. The organic phase (LAP), now the product-bearing stream, overflows from the upper disengagement section and is gravity fed to the bottom of the 1S Column where it forms the continuous phase.

The aqueous stream (LAW) leaving the 1A Column, bearing the bulk of the cerium, rare earths, and sodium, flows by gravity from the lower disengagement section to the LAW Receiver Tank (TK-30-2). (See Section C. 1.6 for further routing.)

In the 1S Column, the organic is contacted with an aqueous scrub stream (LSS) for reduction of the sodium concentration. The scrub solution is composed of citric acid for pH control and a small concentration of DTPA complexing agent to remove trace amounts of undesired metallic impurities carried over from the 1A Column. The LSS butt is pumped from TK-29-1F to an in-line blending tee for mixing with water to provide the desired concentration and flow rate as the LSS stream to the top of the 1S Column. After passing through the organic-continuous 1S Column the aqueous stream enters the bottom disengagement section where the aqueous-organic interface is located and separation of the phases is effected. The aqueous waste scrub stream (LSR) is then jetted to the upper part of the 1A Column. The organic (1SP) overflows from the top of the column to the 1BF Pump Tank (TK-28-4).

1.3 1B Column

The 1BF Pump Tank (TK-28-4) continuously receives the 1S (organic overflow from the 1S Column) and pumps it to the bottom feed point of the 1B Column (TK-28-1) where it becomes the continuous phase. Strontium is stripped from the organic phase with dilute citric acid (1BX). The 1BX citric acid butt is pumped from TK-28-1F to an in-line blending tee for mixing with water to provide the desired concentration and flow rate to the top of the 1B Column. The interface in the organic-continuous column is located in the bottom disengagement section. The exiting aqueous phase (1BP), bearing about 99 percent of the strontium entering the column, the sodium not removed in the 1S Column, the citrate strip solution, and a trace amount of calcium, flows by gravity to the 1BP Receiver (TK-28-2). The organic stream containing small amounts of calcium and strontium overflows from the top of the column to the 1CF Pump Tank (TK-27-4).

1.4 Solvent Treatment

The 1CF Pump Tank (TK-27-4) continuously receives the organic overflow from the 1B Column and pumps it to the bottom feed point of the 1C Column (TK-27-1) where it becomes the dispersed phase since the 1C Column

is operated aqueous continuous with a top interface. The calcium, strontium, and any rare earths which may be left in the organic are removed by a sodium hydroxide-sodium tartrate wash solution (10X). The 10X butt is gravity fed from an AMU tank to an in-line blending tee for mixing with demineralized water to the desired concentration and flow rate as the 10X stream to the top of the 1C Column where it becomes the continuous phase. The aqueous stream leaving the 1C Column (1CP) flows by gravity from the lower disengagement section to the 1CP Receiver (TK-27-2). The washed organic stream (1CW) overflows from the top of the column to the 1CW Receiver (TK-26-3). It is then transferred via TK-27-3 and TK-26-1 to the 1AX Makeup Tank (TK-28-3) where it is butted with 12.2 M nitric acid (10B), gravity fed from TK-28-3C to obtain the desired acid to salt ratio of the D2EHPA for pH control in the 1A Column. TK-28-3C is flushed with a small volume of water to reduce the residual acid holdup and minimize tank corrosion. The flush water is also added to TK-28-3. Periodically, the aqueous heel in TK-28-3 is jetted to the Low-Level Waste Receiver (TK-24-1). The butted organic is pumped to the 1AX Pump Tank (TK-30-3) for reuse in the columns.

1.5 Strontium Product Concentration

The strontium product (1BP) is pumped on a semi-continuous basis from the 1BP Receiver (TK-28-2) to the Cell 5 concentrator (E-5-2) where it is concentrated. Nitric acid and hydrogen peroxide are added to E-5-2 during concentration to decompose the residual citrate. The peroxide is added to the bottom of the concentrator through the discharge line from the TK-5-2F scale tank. The nitric acid is pumped from the TK-5-2A scale tank. The degree of concentration is limited by the heat removal capacities of the purified strontium product storage tanks. The concentrator is operated on either a batch basis or an intermittent overflow basis depending on conditions existing at the time. When the desired concentration is attained during batch operation, the concentrator is shut down, and the concentrated solution is cooled before being jetted to the Concentrate Receiver (TK-5-1) for sampling. When the desired concentration is attained during intermittent overflow operation, the diaphragm-operated valve between E-5-2 and TK-5-1 is opened to permit a small batch gravity transfer of solution to TK-5-1 where cooling takes place. This mode of operation reduces thermal shock on the E-5-2 tube bundle due to less frequent cooling. Concentrated purified strontium product is jetted from TK-5-1 to a storage tank.

1.6 Waste Handling

The 1A Column aqueous waste stream (1AW) is collected batchwise in the 1AW Receiver (TK-30-2) and jetted to the Waste Receiver (TK-9-1) for interim storage and sampling if necessary. It is then jetted to the High-Level Waste Receiver (TK-25-2) for neutralization and disposal or to the PAW Supernatant Receiver (TK-9-2) for rework through the 1A Column via TK-29-2 and TK-29-3.

The 1C Column aqueous waste stream (1CP) is collected batchwise in the 1CP Receiver (TK-27-2) and jetted to the 1CP Contactor (TK-26-2) for sampling to confirm that it meets disposal specifications. The contents of TK-26-2 are then jetted to the High-Level Waste Receiver (TK-25-1) for disposal.

2. Solvent Extraction Purification of Promethium

During normal waste management processing operations no attempt is made to separate promethium from cerium in the 1C Column. Essentially all of the cerium, promethium and other rare earths are stripped into the 1CP aqueous waste stream and discarded to the High-Level Waste Receiver (TK-25-1). Occasions may arise, however, when it will be necessary to recover a purified promethium product during processing of the Purex acid waste. When a purified promethium product is desired, the separation from cerium is made in the 1C Column. This is accomplished by oxidizing the Ce(III) to Ce(IV) so that cerium-144 is retained in the organic phase while americium and the trivalent lanthanides, including promethium-147, are stripped into the aqueous phase. The aqueous phase is a nitric acid solution containing the strong oxidant, persulfate, plus silver ion as a catalyst. Jumper changes are necessary in Cells 27 and 30 to provide the proper routing for the 1CF stream and to provide an organic scrub stream to the bottom of the 1C Column.

2.1 Promethium-Cerium Separation

The 1CF Pump Tank (TK-27-4) continuously receives the organic overflow from the 1B Column and pumps it to the intermediate feed distributor of the 1C Column where it becomes the dispersed phase since the 1C Column is operated aqueous continuous with a top interface. The aqueous strip streams, nitric acid-persulfate (1CX-1) and nitric acid-silver nitrate (1CX-2) are gravity fed from separate AMU tanks to an in-line blending tee for mixing to the desired concentration and flow rate as the 1CX stream to the top of the 1C Column where it becomes the continuous phase. An organic scrub stream (1CS) is pumped from the 1AX Pump Tank (TK-30-3) to the bottom feed point of the 1C Column to extract cerium from the aqueous phase below the intermediate feed distributor and thus reduce cerium contamination of the promethium product. The aqueous stream leaving the 1C Column (1CP), bearing ~98% of the promethium and ~3% of the cerium entering the column, flows by gravity from the lower disengagement section to the 1CP Receiver (TK-27-2). The cerium-bearing organic stream (1CW) overflows from the top of the column to the 1CW Receiver (TK-26-3).

2.2 Solvent Treatment

The solvent received in TK-26-3 from the 1C Column is pumped batchwise to TK-27-3 where it is contacted with a nitric acid-sodium nitrite strip solution. The sodium nitrite accelerates the reduction of Ce(IV) to Ce(III) and the subsequent transfer of cerium to the aqueous phase. The strip solution is gravity fed to TK-27-3 from AMU TK-H-321 (via the 2707 HDR). After each contact of organic and strip solution, an appropriate settling time is allowed for separation of the phases. The organic is then decanted to TK-26-1 where it is contacted with a sodium hydroxide-sodium tartrate wash solution (1OS) for removal of yttrium and traces of rare earths. The D2EHPA degradation product mono(2-ethylhexyl)phosphoric acid is also removed. After an appropriate settling time to allow separation of the phases, the organic is pumped to the 1AX Makeup Tank (TK-28-3).

In TK-28-3 the washed organic is butted with 12.2M nitric acid (100 butt) gravity fed from TK-28-3C to obtain the desired acid to salt ratio of the D2EHPA for pH control in the 1A Column. TK-28-3C is flushed with a small volume of water to reduce the residual acid holdup and minimize tank corrosion. The flush water is also added to TK-28-3. Periodically, the aqueous heel in TK-28-3 is jetted to the Low-Level Waste Receiver (TK-24-1). The butted organic is pumped to the 1AX Pump Tank (TK-30-3) for reuse in the columns.

The cerium product contained in the TK-27-3 aqueous phase is jetted to the High-Level Waste Receiver (TK-25-1) for neutralization and disposal. The aqueous wash solution in TK-26-1 is jetted to the High-Level Waste Receiver (TK-25-2) for disposal.

2.3 Promethium Product Purification and Concentration

The promethium-bearing aqueous stream (1CP) collected in TK-27-2 is transferred batchwise to the 1CP Contactor (TK-26-2) for removal of the sulfate, silver, and sodium ions resulting from the silver-catalyzed persulfate oxidation of Ce(III) to Ce(IV). Removal of the sulfate is necessary to prevent precipitation of double rare-earth sulfates and to allow concentration of the promethium fraction to volumes small enough for storage. The aqueous solution is butted with sodium hydroxide and sodium tartrate for pH adjustment. The tartrate prevents precipitation of rare earth sulfates when the sodium hydroxide is added. The butted solution is contacted with fresh D2EHPA pumped from TK-MO154 via the 1545 header. After an appropriate settling time for separation of the phases, the aqueous waste is jetted to the High-Level Waste Receiver (TK-25-1) for disposal.

The organic is then stripped with strong nitric acid for recovery of the promethium. After an appropriate settling time for separation of the phases, the stripped organic is pumped to the 1AX Makeup Tank (TK-24-3). The aqueous promethium product stream is transferred to an intermediate storage tank prior to concentration. Storage tank (TK-36-2) was originally scoped for this service as part of a separate project but was not installed as part of Phase III.

A concentrator and concentrated promethium storage tanks in Cells 36 and 37 were also scoped for another project but were not installed for Phase III of the Waste Management Program. Until facilities are provided, concentration of promethium is performed in the Cell 5 concentrator on a campaign basis in conjunction with strontium concentration. The concentration operation is similar to that outlined in Sections B 2.6 and C 1.5 of this manual. The main difference in operation is the addition of sucrose from TK-5-2F to the bottom of E-5-2 during concentration to decompose the nitric acid in the dilute promethium product stream. The concentrated promethium product is collected in the Concentrate Receiver (TK-5-1) for sampling and then jetted to storage (none exists at the time of manual preparation).

D. SOLVENT EXTRACTION STARTUP AND SHUTDOWN PROCEDURES

The preceding sections (B. 2.0 and C.) deal with steady-state operation of the solvent extraction system. This section outlines the solvent extraction system startup and shutdown procedures. Since the process status preceding startup or shutdown may vary widely, the choice of specific procedures is made at the time of startup or shutdown. These procedures are based largely on several years of successful solvent extraction column operating experience at the Strontium Semiworks.

1 Startup Procedures

In order to avoid unnecessary waste losses or an off-standard strontium product stream in establishing steady-state operation, the following sequence is usually followed in startup of the solvent extraction system:

- (a) Make up "cold" feed, organic extractant, and aqueous chemical streams.
- (b) Establish aqueous seal in each column.
- (c) Introduce organic to all columns.
- (d) Initiate flow of aqueous chemical streams.
- (e) Establish interfaces.
- (f) Initiate "cold" feed flow to the columns.
- (g) Establish steady-state conditions.

If the columns have not been completely shutdown, all of the above operations may not be necessary to establish column operation.

1.1 Cold Feed Makeup

A synthetic feed having a composition and specific gravity roughly resembling that of the LAF stream to be processed is prepared in TK-29-2. The synthetic feed which contains sodium nitrate, complexant, buffering agent and tartaric acid is adjusted to the approximate "hot" feed pH. Sufficient synthetic feed is prepared to provide approximately 8 hours of column operation. Processing of the synthetic feed prior to introduction of normal LAF to the columns assists in establishment of steady-state conditions, evaluation of equipment performance, and minimization of waste losses.

The cold chemical solutions, 1SS Butt, 1BX Butt, and 1CX Butt are also prepared prior to column startup.

1.2 Filling Columns and Establishing Interfaces

The first condition that is established in the columns is the formation of an aqueous seal by adding the appropriate aqueous stream to each column to a predetermined interface level. The purpose of the seal is to prevent trapping of any organic phase (subsequently introduced) in the bottom effluent lines which normally handle the aqueous phase on all columns. Dilute nitric acid or water is added from scale tank TK-30-1-C to establish the interface position on the 1A Column. Water can also be added via the pulser purge line.

Once the seals have been established, the 1AX extractant flow to the 1A Column is started. The organic fills and overflows each column - 1A, 1S, 1B, and 1C - in turn. The desired liquid levels in the intermediate pump tanks, TK-28-4 and TK-27-4, are established and maintained. As each of the 1A, 1S, and 1B Columns is filled with organic extractant and the pulsers are started, the aqueous stream flows are established to move the dispersed phase through the plate perforations and obtain intimate contact between the phases. The 1C Column pulser is started before the organic enters the column. Pulsers are not started until the pulse legs are completely purged of air either by process solution or by water addition to the pulse leg. As the "cold" aqueous streams are started and the rates manually adjusted to the desired initial flow rate, the interfaces are established at the desired location and placed on automatic control. Flow rates of the cold aqueous streams are also put on automatic control. During this initial startup period transfer of the 1SR stream by jet from the 1S Column to the 1A Column is started.

After establishing the organic and cold aqueous stream flows, synthetic feed is introduced to the 1A Column at the desired initial rate, then put on automatic control. Operation with the synthetic feed and cold streams is normally continued for several hours until the columns are operating smoothly and the flowsheet pH conditions are essentially established, especially in the 1A Column.

1.3 Establishment of Flow Rates

The strontium, rare earth and other fission product-bearing 1AF stream is started after all columns are operating smoothly on "cold" streams. The "hot" 1AF stream is gradually blended with the synthetic feed and started to the column. While the columns are reaching steady-state operating conditions, readjustments of the interface controllers are necessary since the specific gravity of the solutions change due to the introduction of the "hot" 1AF. Adjustments to pulser frequency are made at this time also.

Until the 1A, 1S and 1B Columns reach steady-state flowsheet pH conditions, strontium losses to the 1AW or 1CP streams or rare earth and other fission product contamination in the strontium product stream may be excessive. The

use of synthetic feed at startup is designed to minimize off-standard conditions. Provision has been made for reworking off-standard LAW or strontium product material as indicated in Section F of this chapter. A direct routing for rework of LCP has not been established at the time of manual preparation.

When steady-state conditions have been established and appropriate flow rate checks have been made, the process stream flow rates are gradually increased to flowsheet levels under automatic control. Pulser frequencies are also increased to the desired values at this time.

1.4 Startup from Equilibrium Shutdown

When the columns are started from an equilibrium shutdown (see Section 2.0), air pressure is removed from the column pulse legs. After a waiting period to allow leakage of air past the pulser pistons, the pulsers are started. This time period was established during functional testing. The LAX, LSS, LBX and LCX stream flows are then started to establish operating conditions and for establishment of interfaces. The LAF flow is then started and the rate increased as outlined in Section D. 1.3.

1.5 Startup from Stripping Shutdown

When the columns are started from a stripping shutdown (see Section 2.0), air pressure is removed from the column pulse legs. After a waiting period to allow leakage of air past the pulser piston, the pulsers are started. This time period was established during cold testing. The LAX, LSS, LBX and LCX stream flows are then started and the column interfaces are established. Synthetic feed is then introduced to the LA Column at the desired initial rate and put on automatic control. Operation with the synthetic feed and cold streams is normally continued for several hours until the columns are operating smoothly and the flowsheet pH conditions are essentially established, especially in the LA Column. Introduction of the "hot" LAF and establishment of flow rates is then completed as outlined in Section D. 1.3.

2 Shutdown Procedures

Column shutdowns are of three types: 1) Equilibrium; 2) Stripping; and 3) Complete. An equilibrium shutdown is made if the downtime is to be of short (16 to 24 hours) duration and the cause of the downtime is not directly associated with any of the columns. Maximum length of downtime of this type is dependent on potential loss of complexant due to decomposition by radiation. A stripping shutdown is made if the downtime is to be of intermediate or long duration due to major repair work or to segregate certain feed campaigns. A complete shutdown is made if the downtime is to be of long duration, if the cause of the downtime is directly associated with any of the columns, or if feed campaigns must be segregated. Process status at the time of shutdown dictates the degree of column stripping and tank cleaning required. Rework of shutdown product and waste streams is covered in Section F of this chapter.

2.1 Equilibrium Shutdown

When the B-Plant columns are placed in an "equilibrium" shutdown condition, all aqueous and organic stream flows, both "hot" and "cold", are stopped. The pulsers also are stopped to maintain as nearly as possible a "status quo" condition within the columns. When the pulsers are stopped, air is introduced to the pulser legs to prevent leakage of process solutions past the pulser piston. Air is not to be introduced while the pulser is operating. It may be necessary to add dilution water through the pulser leg of the 1C Colum to maintain the temperature below 65°C in the bottom disengaging section since self-heating of the aqueous phase may be excessive.

2.2 Stripping Shutdown

When the B-Plant columns are given a "stripping" shutdown, the columns are stripped and left full of the continuous phase. The 1AF, 1BF and 1CF Pump Tanks and the waste and product tanks are emptied. The sequence of events is essentially as follows: Synthetic feed is prepared and added to the 1AF Makeup Tank a few hours prior to shutdown to flush "hot" 1AF from the feed system and the columns. At the completion of synthetic feed processing, the 1AX, 1SS, 1SR, 1BX and 1CX streams are continued for 30 to 60 minutes to complete stripping of the columns. During this time, the 1A column interface is gradually lowered and the interface solids and a small amount of organic are jetted to the 1AW Receiver (TK-30-2). On completing the interface solids removal, the interface level is established. At the completion of the 30-60 minute stripping period, the 1AX, 1SS and 1SR flows are discontinued. The 1BX and 1CX flows are continued until the 1BF and 1CF Pump Tanks (TK-28-4 and TK-27-4) contain minimum pump heels and are then stopped. Pulsing is continued for a period of time to complete phase separation in the columns. When pulsing is discontinued, air is introduced to the pulser legs to prevent leakage of process solutions past the pulser piston. Air is not introduced while a pulser is operating. Final interface adjustments are made and the column letdown valves are closed.

At the completion of synthetic feed processing, the aqueous heels in the 1AF Makeup and Pump Tanks (TK-29-2 and TK-29-3) are jetted to waste. The two tanks are then flushed with dilute sodium hydroxide and the flushes are jetted to waste. Heels in the various waste and product tanks are disposed of as necessary to accomplish the purpose of the shutdown.

2.3 Complete Shutdown

When the B-Plant columns are completely shut down, the columns are stripped and emptied together with the intermediate pump tanks. The sequence of events is essentially a reversal of the startup procedure outlined in Section D. 1.0. Sufficient synthetic feed solution is prepared and added to the 1AF Makeup Tank a few hours prior to shutdown to flush "hot" 1AF from the feed system and the columns.

At the completion of synthetic feed processing, the aqueous heels in the 1AF Makeup and Pump Tanks (Tk-29-2 and Tk-29-3) are jetted to waste. The two tanks are then flushed with dilute sodium hydroxide to remove any complexant-rich heels. The flushes are also jetted to waste. When the tanks are empty, dilute nitric acid to be used for displacement of the column organic inventories is added to Tk-29-2 and transferred to Tk-29-3.

Meanwhile, the 1AX, 1SS, 1SR, 1BX and 1CX flows are continued to complete stripping of the columns. At the completion of a 30 - 60 minute stripping period, the 1AX, 1SS and 1SR flows are stopped while the 1BX and 1CX flows are continued. The 1A Column interface is then gradually lowered and the interface solids and a small amount of organic are jetted to the 1AW Receiver (TK-30-2). On completion of the interface solids removal, the interface level is reestablished with dilute nitric acid from TK-29-3 and flow is continued from TK-29-3 to T-30-1 to TK-30-2 for a short period of time to strip the organic in the column. The dilute nitric acid flow is then stopped and the interface is again jetted to TK-30-2 as above.

At the completion of the second interface removal, the 1A Column letdown valve is closed and dilute nitric acid is pumped from TK-29-3 to the 1A Column to displace the organic in the 1A and 1S Columns. When the organic is completely displaced from the 1A and 1S Columns, the aqueous flow is continued to displace the organic from the 1B and 1C Columns. The 1BF and 1CF pumps are operated during this part of the process. The 1BP and 1CP letdown valves are closed during this phase of the operation. The 1BX flow is discontinued when the aqueous overflow to TK-27-4 starts. The 1CX flow is discontinued when aqueous overflow to TK-26-3 starts. When the organic is purged from all of the columns, dilute nitric acid flow is discontinued.

Disposal of the solutions in the columns depends on the status of equipment at the time of shutdown. If the columns are to be emptied, pulser operation is stopped and the columns are emptied to waste tanks. If the columns are to be left full, air pressure is applied to the pulser legs to prevent leakage past the piston. The air pressure required for each column was calculated and checked during functional testing.

E. DETECTION AND REMEDY OF OFF-STANDARD CONDITIONS

Off-standard conditions which may develop during the operation of the solvent extraction system are those processing circumstances which result in excessive strontium waste losses, inadequate decontamination of the strontium product, and inadequate decontamination of the promethium product. The overall plant yield of the strontium and promethium, as defined by the chemical flowsheet, is expected to be better than 95 percent on a sustained operating basis. Tentative specifications for rare earth, other fission product, and impurity content in the strontium and promethium product streams are presented in Chapter I, and more recent specifications are given in Reference 5.

The purpose of this section is to discuss generally the detection and remedy of off-standard conditions occurring in the solvent extraction equipment with particular emphasis being placed on the value of certain instruments as an aid in interpreting abnormal column operation. More meaningful interpretation of the data can be made as experience is gained in operating the processes. Many of the statements made in this section are based on anticipated or theoretical results as determined by the best knowledge at the time of writing. A detailed tabulation of off-standard conditions, their common symptoms, and possible remedies is presented in Tables V-3 and V-4.

1. Methods of Detecting Off-Standard Conditions

1.1 Instruments

Controlled operation of the solvent extraction columns is accomplished by means of six general types of instruments, as follows:

- (a) The recording - controlling electronic rotameters which establish the flow rates of the various feed streams to all columns.
- (b) The air-purge instruments which record the specific gravity of the solution in the upper disengaging section of the column and the differential pressure across the upper part of the column, including the upper disengaging section and the entire cartridge assembly on the 1A, 1S, 1B, and 1C Columns. On the 1C Column there is an additional purge instrument which records the differential pressure across the lower part of the cartridge assembly.
- (c) The gamma energy monitoring instruments which are of two types: 1) gamma spectrometers which incorporate pulse height analyzers for specific energy level detection; and 2) ion chambers which measure gross gamma activity. Probe wells are available to permit continuous monitoring of the lines containing the 1AP, 1AW, 1BP, 1BW, 1CW, and 1CP streams. The gamma spectrometers monitor an individual energy level or scan the energy spectrum between preset levels within the overall range of 0.05 to 2.0 MEV. This flexibility permits the detection of various fission products including rare earths and other emitters of gamma energy within this range.
- (d) The electronic float type controllers which establish the interface position on all columns by controlling the effluent aqueous stream flow rates.

- (e) The temperature sensing and recording instruments which indicate the temperature in both the top and bottom disengaging sections of all columns.
- (f) The pH monitors which measure and record the pH of the 1AF, 1AW, 1BP, and 1CP streams when the samplers at the individual locations are operated.

Under normal operating conditions at a given processing rate, the instrumentation will indicate that almost constant physical and chemical conditions exist in the process. While a single instrument may indicate a trend toward abnormality, it usually takes proper interpretation of the data gathered from several related sources to determine the specific off-standard condition that has developed.

1.2 Samples

Samples obtained at several tank and in-line locations permit analysis of the process solutions by the control laboratory or by the pH monitors noted in Section E 1.1. Analytical data thus obtained provide a valuable means for determination of off-standard conditions. In particular, adequate pH control is essential to efficient operation of the solvent extraction system.

2. Excessive Product Losses

The main product resulting from operation of the solvent extraction system is strontium-90. Promethium-147 can be recovered from the rare earth fraction if the demand arises. Excessive strontium and promethium losses are generally detected by routine sampling, gamma energy monitoring of process streams, or both. Specific gravity and differential pressure instruments do not give positive indications of excessive losses. (See Section E 3.0 if flooding is involved.)

Process stream gamma monitoring should prove to be a very useful method of determining excessive product losses. However, due to the complex mixtures of nuclides present in many of the solvent extraction system streams, interpretation of the gamma spectrometer data obtained is difficult. Detection of excessive strontium losses is possible only if large amounts of strontium-89 are associated with the beta-emitting strontium-90 by detecting specific gamma energy peaks of the metastable yttrium-89 daughter. Yttrium-89 is present in the 1AW and 1BW streams. Detection of excessive promethium losses in the 1AW, 1BP, and 1CW streams is possible only if large amounts of promethium-148 present in PAW and ZAW are associated with the beta-emitting promethium-147. Detection of europium-154 may be used in estimating promethium losses since the nuclides behave similarly. As experience is gained from the correlation of B-Plant in-line analyses, sophisticated laboratory multichannel gamma analyses techniques, and other laboratory analytical methods, confidence in the in-line monitor data will increase.

Once a loss is confirmed, a check of the controlled flows and operating conditions is usually sufficient to locate the off-standard condition. The most likely cause for excessive losses of strontium is loss of pH control in the 1A and 1B columns. The most likely cause for excessive losses of promethium is loss of pH control in the 1A Column. Pulsing conditions, improper flow ratios, and non-flowsheet stream compositions are also potential causes.

3. Column Flooding

Whenever the holdup of the dispersed phase in a solvent extraction column plate section increases to a value which interferes with free counter-current phase flow, the conditions for a flood have been established. If the approach to a flooding condition is made gradually, the dispersed phase buildup is localized and, depending on flow conditions, may tend to disperse and reform as a cyclic local flood. Complete flooding caused by aggravation and growth of a local flood is characterized by either the aqueous or the organic phase leaving the column at the end where it entered. Development of a flooding condition within a solvent extraction column, depending on degree, lowers the column's efficiency. As a consequence, increased losses of strontium or promethium, or an increase in impurity content of the respective product streams is apt to result.

In those columns which operate with the organic phase continuous by means of a bottom interface, the differential pressure increases as the aqueous holdup within the column increases. An increased holdup of aqueous phase also tends to lower the interface position which is indicated on the interface recorder-controller. Since the interface instrument controls the rate of aqueous effluent from the column, an increase in aqueous holdup also becomes apparent through a reduction in the flow of the 1AW, 1SR, or 1BP stream.

For the 1C Column, which has a top interface and a continuous aqueous phase, the reverse of the above instrument behavior is generally true. An increase in the organic holdup in the column is reflected by a decrease in differential pressure, rising interface, and increased aqueous 1CP flow.

Generally, a flooded column is returned to normal operation by reducing influent stream rates, the pulse frequency, or both.

4. Emulsion

Excessive emulsification in the plate section of a pulse column may result from the presence of excessive concentrations of emulsion-stabilizing solid impurities such as ferric hydroxide, silica, or zirconium phosphate (from TBP decomposition). Emulsions may also form when the organic phase is contacted with an aqueous phase of low ionic concentration. The 1S Column is particularly susceptible to this latter cause. Emulsification in the plate section is often accompanied by foaming and improper phase

disengagement in the column disengaging section, particularly at the interface end.

Severe emulsification in the column plate section results in partial coalescence of the dispersed phase and may impair decontamination and cause increased and fluctuating strontium losses. The instrument indications and consequences of a severely emulsified condition in a column plate section are similar to those of local flooding. Distinguishing between a flooded and an emulsified condition may require observation and interpretation of equipment performance over a period of several hours, including the taking of special samples. Severe emulsification in a column plate section is usually remedied in the same manner as a flooding condition; that is, by reducing flow rates and/or the pulse frequency. If emulsification occurs in the 1S Column due to third phase formation, the 1AF and 1AX flow rates are reduced while the 1SS stream is continued at full rate to scrub out the third phase. Rates are then gradually increased to the proper ratios. Addition of Mistron to the 1AF was found to be effective in pilot plant studies when the emulsification was caused by solids.

A foaming or emulsified condition in a disengaging section is usually detected by erratic behavior of the interface control system and in the 1C Column by fluctuation of the apparent specific gravity in the top disengaging section. An emulsion in a column disengaging section often has its counterpart in the plate section and is thus often accompanied by column operating instability and malperformance. If the emulsified condition is not alleviated by the remedies mentioned above, or by increasing the TBP concentration of the solvent, a shutdown and flush of the system may be necessary in order to overcome the difficulty. A general consequence of disengaging section emulsification is excessive entrainment of the wrong phase, which may have deleterious effects on the process as discussed below.

5. Excessive Entrainment

During normal column operation some entrainment of aqueous in the organic and vice versa is always occurring. Entrainment of the order of 0.1 to 0.5 percent by volume of the opposite phase may be considered as normal. Phase emulsification in a disengaging section always leads to increased entrainment and, depending on the type of column involved, may produce any of several undesirable results. In the 1A and 1S Columns, entrainment of aqueous in the overflowing organic phase generally is detected by a decline in the decontamination performance of the columns since the aqueous particles are usually associated with metallic impurities. Organic entrainment in the aqueous phase, such as that which could occur in the bottom section of the 1A and 1B Columns, results in solvent loss. In addition, introduction of excessive quantities of solvent to the 1BP concentrator causes a buildup of TBP hydrolysis products in the concentrated solution. Also, prevention of organic-phase entry into the concentrator provides a desirable added safety factor against a possible "red oil" reaction.

6. Poor Product Quality

Poor product quality is defined as inadequate removal of metallic impurities, rare earths, and other fission products from the strontium product stream, and inadequate separation of cerium, strontium, and metallic impurities from the promethium product stream. All of these off-standard conditions can be detected by routine laboratory analyses of process samples. In addition, it should be possible to detect excessive amounts of gamma emitting rare earths and other fission products in the LBP and LCP streams by the stream gamma monitors.

Poor decontamination from metallic impurities without coincident column flooding or emulsion may be due to low complexant concentrations in the 1A and 1S Columns. Poor separation of the rare earths and other fission products from strontium in the 1A, 1S, and 1B Columns may be due to improper pH control. Poor separation of cerium from promethium in the 1C Column may be due to inadequate oxidation of the cerium or to an inadequate LCS flow rate.

F. REWORK OF OFF-STANDARD PROCESS STREAMS

Any required rework of off-standard process streams in B-Plant will normally involve one of the following streams:

- (a) The strontium product stream (LBP) - to decontaminate the strontium from excessive metallic impurity, rare earth and other fission product activity.
- (b) The 1A Column aqueous waste stream (1AW) - to recover excessive strontium losses.
- (c) The 1C Column aqueous stream (1CP) - to recover excessive strontium losses.
- (d) The promethium product stream (1CP) when making a cerium-promethium separation - to decontaminate the promethium from excessive cerium and/or strontium activity.
- (e) The cesium product stream - to remove excess sodium.
- (f) Ion exchange wastes - to recover excessive cesium losses.

Methods available for reworking these off-standard streams are discussed in this section. The decision to rework is arrived at in each individual case on the basis of a number of factors. The effect of off-standard strontium, promethium, or cesium product compositions upon subsequent processing (in the case of product streams) or the value of the strontium, promethium, or cesium recovered by rework (in the case of waste streams), is weighed against the cost of reprocessing in each instance.

1. Off-Standard Strontium Product

Off-standard strontium product can be routed from the LBP Receiver (TK-28-2) to the LAF Makeup Tank (TK-29-2) via the Cell 5 Concentrator (E-5-2) and the concentrate Receiver (TK-5-1) for rework through the 1A Column. Stored concentrated strontium product can be transferred to TK-29-2 via TK-9-2.

2. Off-Standard Promethium Product

Off-standard promethium product can be routed from the LCP Contactor (TK-26-2) to the LAF Makeup Tank (TK-29-2) via the High-Level Waste Receiver (TK-25-1). A rework route not initially existing which would eliminate gross contamination of the promethium product would involve transfer of the organic phase from the extraction operation in the LCP Contactor (TK-26-2) to the LBP Pump Tank (TK-28-4).

3. Off-Standard Cesium Product

Off-standard cesium product can be routed from the LXP Concentrate Receiver (TK-20-1) to the Cesium Supernatant Receiver (TK-17-2) via TK-17-1 to be blended with incoming feed for rework. When TK-14-2 and TK-17-1 both contain concentrated cesium product, a jumper change is required to jet the contents of TK-20-1 to TK-17-2.

4. Ion Exchange Wastes

Ion exchange wastes collected in TK-18-1 can be jetted back to TK-17-2 for rework if necessary.

5. Solvent Extraction Wastes

1A Column aqueous wastes (1AW) collected in the Waste Receiver (TK-9-1) can be routed to TK-9-2 for rework through the 1A Column via TK-29-2 and TK-29-3. 1C Column aqueous wastes (1CP) collected in the LCP Receiver (TK-27-2) and the LCP Contactor (TK-26-2) can be routed from TK-26-2 to the LAF Makeup Tank (TK-29-2) via the High-Level Waste Receiver (TK-25-1).

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DETECTION AND REMEDY C
HIGH SOLVENT EXT

<u>Off-Standard Conditions</u>	<u>How Detected</u>	<u>Lik</u>
A. High Strontium loss to the 1AW.	(1) By analysis of the aqueous waste in TK-9-1. (2) By analysis of the 1AW Receiver Tank (TK-30-2) sample. (3) By analysis of the 1AW in-line sample.	(1) Flow rate ratio) a) High 1 ratio) b) Low 1 ratio) (2) Stream c a) Low 1 1AX. b) Low 1 c) Low c in 1A d) High : 1AF (3) Low pH: a) Low e b) High : column (4) Flooding (5) Pulse fr optimum a) Frequ b) Air ir
B. High rare earth loss to the 1AW. (Cerium contamination of cesium bearing waste)	(1) By analysis of the aqueous waste in TK-9-1. (2) By analysis of the 1AW Receiver Tank (TK-30-2) sample.	(1) See (1) a (2) Stream c a) Low o centra b) High c 1AF. (3) High pH: (4) Flooding (5) Pulse fr off optin a) Frequ b) Air in (6) Low tem
C. High promethium loss to 1CW during separation of cerium and promethium.	(1) By analysis of the 1CW sample. (2) By in-line gamma energy analysis of the 1CW stream during PAW or ZAW processing.	(1) Low 1CX

OFF-STANDARD CONDITIONS

EXTRACTION WASTE LOSSES

<u>Effect Cause</u>	<u>Detection of Cause</u>	<u>Remedy</u>
<p>1. Rates:</p> <p>1AF (high aq/org flow)</p> <p>1AX (high aq/org flow)</p> <p>2. Stream compositions:</p> <p>D2EHPA concentration in 1AF</p> <p>3. Low pH:</p> <p>1AW concentration in 1AX.</p> <p>4. Strontium concentration in 1AF.</p> <p>5. Strontium reflux from 1S due to low 1SS pH.</p> <p>6. Pulse frequency or amplitude off conditions.</p> <p>7. Pulse leg.</p>	<p>(1) Rates:</p> <p>a) Flow recorder on 1AF</p> <p>b) Flow recorder on 1AX.</p> <p>(2) Stream compositions:</p> <p>a) Instrument specific gravity readings.</p> <p>b) Analysis of samples.</p> <p>(3) Low pH:</p> <p>a) 1AW in-line pH monitor.</p> <p>b) Analysis of samples.</p> <p>(4) Flooding:</p> <p>a) Increase in column differential pressure readings.</p> <p>b) Interface and-or 1AW flow variations.</p> <p>(5) Pulse frequency or amplitude:</p> <p>a) Frequency count.</p> <p>b) Decrease in column differential pressure due to decreased amplitude-frequency product.</p>	<p>(1) Rates:</p> <p>Adjust flows to proper ratios.</p> <p>(2) Stream compositions:</p> <p>a) Butt to specifications; or</p> <p>b) Adjust flow rates to compensate.</p> <p>1) If low D2EHPA or TBP concentrations exist, raise 1AX rate.</p> <p>2) If high strontium concentration exists in 1AF, lower 1AF rate or increase 1AX rate.</p> <p>(3) Low PH:</p> <p>a) Butt 1AF or 1SS with sodium hydroxide or buffer.</p> <p>(4) Flooding: (see text)</p> <p>a) Decrease flow rates.</p> <p>b) Adjust frequency.</p> <p>(5) Pulse:</p> <p>a) Adjust frequency.</p> <p>b) Shut down for maintenance of pulser.</p>
<p>8. See (1) above.</p> <p>9. Stream compositions:</p> <p>10. High complexant concentration in 1AF.</p> <p>11. Cerium concentration in 1AF.</p> <p>12. High pH:</p> <p>13. 1AW in-line pH monitor.</p> <p>14. Analysis of samples.</p> <p>15. Flooding:</p> <p>16. Increase in column differential pressure readings.</p> <p>17. Interface and-or 1AW flow variations.</p> <p>18. Pulse frequency or amplitude:</p> <p>19. Frequency count.</p> <p>20. Decrease in column differential pressure due to decreased amplitude-frequency product.</p> <p>21. Low temperature:</p> <p>22. Temperature recorders for 1AF feed tank and 1A column.</p>	<p>(1) See (1) above.</p> <p>(2) Stream compositions:</p> <p>a) Instrument specific gravity readings.</p> <p>b) Analysis of samples.</p> <p>(3) High pH:</p> <p>a) 1AW in-line pH monitor.</p> <p>b) Analysis of samples.</p> <p>(4) Flooding:</p> <p>a) Increase in column differential pressure readings.</p> <p>b) Interface and-or 1AW flow variations.</p> <p>(5) Pulse frequency or amplitude:</p> <p>a) Frequency count.</p> <p>b) Decrease in column differential pressure due to decreased amplitude-frequency product.</p> <p>(6) Low temperature:</p> <p>a) Temperature recorders for 1AF feed tank and 1A column.</p>	<p>(1) See (1) above.</p> <p>(2) Stream compositions:</p> <p>a) Butt to specifications; or</p> <p>b) Reduce 1AF rate or increase 1AX rate if high cerium concentration exists in 1AF.</p> <p>(3) High pH:</p> <p>a) Butt 1AF or 1SS with nitric acid.</p> <p>(4) Flooding: (see text)</p> <p>a) Decrease flow rates.</p> <p>b) Adjust pulse frequency.</p> <p>(5) Pulse:</p> <p>a) Adjust frequency.</p> <p>b) Shut down for maintenance of pulser.</p> <p>(6) Low temperature:</p> <p>a) Increase temperature of 1AF.</p>
<p>23. Nitric acid concentration.</p>	<p>(1) Analysis of 1CX and 1CW samples.</p>	<p>(1) Increase nitric acid concentration of 1CX.</p> <p>(2) Increase 1CX flow rate.</p>

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DETECTION AND REMEDY OF POOR STRONTIUM AND PRO

Off-Standard Conditions	How Detected	Likely Causes
A. High fission product (Zr-Nb-95, Ru-106, Cs-137) concentration in 1BP.	(1) By analysis of the 1BP in-line sample. (2) By in-line gamma energy analysis of 1AP and 1BP streams. (3) By analysis of the 1BP stream.	(1) Flow rates: a) High 1AF/1AX flow b) Low total flow rate (2) Flooding. (3) High temperature
B. High metallic impurity concentration in 1BP	(1) By analysis of the 1BP in-line sample.	(1) Low complexant concentration in 1SS. (2) For high sodium: a) High sodium in 1A or 1B b) High pH in 1A or 1B c) Low buffer concentration d) High 1SS pH. e) Low 1SS flow. (3) For high calcium: a) Low pH in 1B column (4) Flooding and entrainment in columns.
C. High rare earth concentration in 1BP.	(1) By analysis of the 1BP in-line sample. (2) By in-line gamma energy analysis of the 1BP stream.	(1) Low pH in 1B column (2) High 1BX flow rate (3) Flooding.
D. High strontium loss to the 1BW and high strontium contamination of promethium product (1CP).	(1) By analysis of the 1CP in-line sample. (2) By in-line gamma energy analysis of the 1BW and 1CP streams.	(1) High pH in 1B column (2) High sodium in 1B column buffer concentration or high sodium in 1B (3) Low acid content in 1B column (4) Low acid content of 1B column (5) Low 1BX acid flow (6) High 1AF strontium (7) High 1AF/1AX flow
E. High cerium concentration in promethium product during separation of cerium and promethium.	(1) By analysis of the 1CP sample from TK-26-2. (2) By in-line gamma energy analysis of the 1CP stream.	(1) Inadequate oxidation a) Low persulfate concentration b) High silver concentration (2) Low 1CS flow rate. (3) High 1CX flow rate (4) Low 1CF flow rate. (5) Improper 1CS/1CF ratio
F. High metallic impurity concentration in promethium product. (Ca, Fe, Al)	(1) By analysis of the 1CP in-line sample. (2) By analysis of the 1CP sample from TK-26-2.	(1) High iron, aluminum (2) Low complexant concentration in 1SS (3) High 1CX nitric acid (4) High 1CX flow rate

OFF-STANDARD CONDITIONS

METHIUM PRODUCT QUALITY

se	Detection of Cause	Remedy
low ratio. through 1A column.	(1) Rates: a) Flow recorder on 1AF. b) Flow recorder on 1AX.	(1) Rates: Adjust flows to proper ratios.
n 1A column.	(2) Flooding: a) Instrument specific gravity readings. b) Interface or 1AW flow variations.	(2) Flooding: (see text) a) Decrease flow rates. b) Adjust pulse frequency.
ncentration in 1AF or	(3) High temperature: a) Temperature recorder for 1AF pump tank and 1A column.	(3) High temperature: a) Decrease temperature of 1AF.
AF or 1AX. 1S column. centration in 1SS.	(1) Analysis of 1AF or 1SS samples. (2) For high sodium: a) Analysis of 1AF, 1AX, or 1SS samples. b) 1SS flow recorders. (3) For high calcium: a) 1BP in-line pH monitor. b) Analysis of samples.	(1) Butt 1AF or 1SS to specifications. (2) Adjust 1AF, 1AX, or 1SS flow rates. (3) Adjust pH of 1BX stream.
lumn. nment from 1A and 1S	(4) Flooding: a) Increase in column differential pressure readings. b) Interface or 1AW flow variations.	(4) Flooding: (see text) a) Decrease flow rates. b) Adjust pulse frequency.
nn.	(1) Low pH: a) 1BP in-line pH monitor. b) Analysis of samples. (2) Flow recorders on 1BX chemical and water addition. (3) Flooding: a) Increase in column differential pressure readings. b) Interface and-or 1BP flow variations.	(1) Low pH: a) Butt 1BX with sodium hydroxide. (2) Reduce 1BX flow rate. (3) Flooding: (see text) a) Decrease flow rates. b) Adjust pulse frequency.
nn. column caused by low n in 1SS, low 1SS flow, AF or 1AX. 1B column when high sts. 1BX.	(1) High pH: a) 1BP in-line pH monitor. b) Analysis of 1BP samples. (2) Analysis of 1AF, 1AX, 1SS, or 1BP samples. (3) Analysis of 1BX samples. (4) Flow recorder on 1BX chemical addition. (5) Rates: a) Flow recorder on 1AF. b) Flow recorder on 1AX.	(1) Butt 1SS with buffer. (2) Increase nitric acid concentration in 1BX. (3) Increase 1BX flow. (4) Reduce 1AF flow or adjust 1AF and 1AX flows to the proper ratio.
concentration. ratio. n of Ce(III) to Ce(IV): concentration. centration.	(1) Analysis of persulfate and silver nitrate solutions. (2) 1CS flow recorder. (3) 1CX flow recorder. (4) 1CF flow recorder.	(1) Butt 1CX solution with persulfate or silver nitrate. (2) Increase 1CS flow rate. (3) Adjust 1CX flow rate. (4) Adjust 1CF flow rate.
flow ratio. m, or calcium in 1AF. 1AF or 1SS. d concentration.	(1) Analysis of 1AF and 1SS samples. (2) Analysis of 1CX samples. (3) 1CX flow recorder.	(1) Decrease 1AF flow rate. (2) Butt 1AF or 1SS streams with complexant. (3) Adjust 1CX nitric acid content. (4) Adjust 1CX flow rate.

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Basic Flowsketch of

SOLVENT EXTRACTION

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STM

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1CA

IAF PUMP TANK TK-29-3 4000 GAL

IAF COLUMN T-29-1

IAF RECEIVER TK-30-2 4000 GAL

IAF PUMP TANK TK-30-3 4000 GAL

CONDENSER E-5-3

SR. PRODUCT CONCENTRATOR E-5-2 470 GAL.

SR. CONCENTRATOR RECEIVER TK-5-1 700 GAL.

IBP RECEIVER TK-28-2 2000 GAL

ICW RECEIVER TK-26-3 2600 GAL

ICW CONTACTOR TK-27-3 3800 GAL

ORGANIC CONTACTOR TK-26-1 4000 GAL

IAW MAKEUP TANK TK-28-3 4000 GAL

ORGANIC TREATMENT

WASTE RECEIVER TK-9-1 5000 GAL

HIGH-LEVEL WASTE RECEIVER TK-25-2 7000 GAL

HIGH-LEVEL WASTE RECEIVER TK-25-1 7000 GAL

TO INTERM STORAGE 241A ORAX FARM

LOW LEVEL WASTE RECEIVER TK-24-1 3,900 GAL

LOW LEVEL WASTE CONCENTRATOR E-23-3 3000 GAL

NON-BOILING WASTE CONCENTRATE TK-23-1 800 GAL.

CONDENSER E-23-4

TO CRIB

TO IN-TANK SOLIDIFICATION

CELL NO. & VESSEL POSITION

TANK VOLUME

CONCENTRATION & STORAGE

END

IAF FEED TANK TK-29-3 4000 GAL

WASTE ROUTING FOR NON ROUTINE MODIFIED FLOW SHEET OPERATIONS SHOWN IN MORE DETAIL ON FIGURES X-3, X-4, X-5, X-6, X-7, X-8, AND X-9

WASTE HANDLING

Waste Management Processes

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FIGURE V-2

on - Current Acid Waste

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FIGURE V-3

tion - Acid Sludge Waste

SULFATE PRECIPITATION

- 1) PAS from 244-CR
- 2) Bisulfate Butt ($6M NaHSO_4$)
- 3) pH Adjustment ($1.8M Na_2CO_3$)
- 4) Lead Nitrate Add ($1M Pb(NO_3)_2$)
- 5) Precipitation Supernatant
(The following steps are performed after every third sulfate strike)
- 6) Cake Wash (DW)
- 7) Slurry Water (DW)
- 8) Cake Slurry

CARBONATE METATHESIS
(Performed after every third sulfate strike)

- 9) Metathesis Solution Add
($5M NaOH$, $0.5M Na_2CO_3$)
- 10) Metathesis Supernatant
(Waste)
- 11) Cake Washes ($0.1M Na_2CO_3$)
- 12) Cake Dissolvent ($1.2M HNO_3$)
- 14) Dissolved Cake
- 15) Water Flush (DW)

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FIGURE V-4

Extraction - 1A and 1S Columns

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FIGURE V-5

Partition and Strip - 1B and 1C Columns

FIGURE V-5

Partition and Strip - 1B and 1C Columns

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Strontium Product (F)

FIGURE V-6
Concentration and Storage

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FIGURE V-7
Organic Treatment

FIGURE V-7
Organic Treatment

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NOTE:
ALTERNATE ROUTING FOR
IX COLUMN BACK FLUSH

FIGURE V-8
Cesium Ion Exchange

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Cesium Produ

FIGURE V-9

Cesium Concentration and Storage

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TABLE V-5
LEGEND AND NOTES USED IN FIGURES

- A - Agitator
- BLI - Bed Level Indicator
- CV - Condenser Vent
- DPR - Differential Pressure Recorder
- DA - Dilution Air
- DW - Demineralized Water
- FIQ - Flow Indicator Integrator
- FRC - Flow Recorder Controller
- FRQ - Flow Recorder Integrator
- IFRC - Interface Recorder Controller
- LLI - Liquid Level Indicator
- M - Electric Motor
- P - Pump
- PA - Pressure Alarm
- PI - Pressure Indicator
- pHI - pH Indicator
- RC - Ratio Controller
- RR - Radiation Recorder
- RW - Raw Water
- SGR - Specific Gravity Recorder
- SGRC - Specific Gravity Recorder Controller
- SI - Speed Indicator
- SPL - Sampler
- SPR - Static Pressure Recorder
- STM - Steam
- T - Trap
- TI - Temperature Indicator
- TIC - Temperature Indicator Controller
- TR - Temperature Recorder
- TRC - Temperature Recorder Controller
- VI - Vibration Indicator
- WFI - Weight Factor Indicator
- WFR - Weight Factor Recorder
- WFRC - Weight Factor Recorder Controller
- WFRC A - Weight Factor Recorder Controller Alarm

Notes:

1. Normal maximum working volume is approximately 80% of the listed volume.

CHAPTER VIAQUEOUS AND ORGANIC MAKE-UP

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CHAPTER VIAQUEOUS AND ORGANIC MAKE-UPA. INTRODUCTION

The concurrent processing of Purex Acid Waste (PAW and ZAW), acidified sludge waste (PAS and RAS), and stored supernatant liquid wastes (PSN, RSN, PSS, and RSS) in the Waste Fractionization Plant utilizes precipitation, solvent extraction and ion exchange processes. Current wastes and sludge wastes are processed through solvent extraction equipment on a campaign basis. Twice as much time is allowed for processing current waste as is allowed for processing sludge waste. Once or twice a year the solvent extraction equipment may be used to further purify the strontium inventory as feed material for the fission product program. Based on a 72 per cent operating efficiency, the solvent extraction equipment is used approximately 155 days a year for current waste (30 days for Zirflex waste and 125 days for normal and enriched uranium waste), 78 days a year for sludge waste, and 15 days a year for strontium purification.

The precipitation process is used to prepare feed material for the solvent extraction process by removing a large portion of the iron, aluminum, and magnesium from sludge waste. Crude feed material prepared from sludge waste for the solvent extraction process is accumulated and stored in a 12,000 gallon tank located in Cell 33. The precipitation process operates independently of the solvent extraction process; therefore, based on a 72 per cent operating efficiency, it is operated approximately 260 days a year.

The ion exchange process is used to recover cesium from stored supernatant waste. The ion exchange process operates independently of the precipitation and the solvent extraction processes, and if operated 260 days a year, could accomplish 200 ion exchange cycles.

Depending on which type of feed is being processed, between 40,000 and 80,000 gallons of aqueous chemical solution and between 10,000 and 15,000 gallons of organic chemical solutions per day will be required. The make-up of these chemical solutions will involve using 23 different chemicals, including process water and inorganic ion exchangers in 36 different solutions.

In order to meet potentially usable fission product isotopic specification, impurity limits are placed on the essential materials used in chemical processing and on the uranium metal used for reactor fuel. Limits on alkaline earth elements are needed because these elements are common contaminants in the essential materials and adversely affect strontium product quality. Cesium and cerium are uncommon contaminants; however, the amounts of these elements added with the essential materials must be limited to prevent isotopic dilution of recovered fission products.

The volume and composition of the "cold" process streams needed for processing the waste solutions in the Waste Fractionization Plant are discussed in Part B of this chapter. The essential materials required to make up the cold process streams are discussed in Part C. Part D discusses the source and storage of process chemicals, while the make-up and distribution of the various process streams are discussed in Part E.

B. VOLUME AND COMPOSITION OF AQUEOUS AND ORGANIC STREAMS

1. Current Acid Waste

1.1 PAW

Based on processing 3200 gallons of PAW a day (7000 gallons of IAF), operation of the Waste Fractionization Plant (B-Plant) requires the input of 22 process streams exclusive of the feed material. These "cold" process streams consist of 19 different compositions requiring 13 different chemicals. The total volume of the solutions comes to over 22,000 gallons a day. Approximately 98 per cent of the organic extractant is recycled. Freshly prepared solvent is added periodically to maintain the desired in-plant solvent inventory. The composition and the daily volume requirements for the process streams used for processing PAW are shown in Table VI-1. The volumes and compositions are based on the conceptual flowsheets presented in Chapter IV, Figures IV-1, IV-48, IV-55, and IV-58.

1.2 ZAW

Waste generated by processing zirconium-jacketed fuel elements (Zirflex Processing) are processed in B Plant in a manner similar to that used for processing PAW. The major processing differences between the two types of waste are in the solvent extraction flowsheet as shown in Figure IV-49. Based on processing 2900 gallons of ZAW a day (7800 gallons of IAF), operation of B Plant requires the input of 22 "cold" process streams. As with PAW, the cold process streams consist of 19 different compositions requiring 13 different chemicals, but in proportions different from that required for PAW processing. The total volume of solutions comes to over 26,000 gallons; however, 98 per cent of the organic extractant is recycled. The composition and daily requirements for the cold process streams used for processing ZAW are shown in Table VI-2. These compositions and volumes are based on the conceptual flowsheets presented in Chapter IV.

2. Acidified Sludge Waste

Based on the processing of 4800 gallons of acidified sludge waste (PAS) per day through the sulfate precipitation step to remove iron and aluminum and the processing of 4000 gallons per day of solvent extraction feed (IAF) prepared from sludge waste, operation of the Waste Fractionization Plant requires the input of 20 "cold" process streams. These process streams are of 19 different compositions requiring 14 different chemicals. Approximately 8000 gallons of solution per day are required for the iron and aluminum removal step (sulfate precipitation

TABLE VI-1
AQUEOUS AND ORGANIC PROCESS STREAMS FOR PROCESSING CURRENT WASTE

Basis: 1600 gal. PAW/batch
3200 gal. PAW/day (2 batches/day)
7000 gal. 1AF/day

Function	Stream Designation	Stream Composition	Gal. Batch	Gal. sol'n. per day	SpGr
Solids Leaching	Water leach	H ₂ O	435	870	1.00
	Acid leach	4M HNO ₃	320	640	1.13
	QT leach	1.5M NaOH, 0.1M tartrate	480	960	1.06
	Cake removal	6M NaOH	150	300	1.22
Feed Butt	Buffer butt	11.5M HAcOH (hydroxyacetic acid)	60	120	1.23
	Chelate butt	1.57M Na ₃ HEDTA	550	1100	1.32
	Tartrate butt	4M tartaric acid	10	20	1.26
	pH adjust	19M NaOH	5	10	1.53
Extractant	1AX	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent ⁻		7000 (140)*	0.80
Scrub	1SS butt	2.5M HAcOH, 0.1M NaOH, 0.02M Na ₃ HEDTA, pH 1.8		340	1.02
	1SS dilution water	H ₂ O		1100	1.00
Strontium Strip	1BX butt	1M HNO ₃		30	1.03
	1BX dilution water	H ₂ O		1400	1.00
Cerium-Rare Earth Separation	1CX-1	2M HNO ₃ , 0.5M Na ₂ S ₂ O ₈		530	1.09
	1CX-2	2M HNO ₃ , 0.02M AgNO ₃		200	1.07
	1CS	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent ⁻		1400 (30)*	0.80
Cerium Strip	Ce strip(a)	2.1M HNO ₃	1224	1400	1.07
	Ce strip(b)	3.0M NaNO ₂	20	80	1.12
Organic Wash	1OS	2.5M NaOH, 0.1M citrate	428	1700	1.10
Organic Butt	1OO butt	12.2M HNO ₃	37	150	1.35
Sulfate Removal	pH adjust	3.6M NaOH, 0.12M HAcOH	243	460	1.15
	Extractant	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent ⁻	850 (17)*	1600 (32)*	0.80
	RE strip	1M HNO ₃	600	1100	1.03
	Acid kill	1.4M sugar	22	40	1.18

* Approximately 98 percent of the organic extractant is recycled. The number in parenthesis represents the 2 percent of new extractant needed to replace that lost during processing.

TABLE VI-2
AQUEOUS AND ORGANIC PROCESS STREAMS FOR PROCESSING ZIRFLEX ACID WASTE

Basis: 1200 gal. ZAW/batch
2900 gal. ZAW/day
7800 gal. 1AF/day

Function	Stream Designation	Stream Composition	Gal. Batch	Gal. sol'n. per day	SpGr
Solids Leaching	Water leach	H ₂ O	325	790	1.00
	Acid leach	4M HNO ₃	320	770	1.13
	QT leach	1.5M NaOH, 0.1M tartrate	360	870	1.06
	Cake removal	6M NaOH	110	270	1.22
Feed Butt	Buffer butt	11.5M HAcOH (hydroxyacetic acid)	56	140	1.23
	Chelate butt	1.57M Na ₃ HEDTA	1032	2500	1.32
	Tartrate butt	4M tartaric acid	11	27	1.26
	pH adjust	12.2M HNO ₃	16	39	1.35
Extractant	1AX	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent ⁻		7800 (160)*	0.80
Scrub	1SS butt	2.5M HAcOH, 0.1M NaOH 0.02M Na ₃ HEDTA, pH 1.8		380	1.02
	1SS dilution water	H ₂ O		1200	1.00
Strontium Strip	1BX butt	1M HNO ₃		30	1.03
	1BX dilution water	H ₂ O		1500	1.00
Cerium- Rare Earth Separation	1CX-1	2M HNO ₃ , 0.53M Na ₂ S ₂ O ₈		590	1.09
	1CX-2	2M HNO ₃ , 0.02M AgNO ₃		200	1.07
	1CS	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent ⁻		1600 (32)*	0.80
Cerium Strip	Ce strip(a)	2.1M HNO ₃	1224	1800	1.07
	Ce strip(b)	3.0M NaNO ₂	20	87	1.12
Organic Wash	1OS	2.5M NaOH, 0.1M citrate	428	1900	1.10
Organic Butt	1OO butt	12.2M HNO ₃	37	160	1.35
Sulfate Removal	pH adjust	3.6M NaOH, 0.12M HAcOH	243	530	1.15
	Extractant	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent ⁻	850 (17)*	1900 (38)*	0.80
	RE strip	1M HNO ₃	600	1300	1.03
	Acid kill	1.4M sugar	22	50	1.18

* Approximately 98 percent of the organic extractant is recycled. The number in parenthesis represents the 2 percent of new extractant needed to replace that lost during processing.

and carbonate-hydroxide metathesis) and 34,000 gallons of solution per day are required for the solvent extraction process. As mentioned earlier, the iron and aluminum removal step operates independently of the solvent extraction process for approximately 260 days a year. The solvent extraction process operates approximately 80 days a year processing sludge waste. As is the case with current acid waste, approximately 98 per cent of the organic solvent is recycled. Compositions and daily volume requirements for the "cold" process streams used for processing sludge waste are shown in Table VI-3. These compositions and volumes are based on the conceptual flowsheets presented in Chapter IV, Figures IV-3, IV-50, and IV-58.

3. Strontium Purification

Once or twice a year, crude strontium recovered from current and sludge waste may be purified by a solvent extraction process to prepare feed material for the fission product program. The same solvent extraction equipment that is used to recover strontium and rare earths from current and sludge waste is used to purify the crude strontium. Flowsheets for the purification of strontium are based on the amount of impurities, particularly calcium, present in the crude strontium. Flow ratios, and consequently the required volumes of process streams, vary somewhat for different batches of crude strontium. The volumes and compositions of the process streams needed to purify crude strontium recovered from current and sludge waste are shown in Table VI-4. The flowsheets are based on strontium to calcium ratios of 4.8 for crude strontium recovered from current waste, and 1.0 for crude strontium recovered from sludge waste. As in other solvent extraction processes, approximately 98 per cent of the organic solvent is recycled.

4. Stored Supernatant Waste

Because stored supernatant waste is processed batchwise in an ion exchange process, the chemical requirements stated in Table VI-5 are on a per cycle or per batch basis. The per day requirements can be determined by multiplying the per cycle requirements by 24/31 (assuming 31 hours per cycle). Operation of the cesium recovery ion exchange process will require the input of five process streams including process water and ion exchange medium for bed make-up. However, ion exchange medium will be added only when the performance of the ion exchange column indicates the needs to be replenished. The four aqueous process streams will constitute a volume of 33,000 gallons per cycle and will use three chemicals including water. Approximately 90 per cent of the cesium eluting agent (ammonium carbonate-ammonium hydroxide) is recovered from the cesium product and recycled. Fresh eluting agent is prepared by absorbing ammonia and carbon dioxide gases in water. Composition and the per cycle requirements for the process streams used for processing stored supernatant waste are shown in Table VI-5.

C. ESSENTIAL MATERIALS: REQUIREMENTS AND SPECIFICATIONS

To prevent isotopic dilution of strontium, cerium, and cesium products, the essential materials used in the Waste Fractionization

TABLE VI-3
AQUEOUS AND ORGANIC PROCESS STREAMS FOR PROCESSING ACIDIFIED SLUDGE WASTE

Basis: 4800 gal. PAS/batch for Fe-Al Removal*
4000 gal. 1AF/day for solvent extraction

Function	Stream Designation	Stream Composition	Gal. Batch	Gal. sol'n. per day	SpGr
Iron-Aluminum Removal	BS add	6M NaHSO_4	1410*		1.44
	pH adjust	1.8M Na_2CO_3	2256*		1.21
Sulfate Precipitation	Pb carrier	1M $\text{Pb}(\text{NO}_3)_2$	174*		1.28
	Sul. cake wash	H_2O	1200*		1.00
	Slurry water	H_2O	480*		1.00
Metathesis	Met. sol'n.	4.3M NaOH , 0.43M Na_2CO_3	800		1.20
	Car. cake wash	0.1M Na_2CO_3	1200*		1.00
	CC dissolve	2.2M HNO_3	480		1.07
Feed Butt (for 3200 gal. 1AF)	Dil. water	H_2O	479	600	1.00
	Buffer butt	11.5M HAcOH (hydroxyacetic acid)	139	170	1.23
	Chelate butt	1.57M Na_3HEDTA	510	640	1.32
	Tartrate butt	4M tartaric acid	20	25	1.26
	pH adjust	19M NaOH	102	130	1.53
Extractant	1AX	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent		12,000 (240)**	0.80
Scrub	1SS butt	2.5M HAcOH , 0.15M NaOH pH 1.8		480	1.19
	1SS dilution water	H_2O		1900	1.00
Strontium Strip	1BX butt	1M HNO_3		180	1.03
	1BX dilution water	H_2O		5800	1.00
Calcium Strip	1CX	0.2M HNO_3		2400	1.01
	1CS	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent		2400 (48)**	0.80
Rare Earth Strip	RE strip	2M HNO_3	1440	3800	1.07
	Acid kill	1.4M sugar	63	170	1.18
Organic Wash	1OS	2.5M NaOH , 0.1M citrate	360	2900	1.10
Organic Butt	1OO butt	12.2M HNO_3	31	250	1.15

* Used in three equal portions

** Approximately 98 percent of the organic extractant is recycled. The number in parenthesis represents the 2 percent of new extractant needed to replace that lost during processing.

TABLE VI-4
AQUEOUS AND ORGANIC PROCESS STREAMS FOR PURIFYING CRUDE STRONTIUM

Basis: Crude Sr from PAW-ZAW 6000 gal. 1AF/day Crude Sr from PAS 3000 gal. 1AF/day					
<u>Function</u>	<u>Stream Designation</u>	<u>Stream Composition</u>	<u>PAW-Sr gal.sol'n. day</u>	<u>PAS-Sr gal.sol'n. day</u>	<u>SpGr</u>
Feed Butt	Buffer butt	10M acetic acid	1400	1400	1.06
	Chelate butt	1.05M Na ₅ DTPA	490	270	1.32
	pH adjust	19M NaOH	410	420	1.52
Extractant	1AX	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent	11000 (220)*	11000 (220)*	0.80
Scrub	1SS butt	2.1M citric acid, 0.6M Na ₅ DTPA	340	300	1.14
	1SS dilution water	H ₂ O	3000	2700	1.00
Strontium Strip	1BX butt	3M citric acid	920	700	1.23
	1BX dilution water	H ₂ O	1800	1400	1.00
Citrate Kill	1BP peroxide	3.7M H ₂ O ₂	3000	2300	1.04
	1BP acid butt	12.2M HNO ₃	450	360	1.35
Organic Wash	1CX	2M HNO ₃	6000	3000	1.07
	1OS-1	2M NaOH	21000	11000	1.08
	1OS-2	2M HNO ₃	6000	3000	1.07

* Approximately 98 percent of the organic extractant is recycled. The number in parenthesis represents the 2 percent of new extractant needed to replace that lost during processing.

TABLE VI-5
AQUEOUS PROCESS STREAMS FOR PROCESSING STORED SUPERNATANT WASTES

Basis: 46,450 gal. PSN/day (60,000 gal. cycle)				
<u>Function</u>	<u>Stream Designation</u>	<u>Stream Composition</u>	<u>Amount Cycle</u>	<u>SpGr</u>
Inorganic Ion Exchanger Addition	Bed make-up	Zeolite AW-500	200 lbs.*	0.8
Column Wash	Column wash	H ₂ O	4500 gal.	1.0
Sodium Removal	Sodium eluent	0.2M (NH ₄) ₂ CO ₃ 0.1M NH ₄ OH	12,000 gal.	1.0
Column Wash	Column wash	H ₂ O	4500 gal.	1.0
Cesium Eluent	Eluent	3M (NH ₄) ₂ CO ₃ , 2M NH ₄ OH	12,000 gal.** (120)	1.11

* Inorganic ion exchanger will be added only when needed.

** Approximately 90 percent of the eluent is recycled. The number in parenthesis is the amount of solution which must be added to make-up for that lost during processing.

Plant recovery operations should be as free from these elements as reasonably possible. There is no concern about the isotopic dilution of promethium as it does not exist in nature; however, it is desirable to minimize the amounts of other rare earths added with the process chemicals. Other elements, such as the alkaline earths, behave like strontium in D2EHPA solvent extraction and can constitute a product purity problem if they are not limited in the essential materials.

The alkaline earths, including strontium, are commonly present as contaminants in some essential materials; therefore, alkaline earth limits are required on those essential materials used in strontium processing. Table VI-6 shows the amount of impurities which could be added to the strontium product by way of the essential materials during the processing of one ton of irradiated uranium metal through the Purex Plant, the Waste Fractionization Plant, and the strontium purification cycle, assuming impurity limits listed in the Essential Materials Manual are reached.

TABLE VI-6
POTENTIAL SOURCES OF ALKALINE EARTH IMPURITIES IN
STRONTIUM PRODUCT FROM PROCESSING ONE TON OF URANIUM

Material	lb. used Ton U	Impurity Limit (ppm)			Amount added / Ton Uranium					
		Sr	Ca	Mg	Sr		Ca		Mg	
					gms	%	gms	%	gms	%
Uranium	2000	1	5	10	.907	51.8	4.53	38.5	9.07	88.8
Purex Processing										
Nitric Acid	330	0.2	2	1	.030	1.7	.30	2.5	.15	1.5
Ferrous Sulfamate	27	10	80	1	.123	7.0	.98	8.3	.01	0.1
Hydrazine	1	1	20	1	nil	-	.01	0.1	nil	-
Sulfamic Acid	5	10	40	1	.011	0.6	.02	0.2	.09	0.9
Sodium Nitrite	13	2	20	2	.012	0.7	.12	1.0	.01	0.1
Sugar	49	3	16	1	.066	3.8	.36	3.1	.02	0.2
Process Water	100,000	.005	0.1	.003	.227	13.0	4.54	38.6	.14	1.4
Total Purex Processing					.469	26.8	6.33	53.8	.42	4.1
Total in PAW (Uranium+Purex)					1.376	78.6	10.86	92.3	9.49	92.9
B-Plant Mainline										
Process Water	510	.005	0.1	.003	.001	0.1	.02	0.2	nil	-
Nitric Acid	17	0.2	2	1	.001	0.1	.02	0.2	.01	0.1
Sodium Hydroxide	7	20	40	10	.064	3.7	.13	1.1	.03	0.3
Tartaric Acid	3	2	20	10	.003	0.2	.03	0.3	.01	0.1
Hydroxyacetic acid	18	1	10	2	.008	0.5	.08	0.7	.02	0.2
HEDTA	62	2	10	10	.056	3.2	.28	2.4	.28	2.7
Total B-Plant Mainline					.133	7.6	.56	4.8	.35	3.4
Strontium Purification										
Process Water	13	.005	0.1	.003	nil	-	nil	-	nil	-
DTPA	1	100	300	400	.045	2.6	.14	1.2	.18	1.8
Acetic Acid	2	100	100	100	.091	5.2	.09	0.8	.09	0.9
Sodium Hydroxide	1	20	40	10	.009	0.5	.02	0.2	nil	-
Citric Acid	2	100	100	100	.091	5.2	.09	0.8	.09	0.9
Hydrogen Peroxide	1	10	10	10	.005	0.3	.01	0.1	.01	0.1
Nitric Acid	1	0.2	2	1	nil	-	nil	-	nil	-
Total Strontium Purification					.241	13.8	.35	3.0	.37	3.6
Total Added					1.750	100	11.77	100	10.21	100

TABLE VI-7
ESSENTIAL MATERIALS FOR WASTE FRACTIONIZATION

Materials that are normally liquid		Formula	Formula Weight	Wt. %	Moles per Liter		SpGr
Chemical Name							
Acetic Acid		CH ₃ COOH	60	100 80 57	17.4 14.25 10		1.05 1.07 1.06
DTPA							
pentasodiumdiethylenetriaminepentaacetate			503	41	1.05		1.32
Chel DTPA-41 (1)		NaOOCCH ₂					
DTPA NA 5-80 (2)		NCH ₂ CH ₂ NCH ₂ CH ₂ N					
Versenex (3)		CH ₂ COONa					
D2EHPA							
Di(2-ethylhexyl)phosphoric acid		CH ₃ CH ₂					

- (1) Trade name of Geigy Chemical Corp.
(2) Trade Name of Pfizer Chemicals
(3) Trade name of Dow Chemical Co.

Cesium, cerium, manganese and the rare earths are uncommon contaminants in the essential materials used in the Waste Management Plant; therefore, limits for these elements are not included in essential materials specifications. Periodically, the essential materials are monitored for the presence of cesium, cerium, manganese, and rare earths, and any unfavorable trends in the quantities of these elements entering the process can be corrected by the Production Section.

Purchase specifications for the essential materials required by the Waste Fractionization Plant are included as Appendix A to this chapter. The chemical name, the common or trade names, the chemical formula, and the formula weight of the essential materials used or proposed for future use in the Waste Fractionization Plant are given in Table VI-7. In addition, the expected concentration, specific gravity, and moles per liter of the liquid essential materials are given. With the crystalline essential material chemicals is a table showing the weight percent, grams per liter, pounds per gallon, molarity, and specific gravity of selected aqueous stock solutions made from these chemicals.

1. Current Acid Waste

The essential materials required for processing 3200 gallons of ZAW per day are shown in the table below. The impurity limits for the alkaline earths and the percent of impurities the essential materials could contribute to the strontium product should the impurity limit be reached are shown in Table VI-6 in detail as well as in the table below. As mentioned earlier in this section, the rare earths are uncommon contaminants; therefore, no impurity limits are set on those essential materials which affect only rare earth recovery.

TABLE VI-8
ESSENTIAL MATERIALS REQUIRED FOR PROCESSING CURRENT ACID WASTE

Material	lbs/day		Impurity Limit (ppm)			% Contributed (PAW)		
	PAW	ZAW	Sr	Ca	Mg	Sr	Ca	Mg
Hydroxyacetic Acid	1500	1700	1	10	2	0.5	0.7	0.2
Na ₃ HEDTA	5000	11,000	2	10	10	3.2	2.4	2.7
Nitric Acid	5200	6400	0.2	2	1	0.1	0.2	0.1
Sodium Hydroxide	3100	3200	20	40	10	3.7	1.1	0.3
Tartaric Acid	220	240	2	20	10	0.2	0.3	0.1
Process Water	80,000	90,000	0.005	0.1	0.003	0.1	0.2	nil
Sodium Persulfate	560	620	Used for promethium recovery					
Silver Nitrate	6	6	Used for promethium recovery					
Sodium Nitrite	140	150	Used for promethium recovery					
Sugar	150	190	Used for promethium recovery					
D2EHPA	160	190	Impurities removed by solvent treatment					
TBP	90	100	Impurities removed by solvent treatment					
Hydrocarbon Diluent	1300	1400	Impurities removed by solvent treatment					
Citric Acid	270	300	Impurities removed by solvent treatment					

As can be seen by the above table, the amount of essential materials required to process ZAW is somewhat higher than the amount of essential materials required for PAW. The percent of impurities contributed to the strontium product by the essential materials would,

therefore, be proportionally higher than the percentages listed in the table which is based on PAW. The amount of impurities added by B-Plant processing to the product are small compared to the impurities present in the uranium metal and those added during Purex processing.

2. Acidified Sludge Waste

Iron, aluminum, and manganese are removed from acidified sludge waste by means of a precipitation process operated independently of the solvent extraction process. Because the precipitation process is independent of the solvent extraction process, it can operate essentially continuously as needed. The solvent extraction feed material prepared by the precipitation process is accumulated over a period of time, and processed through the solvent extraction equipment on a campaign basis.

TABLE VI-9
ESSENTIAL MATERIALS REQUIRED FOR PROCESSING STORED SLUDGE WASTE

Material	lbs/day	Impurity Limit (ppm)			% Contributed		
		Sr	Ca	Mg	Sr	Ca	Mg
<u>Precipitation Process for Removal of Iron and Aluminum</u>							
Lead nitrate	400	50	50	10	9.4	4.3	1.4
Sodium bisulfate	7100	2	10	10	6.6	15.3	25.3
Sodium carbonate	3300	10	30	20	15.3	21.2	23.5
Sodium hydroxide	960	20	40	10	9.0	8.3	3.4
Process water	54,000	0.005	0.1	0.003	0.1	1.2	0.1
<u>Solvent Extraction Process</u>							
Hydroxyacetic acid	2000	1	10	2	0.3	1.4	0.5
Na ₃ HEDTA	2900	2	10	10	0.9	2.1	3.4
Nitric acid	6400	0.2	2	1	0.1	0.6	0.5
Sodium hydroxide	3300	20	40	10	30.0	27.7	11.5
Process water	140,000	0.005	0.1	0.003	0.1	0.5	nil
Tartaric acid	130	2	20	10	nil	0.2	0.2
Sugar	640	Used for promethium recovery					
D2EHPA	230	Impurities removed by solvent treatment					
TBP	130	Impurities removed by solvent treatment					
Hydrocarbon diluent	1800	Impurities removed by solvent treatment					
Citric acid	460	Impurities removed by solvent treatment					

The essential materials required for processing 4000 gallons of Purex Acid Sludge (PAS) a day through the precipitation process is shown in the Table (VI-9) below. The table also shows the essential materials required for processing 4000 gallons per day of solvent extraction feed prepared from sludge waste. Because the alkaline earth impurity content varies widely with various feeds, it is not practical to show the effect of essential materials impurities on the total impurities found in the strontium product. However, the table below does show the impurity limits for the alkaline earths and the per cent of impurities the essential materials used in waste fractionization and strontium purification could contribute to the strontium product should the impurity limit be reached.

3. Stored Supernatant Waste

Cesium is recovered from stored supernatant waste by an ion exchange process. The time cycle for each ion exchange cycle (loading, washing, and eluting the column) is between 30 and 35 hours. Periodically fresh inorganic ion exchanger is added to the ion exchange column to replace the amount lost during each cycle by attrition. The amount of inorganic ion exchanger lost each cycle is estimated to be around 200 pounds. The sodium eluent or sodium wash, which is a dilute ammonium carbonate and ammonium hydroxide mixture, is made by absorbing carbon dioxide gas and liquified ammonia gas in water. Cesium product eluent, which is a more concentrated ammonium carbonate and ammonium hydroxide mixture, is recovered by distillation from the cesium product. About 2.5 per cent of the ammonia and 7 per cent of the carbon dioxide present in the cesium eluent are lost each cycle and must be replaced. In addition to the ammonia and carbon dioxide lost each cycle, up to 10 per cent of the total ammonia and carbon dioxide required is lost through physical process losses and has to be replaced.

The essential materials required for processing a 60,000 gallon batch of supernatant waste are shown in the table below.

TABLE VI-10
ESSENTIAL MATERIAL REQUIRED FOR PROCESSING SUPERNATANT WASTE

<u>Material</u>	<u>Function</u>	<u>Amt. /cycle</u>
Zeolite inorganic ion exchanger	Bed Make-up	200 lbs. (1)
Ammonia	Sodium Eluent	850 lbs.
Carbon Dioxide	Sodium Eluent	880 lbs.
Process water	Sodium Eluent	98,000 lbs.
Ammonia	Cesium Eluent Make-up	340 lbs.
Carbon Dioxide	Cesium Eluent Make-up	930 lbs.

(1) Ion exchange medium is added only when operating characteristics of the column indicates it needs additional medium.

4. Strontium Purification

As mentioned in Section A, once or twice a year crude strontium recovered from current and sludge waste is purified by a solvent extraction process to prepare feed material for the fissior product program. The impurities in the crude strontium fractions recovered from current waste differ widely from the impurities in crude strontium recovered from sludge, particularly in the amount of calcium present. The flow-sheet used is dependent on the impurities present; therefore, the amount of material required to process crude strontium from current and stored waste are different.

4.1 Purification of Strontium Recovered From Current Waste

The essential materials required for processing 6000 gallons a day of solvent extraction feed prepared from the crude strontium recovered from current waste are given below. The impurity limits for the alkaline earths and the percent of impurities the essential materials could contribute to the strontium product should the impurity limit be reached are shown in Table VI-6 in detail as well as in the Table VI-11 below.

TABLE VI-11
ESSENTIAL MATERIALS REQUIRED FOR PURIFYING
STRONTIUM RECOVERED FROM CURRENT WASTE

<u>Material</u>	<u>lbs/day</u>	<u>Impurity Limit (ppm)</u>			<u>% Contributed</u>		
		<u>Sr</u>	<u>Ca</u>	<u>Mg</u>	<u>Sr</u>	<u>Ca</u>	<u>Mg</u>
Acetic acid	7000	100	100	100	5.2	0.8	0.9
Na ₅ DTPA	3000	100	300	400	2.6	1.2	1.8
Citric acid	5600	100	100	100	5.2	0.8	0.9
Hydrogen peroxide	3200	10	10	10	0.3	0.1	0.1
Nitric acid	17,000	0.2	2	1	nil	nil	nil
Sodium hydroxide	16,000	20	40	10	0.5	0.2	nil
Process water	300,000	0.005	0.1	0.003	nil	nil	nil
D2EHPA	200	Impurities removed by solvent treatment					
TBP	100	Impurities removed by solvent treatment					
Hydrocarbon diluent	1300	Impurities removed by solvent treatment					

It should be pointed out that a portion of the nitric acid, sodium hydroxide, and process water is used to treat the solvent and therefore will not contribute impurities to the strontium product. The percent contributed above takes this into consideration.

4.2 Purification of Strontium Recovered From Acidified Sludge Waste

The essential materials required for processing 3000 gallons per day of solvent extraction feed prepared from the crude strontium recovered from stored sludge are given in the table below. The impurity limits for the alkaline earths and the percent of impurities the essential materials used in waste fractionization and strontium purification could contribute to the strontium product should the impurity limit be reached are also shown in the table below.

TABLE VI-12
ESSENTIAL MATERIALS REQUIRED FOR PURIFYING
STRONTIUM RECOVERED FROM STORED WASTE

<u>Material</u>	<u>lbs/day</u>	<u>Impurity Limit (ppm)</u>			<u>% Contributed</u>		
		<u>Sr</u>	<u>Ca</u>	<u>Mg</u>	<u>Sr</u>	<u>Ca</u>	<u>Mg</u>
Acetic acid	7000	100	100	100	14	6.5	10.8
Citric acid	5500	100	100	100	2.0	0.9	1.5
Na ₅ DTPA	1900	100	300	400	3.9	5.4	11.9
Hydrogen peroxide	2400	10	10	10	0.5	0.2	0.4
Nitric acid	9000	0.2	2	1	nil	nil	nil
Sodium hydroxide	10,000	20	40	10	1.1	1.0	0.4
Process water	170,000	0.005	0.1	0.003	nil	nil	nil
D2EHPA	200	Impurities removed by solvent treatment					
TBP	100	Impurities removed by solvent treatment					
Hydrocarbon diluent	1300	Impurities removed by solvent treatment					

D. SOURCE AND STORAGE OF PROCESS CHEMICALS

1. Acetic Acid

Acetic acid is received in railway tank cars as an 80 weight per cent aqueous solution. The acetic acid is stored in three 8000-gallon vertical stainless steel tanks ST-131, ST-132, and ST-133 located in the 211-B chemical tank farm. Because of the potential fire hazard of acetic acid, the three storage tanks are surrounded by a 3-foot concrete dike. The storage tanks also have an inert gas blanket system, and carbon dioxide purged weight factor instruments. The acetic acid storage

tanks are lagged and heated, and the piping system is steam-traced to prevent the acid from freezing. From the Chemical Tank Farm the acetic acid is pumped to weigh tank WT-503 on the third floor mezzanine of the 271-B Building.

2. Ammonia

Anhydrous ammonia is received in tank trucks and stored in a 12,200 gallon pressure vessel SN-172 which is located in the 211-B Chemical Tank Farm.

3. Carbon Dioxide

Liquified carbon dioxide is received in the 211-B tank farm in tank trucks and is stored in a 24-ton refrigerated storage tank SB-191 located in the 211-B chemical tank farm.

4. Citric Acid

Citric acid is received as a bulk crystalline dry chemical and is stored on the third floor of the 271-B Building.

5. DTPA

The sodium salt of diethylenetriaminepentaacetic acid is received in tank cars as a 40 weight percent aqueous solution. The material is stored in an 11,500-gallon horizontal tank SK-161, located in 211-B chemical tank farm.

6. D2EHPA

The organic solvent di(2-ethylhexyl)phosphoric acid is received in 55-gallon drums. The drums are stored on the loading platform of the 276-B Building (organic make-up building) until they are needed.

7. HEDTA

The sodium salt of the chelating agent hydroxyethylethylenediaminetriacetic acid is received in tank cars as a 40 weight per cent aqueous solution. The material is stored in four 8000-gallon vertical stainless steel tanks, SE-125, SE-126, SE-127, and SE-128, located in the 211-B chemical tank farm. Tanks SE-125, SE-126, and SE-127 are lagged and equipped with steam coils to keep the material from freezing. Tank SE-128 can be used for emergency chelate storage, but is neither lagged nor equipped with a steam coil.

8. Hydrogen Peroxide

Hydrogen peroxide is received in 30-gallon drums as a 12 weight percent aqueous solution. The drums are both stored and used on the third floor of the 271-B Building.

9. Hydroxyacetic Acid

Hydroxyacetic (glycolic) acid is received in railway tank cars as a 70 weight percent aqueous solution. The solution is stored in three 8000-gallon vertical stainless steel tanks, SF-120, SF-121, and SF-122, located in the 211-B chemical tank farm.

10. Lead Nitrate

Lead nitrate is received as a bulk crystalline dry chemical in bags, and is stored on the third floor of the 271-B Building. At the time this chapter was written litharge, PbO, dissolved in nitric acid was being considered as a substitute for lead nitrate. Litharge would also be received as a bulk dry powder in bags and stored on the third floor of the 271-B Building.

11. Nitric Acid

Nitric acid is received in tank trucks as a 57 weight percent aqueous solution. The acid is stored in three 8000-gallon stainless steel storage tanks, SA-101, SA-102, and SA-103, located in the 211-B chemical tank farm.

12. N-Paraffin Hydrocarbon

The organic diluent n-paraffin hydrocarbon (NPH) is received in railway tank cars and stored in two mild steel storage tanks buried underground adjacent to the 276-B (organic make-up) building. Tank SO-151 has a capacity of 20,000 gallons and tank SO-152 has a capacity of 11,500 gallons.

13. Process Water

Demineralized process water is prepared from the 200 East Area Sanitary water supply by means of a two-stage ion exchange unit. The ion exchange unit is a commercial water demineralizer built by the Graver Water Conditioning Company of New York. The unit was originally purchased in 1953 as part of the Purex prototype equipment and installed in the 321 Building. Later the equipment was moved to the Semiworks in the 200 East Area. Finally the demineralizer was moved to its present location in the 211-B chemical tank farm along with the enclosing steel and transite building 217-B. The first stage of the demineralizer is a hydrogen unit or cation exchanger filled with a strongly acidic ion exchange medium Nalcite HCR-W (Dowex 50W). The second stage of the unit was originally a mixed bed unit containing both anion and cation exchange medium; however, the unit was converted to an anion unit containing a weakly basic ion exchange medium such as Amberlite IRA-93. Converting the mixed bed unit to an anion unit had the advantage of having the same ion exchange media in the B-Plant unit as are in the Purex units. The water demineralizer is capable of supplying 240,000 gallons of water at a rate of 50 gpm between regeneration periods. The treated water has the following specifications:

Total hardness (as CaCO_3)	less than 2	ppm
Calcium	" "	0.2 ppm
Magnesium	" "	0.01 ppm
Strontium	" "	0.01 ppm
Sodium	" "	0.1 ppm
Chloride (as NaCl)	" "	0.6 ppm
Sulfates (as Na_2SO_4)	" "	1.5 ppm
Dissolved solids	" "	4.5 ppm
Silica (as SiO_2)	" "	7.5 ppm
pH		5 to 8

An engineering flow diagram of the water demineralizer and the operating sequence for regenerating the demineralizer are included at the end of this chapter as Appendix B.

14. Silver Nitrate

Silver nitrate is received as a dry solid crystalline chemical in five-pound cartons. The chemical is stored on the third floor of the 271-B Building.

15. Sodium Bisulfate

Sodium bisulfate is received as a bulk dry chemical and is stored on the first floor of the 271-B Building.

16. Sodium Carbonate

Sodium carbonate is received as a bulk dry chemical and is stored on the first floor of the 271-B Building.

17. Sodium Hydroxide

Caustic solution is received in railway tank cars as a 50 per cent aqueous solution. The caustic solution is stored in three 16,000-gallon mild steel horizontal tanks, SQ-141, SQ-142, and SQ-143, located in the 211-B chemical tank farm. The caustic storage tanks are lagged and steam-heated. All exterior caustic lines are also lagged and steam-traced.

18. Sodium Nitrite

Sodium nitrite is received as a bulk dry chemical and is stored on the third floor of the 271-B Building.

19. Sodium Persulfate

Sodium persulfate is received as a bulk dry chemical and is stored on the third floor of the 271-B Building.

20. Sugar

Sugar used for denitrating product streams is received as a bulk dry crystalline chemical and is stored on the third floor of the 271-B Building.

21. Tartaric Acid

Tartaric Acid is received as a bulk dry crystalline chemical and is stored on the third floor of the 271-B Building.

22. TBP

Tributyl phosphate used in solvent make-up is received in 55-gallon drums and is stored on the loading platform of the 276-B Building. Care must be taken not to confuse TBP and D2EHPA drums which are stored in the same location.

23. Zeolite

The ion exchange medium zeolite AW-500 is received as bulk dry material and is stored on the third floor of the 271-B Building.

E. Make-up and Distribution of Cold Process Streams

The fractionization of wastes in the Waste Management Plant involves a number of independent but interrelated unit operations and processes. As many of the process solutions are common to the processing of different types of waste, the make-up and distribution of the process streams are discussed for each of the different functions or operations performed in the Waste Management Plant.

1. Stock chemicals and solutions1.1 Process Water

Process or demineralized water is pumped from the Demineralized Water storage tank SD-111 and is delivered through the 111 Process Water Header throughout the operating gallery in the 211-B Building, and the Aqueous Make-up (AMU) areas located on the first and third floors of the 271-B Building.

1.2 Nitric Acid

Nitric acid, nominally 60 per cent nitric acid, is pumped from the nitric acid storage tanks, SA-101, SA-102, and SA-103, through the 1037 Nitric Acid Header to the third floor of the 271-B Building. The 1037 Nitric Acid Header supplies nitric acid to 27-3-A, cerium strip make-up tank, H-305 Utility tank, Scale Tank WT-501, and nitric acid storage tank H-309. Nitric acid is distributed to the operating gallery from the H-309 tank by way of the 309 Header.

1.3 Sodium Hydroxide (Caustic)

Fifty per cent sodium hydroxide is pumped from the caustic storage tanks SQ-141, SQ-142, and SQ-143 to AMU tanks H-301-1, H-303, H-304, H-305, H-402-1, H-310, and H-311, all located on the third floor of the 271-B Building and to tank 102 on the first floor of the 271-B Building. Sodium hydroxide is distributed throughout the operating gallery by way of the 310-311 Header which comes from the caustic storage tanks H-310 and H-311.

1.4 Chelates or Complexants

1.4.1 HEDTA

The chelating or complexing agent HEDTA is pumped from the chelate storage tanks SE-125, SE-136, SE-127, and SE-128, directly to the Feed Butt Make-up Tanks H-315 and H-316 on the third floor of the 271-B Building.

1.4.2 DTPA

The chelating agent DTPA, used only for strontium purification, is pumped from DTPA storage tank SK-161 to AMU tank H-301, ISS Butt Make-up, and scale tank 29-2-B, 1AF make-up scale tank located in the operating gallery.

1.5 Buffering Agents

1.5.1 Hydroxyacetic Acid

Hydroxyacetic acid buffering agent is pumped from storage tanks SF-120, SF-121, and SF-122 to scale tank WT-502 which is located on the third floor mezzanine of the 271-B Building.

1.5.2 Acetic Acid

Acetic acid buffering agent is pumped from storage tanks ST-131, ST-132, and ST-133 to scale tank WT-503 which is located on the third floor mezzanine of the 271-B Building.

1.6 3 M Citric Acid

A 3 M stock citric acid solution is made up in tank H-302 located on the third floor of the 271-B Building using water from the 111 Header and solid citric acid.

1.7 Sugar Solution

A 1.4 M sugar solution is made up in tank H-403 located on the third floor of the 271-B Building using water from the 111 Header and crystalline sugar.

1.8 Hydrocarbon Diluent

Hydrocarbon diluent is pumped from the underground diluent storage tanks SO-151 and SO-152 to the solvent make-up tank MO-154 located in the 276-B Building.

1.9 D2EHFA

Solvent D2EHFA is pumped from the drums in which it is received with an air-powered drum unloading pump to tank O-201 in the 276-B organic make-up building. From tank O-201 D2EHFA is pumped to the solvent make-up tank MO-154 as needed.

1.10 TBP

TBP is pumped from the drums in which it is received with an air-powered drum unloading pump to Tank O-202 located in the 276-B Building. From O-202 the TBP is pumped to the solvent make-up Tank MO-154 as needed.

1.11 Lead Nitrate Solution

A 1 M lead nitrate solution is made up in Tank H-401 which is on the third floor mezzanine of the 271-B Building. The lead nitrate solution is made by dissolving crystalline lead nitrate in water. An alternate method dissolving litharge (PbO) in nitric acid has been proposed.

1.12 Sodium Bisulfate Solution

A 6 M sodium bisulfate solution is made up in Tank 101, which is located on the first floor of the 271-B Building. The solution is made by dissolving solid sodium bisulfate in water.

1.13 Sodium Carbonate Solution

A 1.8 M sodium carbonate solution is made up in Tank 102 by dissolving soda ash in water. The 102 tank is located on the first floor of the 271-B Building.

2. Leaching of Solids in Current Acid Wastes

The sugar denitrated acid waste from the Purex Plant contains an appreciable amount of solid material. Over 50 per cent of the strontium and 70 per cent of the promethium present in the waste may be associated with these solids. The solids are centrifuged from the waste solution and strontium and rare earths are leached from solids with water, a nitric acid solution, and a caustic-tartrate solution according to the flowsheet shown in Figure IV-1. A flow diagram for the process solutions required for leaching Purex Acid Waste is shown in Figure VI-1 and the composition of the process streams are shown in the following table.

TABLE VI-13
PROCESS SOLUTIONS REQUIRED FOR LEACHING CURRENT ACID WASTES

<u>Process Stream</u>	<u>Make-up Tank</u>	<u>Composition</u>
Water leach	12-2-B	H ₂ O
Acid leach	12-2-C	4 <u>M</u> HNO ₃
Caustic-tartrate leach	H303-H304	1.5 <u>M</u> NaOH, 0.1 <u>M</u> Tartaric acid
Cake removal	12-2-C	6 <u>M</u> NaOH

Water from the 111 Header is added to the centrifuge from scale tank 12-2-B which is located in the operating gallery.

The acid leach is made up in scale tank 12-2-C with water from the 111 Header and nitric acid from the 309 Header.

The caustic-tartrate leach is made up in AMU tanks H303 and H304 with water from the 111 Header, sodium hydroxide either directly from the caustic header or from the caustic head tank, H301-1, and solid tartaric acid. After being made up, the caustic-tartrate leach is dropped to scale tank 12-2-B, which is located in the operating gallery, via the 303-304 Header.

The solution used to remove the leached solids from the centrifuge is made up in scale tank 12-2-C with water from the 111 Header, and sodium hydroxide from the 310-311 Header.

FIGURE VI-1

Flow Diagram for Process Solutions
Required for Leaching Purex Acid Waste

3. Iron and Aluminum Removal Precipitation Process

A sulfate precipitation process is used to remove the bulk of the iron, manganese, and aluminum present in acidified sludge waste. In the flowsheet shown in Figure IV-3, the alkaline earths and the rare earths along with the lead carrier ion are precipitated as sulfates, metathesized to carbonate, then dissolved with nitric acid. A flow diagram for the process solutions is shown in Figure VI-2 and the composition of the process streams is shown in the following table.

TABLE VI-14
PROCESS SOLUTIONS REQUIRED FOR THE PRECIPITATION PROCESS

<u>Process Stream</u>	<u>Make-up Tank</u>	<u>Composition</u>
Bisulfate Add	Tank 101	6M NaHSO_4
pH Adjust	Tank 102	1.8M Na_2CO_3
Lead Addition	H401	1M $\text{Pb}(\text{NO}_3)_2$
Water Wash and Cake Slurry	31-3-A and 32-3-C	H_2O
Metathesis Solution	31-3-F	4.3M NaOH , 0.43M Na_2CO_3
Carbonate Cake Wash	31-3-F	0.1M Na_2CO_3
Cake Dissolvent	32-2-C	5.5M HNO_3

Sodium bisulfate is made up in the 101 tank using process water and solid sodium bisulfate. The sodium bisulfate solution is pumped to scale tank 31-3-A which is located in the operating gallery. From 31-3-A the bisulfate solution is dropped to the precipitator tank 31-3. Sodium carbonate is made up in Tank 102 using process water and solid sodium carbonate (soda ash). The sodium carbonate solution is pumped to scale tank 31-3-F which is located in the operating gallery, and from there dropped to Tank 31-3.

Lead nitrate solution is made up in tank H-401 which is located on the mezzanine of the AMU area on the third floor of the 271-B Building. Process water and crystalline lead nitrate are used for making up the lead nitrate solution. An alternate method of making lead nitrate solution by dissolving litharge (PbO) in nitric acid has been proposed. The same make-up tank will be used if dissolved litharge is adopted. The lead nitrate solution is dropped to scale tank 31-3-E via the 401 header. From tank 31-3-E the solution is added to process tank 31-3.

Wash water for the sulfate precipitate is obtained from the 111 Header and is added to the precipitator via the 31-3-A scale tank. Water to slurry the precipitate from the centrifuge is added via the 32-2-C scale tank.

The metathesis solution is made up in scale tank 31-3-F using 50 per cent NaOH from the 310-311 Header, sodium carbonate from the 102 Header, and water from the 111 Header.

The metathesis cake wash is also made up in scale tank 31-3-F using water from the 111 Header and sodium carbonate from the 102 Header.

The carbonate cake is dissolved with nitric acid solution made up in scale tank 32-2-C using water from the 111 Header and nitric acid from the 309 Header.

FIGURE VI-2

Flow Diagram for the Process Solutions
Required for the Precipitation Process

4. Solvent Extraction Feed Make-Up

Feed materials for the solvent extraction process are made up by adding a buffering agent and a chelating agent to a crude feed solution and adjusting the pH of the solutions to the desired values with sodium hydroxide or nitric acid. Hydroxyacetic acid is used as the buffering agent when processing PAW, ZAW, and PAS as it has high buffering capacity at pH 4. Because acetic acid has a high buffering capacity at the required pH of 4.9, it is used as the buffering agent during the purification of the crude strontium fraction. The choice of chelating agent or agents is somewhat uncertain and subject to change through optimization of flowsheets by plant tests. At the time this chapter was written, HEDTA, with a small amount of tartaric acid, was the chelating agent being considered for processing PAW, ZAW, and PAS. DTPA was the chelating agent being considered for purifying the crude strontium fraction. The basis for choosing chelating agents and buffering agents is discussed in detail in Chapter IV.

In making up solvent extraction feed solutions the feed butts may be added as separate chemical additions or the butts may be combined in the feed butt make-up tank and added as a mixture. In the table below, the feed butts are expressed as separate solutions; however, the solutions are combined as a mixture before being added to the IAF make-up tank. A flow diagram for the process solutions is shown in Figure VI-3.

TABLE VI-15

PROCESS SOLUTIONS REQUIRED FOR SOLVENT EXTRACTION FEED MAKE-UP

<u>Process Stream</u>	<u>Make-up Tank</u>	<u>Composition</u>
Feed butts for PAW, ZAW and PAS		
Chelate butt	H315 and H316	1.57M Na_3HEDTA
Buffer butt	H315 and H316	11.5M Hydroxyacetic acid
Tartrate butt	H315 and H316	4M Tartaric acid
pH adjust	29-2-B	19M NaOH for PAW and PAS 12.2M HNO_3 for ZAW
Feed butts for strontium purification		
Chelate butt	29-2-B	1.05M Na_5DTPA
Buffer butt	H315 and H316	10M Acetic acid
pH adjust	29-2-B	19M NaOH

When processing PAW, ZAW, and PAS, liquid chelating agent is pumped from the 211-B chemical tank farm to tanks H-315 and H-316, the feed butt make-up tanks. Hydroxyacetic acid buffer is added to H-315 and H-316 from weigh tank WT-502. The tartaric acid butt is made up in H-316 and H-315 from solid tartaric acid and process water from the 111 Header. The feed butts are dropped from the make-up tanks to scale tank 29-2-A located in the operating gallery via the 315-316 Header. The pH of the feed solution is adjusted with sodium hydroxide or nitric acid added from scale tank 29-2-B which is also located in the operating gallery. Sodium hydroxide for 29-2-B is obtained from the 310-311 Header, and nitric acid is ob-

tained from the 309 Header. Process water is also available to scale tanks 29-2-A and 29-2-B from the 111 Header. Additional adjustment of the feed solution can be made in the IAF feed tank 29-3 by additions from H-315 and H-316 through scale tank 29-3-E.

When purifying the crude strontium fraction, the chelate butt is pumped from the 211-B tank farm to scale tank 29-2-B which is located in the operating gallery. The acetic acid buffer is added to H-315 and H-316 from weigh tank WT-503. From H-315 and H-316 the buffer butt is dropped to scale tank 29-2-A. The pH is adjusted with caustic or acid from the 29-2-B tank.

FIGURE IV-3

Flow Diagram for Process Solutions Required for
Solvent Extraction Feed Make-Up

5. Solvent Extraction Processes

5.1 Purex Acid Waste, Zirflex Acid Waste, and Purex Acid Sludge Waste

In the solvent extraction process for PAW, ZAW, and PAS, strontium and the rare earths are extracted into the organic phase in the IA column and impurities are scrubbed from the organic phase in the IS column. Strontium is selectively stripped from the organic phase in the IB column.

When processing PAW and ZAW the IC column is used to separate cerium and the rare earths. The rare earths are purified further by a batch extraction and strip in process tank 26-2, while cerium is stripped from the organic phase in process tank 27-3.

When PAS is being processed it is not necessary to separate cerium from the rare earths as the cerium has decayed to low levels. Therefore, the IC column is used to get additional decontamination from calcium by selectively stripping calcium from the organic phase. The rare earths are stripped from the organic phase by batch contact in process tank 27-3.

A flow diagram for the process solutions required for the solvent extraction processing of PAW, ZAW, and PAS is shown in Figure IV-4. The composition of the process streams and the tanks in which they are made up is shown in Table VI-16 on page 628.

The organic IAX-Butt is made up in the organic make-up tank MO-154 located in the organic building, 276-B. The hydrocarbon diluent is pumped from underground storage tanks SO-151 and SO-152, and D2EHPA and TBP are pumped from storage tanks O-201 and O-202 as needed. The IAX Butt may vary somewhat depending on what is needed to adjust the solvent to the required composition. From MO-154, the IAX Butt is pumped to process tanks 28-3, the IAX make-up tank, or 26-2, the promethium batch contactor tank as needed.

The ISS-Butt is made up in tanks H-301 and H-402 with hydroxy-acetic acid from weigh tank H-502, sodium hydroxide from head tank H-301-1 or H-402-1 and chelating agent, if required, from the chelate header (HEDTA Header). From the make-up tanks, the ISS-Butt is dropped to scale tank 29-1-F located in the operating gallery. From 29-1-F the ISS-Butt is pumped to a blend tee where it is diluted to ISS composition with process water from the 111 Header and is delivered directly to the IS column.

IBX-Butt is also made up more concentrated than IBX composition. It is made up in tank H-312 with water from the 111 Header, and nitric acid from weigh tank H-501. From H-312 the IBX-Butt is dropped to scale tank 28-1-F located in the operating gallery and from there it is pumped to a blend tee where it is diluted to IBX composition with water from the 111 Header and is delivered directly to the IB column.

FIGURE VI-4

Flow Diagram for Process Solutions Required for
Solvent Extraction Processing PAW, ZAW, and PAS

TABLE VI-16

PROCESS SOLUTIONS REQUIRED FOR SOLVENT EXTRACTION PROCESSES

<u>Process Stream</u>	<u>Make-up Tank</u>	<u>Composition</u>
	<u>PAW-ZAW</u>	
1AX butt	MO-154	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent*
1CS butt		
1SS butt	H301 and H302	2.5M HAcOH, 0.1M NaOH, 0.2M Na ₃ HEDTA, pH 1.8
1BX butt	H312	1.0M HNO ₃
1CX-1	H313 and H314 (27-1-A and 27-1-B)	2.0M HNO ₃ , 0.53M Na ₂ S ₂ O ₈
1CX-2	H318 and H319 (27-1-C and 27-1-D)	2.0M HNO ₃ , 0.02M AgNO ₃
Cerium Strip(a)	H321 (27-3-A)	2.1M HNO ₃
Cerium Strip(b)	H320 (27-3-B)	3M NaNO ₂
Rare Earth Purification		
pH adjust	26-2-A	3.6M NaOH, 0.12M HAcOH
Extractant	MO-154	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent*
RE Strip	26-2-A	1.0M HNO ₃
	<u>PAS</u>	
1AX butt	MO-154	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent*
1SS butt	H301 and H302	2.5M HAcOH, 0.15M NaOH, pH 1.8
1BX butt	H312	1.0M HNO ₃
1CX	H313, H314, H318, and H319	0.2M HNO ₃
RE Strip	H321	2M HNO ₃

* Nominal composition; may vary depending on requirements.

Two ICX solutions are made up when either PAW or ZAW is being processed. ICX-1 is made up in H-313 and H-314 with water from the 111 Header, nitric acid from weigh tank 501, and solid sodium persulfate. ICX-2 is made up in H-318 and H-319 with water from the 111 Header, nitric acid from weigh tank H-501, and solid silver nitrate. ICX-1 and ICX-2 are blended together at a blending tee and delivered to the IC column. When sludge waste is being processed, the ICX stream is 0.2 M HNO₃ and contains no silver or persulfate. The dilute acid used as ICX when sludge waste is being processed is made up in the same make-up tanks that the silver and persulfate ICS solutions are made up in and delivered to the IC column through the same routing.

When current acid waste is being processed cerium is stripped from the organic phase by a batch process. The strip solution, Ce-Strip (a), is made up in H-321 with nitric acid either from weigh tank H-501 or directly from the nitric acid header and water from the 111 Header. A second strip, Ce-Strip (b), is made up in tank H-320 with water from 111 Header and solid sodium nitrite. Both cerium strip solutions are dropped by gravity directly to process tank 27-3. When sludge waste is being processed, the rare earth strip is made up in H-321 with acid from weigh tank H-501 or from the nitric acid header, and water from the 111 Header. The rare earth strip is also dropped by gravity directly to process tank 27-3.

Aqueous solutions for the rare earth purification (sulfate removal) step, which is a batch process, are made up in scale tank 26-2-A located in the operating gallery. For pH adjust, the hydroxy-acetic acid is obtained from the 301 header which contains ISS-Butt solution, additional caustic is obtained from the 310-311 Header, and water is obtained from the 111 Header. The rare earth strip solution is also made up in scale tank 26-2-A with nitric acid from the 309 Header and water from the 111 Header.

5.2 Strontium Purification Process

Periodically the crude strontium fraction is purified in the solvent extraction equipment to prepare feed material for the fission product program. The strontium is extracted into the organic phase in the IA column, certain impurities are scrubbed from the organic phase in the IS column, and the strontium is stripped from the organic phase in the IC column. Stripping is done at a pH which provides for a separation of strontium from calcium. A flow diagram for the process solutions required for strontium purification is shown in Figure VI-5, and the composition of the process streams is shown in the following table.

TABLE VI-17
PROCESS SOLUTIONS REQUIRED FOR THE
SOLVENT EXTRACTION PURIFICATION OF STRONTIUM

<u>Process Stream</u>	<u>Make-up Tank</u>	<u>Composition</u>
IAX Butt	MO154	0.3M D2EHPA, 0.2M TBP, hydrocarbon diluent [*]
ISS Butt	H301	2.1M Citric acid, 0.6M Na ₅ DTPA
IBX Butt	H312	3M Citric acid
Citrate Kill	H305	3.7M H ₂ O ₂
Acid Butt	H305	12.2M HNO ₃

* Nominal composition; may vary depending on requirement.

The IAX-Butt for strontium purification is made up in the same way as it is for the other solvent extraction processes. (See Section E 5.1 above.)

The ISS-Butt is made up in Tank H-301 with water from the 111 Header, solid citric acid, and DTPA pumped in from the DTPA storage tank in the 211-B tank farm. The ISS-Butt is dropped to scale tank 29-1-F located in the operating gallery from where it is pumped to a

blending tee where it is blended with proper proportion of water to ISS concentration, and delivered to the IS column.

The IBX Butt is made up in tank H-312 with water from the 111 Header, and solid citric acid. The IBX-Butt is dropped to scale tank 28-1-F in the operating gallery from where it is pumped to a blend tee, mixed with the proper proportion of water, and delivered to the IB column.

The hydrogen peroxide used to destroy the citric acid in the strontium product concentrator, and the nitric acid needed to maintain the acidity of the strontium product are added from Utility Make-Up tank H-305, through scale tank 5-2-F to strontium concentrator E-5-2.

FIGURE VI-5

Flow Diagram for Process Solutions Required for the Solvent Extraction Processing for Purifying Strontium

6. Solvent Treatment

The organic solvent used in the solvent extraction processes, both column and batch, must be treated to remove metal contaminants and solvent degradation products. An effective method of treating the solvent is to wash the solvent with a sodium hydroxide solution containing a complexing agent such as citrate. A flow diagram for the process solutions required for treating solvent is shown in Figure VI-6 and the composition of the solutions is shown in the following table:

TABLE VI-18

PROCESS SOLUTIONS REQUIRED FOR SOLVENT TREATMENT

<u>Process Stream</u>	<u>Make-up Tank</u>	<u>Composition</u>
IOS	26-1-A	2.5M NaOH, 0.1M Na ₃ Citrate
1CN (alternate during Sr Purification)	H313 and H314	2.5M NaOH, 0.1M Na ₃ Citrate
1AN acid butt	28-3-C	12.2M HNO ₃

The solvent wash solution, IOS, is made up in scale tank 26-1-A located in the operating gallery. Citric acid is available from the 302 Header, water from the 111 Header, and sodium hydroxide from the 310-311 Header. During strontium purification the IC column can be used to wash the solvent. If this mode of operation is used the solvent wash is made up in H-313 and H-314 with solid citric acid, sodium hydroxide from the caustic header, and water from the 111 Header.

After washing with caustic the solvent is transferred to process tank 38-3 where it is converted to the acid form by butting with nitric acid. The nitric acid butt is added from scale tank 28-3-C located in the operating gallery.

7. Ion Exchange Process for the Recovery of Cesium

Cesium present in the stored alkaline supernatant solutions is absorbed on a synthetic ion exchange medium. Sodium is washed from the ion exchange medium with a dilute solution of ammonium carbonate and ammonium hydroxide. The cesium is subsequently eluted from the ion exchange medium with a concentrated solution of ammonium carbonate and ammonium hydroxide. Flowsheets for the recovery of cesium are shown in Figures IV-72 and IV-73, Chapter IV. Ammonium carbonate-ammonium hydroxide solutions are made by absorbing anhydrous ammonia gas and carbon dioxide gas in water. Approximately 90 per cent of the ammonium carbonate-ammonium hydroxide eluent is recovered and recycled. A flow diagram for the process chemicals required for ion exchange processing for the recovery of cesium is shown in Figure VI-7 and the composition of the streams is shown in Table VI-19 on page 633.

FIGURE VI-6

Flow Diagram for Process Solutions
Required for Solvent Treatment

TABLE VI-19

PROCESS SOLUTIONS REQUIRED FOR THE ION EXCHANGE PROCESS

Process Stream	Make-up Tank	Composition
Bed Make-up	H317	Zeolite AW-500 and water
Na Eluent	MNB173	$0.2\text{M}(\text{NH}_4)_2\text{CO}_3$, $0.1\text{M}\text{NH}_4\text{OH}$
Cesium Eluent	TK-21-1	$2\text{M}(\text{NH}_4)_2\text{CO}_3$, $2\text{M}\text{NH}_4\text{OH}$
Column Wash #2 (S and SX supernates only)	18-3-S	$19\text{M}\text{NaOH}$

FIGURE VI-7

Flow Diagram for Process Solutions Required for
The Ion Exchange Process for Recovering Cesium

The ion exchange medium for the bed make-up is slurried directly into the ion exchange column from Tank H-317. The ion exchange medium is a solid material, and water is obtained from the 111 Header.

The sodium eluent is made up in Tank MNB-173, which is located in the 211-B Chemical tank farm, by absorbing ammonia gas and carbon dioxide gas in water. Demineralized water from the 111 Header is used. The ammonia comes from the anhydrous ammonia storage tank SN-172, and the carbon dioxide comes from the CO₂ storage SB-191. From make-up tank MNB-173 the sodium eluent solution is pumped to the ion exchange feed tank 18-3.

Cesium eluent is recovered in process tank 21-1. Additional eluent is made up in tank 21-1 by absorbing ammonia gas from the 172 Header, and carbon dioxide gas from the 191 header in water in tank 21-1. Alternately, additional cesium eluent could be made up in tank MNB-173 by absorbing ammonia and carbon dioxide in water, and pumping the resulting solution to tank 21-1.

When S and SX supernates are processed, the ion exchange column is washed with 1 M NaOH following cesium elution step to remove any aluminum which may have precipitated in the ion exchange bed. The sodium hydroxide solution is made by pumping 19 M NaOH from scale tank 18-3-C to a blending tee where it is diluted with process water from the 111 Header and delivered to the IX column. The 19 M NaOH is obtained from the 310-311 Header.

8. Waste Treatment

High level wastes are collected in process tanks 25-1 and 25-2 where they are neutralized with sodium hydroxide. Low level wastes are collected in tank 24-1, the feed tank for the low level waste concentrator, where sodium hydroxide can be added if needed to neutralize the waste before it is concentrated. A flow diagram for the sodium hydroxide additions to the waste handling facilities is shown in Figure VI-8.

FIGURE VI-8

Flow Diagram for Caustic Addition to
Waste Handling Facilities

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APPENDIX A

PURCHASE SPECIFICATIONS FOR B-PLANT ESSENTIAL MATERIALS

Material and Number Test	Specification	Sample Frequency
Acetic Acid, 064		
Assay	min 80 Wt. %	each shipment
Residue	max 0.01 Wt. %	each shipment
Chloride	max 0.01 Wt. %	each shipment
Ammonia, anhydrous, technical liquefied	min 99.5 vol. %	on request
Carbon dioxide, compressed gas, commercial grade, 0270	min 99.5 vol. %	on request
Citric Acid, 285		
Acidity as citric acid	min 99.5 Wt. %	each shipment
Residue	max 0.01 Wt. %	each shipment
Chloride	max 0.01 Wt. %	each shipment
Phosphate	max 0.001 Wt. %	each shipment
DTPA (sodium salt), 705	min 40 Wt. %	
SpGr 25/25	min 1.30	each shipment
pH	11 to 14	each shipment
CaCO ₃ Value	80 $\pm$ 2	each shipment
Sr	max 100 ppm	on request
Ca	max 300 ppm	on request
Mg	max 400 ppm	on request
D2EHPA, 384		
Acidity as D2EHPA	min 95 - max 100 %	each shipment
SpGr 20/20	0.970 to 0.984	each shipment
Refractive Index	N ²⁰ D 1.443	
Solubility in water	max 0.01 Wt. % 20C	
Water Content	max 2.4 Wt. % 20C	
Flash Point	385 C	
HEDTA (sodium salt), 668	min 40 Wt. %	
SpGr 25/25	min 1.28	each shipment
pH	11 to 14	each shipment
CaCO ₃ Value	120 $\pm$ 5	each shipment
Sr	max 2 ppm	on request
Ca	max 10 ppm	on request
Mg	max 10 ppm	on request
Hydrogen Peroxide, 526		
Assay	12 to 15 Wt. %	each shipment
Fe	max 0.5 ppm	each shipment
Residue	max 0.01 Wt. %	each shipment
Sr	max 10 ppm	on request
Ca	max 10 ppm	on request
Mg	max 10 ppm	on request

Hydroxyacetic Acid, 524		
Acidity as glycolic acid	min 70 Wt. %	each shipment
Chloride	max 0.2 Wt. %	each shipment
Residue	max 0.1 Wt. %	each shipment
Sr	max 1 ppm	each shipment
Ca	max 10 ppm	on request
Mg	max 2 ppm	on request
Lead Nitrate, 576		
Pb	min 62 Wt. %	on request
Chloride	max 0.01 Wt. %	on request
Sr	max 50 ppm	each shipment
Ca	max 50 ppm	each shipment
Mg	max 10 ppm	each shipment
Mn	max 50 ppm	each shipment
Nitric Acid, 0670		
Acidity as HNO ₃	min 57 Wt. %	each composite*
Chloride	max 0.05 Wt. %	each composite*
Residue	max 0.01 Wt. %	each composite*
Sr	max 0.2 ppm	one per month
Ca	max 2 ppm	one per month
Mg	max 1 ppm	one per month
Phosphate	max 0.003 Wt. %	one per month
n-paraffin hydrocarbon, 669		
Source	min 97 Wt. %	
B. P.	South Hampton Co. min 99 Wt. % in the C-10 to C-14 range	on request
Flash Point	155 to 160 F	
SpGr 60/60 F	0.74 to 0.76	each shipment
Viscosity	max 2.5 n/100 25 C	each shipment
Aromatics	max 0.2 Wt. %	each shipment
Olefins	max 0.5 Bromine No.	each shipment
Silver Nitrate, 775		
Assay	min 99.8 Wt. %	on request
Chloride	max 0.002 Wt. %	on request
Sodium Bisulfate, Hydrated		
Acidity as H ₂ SO ₄	34.5 to 36.5 Wt. %	each shipment
Chloride	max 0.1 Wt. %	each shipment
Sr	max 2 ppm	each shipment
Ca	max 10 ppm	each shipment
Mg	max 10 ppm	each shipment
Sodium Carbonate, 785		
Na ₂ O	min 57.3 Wt. %	on request
Water Insoluble	max 0.1 Wt. %	each shipment
Sr	max 10 ppm	each shipment
Ca	max 30 ppm	each shipment
Mg	max 20 ppm	each shipment

* Composite of samples from 10 truck loads.

Sodium Hydroxide, 0800

Na₂O

Chloride

Sr

Ca

Mg

38.9[±]1 Wt. %

max 0.9 Wt. %

max 20 ppm

max 40 ppm

max 10 ppm

each shipment

each shipment

each shipment

each shipment

each shipment

Sodium Nitrite, 810

Assay

Water Insoluble

min 99 Wt. %

max 0.05 Wt. %

each shipment

each shipment

Sodium Persulfate, 752

Assay

Chloride

Water Insoluble

min 97 Wt. %

max 0.01 Wt. %

max 0.01 Wt. %

each shipment

each shipment

each shipment

Sugar, 842

Sugar Content

Residue

Water Insoluble

min 99.5 Wt. %

max 0.01 Wt. %

Max 0.01 Wt. %

on request

on request

each shipment

Tartaric Acid, 0910

Acidity as Tartaric Acid

Chloride

Residue

min 99.4 Wt. %

max 0.01 Wt. %

max 0.02 Wt. %

each shipment

each shipment

each shipment

Tributyl Phosphate, 0920

Butanol

Acidity

Suspended Solids

SpGr 20/20

Turbidity

max 0.05 Wt. %

max 0.02N

max 0.01 Wt. %

0.973 to 0.983

to pass test

each shipment

each shipment

each shipment

each shipment

each shipment

Zeolite Ion Exchanger

AW-500, Linde

Division of Union Carbide

WATER DEMINERALIZER REGENERATION PROCEDURECation (Hydrogen) Unit

1. Backwash at 55 gpm for 22 minutes.
2. Treat ion exchange bed with 2 percent H_2SO_4 for 27 minutes by adjusting flows to give 5.5 gpm 20% H_2SO_4 and 55.5 gpm water.
3. Treat bed for 9 minutes with 5 percent H_2SO_4 by adjusting flows to give 16 gpm 20% H_2SO_4 and 56 gpm water.
4. Displace acid with 56 gpm water for 14 minutes.
5. Rinse bed with 70 gpm water for 70 minutes.

Anion Unit

1. Backwash at 20 gpm for 10 minutes.
2. Treat ion exchange bed with 2 percent NaOH by adjusting flows to give 7 gpm 10% NaOH and 24 gpm water for 30 minutes.
3. Displace caustic with 24 gpm water for 8 minutes.
4. Rinse bed with 60 gpm water for 60 minutes.

WASTE MANAGEMENT TECHNICAL MANUAL

PART IV: B-PLANT PRODUCT AND WASTE HANDLING

CHAPTER VII

ISOTOPE STORAGE

by

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CHAPTER VIIISOTOPE STORAGEA. INTRODUCTION

When the wastes are first released from the Purex Plant as PAW (Purex Acid Waste), the majority of the thermal heat released during radioactive decay is associated with the short half-life isotopes. The total amount of heat released decreases rapidly as the quantities of these short half-life isotopes decrease; hence, the percentage of heat released by specific isotopes changes over a period of time due to differences in their half-lives. As an illustration, the isotopes of strontium and cesium contribute less than 20 percent of the total heat liberated by beta decay when the waste is released from the Purex plant; but after ten years these two isotopes contribute 95 percent of the heat associated with beta decay. Likewise, the gamma watts liberated by cesium when the waste is released from the Purex plant is approximately one percent; however, after ten years' time, practically all of the thermal watts associated with gamma decay is from cesium. The continuous release of heat over an extended period from these isotopes requires their separation from the rest of the waste before solidification can be effected. The separation of strontium and cesium (assuming 10-year decay) will allow the remainder of the wastes to be safely solidified.

If the heat liberated from strontium 89 is considered with the other short half-life isotopes, strontium 90 and cesium 137 contribute less than 2 percent of the total beta watts present in Purex Acid Waste.

B. STRONTIUM

Two isotopes of strontium have to be removed from current wastes because of the amount of thermal energy released. Strontium-90 has a half-life of twenty-eight years. It is a pure beta emitter; its daughter yttrium-90 emits a 0.2 and 1.7 Mev Gamma. See Reference 1. Since the half-life of the daughter is 64.2 hours, the emission of these gammas reaches a maximum and is then in equilibrium with the parent. Together, strontium-90 and yttrium-90 produce 6.8 thermal watts of energy per kilocurie of strontium-90 which is 23.2 BTU/hr per kilocurie. Strontium-89 has a half-life of 50.4 days and produces 3.4 thermal watts or 12 BTU/hr per kilocurie. Since the ratio of

B. STRONTIUM (Continued)

strontium-89 to strontium-90 is about ten to one in fresh Purex acid waste, most of the heat liberated from these isotopes is from strontium-89.

After a year of storage, the strontium-89 has decayed to an insignificant amount with respect to strontium-90; consequently, the amount of heat liberated by the strontium isotopes is reduced by a factor of approximately five. Storage of strontium isotopes is limited by the heat-removing capabilities of the tank cooling system.

Tanks for storage of strontium-89 and -90 mixture separated from fresh PAW must have coils of sufficient cooling capacity to absorb the total heat released from both isotopes.

During a campaign to separate a mixture of strontium-89 and -90 from PAW with the concentrate being stored in Tank 6-1 or 6-2, each day of processing adds a given quantity of concentrate to the storage tank resulting in continuously changing amounts of heat liberated from the mixture. The strontium-90 isotope, with a long half-life, continuously produces a constant amount of heat per unit volume and this rate of heat release is a function of the quantity of Sr^{90} present. The heat produced by a unit volume of strontium-89, with a half-life of 50.4 days, varies with time in storage. To calculate the curies or heat released from strontium-89 solutions accumulated in the storage tanks versus time, the following is presented.

The constant λ is known as the decay constant. Since the half-life of Sr^{89} is known to be 50.4 days, the value of λ can be derived from the exponential law $A = A_0 e^{-\lambda t}$ in terms of $t_{1/2}$. See Reference 1.

$$\ln \frac{1}{2} = -\lambda t_{1/2}$$

or

$$\lambda = \frac{\ln 2}{t_{1/2}} = \frac{0.69315}{50.4} = 0.0138$$

Assuming a constant amount of PAW is being processed for strontium each day, the exponential law can be expanded to

$$(1) \quad A_{n+1} = A_n e^{-\lambda h} + IRh \quad (\text{Sr}^{89} \text{ only})$$

where A_n is the number of curies in the tank at the beginning of the n^{th} day, $A_n e^{-\lambda h}$ is the curies remaining from A_n due to radioactive decay, IRh is the curies added during the n^{th} day, and h is a one-day step in time. Since there are no curies in the tank at the start of the first day, $A_0 = 0$.

Since $h = 1$, equation (1) can be written as:

$$(2) \quad A_{n+1} = A_n e^{-\lambda} + IR$$

When the decay of the Sr^{89} per day equals the amount added, the system will be in equilibrium and

$$A_n = A_{n+1}$$

and

$$A = A e^{-\lambda} + IR$$

or

$$A(1 - e^{-\lambda}) = IR$$

thus

$$(3) \quad A_{\text{equilibrium}} = \frac{IR}{1 - e^{-\lambda}} = \frac{IR}{1 - e^{-\frac{0.69315}{50.4}}} = \frac{IR}{1 - e^{-0.0136}}$$

For the desired tabular results on any day, the number of curies in the tank for $n = 1, 2, 3, \dots$ is

$$A_1 = 0e^{-\lambda} + IR = IR$$

$$A_2 = A_1 e^{-\lambda} + IR$$

$$A_3 = A_2 e^{-\lambda} + IR$$

$$A_{n+1} = A_n e^{-\lambda} + IR$$

Equation (3) is a linear, first order difference equation with constant coefficients, and therefore solved

$$(4) \quad A_n = \left[\frac{IR}{1 - e^{-\lambda}} \right] \left[1 - e^{-n\lambda} \right]$$

let $A_c = A_{\text{equilibrium}} = \frac{IR}{1 - e^{-\lambda}}$ then the following can be deduced

$$(a) \quad A_0 = A_e (1 - e^{-0\lambda}) = 0$$

$$(b) \quad A_{25} = A_e \left(1 - e^{-\left[\frac{\ln 2}{50.4}\right]25} \right) \approx A_e \left(1 - \frac{\sqrt{2}}{2} \right) \approx 0.293 A_e$$

$$(c) \quad A_{50} = A_e \left(1 - e^{-\left[\frac{\ln 2}{50.4}\right]50} \right) \approx A_e (1 - 0.5) \approx 1/2 A_e$$

(In 50 days one half the equilibrium curies are contained in the storage tank)

B. STRONTIUM (Continued)

$$(d) \quad A_{100} = A_e \left(1 - e^{-\left(\frac{\ln 2}{50.4}\right) 100} \right) \approx A_e \left(1 - \frac{1}{4} \right) \approx \frac{3}{4} A_e$$

$$(e) \quad A_{150} = \frac{7}{8} A_e$$

$$(d) \quad A_{200} = \frac{15}{16} A_e, \text{ etc.}$$

Tables VII-1 through VII-5 and Figures VII-1 through VII-5 are based on input rates of strontium-89 between 2×10^5 and 1×10^6 curies per day, the associated amount of strontium-90 being one-tenth the quantity of the lighter isotope. The calculations are based on a 100-day process cycle with the isotopic mixture assumed to be constant during the separation from the other fission products.

The total heat introduced in the storage tank during the first day of processing is approximately 83 percent from strontium-89 and about 17 percent from strontium-90. However, at the end of the processing cycle (the 100th day), strontium-89 contributes approximately 72 percent of the heat, and 28 percent by strontium-90. This is apparent by observing Figures VII-1 through VII-5 because the curve for the P/hr liberated by strontium-90 is nearly linear; but the curve for strontium-89 (half-life of 50.4 days) slowly approaches equilibrium, i.e., the maximum heat is liberated at a given input rate.

In actual processing, PAW is accumulated in the 244 AR Vault, and the strontium-89 concentration is not constant as assumed in the calculations. In addition, a one-hundred-day processing campaign may not be attained. However, this length of time was selected to show graphically that, over a period of time, the heat output of the strontium-90 gradually increases while heat from strontium-89 begins to level off.

Figure VII-6 is a comparison of the total heat evolved versus time from Figures VII-1 through VII-5.

Figure VII-7 depicts the resultant heat versus time curves after a campaign is completed and no additional curies of either isotope are added to the tank. The values used in Figure VII-7 were the maximum BTU/hr obtained at the 100th day from Table VII-5 and Figure VII-5. However, regardless of actual values, the shape of the curve for the total heat evolved from both isotopes will be the same provided the ratio of isotopes remains constant.

TABLE VII-1

Days	Curies Sr ⁸⁹	BTU/hr Sr ⁸⁹	BTU/hr Sr ⁹⁰	BTU/hr TOTAL
5	9.73x10 ⁵	1.07x10 ⁴	2.32x10 ³	1.30x10 ⁴
10	1.88x10 ⁶	2.07	4.64	2.53
15	2.73	3.00	7.00	3.70
20	3.52	3.87	9.30	4.80
25	4.26	4.68	1.16x10 ⁴	5.85
30	4.95	5.45	1.39	6.85
35	5.59	6.15	1.62	7.78
40	6.20	6.82	1.86	8.67
45	6.76	7.43	2.09	9.52
50	7.28	8.01	2.32	1.03x10 ⁵
55	7.77	8.55	2.55	1.11
60	8.23	9.05	2.78	1.18
65	8.65	9.52	3.02	1.25
70	9.05	9.96	3.25	1.32
75	9.42	1.04x10 ⁵	3.48	1.38
80	9.77	1.07	3.71	1.44
85	1.01x10 ⁷	1.11	3.94	1.50
90	1.04	1.14	4.18	1.56
95	1.07	1.17	4.41	1.61
100	1.09	1.20	4.74	1.67

Input Rate Sr⁸⁹ = 2.0×10^5 curies/day
 Sr⁹⁰ = 2.0×10^4 curies/day

Calculated Equilibrium Heat Generation Rate

$$\text{Sr}^{89} = 1.61 \times 10^5 \text{ BTU/hr}$$

TABLE VII-2

Days	Curies Sr ⁸⁹	BTU/hr Sr ⁸⁹	BTU/hr Sr ⁹⁰	BTU/hr TOTAL
5	1.95x10 ⁶	2.14x10 ⁴	4.64x10 ³	2.60x10 ⁴
10	3.76	4.14	9.28	5.07
15	5.46	6.00	1.39x10 ⁴	7.39
20	7.04	7.75	1.86	9.60
25	8.52	9.37	2.32	1.17x10 ⁵
30	9.90	1.09	2.78	1.36
35	1.12x10 ⁷	1.23	3.25	1.55
40	1.24	1.36	3.71	1.73
45	1.35	1.49	4.18	1.90
50	1.46	1.60	4.65	2.06
55	1.55	1.71	5.00	2.20
60	1.65	1.81	5.46	2.35
65	1.73	1.90	5.93	2.48
70	1.81	1.99	6.49	2.64
75	1.88	2.07	6.96	2.77
80	1.95	2.15	7.42	2.89
85	2.02	2.22	7.88	3.01
90	2.08	2.29	8.35	3.12
95	2.14	2.35	8.81	3.23
100	2.19	2.41	9.28	3.34

Input Rate Sr⁸⁹ = 4.0x10⁵ curies/day
Sr⁹⁰ = 4.0x10⁴ curies/day

Calculated Equilibrium Heat Generation Rate

$$\text{Sr}^{89} = 3.22 \times 10^5 \text{ BTU/hr}$$

TABLE VII-3

Days	Curies Sr ⁸⁹	BTU/hr Sr ⁸⁹	BTU/hr Sr ⁹⁰	BTU/hr TOTAL
5	2.92x10 ⁶	3.21x10 ⁴	6.96x10 ³	3.91x10 ⁴
10	5.64	6.21	1.39x10 ⁴	7.61
15	8.19	9.01	2.09	1.11x10 ⁵
20	1.06x10 ⁷	1.16x10 ⁵	2.78	1.44
25	1.28	1.41	3.47	1.75
30	1.48	1.63	4.17	2.05
35	1.68	1.85	4.86	2.33
40	1.86	2.04	5.56	2.60
45	2.03	2.23	6.25	2.85
50	2.18	2.40	6.94	3.10
55	2.33	2.56	7.64	3.33
60	2.47	2.71	8.34	3.55
65	2.60	2.86	9.03	3.75
70	2.72	2.99	9.72	3.96
75	2.83	3.11	1.04x10 ⁵	4.11
80	2.93	3.22	1.11	4.33
85	3.03	3.33	1.18	4.51
90	3.12	3.43	1.25	4.68
95	3.20	3.52	1.32	4.84
100	3.28	3.61	1.39	5.00

Input Rate Sr⁸⁹ = 6 x 10⁵ curies/day
 Sr⁹⁰ = 6 x 10⁴ curies/day

Calculated Equilibrium Heat Generation Rate

$$\text{Sr}^{89} = 4.83 \times 10^5 \text{ BTU/hr}$$

TABLE VII-4

Days	Curies Sr ⁸⁹	BTU/hr Sr ⁸⁹	BTU/hr Sr ⁹⁰	BTU/hr TOTAL
5	3.89x10 ⁶	4.28x10 ⁴	9.28x10 ³	5.21x10 ⁴
10	7.53	8.28	1.86x10 ⁴	1.01x10 ⁵
15	1.09x10 ⁷	1.20x10 ⁵	2.78	1.48
20	1.41	1.55	3.71	1.92
25	1.70	1.87	4.64	2.34
30	1.98	2.18	5.57	2.74
35	2.24	2.46	6.49	3.11
40	2.48	2.73	7.42	3.47
45	2.70	2.97	8.35	3.81
50	2.91	3.20	9.28	4.13
55	3.11	3.42	1.02x10 ⁵	4.44
60	3.29	3.62	1.11	4.73
65	3.46	3.81	1.21	5.00
70	3.62	3.98	1.30	5.28
75	3.77	4.15	1.39	5.54
80	3.91	4.30	1.48	5.78
85	4.04	4.44	1.58	6.02
90	4.16	4.57	1.67	6.24
95	4.27	4.70	1.76	6.46
100	4.38	4.81	1.85	6.66

Input Rate Sr⁸⁹ = 8×10^5 curies/day
 Sr⁹⁰ = 8×10^4 curies/day

Calculated Equilibrium Heat Generation Rate

$$\text{Sr}^{89} = 6.44 \times 10^5 \text{ BTU/hr}$$

TABLE VII-5

Days	Curies Sr ⁸⁹	BTU/hr Sr ⁸⁹	BTU/hr Sr ⁹⁰	BTU/hr TOTAL
5	4.87x10 ⁶	5.35x10 ⁴	1.16x10 ⁴	6.51x10 ⁴
10	9.41	1.03x10 ⁵	2.30	1.26x10 ⁵
15	1.36x10 ⁷	1.50	3.50	1.85
20	1.76	1.94	4.60	2.40
25	2.13	2.34	5.80	2.92
30	2.48	2.72	7.00	3.42
35	2.80	3.08	8.10	3.89
40	3.10	3.41	9.20	4.33
45	3.38	3.72	1.04x10 ⁵	4.76
50	3.64	4.00	1.16	5.16
55	3.89	4.27	1.28	5.55
60	4.11	4.52	1.40	5.92
65	4.33	4.76	1.51	6.37
70	4.53	4.98	1.62	6.60
75	4.71	5.18	1.73	6.91
80	4.88	5.37	1.84	7.21
85	5.05	5.55	1.96	7.51
90	5.20	5.72	2.08	7.80
95	5.34	5.87	2.20	8.07
100	5.47	6.02	2.32	8.33

Input Rate Sr⁸⁹ = 1 x 10⁶ curies/day
 Sr⁹⁰ = 1 x 10⁵ curies/day

Calculated Equilibrium Heat Generation Rate

$$\text{Sr}^{89} = 8.05 \times 10^5 \text{ BTU/hr}$$

C. CESIUM

The only isotope of cesium that is important to long-term waste storage is cesium-137. This isotope decays by releasing both beta particles and gamma rays and has a half-life of 30 years. Cesium-137 and its short half-life daughter (barium-137 with a half-life of 2.6 minutes) produce 4.8 thermal watts or 16.4 BTU/hr per kilocurie.

Cesium salts, being soluble in neutralized high-level wastes, can be stored in the underground storage tanks during the time when the waste is boiling because the thermal watts contributed are small compared to the total heat being released. When the short half-life isotopes have decayed and cesium becomes the predominant heat producer in the supernatant, the liquid can be pumped to the 221-B building and the cesium separated. A water leach will recover most of the cesium in the sludge. Flowsheets exist for the recovery of cesium from current wastes and will be used if the demand for cesium exceeds the supply available from stored wastes.

Cesium-134 must be considered as a thermal heat source if current wastes are processed for cesium. The half-life is 2.1 years; however, the quantity of the lighter isotope in current wastes is approximately 5 percent of the amount of cesium-137. Cesium-134 releases a total of 10.3 thermal watts of energy or 35 BTU/hr per kilocurie during its decay to the stable barium-134 isotope. In stored wastes, the heat evolved from cesium-134 decreases to an insignificant amount after ten years.

D. STORAGE OF STRONTIUM AND CESIUM

Storage of strontium and cesium in the 221-B Canyon tanks in an aqueous solution is considered to be interim storage. Final storage, permanent storage or semi-permanent storage will be in high-integrity containers probably designed to allow the isotope to be removed if commercial application can be developed. The encapsulation of isotopes may be completed within the B-Plant complex or in a separate building. A prototype packaging system is being developed to demonstrate loading of the strontium-90 or cesium-137 on a synthetic alumino-silicate ion exchanger in a stainless steel container, drying the bed after 500 to 1,000 kilo curies of an isotope have been loaded, and welding the container. Handling techniques during these operations will comply with rigid safety requirements. Storage of these containers may be in a water basin for ease of removing the heat liberated. The water basin technique also provides a means of determining the integrity of the containers by continuously monitoring the water.

Interim storage of strontium product solutions are in the tanks listed in Table VII-6. Since the volume of strontium concentrate added to a storage tanks is small (20 to 40 gallons of concentrate per 100 flow of IAF), no direct cooling from the coils or tube bundles can be attained until the solution level is in contact with the coil or tube bundle. Therefore, tanks which are to receive

D. STORAGE OF STRONTIUM AND CESIUM (Continued)

strontium concentrate during a processing campaign should contain a water butt to raise the solution level so that direct contact is made with the cooling coil or tube bundle before the strontium concentrate is added. Depending upon the quantity and concentration of the solution, the portion of the cooling coil or tube bundle in contact with the solution must have a greater cooling capacity than the total heat emitted from the solution.

A typical (hypothetical) solution heating curve and tank cooling capacity versus tank volume is shown in Figure VII-8. A 250-gallon water butt in the tank is sufficient to maintain the cooling capacity of the coils above the heat evolved from the solution. The vertical drop in the heat output curve is that period of time when Purex acid waste is not being processed but is accumulating in tank 001 in the 244 AR Vault. Other campaign cycles for isolation and concentration of strontium solution from PAW will result in curves similar to that shown. The increase in heat output of the solution and the length of each line segment will depend upon the final concentration of the solution and the length of time of each campaign cycle.

TABLE VII-6
STRONTIUM CONCENTRATE
STORAGE TANKS

<u>Tank</u> <u>Number</u>	<u>Capacity</u> <u>Gallons</u>	<u>Designed Cooling</u> <u>Duty BTU/hr</u>	<u>Volume To</u> <u>First Coil</u> <u>Gallons*</u>
6-1	5000	1,000,000	250
6-2	5000	1,000,000	250
7-1**	5000	500,000	350
7-2**	5000	500,000	350
8-1**	5000	500,000	360
8-2**	5000	500,000	360

* The volume to the cooling jacket is not listed. In some tanks the jacket is lower than the coil or tube bundle and in some other tanks is higher.

** These tanks have cooling jackets.

Cesium is removed from stored supernatant waste solutions and concentrated. Interim storage will be in the tanks listed in Table VII-7. Because the half-life of cesium-137 is 30 years, the quantity of the isotope which can be stored in a given tank will be limited by the cooling capacity of the tank. The decay of cesium-137 produces both beta and gamma radiations totaling 4.8 thermal watts or 16.4 BTU/hr energy per kilocurie. The cesium produce will be concentrated to 20-30 BTU per hour per gallon before it is transferred to a storage tank.

D. STORAGE OF STRONTIUM AND CESIUM (Continued)

Requirements for the tank into which the cesium concentrate is being pumped during a campaign are the same as those for receiving the strontium concentrate; that is, a water butt should be provided so the cooling capacity of the coils (tube bundle) will safely handle the heat evolved from the stored isotope.

TABLE VII-7CESIUM CONCENTRATE
STORAGE TANKS

<u>Tank Number</u>	<u>Capacity Gallons</u>	<u>Designed Cooling Duty BTU/hr</u>	<u>Volume To First Coil Gallons*</u>
14-2**	3900	300,000	500
17-1**	5000	100,000	60

* The volume to the cooling jacket is not listed. In some tanks the cooling jacket is lower than the coil or tube bundle, and in other tanks it is higher.

** These tanks have cooling jackets.

E. RADIOLYSIS OF AQUEOUS SOLUTIONS

Aqueous solutions undergo numerous changes when radioactive materials are present in the solutions. Some of the mechanisms involved are: ionization, transfer of electronic excitation from one molecule to another, electron capture, dissociation of excited vibrational states, neutralization, formation of excited electronic states, and unpredictable reactions.

Hydrogen gas evolution from aqueous solutions has been observed in Purex process vessels, in the 244 CR vault and in B-Plant process vessels at rates up to 1.2 cubic centimeters per watt-hour. See Reference 3. Since the lower explosive limit of hydrogen gas in air is four volume percent, an upper hydrogen gas concentration of two volume percent is specified for operational control purposes. Where normal vessel air in-leakage cannot be guaranteed to dilute evolved hydrogen to less than three volume percent, a minimum air dilution rate of 2.06×10^{-3} cubic feet per watt-hour should be provided by direct air dilution. Table VII-8 presents the minimum air dilution rates required per kilo-curie for the various fission products.

Referring to Table VII-5 and Figure VII-5, the purge air requirements for a strontium-89 and -90 mixture will be nine standard cubic feet per minute (SCFM). The purge air requirements for cesium solution in storage (maximum) is ten SCFM.

E. RADIOLYSIS OF AQUEOUS SOLUTIONS (Continued)TABLE VII-8AIR DILUTION REQUIREMENT FOR VARIOUS FISSION PRODUCTS

<u>Fission Product</u>	<u>Air Dilution Requirement SCF of Air/hr/KCi</u>
Sr ⁸⁹	0.007
Sr ⁹⁰	0.013
Zr•Nb ⁹⁵	0.010
Ru ¹⁰³	0.007
Ru ¹⁰⁶	0.020
Ce ¹⁴¹	0.003
Ce ¹⁴⁴	0.017
Y ⁹¹	0.007
Cs ¹³⁷	0.010
Pm ¹⁴⁷	0.0008

F. FUTURE ISOTOPE SEPARATION

Table VII-9 lists various isotopes which are or may be separated and packaged in the future. The separations technology of these isotopes has been developed except for rhodium, palladium and antimony. The technology for those is being developed. The symbols used in Table VII-9 are:

α alpha particle β+ positron
β- beta particle γ gamma ray

Energies listed after a symbol are presented in decreasing order of abundance. Energies of the radiations are in millions of electron volts. The symbols used for the half-lives are d = days and y = years.

TABLE VII-9

<u>Isotope</u>	<u>Symbol and Isotopic Weight</u>	<u>Half-Life</u>	<u>Decay Mode Energies</u>
Strontium	Sr ⁸⁹	50.4d	β- 1.46
Strontium	Sr ⁹⁰	28 y	β- 0.54
Technetium	Tc ⁹⁹	2.1 x 10 ⁵ y	β- 0.29
Rhodium*	Rh ¹⁰²	210d	β- 1.15; β+ 1.28; γ 0.475
Palladium*	Pd ¹⁰⁷	7x10 ⁶ y	β- 0.035
Antimony*	Sb ¹²⁵	2.7y	β- 0.30, 0.12, 0.62 γ 0.035, 0.67, 0.46
Cesium	Cs ¹³⁷	30y	β- 0.51, 1.18
Cerium	Ce ¹⁴⁴	285d	β- 0.32, 0.19; γ 0.133
Promethium	Pm ¹⁴⁷	2.62y	β- 0.225
Neptunium	Np ²³⁷	2.20x10 ⁶ y	α 4.78, 4.76 γ 0.087, 0.019, 0.030
Americium	Am ²⁴¹	458y	α 5.58, 5.43; γ 0.060
Plutonium	Pu ²³⁹	2.44x10 ⁴ y	α 5.15, 5.13, 5.10 γ 0.053, 0.013

*Separations technology being developed.

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G. APPENDIXDifference Equations

The fundamental problem in the theory of difference equations is in many ways similar to the theory of differential equations with the exception that the mathematical object sought here is a sequence rather than a function. A sequence 's' is defined by associating with every member 'n' of a set of integers, a (real) number 'S_n'.

Two examples are presented to give an intuitive feel for difference equations.

Example 1

Consider the differential equation

$$(1) \quad y' = 2x$$

with the condition that $y = 0$ when $x = 0$. Integrating we have

$$(2) \quad y = \int y' dx = \int 2x dx = x^2 + C$$

where C is the constant of integration. From the condition the constant C is equal to zero in equation 2, the solution to the differential equation 1 is

$$(3) \quad y = x^2$$

The graph for this solution is

Figure 1

The sequence

$$(4) \quad y_n = n^2 \quad n = -2, -1, 0, 1, 2, \dots$$

corresponds to the function $y = x^2$, and the difference equation which corresponds to $y' = 2x$ is

G. APPENDIX (Continued)

$$(5) \quad y_n - y_{n-1} = n^2 - (n-1)^2 = 2n-1 \quad n = -2, -1, 0, 1, 2, \dots$$

with the condition $Y_0 = 0$. From the above construction, it is clear that the sequence (2) is the solution to the difference equation (3).

The usual problem is to find the solution sequence when the difference equation is given. The procedure is analogous to solving differential equations.

Rewriting equation (5)

$$(6) \quad y_n - y_{n-1} = 2n-1 \quad y_0 = 0$$

First the homogeneous equation is solved

$$(7) \quad y_n - y_{n-1} = 0$$

Clearly, $y_n^h = C$ (constant) is a solution to equation (7) since $C - C = 0$.

The particular solution is solved by trial and error in which the following form is tried

$$(8) \quad y_n^p = an^2 + bn$$

substituting equation (8) into (6)

$$\begin{aligned} y_n - y_{n-1} &= an^2 + bn - [a(n-1)^2 + b(n-1)] \\ &= an^2 + bn - an^2 + 2an - a - bn + b = 2n-1 \end{aligned}$$

or

$$2an - a + b = 2n-1$$

therefore

$$2an = 2n \quad \text{which implies} \quad a = 1$$

and

$$-a + b = -1 \quad \text{so} \quad b = 0$$

thus

$$y_n^p = n^2$$

The general solution is the sum

$$y_n = y_n^h + y_n^p$$

or

$$y_n = C + n^2$$

From the condition $Y_0 = 0$, the constant C is equal to zero.

Thus

$$y_n = n^2$$

is the solution to equation (6).

Example 2

The difference equation

$$(1) \quad A_{n+1} = A_n e^{-\lambda} + IR, \quad A_0 = 0, \quad n = 0, 1, 2, \dots$$

describes the curies of material in a waste tank with the assumptions:

- (a) The tank is initially empty ($A_0 = 0$),
- (b) Constant input rate IR (curies/day), and
- (c) The isotope half-life, expressed in days, is $\ln 2/\lambda$

Here n denotes the n^{th} day of the filling, and A_n is the number of curies in the tank on the n^{th} day.

Rewriting equation (1)

$$(2) \quad A_{n+1} - A_n e^{-\lambda} = IR \quad n = 0, 1, 2, \dots$$

with the initial condition $A_0 = 0$.

The homogeneous equation is solved first

$$(3) \quad A_{n+1} - A_n e^{-\lambda} = 0$$

A first trial solution could be

$$(4) \quad y_n^h = Ce^{-n\lambda} \quad \text{where } y^h \text{ is the homogeneous solution}$$

Substituting (4) into (3)

$$(5) \quad y_{n+1}^h - y_n^h e^{-\lambda} = Ce^{-(n+1)\lambda} - Ce^{n\lambda} e^{-\lambda} = 0$$

Thus

$$y_n^h \text{ is a solution for (3)}$$

For a particular solution (Y^P) to (3), the following can be tried

$$(6) \quad y_n^P = a_1$$

$$(7) \quad y_n^P = a_1 + a_2 n, \text{ etc.}$$

Trying (6) as a particular solution to (2) results in

$$y_{n+1}^P - y_n^P e^{-\lambda} = IR$$

$$a_1 - a_1 e^{-\lambda} = IR$$

$$a_1(1-e^{-\lambda}) = IR$$

$$a_1 = \frac{IR}{1-e^{-\lambda}}$$

Thus

$$(8) \quad y_n^p = \frac{IR}{1-e^{-\lambda}}$$

which is the particular solution to (2)

Then

$$(9) \quad y_n = y_n^h + y_n^p = Ce^{-n\lambda} + \frac{IR}{1-e^{-\lambda}}$$

is a general solution. Using the initial condition of $Y_0 = 0$ to evaluate C

$$y_0 = 0 = Ce^{-0\lambda} + \frac{IR}{1-e^{-\lambda}}$$

or

$$C = -\frac{IR}{1-e^{-\lambda}}$$

Thus

$$(9) \quad y_n = \frac{IR}{1-e^{-\lambda}} (1-e^{-n\lambda})$$

is the general solution.

If equation (7) had been substituted as a trial solution, the value of a_2 would be equal to zero and the substitution would reduce to equation (6).

The equation
$$A_n = \frac{IR}{1-e^{-\lambda}} (1-e^{-n\lambda})$$

describes the conditions for the total heat evolved by Sr^{89} during a campaign cycle.

For a more complete presentation, refer to reference 4.

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FIGURE VII-1

Heat Evolved from Strontium Vs Time
 2×10^4 Curies Sr-90 per Day

FIGURE VII-2

Heat Evolved from Strontium Vs Time
 4×10^4 Curies Sr-90 per Day

FIGURE VII-3

Heat Evolved from Strontium Vs Time
 6×10^4 Curies Sr-90 per Day

FIGURE VII-4
Heat Evolved from Strontium Vs Time
 8×10^4 Curies Sr-90 per Day

FIGURE VII-5

Heat Evolved from Strontium Vs Time
 1×10^5 Curies Sr-90 per Day

FIGURE VII-6
Heat Evolved from Strontium Vs Time

FIGURE VII-7
Strontium 89 and 90 Decay Curves

FIGURE VII-8

Tank Volume Vs Tank Cooling Capacity
and Sr-89 and Sr-90 Heat Output

PART IV, Continued

B-PLANT PRODUCT AND WASTE HANDLING

CHAPTER VIII

WASTE HANDLING

By

W. L. Godfrey

PART V

PLANT AND EQUIPMENT

CHAPTER IX

GENERAL DESCRIPTION OF WASTE MANAGEMENT FACILITIES

Rv

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PART V: PLANT AND EQUIPMENTCHAPTER IXGENERAL DESCRIPTION OF WASTE MANAGEMENT FACILITIES

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PART V: PLANT AND EQUIPMENTCHAPTER IXGENERAL DESCRIPTION OF WASTE MANAGEMENT FACILITIES

This chapter presents a general architectural and functional description of those facilities associated with the Waste Management Program. More detailed discussions of equipment, equipment arrangement, flow-sheets, and procedures are found elsewhere in this manual.

A. GENERAL LAYOUT OF PLANT1. Layout of Production Areas

As originally designed, the Hanford Reservation production areas were constructed as essentially independent, self-contained units of the entire production complex. The geographically widely-separated areas were selected to ensure continuity of production in other facilities if one should undergo damage or serious contamination spread. A site plan of the Hanford Reservation is shown in Figure IX-1.

Production units of the complex are located in three general operating areas known as the 100, 200, and 300 Areas. The 300 Area contains a technical library, laboratories, the Plutonium Recycle Test Reactor (PRTR), and other facilities administered by Battelle Memorial Institute, Pacific Northwest Laboratory. Also located in the 300 Area are facilities for the preparation of the uranium fuel elements used in the 100 Area reactors. Douglas United Nuclear operates the fuel preparation facilities.

The 100 Areas, operated for the AEC by Douglas United Nuclear, contain the plutonium production reactors and are situated adjacent to the Columbia River. This location was selected to ensure the availability of an adequate and continuing supply of cooling water to the reactors. The 100 Areas also supply water to the 200 Areas.

A total of nine production reactors has been built. These reactors are called 100-B, 100-C, 100-D, 100-DR, 100-F, 100-H, 100-KE, 100-KW, and 100-N. Technological improvements and improved operating efficiencies have permitted the deactivation of 100-D, 100-DR, 100-H, and 100-F.

After being irradiated in a reactor the uranium fuel elements or "slugs" are discharged from the reactor and stored in a cooling basin to allow short-lived radioactive isotopes to decay. Following the cooling period, the irradiated fuel elements are transported to the 200 Areas in railroad "cask cars" where uranium, plutonium, neptunium, and selected fission products are isolated and purified.

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FIGURE IX-1

Map of the Hanford Reservation

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2. 200 Areas

The chemical processing plants, waste management facilities, and various associated support organizations are located in the 200 Areas. The three 200 Areas, which are situated on a plateau south of the reactor sites, are: 200 East, 200 West, and 200 North.

The 200 North Area, which at present is not being used, contains lag storage facilities for irradiated fuel elements prior to their processing in the 200 East or 200 West chemical separations plants. In addition to the three storage basins located in the 200 North Area, there are three cribs, 216-N-3, 5, and 7, which are presently inactive but may be reactivated if the need should arise.

Facilities located in the 200 West Area are shown in Table IX-1 and facilities located in the 200 East Area are shown in Table IX-2.

Plot plans of the 200 Areas are shown in Figures IX-2 and IX-3.

TABLE IX-1
200 WEST AREA FACILITIES

Bldg. No.	Name and Purpose
202-S	Redox Plant for solvent extraction processing of uranium and plutonium.
222-S	Analytical, research, and development laboratories.
241-S	Redox tank farms for underground storage of high level liquid waste.
241-SX	
221-T	Canyon building used for BiPO ₄ process. Presently used for equipment decontamination by Special Services Sub-Section.
271-T	Service building for 221-T, and offices used by Facilities Engineering Section.
224-T	Concentration building for BiPO ₄ process. Unused at present.
222-T	Offices for Personnel Protection Operation.
241-T	Tank farms for the underground storage of high level waste.
241-TX	
241-TY	
242-T	Waste Evaporator.
221-U	Canyon building containing solvent extraction equipment used for the Uranium Recovery Program. Presently not being used.
271-U	Service building for 221-U, and offices of Document Classification and Custody Operation and Nuclear Materials Sub-Section.
222-U	Laboratory building being used by Battelle-Northwest Laboratories.
224-U	Uranium Oxide conversion plant.
241-U	Tank farm for the underground storage of high level waste.
231-W	Plutonium laboratory of Battelle-Northwest Laboratories.
234-5	Plant and laboratory for the conversion and fabrication of plutonium.
242-Z	Plutonium Reclamation facility.
282-W	Water reservoir.
283-W	Water treatment facility.
284-W	West area steam plant.
272-W	Machine shops.
277-U	Mock-up shops.
277-S	
2704-W	Office buildings.
2704-Z	
2709-W	Mail and duplicating offices.
2719-WA	First Aid.
2723-W	Face mask cleaning and repair facility.
2724-W	Laundry operated by ITT/FSS

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TABLE IX-2
200 EAST AREA FACILITIES

Bldg. No.	Name and Purpose
202-A	Purex plant for solvent extraction processing of uranium and plutonium.
241-A	Purex tank farms for underground storage of high level liquid waste.
241-AX	
244-AR	Vault facility for the handling and transfer of current and stored wastes.
221-B	B-Plant canyon building used for fractionization of wastes.
271-B	Service and office building for 221-B.
222-B	Offices used by plant Accounting operation.
224-B	Concentration building for BiPO ₄ process. Unused at present.
241-B	Tank farms for the underground storage of high level waste and In-Tank Solidification units 1 and 2. (ITS-1 and ITS-2)
241-PX	
241-BY	
200-C	Hot semiworks used to purify strontium and rare earth fractions, and develop flowsheets used in B-Plant.
241-C	Tank farm for underground storage of high level liquid waste.
801-C	Cesium load-out facility used to load cesium into a shipping cask for off-site shipments.
209-E	Critical Mass Laboratory of Battelle-Northwest Laboratories.
275-EA	Essential Materials warehouse.
272-E	Maintenance shops and offices.
274-E	
282-E	Water reservoir and treatment facility.
283-E	
284-E	Steam plant.
2101-M	Graphite building houses certain Atlantic Richfield Hanford Company offices as well as ITT/FSS Electrical Utility Section.
2704-E	Administrative offices.
2713-E	Personnel accounting and security offices.
3719-E	First Aid.

3. Waste Management Facilities

3.1 B-Plant Area

The waste fractionization plant, B-Plant, is located in the northwestern quadrant of the 200 East Area. The name and function of the various installations within the B-Plant area are given in Table IX-3. A more detailed description of B-Plant is given in Section B of this chapter.

3.2 Waste Tank Farms

The term "waste tank farm" or "tank farm" is used to identify a cluster of large underground steel-lined concrete tanks. Neutralized high level radioactive wastes containing virtually all of the chemical salts and radioactive fission products passing through the chemical separations plants are stored in these tanks. If heat from radioactive decay is sufficiently high, solutions in the tank will boil and the tanks must be equipped with vapor handling facilities. These tanks are called boiling tanks, and the farm in which they are located is called a boiling tank farm. Shielding from radiation in the tanks is provided by the several feet of earth covering the tanks.

FIGURE IX-2
Plot Plan of 200 West Area

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FIGURE IX-3
Plot Plan of 200 East Area

FIGURE IX-3

Plot Plan of 200 East Area

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TABLE IX-3
FACILITIES LOCATED IN B-PLANT AREA

<u>Installation</u>	<u>Name</u>	<u>Function</u>
221-B	Processing Building (Canyon Bldg.)	a. Separation, concentration, purification, and storage of selected FP's. b. Waste Handling c. Solvent Recovery
271-B	Service Building	a. Offices b. Aqueous makeup of process chemicals. c. Instrument maintenance shops. d. Cold side ventilation equipment.
211-B	Chemical Tank Farm	Bulk storage of liquid chemicals.
217-B	Demineralizer	Demineralizer for process water.
276-B	Organic Makeup	Storage and makeup of fresh organic.
291-B	Fan House, Exhaust filters, filter instrumen- tation building, and exhaust stack.	Ventilation and vessel vent exhaust fans for process building. Emergency steam turbine fan.
292-B	Stack Sample Building	Sampling equipment for sampling process stack effluents.
282-B	Emergency Raw Water Pump	Emergency raw water well and pump to supply cooling water to process equipment.
222-B	Accounting Offices	Offices for plant accounting operation.
224-B	Concentration Building	Process cells unused at present.
2902-B	Elevated Water Tank	Emergency supply of sani- tary water.
241-BX-154 241-ER-151 241-B-154	Diversion Box Diversion Box Diversion Box	Route waste and other streams to and from 221-B.
216-B-2	Crib	Cooling water and chemical sewer.
216-B-3	Crib	Cooling water and chemical sewer.
216-B-12	Crib	221-B process condensate.
216-B-13	Crib	291-B process stack drain.
216-B-55	Crib	221-B steam condensate.
216-B-56	Organic Crib	221-B organic waste.

Tank farms are designated by the number 241 suffixed by the letter designation of the separation plant they are built to serve. For example, 241-A is the tank farm for the Furex or A plant, while 241-T is the tank farm built to serve the bismuth phosphate process in 221-T. When replacement tank farms are required, they are designated with an X or a Y such as 241-AX, 241-TX, or 241-TY. Common usage generally omits the numerical 241 designation and the tank farms are referred to as A Farm, AX Farm, TX Farm, etc.

There is a total of 12 tank farms located in the Chemical Processing Department's 200 East and 200 West areas containing a total of 149 waste storage tanks. Table IX-4 lists the tank farms, their location, the number of tanks in each farm, and a very general description of the wastes stored in the farm. The tank farms are discussed in more detail in Section C of this chapter.

TABLE IX-4
HIGH LEVEL WASTE TANK FARMS
(See Figures IX-2 and IX-3 for location)

<u>Tank Farm</u>	<u>Location</u>	<u>No. of Tanks</u>	<u>Description of Waste</u>
241-A	200-E	6	Boiling Purex waste
241-AX	200-E	4	Boiling Purex waste
241-S	200-W	12	Non-boiling Redox waste
241-SX	200-W	15	Boiling Redox waste
241-C	200-E	12	Non-boiling coating and miscellaneous waste
241-B	200-E	12	Non-boiling coating, TBP, and miscellaneous waste
241-BX	200-E	12	Non-boiling coating, TBP, and miscellaneous waste
241-BY	200-E	12	Non-boiling coating, TBP, and miscellaneous waste
241-T	200-W	12	Non-boiling coating and miscellaneous waste
241-TX	200-W	18	Non-boiling Redox and miscellaneous waste
241-TY	200-W	6	Non-boiling miscellaneous waste
241-U	200-W	12	Non-boiling coating and Redox waste

3.3 244-AR Vault Area

The 244-AR Vault Area is located approximately 200 feet due west of the 241-A Tank Farm (see Fig. IX-3). The facility will provide waste acidification and transfer capability between the Purex Plant, 241-A and AX Tank Farms, and 221-B Waste Fractionization Plant. A more detailed description of the 244-AR Vault is given in Section D of this chapter.

B. B-PLANT1. Architectural Description

The Waste Fractionization Plant (221-B) is a multi-storied, predominantly reinforced concrete structure, approximately 850 feet in length, 68 feet wide, and 72 feet in height. The building is divided into two major sections: 1) the processing portion which includes the canyon craneway; and 2) the service and operating portion which includes the operating, pipe, and electrical galleries. The canyon cells contain the vessels and associated equipment in which all radioactive solutions entering the plant are processed. The radio-active or "hot" facilities are separated from the service area by massive concrete shielding. Operation of the equipment within the canyon cells is accomplished remotely from the operating gallery. Replacement or maintenance of "hot" equipment requires the use of the remotely operated canyon crane. Remote operation is discussed further in Chapter XII. Figures IX-4 and IX-5 illustrate a typical cross section of the building.

FIGURE IX-4

Cross Section of 221-B and 271-B Buildings
(Based on H-2-33099)

FIGURE IX-5
221-B Canyon Building

2. Canyon

2.1 Process Cells

The canyon consists of 40 equipment cells arranged in a single row running the length of the building. The standard canyon cell is 17 feet 8 inches long, 13 feet wide, and 22 feet high. Each cell is separated from its adjacent cell by a seven-foot thick concrete wall. The cells are equipped with specially designed six-foot thick concrete cover blocks. These cover blocks are designed to prevent the escape of airborne radioactive contamination from the cells to the canyon deck, as well as to provide shielding of the high intensity radiation emanating from the process equipment.

All lines which service the cells are buried in concrete and terminate in a row of "connector nozzles" on the cell walls nine feet below canyon deck level. The elevation of the canyon deck is 711 feet 6 inches, the cell nozzles are 702 feet 6 inches; and the pipe trench nozzles are 704 feet 2 inches. Equipment is placed on the cell floor and held in position by guides built into the cell, thus establishing a standard relationship between the wall connector nozzles and the vessels. This arrangement makes possible the prefabrication of replacement vessels, jumpers, and other equipment for any given location in the cell. The equipment locations and functions carried out in the various cells are shown elsewhere in this manual.

2.2 Pipe Trench

Also located in the canyon and running parallel to the process cells is the pipe trench. A large part of the piping through which inter-cell solution transfers are made is located in the pipe trench. The pipe trench is approximately 8 feet wide, 6 feet deep, and runs from Cell 5 through Cell 40. Lines from the cells pass through the concrete and terminate in connector nozzles in the trench. As in the cells, the piping is in prefabricated sections attached to the nozzles with connector heads. All pipes in the trench are sloped to permit proper drainage. The trench is accessible for remote maintenance via removable concrete cover blocks. Moisture, which may enter the trench from the canyon deck or from piping leaks in the trench itself, is collected in sumps which drain to adjacent process cells. The process cells in turn drain to Cell 10.

2.3 Air Tunnel

Located below the pipe trench is the ventilation air tunnel. Both process cell and vessel ventilating air leave the 221-B Building via this tunnel. The air tunnel measures 10-1/2 feet by 10-1/2 feet and extends from Cell 40 through Cell 5. From the 221-B Building the ventilation air is passed through either the high efficiency filter,

291-B, or the sand filter, 291, then through the exhaust fans. The exhaust fans discharge the ventilation air to the base of the 200-foot process stack.

3. Galleries

The electrical pipe, operating, and crane cab galleries are located at progressively higher levels on the north side of the 221-B Building. The galleries are approximately 14 feet wide and run the length of the building. The electrical, pipe, and operating galleries are isolated from the processing portion of the building by concrete shielding and are provided with an independent air supply. These areas are considered "cold side" zones. The crane cab gallery is open to the canyon and is therefore a regulated or "hot side" zone.

3.1 Crane Cab Gallery

A 75-ton electrically operated overhead railway crane is used for remote handling of equipment in the canyon portion of the building. This crane is provided with a shielded cab which operates behind a five-foot thick parapet wall, thus providing shielding against radiation. The area between the parapet wall and the outer structural wall of the building is known as the "Crane Cab Gallery" or "Craneway". The Crane Cab Gallery can be seen in Figures IX-4 and IX-5. A description of the crane is given in Chapter XII.

3.2 Operating Gallery

Most of the controls, instruments, and data recorders for the cell equipment are located in the operating gallery. Arranged along the length of the operating gallery is a series of panel boards from which control and instrument lines run to the equipment in the cells. Chemical addition "Scale Tanks" are provided at points along the operating gallery with inlet connections to appropriate chemical headers. The chemical makeups are weighed in the scale tanks and are either pumped or gravity-fed to the process vessels located in the canyon.

3.3 Pipe Gallery

The pipe gallery provides space for the non-radioactive piping which serves the in-cell equipment. As remote maintenance is not required in this area all connections are of the normal type. Chemical headers, electrical and steam distribution lines are also located in the pipe gallery.

3.4 Electrical Gallery

The electrical gallery is located in the lowest level of the building. The gallery floor is at the same elevation as the process

cell floor. The main electrical lines and electrical distribution centers are located in the electrical gallery. The main steam line entering the building is also located in this gallery.

4. 271-B Service Building

The 271-B Building is a four-story concrete structure approximately 160 feet long and 48 feet wide attached to the north or gallery side of the 221-B Building. The relationship of 221-B, 271-B, and other buildings in the B-Plant area is shown in Figure IX-6. A cross section of the 271-B Building is shown in Figure IX-5.

The basement floor of the building contains the maintenance and instrument shops, foremen offices, air compressors for building instrument and process air supply, filters for the building ventilation air supply, and electrical distribution panels for 271-B.

The second floor contains administrative and supervisory offices, lunch room facilities, and the dispatcher's office. The communications facilities, which are used for controlling the movement of material and personnel in the building, are located in the dispatcher's office. All magnetically locked doors giving access to the canyon area are controlled from the dispatcher's office.

The third floor contains the bulk of the chemical makeup head tanks and is referred to as the Aqueous Makeup area or AMU. Office space and additional dry chemical storage are also found on this floor.

5. Building Ventilation

The 271-B and 221-B Buildings contain five separate and distinct ventilation systems. One system ventilates the 271-B Service Building; one system ventilates the operating portion of the 221-B Building; a third system supplies ventilation to the process equipment areas of 221-B, while the final two systems ventilate the process vessels themselves. This section describes the building ventilation systems. The vessel vent system is described in the following section. All systems are designed to ensure the flow of air away from the operating and service areas toward the processing areas.

5.1 271-B Ventilation

The 271-B ventilation system is designed around a 59,000 cfm Buffalo Supply Unit. Fresh air is drawn into the building through a vertical duct near the roof. The air passes down through a dry filter, then flows successively through a preheater, a wet filter, and a reheater. The filtered air is fed through supply ducts to the various offices, shops, and corridors in the building. From 271-B a portion

of the air is discharged to atmosphere through blower fans on each level. The remaining flow is into the operating, pipe, and electrical galleries in 221-B.

5.2 221-B Operating Area Ventilation

Ventilation of the operating areas in 221-B is accomplished by feeding fresh, dust-free air from 10 air filtering and heating units distributed along the operating gallery. Each of these units has a capacity of approximately 4500 cfm. This air is joined in the operating gallery by that flowing in from 271-B, and passes through gratings in the floor to the pipe gallery. Air is exhausted to atmosphere from the pipe gallery through nine exhaust fans distributed along its length. The discharge from the electrical gallery is by three exhaust fans.

5.3 221-B Processing Area Ventilation

The ventilation of the process areas is accomplished by feeding fresh, dust-free air from 10 separate 4500 cfm filtering and heating units to various points along the craneway. The air flows over the craneway parapet wall and down to the canyon deck. It is then drawn through calibrated openings around the cover blocks into the pipe trench and process cells. From the process cells and pipe trench air is pulled into the air tunnel through openings in each cell and each section of the pipe trench. As originally constructed, the process cells were connected to the air tunnel by one 10-inch duct in each cell. To prevent significant escape of airborne contamination from an open cell, 12 new 14-inch ventilation openings were provided from each cell. The new ventilation openings, totaling 12 square feet cross sectional area, provides an air flow rate of 37,500 cfm (160 fpm) through an open cell. Total air flow through the canyon is 37,500 cfm with all cell blocks in place and 75,000 cfm with a cell open.

Exhaust air from the process areas passes through the air tunnel to the 291-B exhaust filter. From the filter the air is discharged via the exhaust fans to the 200-foot process stack. A ventilation diagram of the service, operating, and process areas is shown in Figure IX-7.

5.4 291-B Exhaust Filter

The 291-B Exhaust Filter enclosure is a buried concrete structure approximately 51 feet in length, 32 feet wide, and 22 feet high. The existing structure contains two filter cells; the one in use and a spare cell. A cell contains four panels of 40, two feet by two feet absolute (CWS) filters arranged such that the air must pass through two banks of filters before being discharged. In addition to the two banks of absolute filters, a prefilter is located just upstream from the first filter bank. The prefilter consists of one hundred five Varicel-90 filters 20 x 25 x 6 fronted by a glass fiber pad called a Renu Filter*. The prefilters are

* Varicel and Renu are trade names of the American Air Filter Company, Louisville, Kentucky.

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FIGURE IX-6

of B-Plant Area

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FIGURE IX-7

Ventilation Diagram B-Plant Processing and Service Areas

arranged in three panels. The lower panel which is 11 units wide and five units high is stationary. The two upper panels which are five units high and five units wide may be lowered in front of the lower panel, similar to a window sash, removing the upper prefilters from the air stream. The prefilters will be lowered when the pressure drop across it becomes excessive. The Exhaust Filter enclosure is designed to permit the isolation of cells containing plugged or ruptured filters and the activation of the next cell through the use of water seals. Additional cells may be constructed as needed. An isometric view of the Exhaust Filter is shown in Figure IX-8, however, the prefilters have not been included in the drawing.

5.5 291-B Sand Filter

The 291-B Sand Filter was constructed for use in conjunction with the operation of the BiPO_4 process in 221-B. It is designed for up-draft air flow through a multi-layered filter media of graded sand and gravel. The buried concrete filter housing has been left intact and in the event of a sudden or unexpected failure of the absolute filters, the sand filter may be reactivated through the use of water seals; however, air flow from 221-B would be reduced to approximately 37,500 cfm. More complete details of the sand filter may be found in Drawings H-2-1377, H-2-1379 and H-2-1477.

FIGURE IX-8

291-B Exhaust Filter

5.6 291-B Exhaust Fans and Process Stack

The ventilation air from the 221-B is exhausted through a buried duct by fans located in the 291-B area. Two direct drive centrifugal fans, each rated at 37,500 scfm are used for the exhaust system. Each fan is equipped with a radial inlet damper which is used to control the air flow to the fan. The fans are driven by 100 HP, 440 V electric motors and are operated at 1175 rpm. A steam-driven fan, which also has a capacity of 37,500 scfm, serves as an emergency standby in the event of a power or mechanical failure of the electric fans. A vacuum control on the inlet duct automatically starts the steam turbine should the vacuum within the duct drop below 0.2 inch of water.

The ventilation air is discharged to the atmosphere from the top of a 200-foot reinforced concrete stack located adjacent to the fans. The stack is lined with a 5-foot ID acid-proof brick liner. Drainage in the stack is collected in a stainless steel sump pan at the base of the stack, and routed to a crib.

6. B-Plant Vessel Vent Systems

The B-Plant vessel vent equipment is located in Cell 22 and consists of two separate systems. The first system (Vessel Vent No. 1) is designed to vent and filter the gases from those process vessels which do not contain ammonia via Vent Header No. 22. The second system (Vessel Vent No. 2) is designed to vent, scrub, and filter gases from process vessels in which ammonia is present via Vent Header No. 146. A schematic of the Vessel Vent Headers is shown in Figure IX-9. Figure IX-10 is a schematic of the equipment in Cell 22.

6.1 Vessel Vent System No. 1

The vessel vent equipment for the No. 1 system is composed of a steam heater (E-22-3), a high efficiency filter assembly (F-22-5), a steam or air-operated jet (J-22-4), a condenser (E-22-4), a condensate receiving tank (TK-22-1), and a recycle drain pump (PA-22-1). Vent air from the process vessels enters the heater via Header 22 where it is heated above its saturation temperature before entering the filter assembly. In the filter assembly the dry gases are filtered through two banks of high efficiency - absolute type (CWS) filters, then pass to the 1200 cfm jet which discharges to the condenser. Condensable vapors are removed from the gas stream and the non-condensibles are discharged to the air tunnel. The condensed vapor drains into the condensate receiving tank where it is used as recirculating fluid for the Vessel Vent No. 2 ammonia scrubber tower. Excess condensate is pumped to the 216-B-12 crib.

6.2 Vessel Vent System No. 2 (Ammonia present)

The vessel vent equipment for the No. 2 system is composed of an ammonia scrubber tower (T-22-2), a condensate receiving tank (TK-22-1), a recirculating-drain pump (PA-22-1), a steam heater (E-22-7), a prefilter (F-22-6), three high efficiency filter assemblies (F-22-8-1, F-22-8-2, and F-22-9), and a steam or air operated jet (J-22-9). The condensate receiving tank and recirculating-drain pump are common to both vent systems. Contaminated gases from ammonia process vessels enter the ammonia scrubber tower via Header 146. The ammonium carbonate absorber tower in Cell 21 is also vented to the ammonia scrubber tower. Ammonia is scrubbed from the vent gases with condensate from the condensate receiver tank. Gases from the ammonia scrubber tower pass through the heater which raises the temperature of the gas above its saturation temperature and enters the prefilter. The prefilter, a multi-layered fiber glass filter, removes coarse particles from the gas prior to passage through the high efficiency filters. Two stages of double-banked high efficiency - absolute type (CWS) filters are used to assure adequate removal of radionuclide particles from the gas. The first stage high efficiency filter, located in Cell 22, consists of two double CWS filters connected in parallel. The second stage high efficiency filter

is located in a pit behind the 221-B Building adjacent to Cell 22 and consists of one double CWS filter. From the filters the gases pass through a 125 cfm jet also located in the pit behind the 221-B Building. The jet discharges to the 24-inch sewer going to the retention basins.

7. Chemical Tank Farm 211-B

The Chemical Tank Farm 211-B is located north of the 271-B Building and contains bulk storage facilities for many chemicals used in the Waste Fractionization processes. Also contained in this area is the Demineralizer Facility for process water (217-B). A plot plan of the chemical storage area is illustrated in Figure IX-11. Table IX-5 lists the chemical storage tanks by number, capacity, use, service pump number, and tanks and headers served directly by the tank.

TABLE IX-5
CHEMICAL STORAGE TANKS IN 211-B CHEMICAL TANK FARM

Tank	Volume	Chemical	Pump	Headers and Tanks Served
SA-101	8,000	57% Nitric Acid	PSA-5	309 Header, Tanks H302, H303, H304, H309, H318, H319, H321, and H501
SA-102	8,000		PSA-6	
SA-103	8,000			
SF-120	8,000	70% Hydroxyacetic Acid	PSF-3	Tank H502
SF-121	8,000		PSF-4	
SF-122	8,000			
ST-131	8,000	41% HEDTA	PST-15	Tank H503
ST-132	8,000		PST-16	
ST-133	8,000			
SQ-141	18,000	50% NaOH	PSQ-8	217 Bldg., 310-311 Header, Tanks H102, H301, TK301-1, H302, H303, H304, H305, H310, H311, TK402-1
SQ-142	18,000			
SQ-143	18,000			
MNB-173	18,000	Ammonium Carbonate (Make-up Tank)	PSN-7 PSN-7A	173 Header
SE-125	8,000	40% NTA	PSE-19 PCE-10	Tanks H315 and H316. (SE-128 is unlagged and used only as reserve.)
SE-126	8,000			
SE-127	8,000			
SE-128	8,000			
SD-111	18,000	Demineralized Water	PSD-18	111 Header
SN-172	12,200	Anhydrous Ammonia	--	MNB-173, 172 Header
SB-191	24 Ton	Carbon Dioxide	--	MNB-173, 191 Header
SO-151	20,000	n-paraffin hydro-carbon	PSO-22	MO-154
SO-152	11,500			
SK-161	11,500	Spare		

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FIGURE IX-9
Cell Vent Systems

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TK-22-1

Condensate Receiver
560 gal.
Coil Area - 240 ft²
Design Duty - 100,000 BTU/hr

PA-22-1

GPM 17
HP 2
Head 25 ft

T-22-2

Ammonia
Scrubber
Tower

E-22-7

Heater
Coil Area - 20 ft²
Design Duty - 17,000 BTU/hr

FIGURE IX-10

Vessel Vent Equipment

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FIGURE IX-11

Chemical Tank Farm, 211-B

8. Utilities8.1 Steam

The 200 East Area Power House, 284-E, supplies high pressure 225 psig (450 F) steam to B-Plant through an 8-inch overhead line which enters the B-Plant area at the SE corner. High pressure steam to the process stock area (219-B), 222-B Building, and the 224-B Building is supplied by branches from this line. The line continues around the west end of B-Plant and enters 221-B in the vicinity of Cell 37 on the

electrical gallery level. The main steam cut-off valve is located in the electrical gallery at this point. Two PRV stations in the pipe gallery, one near Cell 29 and one near Cell 15, reduce the high pressure steam to medium pressure, 100 psig steam. Low pressure steam used in the building heating system and in process vessel heating coils and jackets is provided by further reducing the medium pressure steam with additional PRV's. Separate PRV's are used to reduce medium pressure steam to 29 psig for the concentrators in Cell 5 and Cell 23. Medium pressure steam for the 271-B Building and the 211-B Tank Farm is supplied through an 8-inch line which leaves the pipe gallery in the vicinity of Cell 20. A simplified schematic of the steam trunk lines is shown in Figure IX-12.

FIGURE IX-12

Schematic of Steam Trunk Lines in 221-B

8.2 Compressed Air Systems

8.2.1 Process Air

Compressed process air for the B-Plant area is supplied from the compressor room in the basement of the 271-B Building. Equipment consists of one Worthington 782 cfm, two-stage duplex compressor and two 335 cfm single-stage Pennsylvania compressors. The compressors are arranged to start automatically as certain prescribed drops occur in header pressure; thus the system will be maintained around 95 psig over a wide range of demand. The air for the compressors is filtered before being compressed. The compressed air is routed through an aftercooler and then into two large air receivers located outside of the 271-B Building.

8.2.2 Instrument Air

Instrument air for the B-Plant area is supplied by a 300 cfm, 100 psig compressor located in the electrical gallery in the 221-B Building. The compressor is equipped with polytetrafluorethylene rings for oil-free operation. Supply air is filtered before being compressed. Interconnections exist between the process and instrument air systems; however, these are used only in an emergency.

8.2.3 Breathing Air

Four Mine Safety Appliance (MSA) clean air blowers with water separators are installed in an enclosure on the south side of the 221-B Building. Two of these blowers, operated by 3 HP Continental Electric motors, deliver 38 cfm of breathing air. The remaining two blowers are each driven by a 5 HP Louis Allis motor and have a combined capacity of 120 cfm. The total flow delivered by the four blowers can supply breathing air to a total of 32 mask outlets. The compressors were manually operated at the time this was written but may be converted to an automatic system through the use of existing line pressure switches. Breathing air is supplied to air manifold stations located in the canyon, the railroad tunnel, the pipe gallery, the operating gallery, and to the 211-B Chemical Tank Farm.

8.3 Raw Water

Raw or untreated water which is used for cooling water and for cell sprays is supplied to B-Plant from the 200 East Reservoir (282-E) through a 12-inch line entering the building on the east end, and a 10-inch line entering the building on the west end. The two lines are joined together in the operating gallery to form a loop system. Emergency raw water is provided from two wells located near the west entrance to the B-Plant enclosure. The diesel-driven pumps with which

the wells are equipped are capable of supplying 550 gpm of emergency cooling water. The emergency water supply is connected to the 10-inch raw water supply line with appropriate hand and check valves.

8.4 Sanitary Water

Sanitary (filtered) water is used in B-Plant for safety showers, drinking and toilet facilities, feed to the 217-B water demineralizer, and as emergency water in wall niches in the 221-B canyon. Lines to the wall niches in the canyon are equipped with backflow preventers as a protection against contaminating the sanitary water. Sanitary water is supplied to the B-Plant area from the 200 East Area filter plant (283-E) through an 8-inch line which enters the building near the northwest corner.

8.5 Process Water

Water used in B-Plant processes is prepared from the 200 East Area filtered water supply. As received, this water contains relatively large quantities of dissolved ionic impurities. Before being used in the process, the ionic impurities must be reduced. Purification is achieved by means of a two-stage ion exchange water demineralization unit. The unit has a capacity of 50 gpm and is regenerated every 8 to 10 days or 240,000 gallons. Regeneration of the units takes about two hours. Impurities present in filtered and process water are shown in Table IX-6. A more complete description of the demineralizer may be found in Chapter VI.

The location and layout of water mains which supply the B-Plant area are shown in Figure IX-6.

8.6 Electrical Power Distribution

Electrical power is furnished to B-Plant facilities by two normal power incoming lines, ES-153 and ES-158, and one emergency line, ES-166. These lines feed 2300 volt switchgear equipment in the 221-B Building electrical gallery. From the 2300 volt switchgears, power is fed to 2300 V/440 V transformers and to 2300 V/110-220 V transformers for power and lighting, respectively. These transformers are located on the north end adjacent to the 221-B Building. The 440 V power from the transformers is distributed to cubicles in the electrical gallery where switchgear equipment and distribution circuits for individual pieces of equipment are located. The lower voltage transformers feed lighting circuits and various small loads. If either one of the normal power incoming lines fail, its load can be switched at the 440 volt level to the other normal line.

A limited amount of emergency power is available to B-Plant in the event both normal electric power supplies fail. At the time this chapter was written only the regulated voltage circuit for instruments and the canyon door latch circuit switched automatically to the emergency line E8-166 when normal power failed. An emergency air compressor, a limited number of ventilation air supply fans, and some emergency lighting circuits will be added to the emergency power supply as power is made available. Emergency power for the 200 East Area is provided by a steam turbine-generator set located in the 284-E power house. Some battery-powered emergency lights, sparsely placed throughout the building, come on automatically in the event of a power failure.

TABLE IX-6
IMPURITIES IN FILTERED AND PROCESS WATER

<u>Constituent</u>	<u>Filtered Water</u>	<u>Process Water Specifications</u>
Total Hardness (as CaCO_3)	55-80 ppm	2 ppm
Calcium	20-40	0.2
Magnesium	4-5.5	0.01
Strontium	0.13*	0.01
Sodium	--	0.1
Chloride (as NaCl)	1-5	0.6
Sulfates (as Na_2SO_4)	14-30	1.5
Dissolved Solids	85-110**	4.5***
Silica (as SiO_2)	3-7.5	7.5
pH	7.6-8.1	5-8

* Raw Water Concentration

** Includes Silicates

*** Excluding Silicates

C. WASTE STORAGE TANK FARMS

The complex of waste storage tanks at Hanford include 149 tanks ranging in capacity from 50,000 to 1,000,000 gallons. These tanks are grouped in twelve tank farms located in the 200 East and 200 West Areas up to ten miles apart. Some general information about these tanks is tabulated in Table IX-7.

TABLE IX-7
WASTE STORAGE TANKS AT HANFORD

<u>Farm</u>	<u>Tanks per Farm</u>	<u>Capacity per Tank, Gallons</u>	<u>Capacity per Farm, Gallons</u>	<u>Year Constructed</u>	<u>Type</u>
A	6	1,000,000	6,000,000	1954-55	Boiling
AX	4	1,000,000	4,000,000	1963-64	Boiling
B	16	54,500 (4) 530,000 (12)	6,578,000	1943-44	Non-Boiling
BX	12	530,000	6,360,000	1946-47	Non-Boiling
BY	12	758,000	9,096,000	1948-49	Non-Boiling
C	16	54,500 (4) 530,000 (12)	6,578,000	1943-44	Non-Boiling
S	12	758,000	9,096,000	1950-51	Non-Boiling
SX	15	1,000,000	15,000,000	1953-54	Boiling
T	16	54,500 (4) 530,000 (12)	6,578,000	1943-44	Non-Boiling
TX	18	758,000	13,644,000	1947-48	Non-Boiling
TY	6	758,000	4,548,000	1951-52	Non-Boiling
U	16	54,500 (4) 530,000 (12)	6,578,000	1943-44	Non-Boiling

1. Non-Boiling Tank Farms

1.1 General Description of Non-Boiling Tank Farms

The tanks in the nine non-boiling tank farms are of three sizes, 54,500 gallons; 530,000 gallons; and 758,000 gallons as indicated in Table IX-7. The 530,000-gallon and the 758,000-gallon tanks are arranged in three, four, or six tank cascades. That is, the tanks are arranged in such a manner that when the first tank in a cascade is filled it overflows to the second tank and so on. Through the years as various programs have been instigated, many of the overflows between tanks in the various cascades have been removed, modified, or blanked off. In 1952 as part of the Uranium Recovery Program, sluice pits, diversion boxes, and transfer lines were installed in the tank farms. Section D of this chapter will discuss the transfer facilities in greater detail.

1.2 Layout of the Non-Boiling Tank Farms

Plot plans of the non-boiling tank farms are shown in Figures IX-13 through IX-19.

1.3 Construction of Non-Boiling Waste Tanks

The non-boiling waste tanks are constructed of reinforced concrete with a mild steel liner on the bottom and side walls. The tanks are placed with the top of the dome about seven feet below the surface of the ground. The earth serves both as shielding and as a sink for dissipation of the heat from radioactive decay. A number of the tanks are equipped with air-cooled reflux condensers. Dry wells located within the tank farms are used to monitor the soil for radioactivity thus serving as a leak detection system.

1.3.1 530,000-Gallon Waste Tank

The 530,000-gallon waste tanks, located in the B, BX, C, T, and U tank farms, are the oldest or first generation waste storage tanks. The tanks are of the type shown in Figure IX-20. They are 75 feet in diameter and store liquid to a depth of 16 feet.

1.3.2 758,000-Gallon Waste Tanks

The 758,000-gallon waste storage tanks, located in the BY, TX, TY and S tank farms, are second generation waste storage tanks. The tanks are similar to the 530,000-gallon tanks in that they are 75 feet in diameter; however, they are designed to hold wastes to a level of 22 feet.

FIGURE IX-14

Layout of BX and BY Tank Farms
(Based on H-2-44501)

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FIGURE IX-15

Layout of C Tank Farm
(Based on H-2-61962)

FIGURE IX-16
Layout of S Tank Farm
(Based on H-2-44511)

FIGURE IX-17
 Layout of T Tank Farm
 (Based on H-2-44511)

FIGURE IX-18

Layout of TX and TY Tank Farms
(Based on H-2-44511)

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FIGURE IX-19

Layout of U Tank Farm
(Based on H-2-44511)

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FIGURE IX-20

Storage Tank for Non-Boiling Waste

1.3.3 54,500-Gallon Waste Tanks

Four smaller tanks are located in each of the B, C, T, and U tank farms. These tanks are 20 feet in diameter and are filled to a depth of 24 feet. The tanks were originally designed to hold a highly radioactive cake from a scavenging-precipitation process on Bismuth Phosphate wastes. However, the tanks were never used for this purpose. Instead, general high-level non-boiling waste solutions are stored in them.

2. Boiling Tank Farms

2.1 General Description of the Boiling Tank Farms

There are three boiling waste tank farms - A, AX, and SX, containing 6, 4, and 15 waste storage tanks, respectively. The SX tank farm was the first tank farm designed specifically to handle boiling waste solutions. The A tank farm was built to handle Purex plant wastes and incorporated a number of new features developed during the operation of the SX tank farm. The AX tank farm, the latest one built, also handles Purex wastes and includes improvements not found in the A farm. These additional features are discussed in the following sections. As with non-boiling tanks, the waste tanks are constructed of reinforced concrete with carbon steel liners on the bottom and side walls. The tanks have a diameter of 75 feet and a height of 44 feet 4 inches from the top of the dome to the bottom of the tank. The working height of the tank, that is the height to which solutions can be stored, is 32.5 feet. The nominal capacity of the tank is one million gallons. The boiling waste tanks are designed to permit self-concentration of the wastes. The vapors are routed through headers to condensers which are vented to the atmosphere through filters. Condensate is either discarded to ground or returned to the waste tank. The contents of the waste tanks are agitated by means of air-lift circulators. Leak detection in the boiling waste tank farms is provided by a system of dry wells or drainage grids. A sketch of a boiling waste tank is shown in Figure IX-21.

FIGURE IX-21

Storage Tank for Boiling Waste

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2.2 241-A and AX Tank Farms

Because of their close proximity to one another, the A and AX tank farms have many common facilities such as the air supply, vent headers and condensers, normal and emergency electrical supply, and a number of miscellaneous services and buildings. The layout of the A and AX tank farms is shown in Figure IX-22. Common facilities include the following:

Process Air - used for the air-lift circulators is supplied by three 50-horsepower, vertical, single cylinder, piston-type units built by the Joy Manufacturing Company. Each compressor has a nominal capacity of 360 cfm with a discharge pressure of 40 psig. The compressors are located in the compressor building, 241-A-701.

Instrument Air - is supplied by two 25 cfm, 35 psig compressors.

Electrical Power - for the A and AX tank farms is supplied from a 300 KVA 2400/480 volt three-phase transformer. Emergency power for the air compressors and other auxiliary equipment is supplied by a 125 KVA diesel-driven generator located in the compressor building. A 35 KVA gasoline-driven generator supplies emergency power to the control building and the emergency cooling water system. Both emergency electrical systems start and switch automatically in the event of a primary power failure.

Vent Header and Condensers - All of the tanks in the A and AX tank farms are connected to a common vent header, sometimes referred to as the vacuum header. Water seals are used to isolate non-boiling tanks from the vent system. Air and water vapor from the waste tanks are routed through the vent system to three surface and two contact condensers located in the condenser building - 241-A-401. Individual condensers can be isolated from the vent system by means of water seals.

The water seals to the contact condensers will automatically blow and activate these condensers when the differential pressure exceeds 30 and 34 inches of water. Other water seals will blow by-passing the condensers should the differential pressure exceed 66 inches of water. Non-condensable gases pass from the condensers, through a deentrainment vessel and are exhausted through filters to the atmosphere. Three exhaust blowers, two in operation and one on stand-by, of 600 cfm keep the vent system under a vacuum. Cooling water for the condensers is supplied by gravity flow from the 201 tank just east of the 202-A (Purex) building. The 750,000-gallon 201 tank is automatically kept filled with used cooling water from 202-A. Condensed vapors are collected in the 14,000-gallon 417 tank. The condensate can either be pumped back to a waste tank, or allowed to overflow to the A-24 crib.

Miscellaneous Service Buildings - Service buildings located in the A and AX tank farm area include a Change House (2707-EB), and a Control House (2711).

A comparison between the A and the AX tank farm is given in Table IX-8, and pertinent features of each tank farm are discussed in the following sections.

TABLE IX-8
A AND AX TANK FARM COMPARISON

	<u>AX Tank Farm</u>	<u>A Tank Farm</u>
Number of tanks	4	6
Maximum volume of concentrated waste that can be stored per tank (gal.)	1,000,000 at 1.8 SpG	840,000 at 1.37 SpG
Vapor Pressure Allowed	2.24 psi	2.25 psi
Tank Dome Live Load	40 psi plus a 50 T concentrated load	28-ton con- centrated load
Earth Cover	6.5 to 7.5 ft	7 ft
Number of Air-lift Circulators	22	4
Leak Detection	Internal	External
Vapor Handling Facilities	---	Common ---
Number of Risers in Tank Dome	54	13
Temperature Elements	59	9

2.2.1 A Tank Farm

A cross-section of a waste storage tank in the 241-A tank farm is shown in Figure IX-23. Each tank is equipped with four air-operated circulators, except tank 101-A, which has 5. The lower end of the circulators are positioned 18 inches from the bottom of the tank. Two circulators are designed for agitation of liquid greater than 19 feet from the bottom. The circulators can "turn over" liquid at up to 4000 gpm with maximum air flow at 10 cfm. Instrumentation on the A farm tanks include electrode type liquid level measurement, weight factor

FIGURE IX-23

Cross Section of A Farm Waste Storage Tank

bubbler tubes, pressure-vacuum instruments, and approximately 9 temperature measuring elements. For leak detection, a system of 44 vertical dry wells plus three laterals under each tank has been installed to permit taking radiation detection probe readings. The three laterals utilize air pressure to force a probe through the horizontal distance.

2.2.2 AX Tank Farm

The waste storage tanks in the 241-AX Tank Farm are basically similar to those in the 241-A Tank Farm. A composite cross-section of an AX Farm tank is shown in Figure IX-24. There are 22 air-lift circulators in the AX Farm tanks, 17 being 22 feet long, and 5 being 17 feet long. The taller circulators require a tank volume of 800,000 gallons to operate, and the shorter ones require a volume of about 600,000 gallons. All of the circulators are located 30 inches from the bottom of the tank. Normally, each circulator requires about 5 cfm of air.

FIGURE IX-24

Cross Section of AX Farm Waste Storage Tank

A total of 59 iron-constantan thermocouples is installed in each of the AX Farm waste storage tanks. Each of the air-lift circulators has a temperature element below it that extends to within three inches of the tank bottom, and is used to help determine malfunction of a circulator. Twenty-one thermocouples are installed within each storage tank's con-

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crete structure. Twelve thermocouples are in thermowells within the storage tanks and are used to measure temperature gradients in the stored waste at four different locations. The remaining thermocouples are located at various places in the tank to record sensitive areas.

Other instrumentation on the AX storage tanks include float-actuated liquid level measuring devices, air-purged dip tubes to sense tank pressure and liquid level in excess of 30.5 feet, sludge level meters, and radiation probes. Each storage tank in the AX Farm has its own internal leak detection system. This consists of a network of drain slots in the concrete base immediately below the carbon steel tank liner. The drain network is connected to a leak detection well from which any leakage can be pumped.

2.3 241-SX Tank Farm

The 241-SX Tank Farm consists of fifteen, 75-foot diameter tanks arranged in five cascades of three tanks each. The layout of the 241-SX Tank Farm is shown in Figure IX-25. The original design provided for four 12-inch risers, four 4-inch risers and one 42-inch riser on each tank; however, modifications to the tank farms have made it necessary to use some of these risers for other purposes. Waste can be routed directly to each tank in the tank farm, or the filling can be done by cascading. Vapor generated by the heat of radioactive waste in the SX Tank Farm is condensed in water-cooled condensers located in the 401 Condenser Building adjacent to tank 106-SX. Vapors from each tank are carried via headers to tank 106-SX where some condensation takes place and entrained liquids drop out. From tank 106-SX, the vapors are routed to the condensers, and uncondensable gases are then exhausted to the atmosphere.

Emergency cooling water for the condensers is provided by two, 150,000-gallon water storage tanks located near the 401 condenser house. Condensate may be routed to a crib, or it may be returned to tank 106-SX or to any of the other tanks.

A special air-purge tank cooler has been installed on tank 108-SX making it necessary to remove that tank from the tank farm vent system. The special equipment consists of a 7000 cfm exhauster, a heater to keep the temperature of the exiting air above the dew point, and a bank of high efficiency filters to remove particulate matter. The air is exhausted to atmosphere through a 15-foot stack in the tank farm.

Air-lift circulators were developed to overcome the bumping phenomenon first observed in tank 101-SX. Tanks 101-SX and 104-SX each contain one air-lift circulator. Tanks 107 through 115 each contain four circulators. Two of the circulators are designed to discharge at the 10-foot level and two discharge at the 15-foot level.

FIGURE IX-25

Layout of SX Tank Farm
(Based on H-2-44511)

Process air for the air-lift circulators is supplied by two, forty-horsepower Fuller rotary type compressors located in the compressor house. Instrument air is supplied by two five-horsepower De Vilbiss piston type compressors also located in the compressor house. The compressors are alternated in service, and are so arranged that the standby unit will start should the operating unit stop.

Each tank 107 through 115 has an instrument shack located adjacent to it. The instrument shacks contain instruments for specific gravity, differential pressure between the inside and outside of the air-lift circulators, air flow to the circulators, temperature measurements, and static pressure.

D. WASTE TRANSFER FACILITIES

1. General Description of Waste Transfer Facilities

In 1952, a network of underground lines and transfer stations was installed to connect many of the underground tanks with the building used to recover uranium from the stored wastes from the bismuth phosphate process. These lines are constructed of stainless steel tubing about three inches in diameter and are contained in concrete trenches. Multiple lines interconnect the older tank farms in each area with a pumping station, and the two pumping stations are interconnected by multiple inter-area transfer lines.

Facilities for transferring wastes between tanks, and for routing wastes to the desired tanks were included in the design of the A and AX Tank Farms. A facility for the accumulation and dissolution of stored sludge waste has been built adjacent to the A and AX Tank Farm. This facility is called the 244-AR Vault.

2. 244-AR Vault

The 244-AR Vault is designed to accumulate and acidify stored sludge waste sluiced from the waste storage tanks in the A and AX Tank Farms. The AR Vault also includes a lag storage tank for current Purex acid waste (PAW and ZAW) enroute to B-Plant for processing and a lag storage tank for neutralized high-level waste (NHW) enroute from B-Plant to the A or AX Tank Farm.

2.1 Layout of 244-AR Vault Area

The layout of the 244-AR Vault Area is shown in Figure IX-26. Facilities included in the AR Vault area include the vault canyon or process area, service building, filter building (291-AR), change house, air compressor, emergency electrical generator, two chemical storage tanks, vessel vent stack (291-AR-B), ventilation stack (291-AR Stack), and sluicing and routing system.

FIGURE IX-26

Layout of 244-AR Vault Area
(Based on H-2-61988)

2.2 Description of 244-AR Vault Buildings

The 244-AR Vault process area consists of a reinforced concrete structure approximately 97 feet long and 21 feet wide. The process area is divided into three cells plus a failed equipment storage area all located below grade level. Two of the cells are 21 feet square and 32 feet 9 inches deep. The 50,000-gallon PAW Transfer Tank (TK-001) is located in one of these cells, and the 50,000-gallon Slurry Accumulator Tank (TK-002) is located in the other. The third cell is 32 feet long, 12 feet wide and 21 feet deep. The 5000-gallon Neutralized High Level Waste Tank (TK-003), and the 5000-gallon Sludge Acidification Tank (TK-004) are located in this cell. The process cells are covered by interlocking concrete cover blocks 5 feet thick. The cover blocks over the equipment storage area are two feet thick.

The area above the cells is enclosed by a reinforced concrete building approximately 36 feet in height above the cover blocks. A remotely operated crane with four 1-ton hoists and one 20-ton hoist operates along rails located 30 feet above the deck. The crane is operated from a control room located midway along and 7 feet south of the canyon building. The reinforced walls of the crane control room provide additional shielding to the crane operator when the cell cover blocks are removed. A periscope and a closed circuit television system in the crane control room provide for remote viewing of operations within the vault process area. The floor plan of the AR Vault is shown in Figure IX-27, and an elevation view is shown in Figure IX-28.

2.3 244-AR Vault Equipment and Facilities

2.3.1 Tanks

Four process tanks, two chemical storage tanks, and an aqueous make-up tank are included in the AR Vault. The function, volume, and major pieces of equipment installed on the tanks are shown in Table IX-9.

2.3.2 Ventilation

Ventilation air for the service area and the crane control room is supplied by a 5700 cfm fan located on the roof of the service area. The air is filtered, water washed, heated and distributed through ducts to the control room, rest room, sample room and crane control room. The air is exhausted to atmosphere from the service area through two 1700 cfm exhaust fans. From the rest room air is exhausted through an 1100 cfm ventilating fan, and from the chemical make-up tank it is exhausted through a 200 cfm exhaust fan. The crane control room is vented to the atmosphere through a dampered port. The sample room is vented through a dampered opening into the canyon. The damper is controlled so the air flow is always into the canyon.

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FIGURE IX-27
Floor Plan of 244-AR Vault
(Based on H-2-61991)

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1
H-2-61991 SCALE: 3/8" = 1'-0"

2
H-2-61991 SCALE: 3/8" = 1'-0"

3
H-2-61991 SCALE: 3/8" = 1'-0"

FIGURE IX-28
 Elevation of 244-AR Vault
 (Based on H-2-61993)

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TABLE IX-9
TANKS IN THE 244-AR VAULT

<u>Tank</u>	<u>Function</u>	<u>Volume, gallons</u>	<u>Equipment</u>
001	PAW Storage	50,000	Pump, agitator
002	Slurry Receiving	50,000	Pump, sluice pump, agitator
003	FP Waste Storage	5,000	Agitator
004	Acidification Tank	5,000	Agitator, Radiation Mon. dry well
A10	Nitric Acid Storage	8,000	Pump
A20	Caustic Storage	1,300	Pump
A30	Aqueous Make-up	800	Agitator

Ventilation air for the canyon and process cells is supplied by a 21,500 cfm supply fan which is also located on the roof of the service building. The filtered, water-washed, and heated air is delivered to the canyon at two places through the roof of the building. The air passes through the canyon and into the process cells through two ducts located at the west end of the building. The air sweeps through all three cells and is exhausted from Cell 1 through an underground duct to the filter building. The filter building provides for filtering the air through two banks of high efficiency filters before exhausting the air to atmosphere through a 61-foot high concrete stack. Two 24,300 cfm exhaust fans are used, one in operation and one on standby. The No. 2 fan is connected to the emergency electrical supply and will automatically start should there be a failure of the normal electric power.

2.3.3 Vessel Vent

The four process vessels, TKS-001, 002, 003, and 004, in the AR Vault are vented by means of a vessel vent header. The off-gases are heated well above the dew point and filtered through two stages of high efficiency filters. The heater and filter are located in Cell 3 of the Vault Canyon. The filtered gases are discharged to atmosphere through a 150-foot vessel vent stack. The vessel vent exhaust fan is rated to deliver 525 cfm at 12 inches of water vacuum.

2.3.4 Pumps

In general the pumps used for process solutions in the AR Vault are single stage vertical centrifugal pumps. Except for a brief description of the Sluice Pump and the Waste Recovery Pump, detailed information about the pumps is included in Chapter X and will not be discussed here.

The Sluice Pump, located in tank 002, is designed to pump the recirculating sluicing solution under high pressure to the sluicing nozzles located in the underground storage tanks. The pump is specified to deliver a solution with a specific gravity of 1.5, a viscosity of 1.02 cps., and a temperature of 176 F at 600 gpm with a 390-foot head.

The Waste Recovery Pump is used to pump the sludge slurry from the underground storage tanks to the Slurry Receiving Tank in the AR Vault. The pump is a single stage suction, vertical centrifugal pump with radial discharge from the impeller. The pump is specified to pump a slurry containing 1 pound per gallon solids having a specific gravity of 2.2 and a maximum dimension of 1.0 inch. The slurry has a specific gravity of 1.6, a viscosity of 0.83 cps at a temperature of 220 F. The normal capacity of the pump is specified to be 660 gpm with a head of 116 feet.

2.3.5 Utilities

Utilities available to the 244-AR Vault include the following:

Water - Filtered untreated water for cooling is supplied from the 200-E raw water supply system through an 8-inch supply line. Sanitary water from the area supply is delivered to the AR Vault through a 6-inch supply line. Emergency cooling water is available from the sanitary water supply by means of an intertie between the sanitary and raw water supply through a back-flow preventer.

Steam - from the 200 E power house is received at 225 psig and reduced to 100 psig for use in jets and the vessel vent off-gas heater. Low pressure, 20 psig, steam is used in the tank coils and in the building heating and ventilation systems.

Electricity - is supplied through a 750 KVA 13,800 volt primary and 480 and 277 volt secondary transformer. Emergency electrical power is supplied from a 90 KVA diesel generator located adjacent to the Vault. The emergency power is sufficient to operate one canyon ventilation exhaust fan and the vessel vent exhaust fan.

Compressed Air - Information on the air compressor that supplies the process and instrument air for the AR Vault was not available when this chapter was written.

2.4 Sluicing Facilities

Facilities for sluice mining sludge from the underground waste storage tanks have been installed in the A Tank Farm. At the time this manual was written sluicing facilities for the AX Tank Farm were in the design stage and are not included here. However, the sluicing equipment in the AX Tank Farm will be similar to that in the A Tank Farm. Facilities needed to sluice mine the underground storage tanks are as follows: 1) a sluice pump and waste recovery pump. (Pumps are discussed in Section D. 2.3.4. and in Chapter X.); 2) pump pits, sluice pits, and diversion boxes all are discussed in Section D. 3.; and 3) sluicing nozzles. The sluicing nozzles are discussed in detail in the references and are described only briefly here. The sluicing nozzles are suspended approximately 31 feet below the support flange into the storage tank. The nozzles may be rotated 360 degrees in the horizontal plane and 110 degrees in the vertical plane. The nozzle has a 1-inch opening and is designed to impinge 75 percent of the stream within a 12-inch diameter circle at a distance of 50 feet at a minimum tip pressure of 100 pounds per square inch. The sluicer is equipped with an electrical driven oscillating cam designed to swing the nozzle through a horizontal arc variable from 5 to 120 degrees at a frequency of 1 cycle per minute.

In A Tank Farm the Waste Recovery Pump is located in the pump pit near the center of the tank. The Waste Recovery Pump is used to pump the slurried sludge loosened by the sluicers from the storage tank, through the 153-A Diversion Box to TK-002 in the AR Vault. Those transfer lines used to transport slurries from the underground tanks to the AR Vault, and sluicing solution back to the tanks are all 6-inch, schedule 40 direct buried carbon steel pipe.

3. A and AX Transfer Facilities

Transfer of solutions into, out of, and within the A and AX Tank Farms is accomplished by means of stainless steel lines contained in concrete trenches or directly buried carbon steel pipe. The lines terminate at risers from the underground tanks, pump pits or sluice pits above the tanks, diversion boxes or diverter stations located in or near the tank farms.

3.1 Pump Pits

Each waste storage tank in the A Tank Farm has a pump pit 12 feet long, 11 feet wide, by 7.5 feet deep with 2.5-foot thick block covers. The pump pits are centered on top of the underground storage tanks. The 42-inch flanged pump riser from the tank and two discharge nozzles are located in the pump pit. One discharge nozzle is connected

to the 4-inch carbon steel inter-tank transfer line V-032 and the other discharge nozzle is for the 6-inch carbon steel line to the 152-A Diversion Box. This latter line is the line through which the sludge slurry will be pumped when the tank is sluice mined. A three-inch drain in the bottom of the pit empties to the tank below. Spray nozzles and nozzles to route water to the pump from an adjacent valve pit are also located in the pump pit. See Figure IX-23 for the location of the pump pit in relation to the rest of the tank.

The pump pits in the AX Tank Farm are 7.5 feet long by 6 feet wide by 7.5 feet deep with 2.5-foot thick cover blocks. The center line of the pump pit is located 7 feet 3 inches from the center of the tank and contains two 12-inch risers for pump mounts. A 4-inch pump pit floor drain extends to within 5 feet of the bottom of the tank. Each pump pit contains two discharge nozzles, one a spare and the other connected to the 3-inch carbon steel pump-out header line 4026. The location of the pump pits can be seen in Figure IX-24.

3.2 Sluice Pits

Each tank in the A Tank Farm has two sluice pits in addition to the pump pit. Sluice pits in the AX Tank Farm were not constructed at the time this manual was written. The sluice pits are 6 feet long, 6 feet wide, by 3-1/2 feet deep and are covered by a two-foot thick cover block. Each pit contains a 12-inch flanged riser for the sluicer, a 4-inch nozzle for sluicing solution, four spray nozzles, and a floor drain back to the waste tank. The sluice pits are located 28 feet from the center of the tank and on four of the tanks are oriented on a NW-SE axis. The reader is referred to Figure IX-29 and the appropriate reference drawings for the proper location of the sluice pits. The sluice pits in the A Tank Farm receive their sluicing solution from the AR Vault via Diversion Box 153-A.

3.3 Diverter Stations

A diverter station operates similar to a switch board in that highly radioactive waste solutions can be routed to a selected underground waste storage tank, the AR Vault, or the CR Vault. This is accomplished by means of diverter tanks within the diverter station. Transfer lines leading into the stations terminate in the diverter tanks. The waste solution overflows the diverter tank through a movable spout into a funnel on a transfer line leaving the station. A routing change is made by moving the spout to the proper funnel. Positioning the spout is done with a shaft that extends through the cover block to a handle located above the station. Illustrations of diverter stations are shown in Figures IX-30 and XII-16. Since diverter tanks rely on gravity flow, the flows are unidirectional and are limited to less than 150 gallons per minute.

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NEW DIVERTER STATION FOR HIGH LEVEL RADIOACTIVE LIQUID WASTES

FIGURE IX-30

Diverter Station

There are two diverter stations associated with the waste transfer facilities in the A and AX Tank Farms. Diverter station 151-AX is 41 feet 4 inches long, 10 feet wide, and 24 feet 10 inches high. The station contains four diverter tanks, C, D, E and F, located in individual cells. An 11,000-gallon stainless steel lined catch tank is located below the diverter tanks. Drainage into the catch tank can be pumped or jetted to diverter tank E or F.

Various high level wastes from the Purex plant are routed to the diverter tanks in the 151-AX station as indicated in Figure IX-31. Depending on the disposition of the waste, it may be routed to an underground storage tank in the A farm, to Tank 003 in the 244-CR Vault, to Tank 001 in the 244-AR Vault, or to one of the two diverter tanks in Diverter Station 241-AX-152.

Diverter Station 152-AX contains two diverter tanks, A and B, located in a common cell. The dimensions of the station are 25 feet 2 inches

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FIGURE IX-31

Simplified Diverter Station Transfer Routes

long, 9 feet wide, and 29 feet 2 inches high. There is also an 11,000-gallon stainless steel lined catch tank located beneath the two diverter tanks in this station. The diverter tanks in the 152-AX station are used to route solutions to the existing tanks in the AX Tank Farm. Stubbed lines exist for four future underground waste storage tanks in the proposed AY Tank Farm. The catch tank in the 152-AX station may be pumped or jetted to diverter tanks D or G in the 151-AX station.

3.4 Diversion Boxes

Diversion boxes are essentially piping "patch boards" which are used to minimize duplication of piping and allow the changing of line routings without the use of valves. Diversion boxes are used when the line must be under pressure while diverter stations are used for gravity flow only. The diversion boxes are concrete pits with the pipes passing through the concrete and terminating in remote connector nozzles inside. Two diversion boxes, 151-A located on the south side of the Purex plant, and 152-A located at the east end of the A Tank Farm were originally used to route all high-level wastes to the various tanks in the A Tank Farm. Now, however, the majority of the high-level waste is handled by the diverter stations discussed in Section D. 3.3 above and the 151-A and 152-A diversion boxes are used to route coating wastes from the Purex plant to the C Tank Farm.

Two new diversion boxes have been built as part of the sludge removal facilities in the A and AX Tank Farms. These two new boxes are the 153-A and the 153-AX Diversion Boxes. The new boxes route the high pressure solution used for sluice mining sludge from the 244-AR Vault to the desired sluice pit on the tank, and route the sludge slurry pumped from the tank to the 244-AR Vault. These routings are shown in Figure IX-29.

An illustration of a diversion box is shown in Figure IX-32 and in Chapter XII, Figure XII-14.

4. Other Waste Transfer Facilities

Other waste transfer facilities which are or may be used in the Waste Management Program are briefly described below. More detailed information may be found in appropriate prints and references.

4.1 244-CR Vault

The 244-CR Vault located in the C Tank Farm contains two 40,000-gallon tanks (001-CR and 011-CR) and two 15,000-gallon tanks (002-CR and 003-CR). The two 15,000-gallon tanks have cooling coils, but the two 40,000-gallon tanks do not. All of the tanks are equipped with agitators, pumps, samplers, and appropriate instrumentation. Tank 003-CR is used as a lag storage tank for acidified sludge waste (FAS) between the AR Vault and B-Plant. The 002-CR tank is used to store miscellaneous special fission product fractions. The two larger tanks, 001-CR and 011-CR, are used to collect and transfer a variety of waste solutions in and out of the C Tank Farm.

4.2 244-BXR, 244-TXR, 244-UR Vaults

There are three other vaults similar in construction to the 244-CR Vault. These are 244-BXR, 244-TXR, and 244-UR Vaults. However, the 244-TXR and 244-UR Vaults do not contain a Oil Tank. At the time this manual was written these vaults were not being used.

4.3 241-WR Diversion Station

The 241-WR Diversion Station is another vault-like structure located adjacent to the 221-U Building. This vault contains nine 50,000-gallon tanks. At the time this section of the manual was being written the 241-WR Vault was not being used.

4.4 Inter-Area Transfer Lines

A 6-line buried pipe encasement connects Diversion Box 154-UX, adjacent to the 221-U Building in 200 West Area with Diversion Box 151-ER southwest of B-Plant in 200 East Area. The 151-ER and the 154-UX Diversion Boxes are each connected to other diversion boxes in their respective areas. Virtually all of the waste storage tanks in all of the tank farms may be connected together through diversion boxes and the inter- and intra-area transfer lines.

4.5 Other Diversion Boxes

Practically all of the lines used to transfer high level waste within or between facilities in the chemical separations complex originate or terminate in Diversion Boxes. The Diversion Boxes serve as "Patch Boards" by which the various facilities may be interconnected. Very likely, all of the many diversion boxes in the 200 Areas will be used in the Waste Management Program at one time or another.

Four diversion boxes, not previously mentioned in other sections of this chapter, have a special use and are listed below.

151-CR - Used to route coating wastes into and out of C Tank Farm.

151-C - Used to route PSN and PSS from the AR Vault and from the pump pit on 101-A Tank to the 105-C Tank.

152-C - Used to route PSN from 105-C to B-Plant.

154-B - B-Plant Diversion Box. PSN from 105-C passes through 154-B enroute to B-Plant as well as 152-C. Non-boiling high-level salt waste from the waste concentrator in Cell 24 is routed to the ITS units in the BY Tank Farm via 154-B.

FIGURE IX-32
Diversion Box

DRAWING INDEX

A drawing index for the entire Waste Management complex would include a number of indexes for separate facilities and projects. A complete index would be quite long; therefore, the index included in this section of the Waste Management Technical Manual includes only a list of the other indexes, a list of the Engineering Flow Diagrams, and a few other pertinent, often-used drawings. The reader should refer to the other drawing lists to find additional information.

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PART V, Continued
PLANT AND EQUIPMENT
CHAPTER X
PROCESSING EQUIPMENT

By

R. A. Kyle

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PART V: PLANT AND EQUIPMENT, ContinuedCHAPTER XPROCESSING EQUIPMENT

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CHAPTER XPROCESSING EQUIPMENTA. INTRODUCTION

The Waste Management facilities involve the operation of a wide variety of process equipment such as tanks, concentrators, condensers, centrifuges, pulse columns, an ion exchange column, an adsorber, and a scrubber. Some of the equipment is new, but a large portion has been relocated from the Uranium Recovery Plant (221-U), T-Plant (221-T), and within B-Plant (221-B) itself.

1. Equipment Notations

The following notations are used in identifying the process equipment:

- A - Agitator
- E - Heat Transfer Equipment
- F - Filter
- G - Centrifuge
- J - Jet
- P - Pump
- PA - Pump Agitator
- T - Tower
- TK - Tank

The process equipment is referenced to a particular cell by an assigned piece number. For example, TK-13-1 denotes Tank (TK), Cell 13 (13), and piece 1 (1). Accordingly, the equipment in the AR and CR Vaults is identified by an AR or CR.

2. Process Equipment Classification

The term "vessel" designates all non-mechanical equipment pieces containing a liquid or gaseous stream. In the Waste Management facilities the following three types of vessels are used:

- 1) Class I vessels are made of stainless steel and are designed to contain radioactive materials. They are designed for remote maintenance and handling.
- 2) Class II vessels are also made of stainless steel but are not intended for radioactive materials. They are designed for contact maintenance.
- 3) Class III vessels are those which are fabricated from materials other than stainless steel and are not designed to contain radioactive materials. They are designed for contact maintenance.

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2.1 Class I Vessels

Class I vessels are essentially of all-welded stainless steel construction with carbon steel used only for necessary external attachments. The carbon steel attachments are protected with a coating of Amercoat* and are not in contact with process solutions. Double butt welds are used for pressure-holding seams where possible. The quality of the welds is controlled by radiographic testing or by other specialized techniques depending on the location of the weld.

Special construction features which allow installation or removal of the equipment with a crane are necessary for remote maintenance of the equipment. Thus, the equipment piece must be provided with remote connector nozzles for lines up to 4 inches in diameter and with remote flanges for larger size lines. The equipment must be provided with lifting bails so placed that when suspended it will be balanced and will hang essentially in its installed position. Dowels and aligning holes or trunnions and trunnion guides are provided to position the equipment in its designated location. The equipment is fabricated to unusually close tolerances in order that replacement equipment or parts may be readily installed.

2.2 Class II Vessels

Class II vessels, like Class I vessels, are of all-welded stainless steel construction with carbon steel used only for supports and attachments not in contact with a process solution. Examples of Class II vessels are the AMU tanks, the head tanks and weigh tanks in the operating gallery, and certain chemical storage tanks in the 211-B Chemical Tank Farm. As the vessels do not contain radioactive solutions it is possible to perform contact maintenance on them and the design tolerances are less stringent than with Class I vessels.

For the design and fabrication of Class II vessels as pressure vessels, the general requirements of the A.S.M.E. Boiler Construction Code were followed. Basic design pressures were taken to be an internal pressure of 15 psig or 110 percent of the operating pressure, whichever is greater, and an external pressure of 5 psig.

For the design and construction of Class II atmospheric tanks, the general requirements of the American Petroleum Institute Standard 12C were followed. Designs were for the maximum internal pressure imposed by a liquid of 1.8 specific gravity with loads due to wind pressure and earthquake forces also considered.

* Trade name of Amercoat Corporation

2.3 Class III Vessels

Specifications for Class III vessels are similar to Class II vessels except the Class III vessels are constructed of materials other than stainless steel. Examples of Class III vessels are the ammonia storage tank, the carbon dioxide storage tank, the caustic storage tanks, and the diluent storage tanks.

B. CANYON AND VAULT TANKS

1. Canyon Tanks

Most of the process tanks in the B-Plant canyon have been re-located from the Uranium Recovery Plant, T-Plant, or other cells in B-Plant. All tanks, except the deep cell tank in Cell 10, are either cylindrical or oval shaped with vertical sides. The 10,000-gallon waste collection tank in Cell 10 is rectangular in shape and has no top. All tanks are equipped with cooling coils except TK-29-4 which is inside TK-29-2. In addition, many of the tanks have water jackets; however, none of these are connected. Table X-1 is a list of the tanks and pertinent data applicable to the tank.

2. Vault Tanks

Four tanks in the 244-AR Vault and tank 003 in the 244-CR Vault are also used in the Waste Management Program. All of these tanks are Class I vessels. Pertinent data pertaining to the tanks in the vaults are listed in Table X-1.

C. SOLVENT EXTRACTION EQUIPMENT

The solvent extraction system, located in Cells 26, 27, 28, 29, and 30, is composed of four pulse columns and associated pumps, tanks, and pulsers. There is a pulse column in every cell but 26. The function of the pulse columns permits the separation of strontium and rare earths from the bulk salts and other fission products.

1. Columns

A pulse column is a type of solvent extraction contactor containing a series of horizontal, perforated plates. In a pulse column an up-and-down pulsing motion is superimposed on the net countercurrent flow of the liquid phases through the column.

The upward and downward pulsing movement of the column contents through the plate perforations provides agitation resulting in intimate mixing of the two countercurrently flowing phases. The pulsing also provides the means for countercurrent flow of the aqueous and organic phases through the columns. Experience indicates that the specific gravity

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TABLE X-1
CANYON AND VAULT TANKS

Tank No.	Name	Dimensions (feet)	Capacity ⁽¹⁾ (gal)	No. of Agitators ⁽²⁾	No. of Pumps ⁽²⁾	No. of Jets ⁽²⁾	Coil Area (sq. ft.)	Design Duty ⁽³⁾ (Btu/hr)	Coil Range ⁽¹⁾ (gal.)	
									From	To
TK-5-1	Strontium Concentrate Receiver	3-1/4x7x4	400	1	0	3	240	480,000 cool	65	416
TK-6-1	Strontium Storage	8ø x 14	4100	1	0	1	420	840,000 cool	227*	1649
TK-6-2	Strontium Storage	8ø x 14	4100	1	0	2	420	840,000 cool	238*	1698
TK-7-1	Strontium Storage	8ø x 14	4100	1	0	2	157	314,000 cool	494	4051
TK-7-2	Strontium Storage	8ø x 14	4100	1	0	2	157	314,000 cool	500*	4000
TK-8-1	Strontium Storage	8ø x 14	4100	1	0	1	157	314,000 cool	499	4022
TK-8-2	Strontium Storage	8ø x 14	4100	1	0	1	157	314,000 cool	516	4026
TK-9-1	Waste Receiver	3ø x 14	4100	1	0	1	157	314,000 cool	432	4035
TK-9-2	Supernatant Storage	3ø x 14	4100	1	0	1	157	314,000 cool	505	4065
TK-10-1	Waste Collection	18x11x7	8000	0	0	1	908	1,816,000 cool	700	7200
TK-11-1	Slurry Tank	4-1/2øx7	650	1	0	2	78	156,000 cool	122	662
TK-11-2	Decant and Metathesis	9ø x 9	3400	1	0	3	300	600,000 cool	100*	1500
TK-12-1	Supernatant Receiver	9ø x 9	3400	1	0	1	118	236,000 cool	551	2964
TK-13-1	Centrifuge Supernatant Receiver	5ø x 9	3400	1	1	4	30	60,000 cool	318	3532
TK-14-1	Undesignated	4-1/2x7	595	1	0	2	78	156,000 cool	98	687
TK-14-2	Cesium Storage	9 x 9	3180			1	118	236,000 cool	491	2939
TK-16-1	Undesignated	6-1/2øx14	2585	1	0	3	70	140,000 cool	305	2007
TK-17-1	Cesium Storage	8ø x 14	3950	1	0	1	228	456,000 cool	173	1476
TK-17-2	Cesium Supernatant Receiver	8ø x 14	4000	1	1	1	100	197,000 cool	110*	950*
TK-18-1	DXF Receiver	9-1/2øx12	1480	1	1	1	52	104,000 cool	100*	507
TK-18-3	DXF Pump Tank	4-1/2øx7	550	1	1	1	40	80,000 cool	25*	324
TK-19-1	DXF Receiver Tank	10x16x14	11,260	2	1	0	160	320,000 cool	600*	2670
TK-20-1	DXF Concentrate Receiver	3-1/4øx7x4	356	1	0	2	240	480,000 cool	62	412
TK-21-1	Cesium Eluent Storage	10x16x14	11,260	2	2	0	160	320,000 cool	500*	2520
TK-22-1	Condensate Receiver	3-1/4x7x4	375	1	1	0	240	2,160,000 heat 480,000 cool	68	417
TK-23-1	Non-boiling Waste Concentrate	3-1/4x7x4	634	1	1	1	128	256,000 cool	57	502
TK-24-1	Low-Level Waste Receiver	10x16x14	11,000	2	1	0	290	580,000 cool	500*	7092
TK-25-1	Cerium Waste Receiver	8ø x 14	3900	1	1	2	435	870,000 cool	150*	2045
TK-25-2	High-Level Waste Receiver	8ø x 14	3900	1	1	2	435	870,000 cool	150*	2096
TK-26-1	Organic Contactor	9ø x 9	3146	1	1	3	68	136,000 cool	302	3358
TK-26-2	ICF Contactor	5x7x12-1/2	2110	1	1	3	48	96,000 cool	150*	610*
TK-26-3	ICW Receiver	5x7x12-1/2	2095	1	1	2	48	96,000 cool	125*	569
TK-27-2	ICF Receiver	5-1/2øx12	1600	1	0	1	52	104,000 cool	60*	460*
TK-27-3	ICW Contactor	7ø x 14	3030	1	1	3	200	400,000 cool	200*	2074
TK-27-4	ICF Pump Tank	2-3/4x5x3-1/2	224	1	1	1	55	110,000 cool	30*	205

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TABLE X-1, continued

Tank No.	Name	Dimensions (feet)	Capacity ⁽¹⁾ (gal)	No. of Agitators ⁽²⁾	No. of Pumps ⁽²⁾	No. of Jets ⁽²⁾	Coil Area (sq. ft.)	Design Duty ⁽³⁾ (Btu/hr)	Coil Range ⁽¹⁾ (gal.)	
									From	To
TK-28-2	LBP Receiver	5-1/2 ϕ x 12	1584	1	1	1	52	104,000 cool	64	561
TK-28-3	LAX Make-up	7 ϕ x 14	3012	1	1	3	200	400,000 cool	189	1934
TK-28-4	LBP Pump Tank	2-3/4x5x3-1/2	228	1	1	1	55	495,000 heat 110,000 cool	30*	202
TK-29-2	LAF Make-up	9-1/2x5x14	3294	1	0	3	200	400,000 cool	237	1636
TK-29-3	LAF Pump Tank	9-1/2x5x14	3319	1	1	2	200	400,000 cool	240	1651
TK-29-4	LSF Pump Tank	1-2/3x8-2/3	66	0	1	0	-	-	-	-
TK-30-2	LAW Receiver	9-1/2x5x14	3300	1	0	3	200	400,000 cool	140*	1500*
TK-30-3	LAX Pump Tank	9-1/2x5x14	3300	1	1	0	200	1,800,000 heat 400,000 cool	209	1634
TK-31-1	PAS Metathesis Tank	5-1/2 ϕ x9	1200	1	0	2	52	468,000 heat 104,000 cool	61	533
TK-31-2	Dissolved Cake Storage	4-1/2 ϕ x 7	572	1	0	1	40	80,000 cool	111	405
TK-31-3	PAS Precipitator Tank	6-1/2 ϕ x13	2561	1	0	2	115	1,030,000 heat 230,000 cool	1370	2636
TK-32-1	Waste Receiver	9-1/2 ϕ x 9	3175	1	0	3	115	230,000 cool	852	3011
TK-33-1	Treated PAS Storage	10x16x14	11,246	2	0	1	160	320,000 cool	562	2555
AR-001	PAW Storage	20 ϕ x19-3/4	36,000	1	1	1	1324	2,650,000 cool	1750	31,500
AR-003	Neutralized High-Level Waste Storage	9-1/2 ϕ x9	4000	1	0	2	219	438,000 cool	460	3570
AR-004	Sludge Waste Acidification	9-1/2 ϕ x9	4000	1	0	2	219	438,000 cool	460	3570
CR-003	PAS Storage	14 ϕ x 12	15,000	1	1	0	586	1,172,000 cool	877	5224

Footnotes:

- ¹ The working capacities and coil ranges were obtained from calibration data. Those marked with an asterisk were estimated.
- ² The number of agitators, pumps, and jets on each tank, as well as the coil area, were obtained from Engineering Flow Diagrams.
- ³ The design cooling duty was computed using the following assumptions:

$$(a) \quad U = 40 \frac{\text{Btu}}{\text{hr.sq.ft.}^{\circ}\text{F}}$$

(b) Cooling water inlet temp. = 70 F; outlet temp. = 90 F

(c) Bulk solution temp. = 130 F; therefore average $\Delta T = 50$ F

For heating, the following assumptions are made:

$$(a) \quad U = 150 \frac{\text{Btu}}{\text{hr.sq.ft.}^{\circ}\text{F}}$$

(b) Average $\Delta T = 60$ F

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difference between the two phases is usually not sufficient to cause a significant countercurrent flow through the small holes in the perforated plates. Consequently, the net flow of the light phase up and the heavy phase down the column is caused almost entirely by the actions of the pulse generator and the stream pumps.

1.1 Column Dimensions and Capacities

The 1A and the 1B Columns are identical. Both have an over-all height of 18.5 feet with a 4 ft by 5 ft by 2 ft high bottom disengaging section. The column proper is 20 inches in diameter. The plate section is 14.5 feet high. The dimensions of the top disengaging section are 4 ft by 4 ft by 2 ft high.

The disengaging sections on the 1S and the 1C Columns have the same dimensions as the 1A and the 1B Columns. However, the 20-inch diameter plate section of the 1S Column is only 10.5 feet in height. The plate section of the 1C Column is 14.5 feet in height, but has an inside diameter of 15.25 inches. Table X-2 lists the pertinent data for the pulse columns. Simplified sketches of the columns are shown in Figures X-1 through X-4.

TABLE X-2
PULSE COLUMNS

Column		Overall Height Feet	Column I. D. Inch	Plate Section Height Feet	Plate Holes Dia. Inch	Hole Centers Inch	Perforations Nozzle Direction	(a) Lower Plate	(a) Column Volume Gal.	Volume ⁽¹⁾ Top Dis. Section Gal.	Volume Plate Contact Section Gal.	Volume Bottom Dis. Section Gal.	Dispersed Phase	Cont. Phase
T-30-1	1A	18.5	20	14.0 ^(a)	0.1875	3/8 Tri.	Down	Yes	731	218	263	250	Aq.	Org.
T-29-1	1S	14.5	20	10.0 ^(b)	0.125	3/8 Tri.	Up	Yes	603	156	195	252	Aq.	Org.
T-28-1	1B	18.5	20	14.0 ^(c)	0.125	3/8 Tri.	Down	Yes	731	218	263	250	Aq.	Org.
T-27-1	1C	18.5	15.25	14.5 ^(d)	0.125	3/8 Tri.	Up	No	600	185	158	257	Org.	Aq.

(a) Two 6.5' sections at 2" plate spacing.

(b) Two 4.5' sections at 2" plate spacing.

(c) Two 6.5' sections at 2" plate spacing.

(d) One 10.33' section at 4" plate spacing.

One 4.0' section at 2" plate spacing.

(e) The lower plate is 6" below the upper section and 6" above the lower section.

(f) To overflow nozzle.

Pilot plant studies indicate that satisfactory operation can be obtained for throughput rates of up to 2300 gallons per hour (total of both phases) in the 1A Column; 1200 gallons per hour in the 1S and 1B Columns; and 1700 gallons per hour in the 1C Column. However, the throughput rates vary with the stream being processed and are usually at least a factor of two under the above rates.

FIGURE X-1
T-30-1, 1A Column

FIGURE X-2

T-29-1, IS Column

FIGURE X-3
T-28-1, 1B Column

1.2 Sieve Plates

The countercurrent flow sections of the four pulse columns are fitted with horizontal stainless steel sieve plates. The plates in the 1S, 1B, and 1C Columns have 1/8-inch diameter holes spaced 3/8-inch apart, center to center, in an equilateral triangular arrangement. The free perforated area of the plate is about 10 percent. The holes in the 1A Column plates are 0.1875 inch in diameter and are spaced in the same array. The free perforated area of the 1A Column plate is about 22 percent. The holes are formed in such a way they act as nozzles which point downward in the 1A and 1B Columns and upward in the 1S and 1C Columns.

All plates are spaced 2 inches apart except for the upper section of the 1C Column which has a four-inch plate spacing.

1.3 Louver Plates

Each of the columns except the 1C Column is equipped with a louver plate located midway up the column six inches above the bottom section of plates and six inches below the upper section of plates. The purpose of the louver plates is to impart a swirling motion to the column contents and to break up channeling. Vertical baffles are placed in front of the louvers to provide additional agitation.

1.4 Cartridge Construction

The stainless steel sieve and louver plates are assembled in a cartridge which can be inserted in the column as a unit. In the 1A, 1S, and 1B Columns, the plates are supported by thirteen, 3/4-inch tie rods connected at the top and bottom of the cartridge to support "spiders". Sections of 3/4-inch schedule 40 pipe slipped over the rods are used to hold the plates apart. For the 1C Column the plates are supported by nine, 1/2-inch diameter tie rods with 1/2-inch schedule 40 pipe used for spacers.

1.5 Distributors

The influent stream distributors are designed to provide reasonably uniform phase distribution across the column cross-section area without unnecessary complexity of design. Each column has a four-nozzle organic distributor located 21-3/16 inches above the bottom of the lower disengaging section which is 3-7/8 inches below the bottom sieve plate. The aqueous distributor in each column is located 7-1/4 inches above the top sieve plate. This aqueous distributor is attached to and is part of the removable cartridge. In addition to these two distributors, the

1A and 1B Columns have a second aqueous distributor located 30 inches below the top of the upper disengaging section which would place it 1-1/16 inches below the top sieve plate. This distributor consists of eight nozzles equally spaced around the column and directed radially towards the center of the column. The 1C Column has an additional organic distributor 77 inches above the bottom of the lower disengaging section which would place it 55-3/16 inches above the lower organic distributor. The design of the intermediate 1C Column distributor is similar to the lower aqueous distributors on the 1A and 1B Columns.

2. Pulse Generators

The aqueous and organic liquid phases in the pulse columns are forced alternately upwards and downwards through the perforated plates in the columns to cause intimate mixing of the phases and, hence, good extraction. The pulsing of the liquid contents of the columns is done by means of reciprocating piston devices called pulse generators. A diagram of the pulse generators is shown in Figure X-5.

The pulse is generated by means of a 16-inch diameter piston. The amplitude of the pulse is preset at two inches in the 1A, 1S, and 1B Columns, and one inch in the 1C Column. However, the frequency of the pulse may be varied from 25 to 90 cycles per minute during column operation. The pulse is transmitted hydraulically to the liquid contents of the solvent extraction column through a pulse leg at the bottom of the column.

2.1 Piston and Cylinder Assembly

The 16-inch piston operates in a cylinder 27 inches long and flanged at the lower end to a reducer which adapts the cylinder to the 8-inch diameter pulse leg. The cylinder head contains a bushing of Graphitar 41 centered concentrically with the bore of the cylinder. The bushing, with a nominal bore of three inches, provides a 0.004 inch diametrical clearance with the piston rod and restricts leakage of vapor and mist from the cylinder. A two-inch overflow line in the cylinder wall just above the piston allows solutions which leak past the piston to flow by gravity to a tank containing a solution of the same phase as is present at the bottom of the column. A 3/32-inch weep hole originally present in each piston has been plugged to reduce the pulse leakage rates to less than 0.2 gpm.

2.2 Pulse Leg

The pulse is transmitted from the pulse generator to the lower disengaging section of the solvent extraction column through an eight-inch diameter pulse leg approximately six feet long. The pulse leg

REFERENCE DRAWINGS
H-2-60992 & H-2-60993

FIGURE X-5
PULSE GENERATOR
PS-27, PS-28, PS-29, PS-30

is equipped with an air or water purge. The air purge is used when the column is shut down to prevent excessive leakage of liquid past the piston. However, before operating the pulse generator the pulse leg must be filled with liquid to provide proper lubrication for the piston. The pulse leg is filled with organic phase for the 1A Column, and with an aqueous phase in the 1S, 1B, and the 1C Columns.

2.3 Motion Box

The motion box reduces the speed of the variable speed electric motor, and converts the rotary motion of the motor to reciprocating motion. The variable speed electric motor is a vertically mounted, 15-horsepower, 440-volt, 3-phase, totally enclosed-fan cooled, 55 C-rise, induction motor having Class B insulation and constant torque loading the motor operates over a speed range of approximately 1800 to 497 rpm from a variable-frequency motor-generator set power supply. The power supply is described in 2.4 below.

The driving motor is directly connected to a worm shaft by means of a spline joint. The worm threads engage a 20-inch diameter worm gear which provides a reduction ratio of 18-1/2 to 1. The worm gear is keyed to a 4-1/4-inch worm gear shaft. The worm gear shaft is provided with an overhanging stub, 3 inches in diameter, which is eccentric to the shaft.

A slide block is fixed to the eccentric shaft of the worm gear by means of lock nuts. The slide block supports a cast iron yoke which is free to move vertically up and down, but is otherwise fixed in position on guide rods. Thus, eccentric movement of the worm gear shaft is transmitted into vertical reciprocating motion. The piston rod is attached to the yoke through the top of the box by means of yoke arms and tie rods. Connections through the top of the box this way reduces the chance of oil leakage through seals.

All moving parts in the motion box are lubricated by oil directed through nozzles to the gear set and moving parts. The motion box contains 20 gallons of oil which is recirculated by means of a gear pump driven from the worm gear shaft. Oil is changed at regular intervals by introducing fresh oil through a remote connector. An overflow line in the motion box allows the waste oil to be flushed to a waste oil container mounted on the side of the unit.

2.4 Electric Power Supply

The electric power supply delivers variable frequency power to the variable speed induction motor that drives the pulse generator. The variable frequency alternating current is generated by means of a General Electric Company Type AT1-924, 9.0/2.75-IVA, 1800/497-rpm, alternator. The alternator is driven by an Easton,

Yale, and Towne type GCA, 15-hp, 1755-rpm, 220/440-volt, 3-phase induction motor, connected through an eddy current coupling adjustable speed drive. The eddy current coupling is an Easton, Yale, and Towne Company model MO-100001-0905 capable of speed variations from 1680 to 100-rpm. The dc current used to excite the field of the alternator is provided by General Electric Company Type B-254, 3-Kw, 1750-rpm, 125-volt, generators directly connected to a standard induction motor. The five alternators (one for each pulser plus a spare) along with the other power supply equipment, are located in the electrical gallery adjacent to Cells 28, 29, and 30.

D. CENTRIFUGES

1. General Description

Cells 12, 13, and 32 each have a centrifuge and a supernatant receiver. The principal components of a centrifuge include: a) a solid cylindrical bowl; b) a vertical spindle from which the bowl is axially suspended; c) an electric motor directly connected to the spindle; and d) an outer cylindrical case which encloses the rotating bowl. These components are mounted on a raised concrete foundation so that the bowl effluent will drain by gravity through an opening near the bottom of the outer cylinder to the supernatant receiver. The entire assembly is designed for remote operation and maintenance. All parts in contact with process solutions or fumes are stainless steel. A sketch of a centrifuge is shown in Figure X-6.

2. Centrifuge Bowl

The bowl of the centrifuge is solid and measures 40 inches in diameter and 24 inches in height. The capacity of the bowl when not spinning is 120 gallons; however, during operation the maximum hold-up is 60 gallons. The hold-up may be reduced by adjusting hydraulically-operated skimmers with which each centrifuge is equipped. Three horizontal baffle plates with weep holes are equally spaced around the inside of the bowl. The bowls and the cases are equipped with sprays supplied by 230-foot head pumps from scale tanks located in the operating gallery.

3. Electrical Features and Instrumentation

A 440-volt, 40-hp electric motor rotates the bowl at 1740 rpm or 870 rpm with a corresponding centrifugal force of 1720 G's (1720 times the force of gravity) and 430 G's. It is possible to obtain other centrifuge speeds by intermittent operation of the drive motor.

A centrifuge is slowed or braked by applying a direct current to the motor windings after the ac power has been removed.

Each centrifuge is equipped with a tachometer, a weight factor manometer, a vibration meter, and a temperature element in the bottom of the bowl.

NOZZLE	SERVICE
A-	CHEMICAL ADDITION
B-	PROCESS INLET
C-	BLANK
D-	PROCESS INLET
E-	SOLUTION OUT
F-	GRAVITY OUTLET TO RECEIVER
G-	LIQUID LEVEL
H-	TEMPERATURE
J-	CASE SPRAY OR CHEMICAL ADDITION
K-	HYDRAULIC CONTROL
L-	POWER TO MOTOR
M-	BOWL SPRAY
N-	LUBE
P-	SPEED INDICATOR

FIGURE X-6

CENTRIFUGE

G-32-2, G-13-2, G-12-2
Reference Drawing H-2-61009

E. ION EXCHANGE COLUMN

The ion exchange column, T-18-2, is a Class I vessel 6 feet in diameter and 15 feet high. For down-flow operation, solutions enter the column at the top through a cage three feet in diameter made of 80 mesh stainless steel screen attached to the inside top of the column. The screen cage covers the outlets to nozzles B, C, F, and H. Solutions are collected near the bottom of the column in a 10-arm "spider" 64 inches in diameter. The arms of the spider are covered with a 50-mesh stainless steel screen. The lower 13 feet of the column are filled with an ion exchange medium which is added to the column as a slurry through a nozzle which by-passes the top screen. The ion exchange media may be removed by jetting it through a drain line located below the bottom collection spider. Instrumentation on the ion exchange column includes an ion exchange medium level indicator, top and bottom pressure indicators, and a temperature indicator. Figure X-7 is a schematic sketch of the ion exchange column.

FIGURE X-7

Ion Exchange Column
Based on H-2-60840

F. CONCENTRATORS AND CONDENSERS

Concentrators are located in Cells 5, 20, and 23. The concentrators are of the vertical-tube, thermal-recirculation, steam-heated variety. The concentrators in Cell 5 and Cell 20 are used to concentrate strontium and cesium product solutions, respectively. The Cell 5 concentrator may also be used to concentrate rare earth solutions if required. Both of these concentrators have been modified from equipment in the Uranium Recovery Plant. The Cell 23 concentrator is of the Purex type. It is used to concentrate liquid wastes with the condensate going to an underground crib, and the concentrated bottoms to an In-Tank Solidification unit via non-boiling waste storage. Pertinent data for the concentrators are listed in Table X-3.

No.	Name	Capacity	Duty BTU/Hr.	Area ft ²	Bundle Description
E-5-2	SR Concentrator	300 Gal.	4, 500, 000	896	307 Vert. Tubes 1" x 12 BWG x 14'2-7/8"
E-20-2	CS Concentrator	300 Gal.	9, 000, 000	896	307 Vert. Tubes 1" x 12 BWG x 14'2-7/8"
E-23-3	Waste Concentrator	3, 000 Gal.	30, 000, 000	1, 850	West-687 Vert. Tubes 1-1/4" x 12 BWG x 10' East-630 Vert. Tubes 1" x 12 BWG x 10'
E-5-3	SR Condenser	----	4, 500, 000	895	342 Hor. Tubes 1" x 12 BWG x 10'
E-20-3	CS Condenser	----	9, 000, 000	895	342 Hor. Tubes 1" x 12 BWG x 10'
E-23-4	Waste Condenser	----	30, 000, 000	1, 340	568 Hor. Tubes 1" x 12 BWG x 9'
E-22-3	Vessel Vent Heater	----	200, 000	190	91 Hor. Tubes 1" x 12 BWG x 8'
E-22-4	Vessel Vent Condenser	----	2, 000, 000	895	342 Hor. Tubes 1" x 12 BWG x 10'
E-22-7	Scrubber Vent Heater	----	50, 000	40	51 Hor. Tubes 1" x 12 BWG x 3'

TABLE X-3
CONCENTRATORS AND CONDENSERS

1. Product Concentrators

The product concentrators each have one tube bundle containing 307 one-inch No. 12 B.W.G. tubes 14 feet 2-3/4 inches long. The outside surface area of the tubes is 1197 square feet. The concentrators

are operated with process solution on the tube side and steam on the shell side. The over-all dimensions of the tube bundle section are 25-1/2 inches in diameter and 15 feet high.

Below the tube bundle is an enlarged section 54 inches in diameter and 12 inches high. Above the tube bundle is the vapor section 54 inches in diameter and 37-1/16 inches high. A reverse-dished impingement plate which deflects the percolated liquid is located in the vapor shell. The impingement plate effects a separation of liquid and vapor. The vapor section and the bottom section are connected with an eight-inch downcomer which allows recirculation of the concentrated liquid.

Directly above the vapor section is a deentrainment section 54 inches in diameter and 32-3/16 inches high containing a mist separator and spray nozzles. The mist separator, consisting of "Z" baffles, removes the entrained droplets of liquid from the vapors and returns the liquid to the deentrainment section through a seal pot. The seal pot prevents vapors from by-passing the impingement plate and traveling directly to the mist separator.

Semicircular baffles, acting as tube supports, are located in the steam chest of each evaporator. The baffles prevent channeling of steam through the tube bundles. Expansion joints in both the evaporator shells and downcomers minimize strain due to large temperature changes. A schematic sketch of the concentrator in Cell 5 is shown in Figure X-8 and a sketch of the concentrator in Cell 20 is shown in Figure X-9.

2. Waste Concentrator

The large waste concentrator in Cell 23 has two removable stainless steel tube bundles located in 55-inch diameter cylinders 14 feet 5 inches high. The two tube bundles are of different design with the west bundle having a surface area of 1850 square feet and the east bundle having a surface area of 1290 square feet. The west bundle has 687 tubes, 1-1/4 inches O.D., No. 12 B.W.G., 10 feet long. The east bundle contains 630 tubes, 1-inch O.D., No. 12 B.W.G., 10 feet long.

A 30-inch diameter draft tower sits between the tube bundles which allows liquid to circulate down the draft tower and back into the bottom of the tube bundle sections. The shells containing the tube bundles are connected to the draft tower by 21-inch diameter pipes at the bottom and by 4-feet 7-inch by 6-foot rectangular ducts on top.

The stripping and deentrainment section is 60 inches in diameter by 7 feet 1-1/8 inches high. It rests on the ducts that join the side cylinders to the top of the draft tube. The vessel contains four sets of spray nozzles located 9 inches, 31 inches, 58 inches and 73

inches below the top of the vessel. Above and below the second set of spray nozzles are two entrainment separator pads. These pads are 6 inches thick and are made of 0.006-inch diameter stainless steel wire. The upper pad has a density of 14 lbs/ft³ and the lower pad has a density of 6 lbs/ft³. A 16-inch flanged nozzle at the top of the deentrainment section is the vapor outlet leading to the condenser.

An overflow column for the concentrated solution is located next to the draft tower. This column, which has a diameter of 18 inches, contains the weight factor and specific gravity dip tubes. An elevation sketch of the concentrator is shown in Figure X-10 and a plan view of the concentrator is shown in Figure X-11.

3. Condensers

The horizontal, multi-pass, water-tube condensers located in Cells 5 and 20, have been modified and relocated from 221-U Building. Each condenser has 342 tubes, 10 feet long. The surface area of the tubes is 895 square feet, and there are 9 tube passes. Seven segmental baffles spaced throughout the length of each condenser distribute the vapor flow through the shell. An expansion joint is provided in the condenser shell to relieve stresses caused by shell temperature changes. Condenser 20-3 is equipped with four water spray nozzles. A sketch of the condenser in Cell 5 is shown in Figure X-12 and a sketch of the condenser in Cell 20 is shown in Figure X-13. Table X-3 lists pertinent data on the condensers.

The condenser on the Waste Evaporator in Cell 23 is also a horizontal, multiple-pass, water-tube type containing 568 tubes 9 feet long. The surface area of the tubes is 1340 square feet. Four segmental baffles serve to channel the vapor flow through the condenser. The cooling water makes six passes through the condenser. The design duty of the condenser is 30 million Btu/hr. Figure X-14 is a sketch of the condenser, and Table X-3 contains pertinent data on the condenser.

G. AMMONIUM CARBONATE ABSORBER

The ammonium carbonate absorber, T-21-2, is used to adsorb ammonia and carbon dioxide gas in water to make a solution of ammonium carbonate and ammonium hydroxide. The absorber which sits on top of TK-21-1 has an over-all height of 6 feet 6 inches, and an outside diameter of 22 inches. A five-foot section of the column is packed with 3/4-inch porcelain Intalox* saddles. Liquid is pumped from TK-21-1 to the top of the tower where it is allowed to trickle down through the packing back into the tank through a sieve plate on the bottom. Gases not absorbed by the recirculated liquid exit the top of the tower and enter the No. 2 vessel vent system in Cell 22. A sketch of the ammonium carbonate absorber is shown in Figure X-15.

* Trade name of U.S. Stoneware Company

FIGURE X-8

E-5-2 Concentrator
Based on H-2-60942

FIGURE X-9

E-20-2 Concentrator
Based on H-2-60945

NOZZLE	SERVICE
A-	STEAM INLET
B-	STEAM INLET
C-	STEAM INLET
D-	STEAM INLET
E-	CONDENSATE OUTLET

NOZZLE	SERVICE
A-	PROCESS IN
B-	CHEMICAL ADDITION
C-	WEIGHT FACTOR & WATER ADDITION
D-	LIQUID RETURN
E-	SPARE
F-	PROCESS OVERFLOW
G-	SPARE
H-	PROCESS OUT
J-	WEIGHT FACTOR & SPECIFIC GRAVITY
K-	TEMPERATURE
L-	SPARE

NOZZLE	SERVICE
A-	STEAM INLET
B-	STEAM INLET
C-	STEAM INLET
D-	STEAM INLET
E-	CONDENSATE OUTLET

FIGURE X-10

E-23-3 Concentrator

FIGURE X-11

E-23-3 Concentrator - Plan View

FIGURE X-12

E-5-3 Condenser
Based on H-2-60948

FIGURE X-13

E-20-3 Condenser
Based on H-2-60948

FIGURE X-14

E-23-4 Condenser
Based on H-2-60854

FIGURE X-15

T-21-2 Ammonia Carbonate Absorber
Based on H-2-60841

H. VESSEL VENT SYSTEMS1. Vessel Vent System No. 1 (Normal)1.1 Vent Gas Heater

The vent gas heater, E-22-3, is 9 feet, 7-1/2 inches long and has an outside diameter of 18 inches. Heat is supplied by 100 psig steam delivered to 91 tubes, 8 feet long. Three segmented baffles distribute the vapor flow through the shell. Figure X-16 is a sketch of the vent gas heater.

FIGURE X-16

E-22-3 Vent Gas Heater
Based on H-2-60843

1.2 Filter

Filter, E-22-5, consists of two banks of two CWS high efficiency fiberglass filters stacked on top of each other. Each filter is 24 inches square and 11-3/4 inches deep. The second bank of filters is located six inches downstream from the first bank.

1.3 Condenser

Condenser, E-22-4, has been relocated from 221-U Building and is nearly identical to the condensers in Cells 5 and 20. The condenser contains 342 tubes arranged for 9 tube passes. There are seven segmented baffles distributed through the length of the condenser. An expansion joint in the condenser shell is provided to relieve stresses caused by shell temperature changes. Condenser is shown in Figure X-17, and pertinent data are given in Table X-3.

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FIGURE X-17

E-22-4 Condenser
Based on H-2-60968

2. Vessel Vent System No. 2 (Ammonia)

2.1 Ammonia Scrubber

The ammonia scrubber tower, T-22-2, which sits on top of TK-22-1, is 16 feet, 8 inches high and has an outside diameter of 26 inches. A large vapor to liquid contact area is provided by 3/4-inch Intalox* porcelain saddles. The packing is 13 feet, 9 inches high and starts one foot above the bottom of the tower. Liquid enters the top of the tower (through one spray nozzle), trickles down through the packing, and drains into TK-22-1 through a dip leg. A York style moisture entrainment separator or demister, located 11 inches above the packing in the center of the tower, is 4-5/8 inches in diameter and 4 inches in height. Figure X-18 is a sketch of the scrubber tower.

FIGURE X-18

T-22-2 Ammonia Scrubber Tower
Based on H-2-60842

* Trade name of U.S. Stoneware Company

2.2 Vent Gas Heater

The vent gas heater, E-22-7, is 56 inches long and has an outside diameter of 12-3/4 inches. Steam at 100 psig is supplied to 51 tubes, 3 feet in length. There are two baffle plates in the heater. Figure X-19 is a sketch of the heater and Table X-3 contains pertinent data.

FIGURE X-19

E-22-7 Heater
Based on H-2-60845

2.3 Filters

A sketch of the fiberglass prefilter, F-22-6, is shown in Figure X-20. Filters F-22-8-1 and F-22-8-2 each consist of two CWS high efficiency fiberglass filters in series. Each CWS filter is 24 inches square and 11-3/4 inches deep. Filter, F-22-9, is located in a pit on the south side of the 221-Building adjacent to Cell 22. The F-22-9 filter is identical to F-22-8. Additional discussion of the vessel vent systems is given in Chapter IX, Section B 6.

FIGURE X-20

Fiberglass Prefilter

I. AUXILIARY EQUIPMENT

The following section on auxiliary equipment deals primarily with the mixing and transfer of solutions in the process.

1. Pumps

The majority of pumps used in the Waste Management Facilities have been relocated from 221-U Building. Those pumps which are new have been built to U-Plant design. Pumps located within the process tanks are supported and fixed on the top of the vessel by means of a mounting flange resting on a nozzle flange. A vertical column, containing the pump stages as an integral part, extends downward the desired distance. The number of stages in the pump is determined by the desired head and capacity required. Solutions enter the pump axially at the lower end of the column and pass vertically upward from stage to stage through the column. The pumped solution is discharged radially through a side arm at the top of the column section just above the mounting flange. The drive shaft extends concentrically through the column and is guided by sleeve bearings lubricated by the pumped solution. The drive shaft is directly coupled to the shaft of the electric pump motor mounted above the mounting flange. The weight of the shaft and the thrust developed during operation are absorbed by the motor bearings. A throttle bushing is provided at the point where the drive shaft emerges from the column section. Leakage past the throttle bushing is returned to the vessel. Table X-4 is a summary of the pumps.

TABLE X-4
PUMP SUMMARY

Pump EPH	Capacity gpm	Head ft	Motor hp	Service	Dimensions (feet)	Pump Heel (gal)
244-AR-P-001	100	355	20	PAW Storage	20 ϕ x 20	400*
244-AR-P-002-1	600	390	150	Slurry Receiver	20 ϕ x 20	14,000*
244-AR-P-002-2	50	38	2	Slurry Receiver	20 ϕ x 20	1,200*
244-CR-P-003	50	100	5	PAS Storage	14 ϕ x 12	584
P-13-1	50	50	2	Centrifuge Supernatant Receiver	9 ϕ x 9	55*
P-17-2	50	80	2	Cesium Supernatant Receiver	8 ϕ x 12	347
P-18-1	50	90	3	IXW Receiver	9-1/2 ϕ x12	45*
PA-18-3	50	90	3	IXF Pump Tank	4-1/2 ϕ x7	25.3
P-19-1	15	110	2	ICP Receiver Tank	10x16x14	787
P-21-1-1	50	80	2	Cesium Eluent Storage	10x16x14	818.6
P-21-1-2	15	70	3	Cesium Eluent Storage	10x16x14	818.6
P-22-1	15	70	2	Condensate Receiver	3-1/4x7x4	22.8
P-23-1	10	25	2	Non-boiling Waste Receiver	3-1/4x7x4	43
P-24-1	45	90	2	Low-Level Waste Receiver	10x16x14	1,244
P-25-1	50	120	5	Cerium Waste Receiver	8 ϕ x 14	137.7
P-25-2	50	120	5	High-Level Waste Receiver	8 ϕ x 14	122.3
P-26-1	75	45	3	Organic Contactor	9 ϕ x 9	1.830
P-26-2	75	117	5	ICP Contactor	5x7x12-1/2	28
P-26-3	75	117	5	ICP Receiver	5x7x12-1/2	31
P-27-3	100	70	5	ICW Contactor	7 ϕ x 14	1,300
P-27-4	5	72	4	ICF Pump Tank	2-3/4x5x3-1/2	126
P-28-2	10	90	5	LEP Receiver	5-1/2 ϕ x12	82.3
P-28-3	100	70	5	LAX Makeup	7 ϕ x 14	1,621.1
PA-28-4	8	72	4	LEF Pump Tank	2-3/4x5x3-1/2	11.8
P-29-3	5	110	6	LAF Pump Tank	9-1/2x5x14	90*
P-30-3	10	110	6	LAX Pump Tank	9-1/2x5x14	92.1

*Estimated Heel

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1.1 Pump Agitators

In several B-Plant tanks, limited space has necessitate modifying existing pumps into pump agitators. The modification consists of drilling three holes in the bowl of the bottom pump stage. A portion of the solution entering the first stage is forced through the holes back into the tank, and a portion passes on to the upper pump stages. Through the use of a diaphragm operated valve on the pump discharge line a pump agitator may be used for two modes of operation: 1) with the pump discharge valve closed, solution will recirculate back to the tank agitating the contents of the tank; 2) with the pump discharge valve open solution will be pumped and agitated simultaneously. It should be pointed out that pump agitators cannot be used for batch contactors because it cannot pump without also agitating the solution.

2. Agitators

Many of the agitators used at B-Plant have been modified and relocated from U-Plant, T-Plant, and within B-Plant. Several different types of agitators are in service. These are summarized in Table X-5.

All of the agitators are of stainless steel construction. The agitator shaft is connected through a flexible coupling to the output shaft of a speed reducer which is directly connected to the shaft of an electric motor. The agitator shaft is fabricated in two sections; the upper portion carries both thrust and radial bearing loads, while the lower portion carries the agitator blades. The two sections are joined together with a rigid, flange-type coupling. The upper section is sealed by a kerosene-lubricated Durametallic seal at the upper end of a cylindrical torque tube welded in the mounting flange. The torque tube also contains a grease-lubricated guide bearing near its lower end to provide shaft support near the point of load application. Contact of process solutions with the guide bearing is prevented by means of positive air pressure introduced to the torque tube. Kerosene drippings from the Durametallic seal and air escape through the clearance between the agitator shaft and the lower end of the torque tube.

3. Transfer Jets

Transfer jets are used for transferring many solutions. The rated water syphoning capacity ranges from 3 to 75 gallons per minute with somewhat smaller jets used in samplers. Solutions transferred by steam jet are diluted 2 to 3 percent. Although steam is usually used for the motive fluid, both water and air may be used. Solutions at temperatures greater than about 145 F can not be jetted because suction of the solution is great enough to cause the solution to vaporize. However, submerged jets are capable of jetting solutions up to about 175 F. When the solution to be jetted vaporizes, the jet is said to be "gassed".

TABLE X-5
AGITATOR SUMMARY

Agitator EPN	Motor Shaft		Type	Impeller		Minimum Volume to Agitate (gal)	Vessel Service	Dimensions (feet)
	hp	rpm		Dia., In.	No. Blades			
244-AR-A-001	50	1800	turb	48	14	1200*	PAW Storage	200x19-3/4
244-AR-A-002	60	1800	turb	48	14	1200*	Slurry Receiver	200x19-3/4
244-AR-A-003	15	1150	turb	20	8	140*	Neutralized High Level Waste Storage	9-1/20x9
244-AR-A-004	15	1150	turb	20	8	140*	Sludge Waste Acidification	9-1/20x9
244-CR-A-003	10	1750	turb	33	70(3)	2019	PAS Storage	140 x 12
A-5-1	2	1150	prop	8	3	140*	Strontium Concentrate Receiver	3-1/4x7x4
A-6-1	7.5	1750	turb	17	8	494.4	Strontium Storage	80 x 14
A-6-2	7.5	1750	turb	17	8	508	Strontium Storage	80 x 14
A-7-1	5	1150	turb	18	4	316	Strontium Storage	80 x 14
A-7-2	7.5	1750	turb	17	8	320	Strontium Storage	80 x 14
A-8-1	5	1150	turb	18	4	324	Strontium Storage	80 x 14
A-8-2	5	1150	turb	18	4	333	Strontium Storage	80 x 14
A-9-1	5	1150	turb	18	4	329	Waste Receiver	80 x 14
A-9-2	5	1150	turb	18	4	320	Supernatant Storage	80 x 14
A-11-1	5	1150	turb	14	4	69	Slurry Tank	4-1/20x7
A-11-2	15	1150	turb	36	8	368	Decant and Metathesis	90 x 9
A-12-1	15	1150	turb	24	4	437	Supernatant Receiver	90 x 9
A-13-1	5	1750	turb	20	8	753.6	Centrifuge Supernatant Receiver	90 x 9
A-14-1	5	1150	turb	14	4	98.4	Undesignated	4-1/20x7
A-14-2	15	1150	turb	24	4	490.8	Cesium Storage	90 x 9
A-16-1	5	1150	turb	14	4	348.6	Undesignated	6-1/20x14
A-17-1	7.5	1750	turb	17	8	423	Cesium Storage	80 x 14
A-17-2	5	1750	turb	17	8	347	Cesium Supernatant Receiver	80 x 14
A-18-1	5	1150	prop	9	3	176.2	LXW Receiver	9-1/20x12
PA-18-3	3	--	pump	--	--	25.3	LXW Pump Tank	4-1/20x7
A-19-1-1	7.5	1750	turb	17	8	1170.4	LCP Receiver Tank	10x16x14
A-19-1-2	7.5	1750	turb	17	8	1170.4	LCP Receiver Tank	10x16x14

TABLE X-5, Continued

Agitator EPN	Motor Shaft		Type	Impeller		Minimum Volume to Agitate (gal)	Vessel Service	Dimensions (feet)
	hp	rpm		Dia., In.	No. Blades			
A-20-1	2	1150 1150	prop	8	3	134.9	LXP Concentrate Receiver	3-1/4x7x4
A-21-1-1	7.5	1750 186	turb	17	8	1169.3	Cesium Eluent Storage	10x16x14
A-21-1-2	7.5	1750 186	turb	17	8	1169.3	Cesium Eluent Storage	10x16x14
PA-22-1	2	--	pump	--	-	22.6	Condensate Receiver	3-1/4x7x4
PA-23-1	2	--	pump	--	-	33	Non-Boiling Waste Concentrate	3-1/4x7x4
A-24-1-1	7.5	1750 186	turb	17	8	1244	Low-Level Waste Receiver	10x16x14
A-24-1-2	7.5	1750 186	turb	17	8	1244	Low-Level Waste Receiver	10x16x14
A-25-1	7.5	1750 186	turb	17	8	408.5	Cesium Waste Receiver	8 1/2 x 14
A-25-2	7.5	1750 186	turb	17	8	399	High-Level Waste Receiver	8 1/2 x 14
A-26-1	5	1150 1150	prop	9	3	1043	Organic Contactor	3 1/2 x 9
A-26-2	5	1150 1150	prop	9	3	280	LCP Contactor	5x7x12-1/2
A-26-3	5	1150 1150	prop	9	3	280	LCP Receiver	5x7x12-1/2
A-27-2	5	1150 1150	prop	9	3	225	LCP Receiver	5-1/2x4x12
A-27-3	5	1150 1150	prop	9	3	530	LCP Contactor	7 1/2 x 14
PA-27-4	5	--	pump	--	-	12.6	LCP Pump Tank	2-3/4x5x3-1/2
A-28-2	5	1150 1150	prop	9	3	206.6	IBF Receiver	5-1/2x4x12
A-28-3	5	1150 1150	prop	9	3	547.1	LAX Makeup	7 1/2 x 14
PA-28-4	2	--	pump	--	-	11.6	IBF Pump Tank	2-3/4x5x3-1/2
A-29-2	7.5	1750 186	turb	17	8	377	LAF Makeup	9-1/2x5x14
A-29-3	7.5	1750 186	turb	17	8	365.6	LAF Pump Tank	9-1/2x5x14
A-30-2	7.5	1750 186	turb	17	8	390*	LAW Receiver	9-1/2x5x14
A-30-3	7.5	1750 186	turb	17	6	355.3	LAX Pump Tank	9-1/2x5x14
A-31-1	2	1150 1150	prop	8	3	212.3	PAS Metathesis Tank	5-1/2x4x9
A-31-2	5	1150 100	turb	18	4	154.9	Dissolved Cake Storage	4-1/2x7
A-31-3	5	1750 150	turb	20	8	306.2	PAS Precipitator Tank	6-1/2x4x14
A-32-1	5	1150 150	turb	24	8	752	Waste Receiver	9-1/2x9
A-33-1-1	7.5	1750 186	turb	17	8	1308.6	Treated PAS Storage	10x16x14
A-33-1-2	7.5	1750 186	turb	17	8	1306.8	Treated PAS Storage	10x16x14

*Estimated volume

4. Gang Valves

Gang valves are used to operate the steam jets in the B-Plant. A gang valve consists of four spring-closed, globe-type valves with all working parts constructed of bronze. The four valves control steam, air, shut-off, and vent. The use of the gang valves prevent back flow of radioactive solutions into the partial vacuum created by condensation of steam in un-purged lines. The following four positions of a gang valve are used:

Position 1. Normal Closed Position

Valve to operating gallery closed, valve to jet is open, steam and air valves are closed.

Position 2. Air Venting of Jet or Sparger

Gallery valve closed, jet and air valve open, steam valve closed.

Position 3. Steam Being Supplied to Jet or Sparger

Gallery valve closed, jet and steam valve open, air valve closed.

Position 4. Jet Vented to Operating Gallery - Maintenance Position

Gallery and jet valves open, steam and air valves closed.

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PART V, Continued
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PART V, Continued
PLANT AND EQUIPMENT

CHAPTER XII
REMOTE OPERATION AND MAINTENANCE

By

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HANFORD ENGINEERING SERVICES

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WASTE MANAGEMENT TECHNICAL MANUALCHAPTER XIIREMOTE OPERATION AND MAINTENANCE

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CHAPTER XIIREMOTE OPERATION AND MAINTENANCE

The high radiation levels prevailing in much of the Waste Management Facilities necessitate interposition of massive shielding between personnel and processing areas. Routine operation and maintenance are carried out in many cases with no access to the process equipment. Instrument control, discussed in Chapter XIII, is extensively used. Methods of remote sampling of process streams for laboratory checks on instrument control, are discussed in Chapter XIV. The methods and equipment used in performing remote operation and maintenance (except process-control instrumentation and sampling) are the subject of this chapter.

A. PRINCIPLES OF REMOTE OPERATION AND MAINTENANCE

The Waste Management process equipment has been designed, insofar as possible, to provide trouble-free service with a minimum of maintenance and attention. However, during the design of this equipment, it was recognized that each item would have a finite life and would require service or replacement at the end of life. For this reason and to provide flexibility to accommodate future design changes, most of the equipment has been designed so that it may be installed or removed remotely.

To avoid exposing personnel to excessive radiation, the equipment is located in heavy-walled concrete "vaults" or "cells", often underground. These vaults are covered with massive concrete cover blocks. The cover blocks have stepped interlocking edges so that an emerging "radioactive ray" originating within the vault must pass through a certain minimum thickness of shielding. When it is necessary to perform work in a vault, the cover blocks may be removed with a crane.

All remote maintenance is accomplished from above using cranes. The cranes not only lift equipment but handle the tools used in remote maintenance. One of the unique features of the Waste Management Facilities is that all equipment is assembled and disassembled vertically. Consequently, the equipment is counter-balanced so that when suspended from a crane hook, it will assume the correct attitude for vertical assembly.

When a cell or vault is first constructed, the actual or "As-Built" dimensions of all fixed-location (embedded in concrete) points are recorded. Such location points include mounting pads, trunnions, dowels, and remote connector nozzles. The "As-Built" dimensions of each item subsequently installed (dunnages, vessels, pumps, jumpers,

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A. PRINCIPLES OF REMOTE OPERATION AND MAINTENANCE (Continued)

et cetera) are similarly recorded. In this manner, all equipment may be prefabricated in the 277 mock-up building which is radioactively "cold", then set into the "hot" cell without exposing personnel to radiation.

Radioactive process fluids naturally "contaminate" all surfaces which they contact; therefore, it is necessary to design and construct equipment that may be contacted by these fluids so it can be removed and decontaminated. To this end, crevices, porous materials, and pockets which will contain liquid pools must be avoided. Process lines are self-draining without low points to trap solutions. Process solutions, if spilled, may contaminate equipment which cannot be decontaminated. Leakage must be minimized if not avoided entirely. All joints are, therefore, located above the static liquid level and are gasketed. Valves are avoided wherever possible and where used are incorporated in jumpers in order to be serviceable should leakage occur. Deep-well type pumps are used where steam jet syphons cannot perform the function satisfactorily. Vessels and potentially radioactively contaminated areas are maintained at a slight vacuum so that all air leakage will be directed into the most contaminated area. The vacuum is maintained by blowers that draw the air from the contaminated area through particulate filters to minimize atmospheric contamination.

Many remotely operated components have been standardized, such as: remote connectors, dowels, studs, nuts, and steam syphons.

B. CRANES

In the Waste Management Facilities, all remote operations are carried out from above using cranes. Bridge cranes are the work horses of the canyon building and mobile cranes are used to service the tank farms, diversion boxes, and vault buildings. The cranes which serve the Waste Management Facilities are described in the following.

1. 221-B Building (B Plant) Canyon Cranes

The "B" Plant Canyon has been provided with two electrically-operated overhead bridge cranes, sharing the same rails. The main crane is used for most remote maintenance operations since the operator is shielded from radiation. The auxiliary crane is used for other tasks where the radiation levels are low. Crane maintenance platforms located at each end of the building provide access to the cranes for servicing.

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B. CRANES (Continued)1.1 Main Crane (CVI 65106 and H-2-33671)

The main crane is located west of the auxiliary crane on their common rails which extend the length of the canyon. The main crane is illustrated in the building cutaway, Figure XII-1. Figure XII-2 is a photograph showing the main crane and the east crane maintenance platform. The crane operator is protected from radiation both by the shielded cab and the parapet wall behind which it travels. The crane cab is air conditioned.

The main trolley runs atop the bridge and carries a 75-ton hoist and a 10-ton hoist. The 10-ton hoist is fitted with an electrically-operated rotary hook. Beneath each of the two bridge girders is a monorail and trolley. Each trolley carries a 1-ton and a 1/2-ton hoist from which hang auxiliary hooks, grabbers, or impact wrenches having 2 or 3-inch sockets. The bridge, the three trolleys, the six hoists, the rotary hook, and the two impact wrenches are controlled from the crane cab.

The area below the crane is illuminated by twenty floodlights on the bridge, four 1,000 watt lamps beneath the trolley, and two 1,000 watt periscope spotlights. The crane operator views the operation through two periscopes or through a closed-circuit television system.

1.1.1 Capabilities

Drawing H-2-44966 shows the crane lifting capabilities. The speeds of the bridge, trolley, 75-ton hoist, and 10-ton hoist are controlled by a drum controller which affords six speeds in either direction (plus a stop position). The maximum speeds are: Bridge travel - 160 FPM, trolley travel - 25 FPM, 75-ton hoist lift - 5 FPM, and 10-ton hoist lift - 35 FPM. It is possible to block the higher speeds so they cannot be used. The trolleys of the monorail hoists travel at 25 FPM and the hoists lift at 21 FPM (both single speed).

1.1.2 Shielding

The crane cab is shielded from direct gamma radiation by the concrete parapet behind which it runs. Protection against scattered radiation is afforded by the steel shielding of the cab which is 4-1/2 inches thick on the top and upper part of the sides, 3 inches thick on the lower part of the sides, and 1-1/2 inches thick on the bottom. The cab is

B. CRANES (Continued)

entered through steel doors 3 inches thick. Steel is used in this structure rather than lead because of the danger that lead might eventually sag and crevices open up through the shield. The periscopes are brought in through a labyrinth on the front wall of the cab. The objective lens systems of the periscopes are exposed to moderately severe gamma bombardment while the crane is moving contaminated equipment. As a result, the lens elements gradually become discolored; but transparency may be restored by heat treatment. Ventilating air is supplied through a shielded duct from a blower mounted on top.

1.1.3 Crane Optical Aids

Because the crane cab in the Canyon Building is separated from the canyon by a 5-foot thick concrete parapet, the operator cannot directly watch the operation of the crane and recourse must be made to optical aids.

Two large periscopes, one on either side of the crane bridge permit the operator to view the crane hooks, impact wrenches and cell equipment with clarity. Although the field of vision is rather limited (to gain magnification) scanning may be obtained at the operator's discretion by electric motors which "telescope" the periscope across the canyon, and rotate it on its axis. The eyepieces are automatically synchronized with the viewing direction of the objective ends of the periscopes so that the operator is always looking in the true direction.

Large negative lenses have been installed on the outboard side of each periscope objective so that when the objective is rotated in this direction, a tremendously increased field of view is obtained. This allows the operator, in one glance, to get a general view of the canyon, to see whether or not all cover blocks are in place, and to see if anyone is on the deck.

A television camera also is installed under the crane bridge. The viewing angle of this instrument is varied by electric motors under the operator's control which rotate the camera on both the horizontal and vertical axes. The "picture" picked up by the camera is transmitted by wire to the crane cab where it appears on the screen of a television monitor. Although the television lacks the definition of the periscope, it has a broad field of view, is not as tiring to the eye, permits quicker scanning of the situation, and affords an additional view from a different angle. Portable, closed-circuit

B. CRANES (Continued)

television systems may be used with the crane when necessary to gain additional viewpoints. The portable television equipment requires "Kluge" setups and is used only when absolutely necessary.

1.1.4 Electrical Services

The crane is supplied with 440 volt, three-phase, 60 cycle power via conductors and collector shoes mounted on the crane. Similar conductors and collectors supply power to the trolley. The monorail trolleys are supplied by festooned cables. The rotary hook and the impact wrenches and/or grabbers are supplied through reel-type cord retractors. A telephone in the cab is connected to the building PAX system. Cab air-conditioning is provided for operator comfort.

1.1.5 Rotary Crane Hook (H-2-44970)

The 10-ton rotary hook was designed to allow the crane greater versatility. A 115 volt DC gear motor drives the hook through a slip clutch set at 60 ft.lb. maximum torque. The load is transmitted from the 10-ton hook to the block by a tapered roller bearing.

1.2 Auxiliary Crane (CVI 76513)

The auxiliary crane operates on the west side of the main crane. The crane operator, having little radiation shielding and no optical aids, views his work directly. The auxiliary crane is therefore used only for work in low level radiation zones.

The main trolley runs atop the bridge and carries a 10-ton hoist. Six-speed drum controllers like those on the main crane are also used to control the bridge, trolley, and hoist movements. The maximum design speeds are: Bridge - 300 FPM, Trolley - 25 FPM, and Hoist - 35 FPM. The lift is 70 feet. The monorail hoists located beneath the two bridge girders are identical with those on the main crane except that the right trolley carries only one cable reel (for supplying power and control to an impact wrench).

Lighting is provided by four 1,000 watt floodlights beneath the trolley and a 400 watt searchlight.

B. CRANES (Continued)1.3 Crane Maintenance Platforms (H-2-2762 and H-2-33125)

Two mobile crane maintenance platforms are provided to service the cranes. Each is mounted on a short section of rails at the end of the canyon and is propelled by driving the wheels through a handcrank mechanism. Access to each platform is provided by a fixed ladder mounted on the canyon end walls. A fixed, caged ladder hangs from the west end platform allowing access at any position along the rails. The east platform is of split-level design, which allows maintenance of the crane on the upper level and of the impact wrenches on the lower. The east platform has a swing-down ladder which may be lowered from the platform by a manually-operated winch.

2. 244 AR Building Canyon Cranes (H-2-62046)

A 20-ton bridge crane spans the 244 AR Building and runs the length of the canyon. Four "I" beams are suspended beneath the bridge girders, two under each girder, providing runways for four 1-ton monorail hoists. Two of the auxiliary hoists carry impact wrenches as shown in Figure XII-3. The cranes are all controlled from the crane control room from which the operator may observe the crane movements through three closed-circuit television systems and a periscope. In event of failure, a manually-operated system is provided to retrieve the bridge to the east end of the canyon where maintenance may be performed by personnel on the crane maintenance platform. The operating characteristics of the cranes are shown in the following Table.

TABLE XII-1

<u>Hoist*</u>	<u>No. Hoists</u>	<u>Capacity (Tons)</u>	<u>Trolley Speed (FPM)</u>	<u>Hoist Speed (FPM)</u>	<u>Maximum Hook Height (Above Canyon Floor, 682) (Ft.)</u>	<u>Lift (Ft.)</u>
Main	1	20	20/10/3	15/7.5/3	30	50
Auxiliary	4	1	30	31/10	26-1/2	59

* Bridge travel speed 10/20/40 FPM.

2.1 Observation System

A monocular periscope from the crane control room penetrates the south wall of the canyon, 9 feet 4 inches from the floor, enabling the operator to view the canyon area. The objective

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B. CRANES (Continued)

lens can scan through a solid angle of 180° . The eyepiece provides magnifications of 2X and 10X and is adjustable in elevation to ensure operator comfort. Each of the three closed-circuit television systems has a 17-inch monitor located within the control room; is shielded from ambient radiation; is contained in a corrosion-resistant housing that may be decontaminated and has remotely-controlled pan, tilt, and zoom mechanisms (pans through 350° , tilts through 90° , and zooms from a focal length of 25 mm to 150 mm). One camera is mounted on the crane, one may be mounted upon any of sixteen wall brackets provided, and the other may be mounted on any of the remaining fifteen wall brackets.

The canyon area is provided with high-intensity lighting along the walls. A ten-foot diameter area of the vault is lighted to an intensity of 100 foot candles by mercury-vapor floodlights on the crane. The lights are controlled from Crane Control Room.

2.2 Crane Maintenance Platform (H-2-62003 and H-2-62004)

In order to service the crane and its associated equipment, a crane maintenance platform is provided at the east end of the canyon. The platform moves along a short section of rail powered by an electric drive motor. The drive motor may be controlled either from the platform or the canyon floor. In order to reach the platform, personnel must climb one of two open ladders to an intermediate platform on the north wall, then up a caged ladder, then onto the crane maintenance platform.

3. Mobile Gantry Crane (CVI 2973)

The gantry crane is used in the Waste Management Facilities for installing and removing pumps, sluicing nozzles, and other equipment; and for making jumper changes in the diversion boxes and vaults.

3.1 Description

The gantry crane is a self-propelled railway crane equipped with two electric hoists (10-ton and 1-ton capacities), and is designed to span diversion boxes and pump, heel, and sluice pits. The crane may be towed from one location to another by lowering rubber-tired wheels which lift the crane from its rails. Crane rails are provided at the 244 CR Vault and the 241-ER-151 diversion box. Figure XII-4 is a photograph of the gantry crane.

B. CRANES (Continued)3.2 Superstructure

The superstructure of the gantry crane is a steel frame, supported on side members equipped with railway wheels, to position the hoist monorail directly over the working area. The monorail is an 18 inch "I" beam, 26 feet 7 inches long, positioned transversely 12 feet 9 inches above the crane rails. One end of the monorail overhangs the railway 8 feet and the other end overhangs 4 feet 7 inches. The side members allow a transverse clearance of 12 feet 8 inches. The center-to-center distance between the 70 pound rails is 14 feet. The gantry crane is also equipped with pneumatic rubber-tired auxiliary wheels which are raised and lowered by 10-ton capacity Porta-Power (No. R-159) hydraulic rams. One pair of wheels is fitted with a towing bar and steering links which permit a minimum turning radius of 19 feet.

3.3 Hooks and Hoists

The crane is equipped with two Yale and Towne Company hoists of 10-ton and 1-ton capacities. Pertinent data concerning the hoists is tabulated below.

TABLE XII-2

Model	<u>Hoist Data</u>	
	XE-1DC30M12	PC-1C38M15
Maximum Clearance Hook Face to Top of Rails	7 Ft.	9 Ft. 10 Inches
Total Lift	30 Ft.	38 Ft.
Hoist Speeds	12 and 4 Ft./Min.	15 and 7.5 Ft./Min.
Trolley Speeds	15 and 5 Ft./Min.	15 and 5 Ft./Min.

3.4 Electrical Services

The required 480 volt, 3-phase electrical supply is brought to the crane through a No. 4, four-conductor cable which is carried on an Applaton cable reel (No. CW-46) mounted at one corner of the superstructure. The crane is self-propelled on the rails at speeds of 40 and 3 Ft./Min. through a gear and shaft system by means of two separate motors mounted on the superstructure.

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B. CRANES (Continued)

A portable pushbutton control panel is provided for operating the crane. The control leads are of sufficient length to allow the operator to be at least 30 feet from either side of the crane. A 200 foot cable is also available to decrease operator proximity.

3.5 Lighting

The crane work area is lighted by six, 750 watt, 110 volt floodlights (Westinghouse type AH-16, Style No. 891 572), which are mounted on the crane superstructure in two banks of three lights each.

3.6 Optical System

A system of mirrors may be employed to assist the crane operator in carrying out remote operation. Binoculars are employed by the operators to aid in viewing the equipment through the mirrors. The portable television system may be used, if necessary, to view operations.

3.7 Rotary Hook (H-2-33551)

The gantry cranes are equipped with an electrically-operated, 10-ton rotary hook. The hook may be rotated either clockwise or counter-clockwise at 2-1/4 RPM. Hook rotation may be started and stopped by engaging or disengaging a magnetic clutch. The control station has two pushbuttons and one selector switch to control the hook. One pushbutton runs the motor "forward", one "reverse" and the selector "locks" or "unlocks" the clutch.

3.8 Operation

The crane and hoists may be operated from any point within 200 feet of the crane through the use of the portable control panel.

Jumper changes and the removal and installation of equipment are observed with the mirror-type viewing system.

The 10-ton capacity hoist is used for handling cover blocks and equipment, while the 1-ton hoist is used with an impact wrench for loosening and tightening remote connectors and equipment hold-down nuts.

B. CRANES (Continued)

4. Boom Cranes

Two boom cranes are assigned permanently to serve the Waste Management Facilities and two are available on a work order basis from "On-Site" services. All are standard industrial models with extendable booms.

4.1 20-Ton Lorain Crane

A Lorain, Series 40, Model MC-414, 20-ton, wheel-mounted, self-propelled crane is assigned to the Waste Management Facilities. Boom sections are available to vary the boom length from 30 feet to 70 feet. This crane is shown performing work in a diversion box in Figure XII-5. The H.O. (Hanford Operations) number of this crane is 17T-10797.

4.2 45-Ton American Crane

An American Model 599T, wheel-mounted, self-propelled, 45-ton crane is available from J. A. Jones Construction Company on work order basis. Boom sections are available to extend the 40 foot (minimum) boom to 110 feet. Its H.O. Number is 17T-19959.

4.3 60-Ton Manitowoc Crane

A 60-ton, wheel-mounted, self-propelled, Model 2900, Manitowoc crane is available on a work order basis from ITT/FSS Road Maintenance Section. Boom sections are available to extend the 40 foot (minimum) boom to 110 feet. Its H.O. Number is 17T-19960.

4.4 100-Ton Manitowoc Crane

A Manitowoc, Model 3900, 3-1/2 yard, 100-ton, track-mounted crane is assigned to the 200 Areas (Isochem, Inc.), and is normally used for construction. Boom sections are available to extend its 50 foot (minimum) boom to 140 feet. Its H.O. Number is 17-10666.

C. REMOTE CONNECTORS

The remote connector is a device for connecting process pipes, auxiliary lines, instrument lines, or electrical lines in areas where radiation levels or radioactive contaminants prohibit human access. The stationary portions of the connectors (always the lower portions) are usually mounted on the cell wall or upon the

C. REMOTE CONNECTORS (Continued)

process vessels. The movable portions (the "uppers") are normally attached to jumpers or to equipment subject to periodic removal. This equipment is arranged and balanced so that, when it is dangled from a crane hook, the "uppers" are properly oriented to engage simultaneously with their assigned "lowers" as the equipment is lowered vertically. The connectors are so designed that once they have been engaged, the equipment will remain in position after release from the crane. The connectors are secured by tightening the nuts with the remote impact wrench.

There are three basic types of connectors - the pipe connector, the electrical connector, and the wedge connector.

1. Pipe Connectors

Pipe connectors are used to connect pipes and multi-passage conduits, and to insert and seal thermocouple wells. Two types of pipe connectors are employed in the Waste Management Facilities, the "Hanford connector" which has a 3-inch hexagonal operating nut and employs flat mating surfaces, and the "Purex connector" which has a 2-inch hexagonal operating nut and spherical mating surfaces. In all other respects the two types are similar but they are not interchangeable. In pipe connectors, the "lowers" are known as "nozzles" while the "uppers" include everything else and are generally called "the connector". Figure XII-6 illustrates the two types of connectors.

Both types of connectors are available in two styles, horizontal or vertical; the connector skirt determines the style. The function of the connector skirt is to locate the connector upon the nozzle and hold it in position until the nut is tightened. In Figure XII-6, the Hanford connector is shown with a horizontal skirt and the Purex connector with a vertical skirt. The horizontal skirts are so shaped that they engage the nozzles and hang cantilevered from them. The vertical skirts are shaped like an inverted funnel in order to locate upon nozzles with vertical axes.

The nut is jacked away from the mating surfaces by tightening the pivoted, operating screw. The nut carries three latches which catch behind the nozzle flange and draw the mating surfaces together upon the gasket. The latches pass through openings in the yoke; and the geometry of these openings, the connector block, and the latches is such that, upon making the connection, the yoke forces the latches in behind the flange and, when breaking the connection, the connector block forces the latches out to clear the flange. Located directly behind the nozzle

C. REMOTE CONNECTORS (Continued)

flange is a "kickplate" which may be a separate or an integral part of the equipment upon which the nozzle is mounted. When loosening the connector, the last few turns of the screw brings the latches against the kickplate forcing the mating surfaces apart, thus overcoming any tendency of the gasket to stick.

1.1 Hanford Connectors (H-2-32700)

Hanford connectors are available in one size only. A variety of blocks and nozzles are available for single 1, 2, and 3-inch pipe connectors, 4-port instrument connections, coaxial recirculation line connections, thermometer well connections, and blank plugs. All connector blocks and nozzles are made of type 304-L stainless steel. Gaskets are spiral wound metal with a filler. Metals available are stainless steel and titanium; fillers are blue African asbestos, teflon, and linear polyethylene.

1.2 Purex Connectors (H-2-32410, H-2-32420, H-2-32430, H-2-32440)

There are four sizes of Purex connectors, 1, 2, 3, and 4-inch IPS. A multitude of connector blocks and nozzles are available for same size, reducing and increasing pipe connections, three-port instrument connection, recirculation connections, thermometer installation, and blank plugs. The connector nozzles are centrifugally cast stainless steel, the spherical mating surface of one type is faced with Stellite #6. The gaskets are teflon or teflon-impregnated asbestos.

2. Electrical Connectors

Electrical connectors are used to connect power, instrumentation, and communication conductors. Two types are employed - the "Hanford connector" which is simply a modification of the Hanford pipe connector and the "Purex connector" which employs the same size operating nut as the Purex pipe connector. Unlike the pipe connectors, the electrical connectors are all "vertical" connectors; that is, the "Nozzles" have vertical axes. Electrical connections are formed between silver-plated bronze contacts held under pressure by a spring. The springs are deformed as the operating screw is tightened.

2.1 Hanford Electrical Connector (H-2-32710)

The Hanford electrical connector, illustrated in Figure XII-7, is essentially the same as the Hanford pipe connector but with six electrical contacts made to accept No. 6 Awg conductors.

C. REMOTE CONNECTORS (Continued)2.2 Purex Electrical Connector (H-2-32400 and H-2-32401)

The Purex electrical connector is illustrated in Figure XII-7. The physical configuration bears little resemblance to the Purex pipe connector except in principle; three latches draw the "upper" down to the "lower" as the nut is tightened. When released, the latches are cammed out to clear the striker flange. They are guided in behind the flange as the screw is tightened. The connector halves are guided together by dowel pins. The several standardized contact arrangements available for the Purex connectors are seven contacts for No. 6 wire, thirteen for No. 6, twenty for No. 14, and thirty-three for No. 16. Also available are arrangements for magnetic shielded and coaxial connections.

3. Wedge Connectors (H-2-33444 and H-2-62081)

Several wedge connectors are utilized in the Waste Management Facilities. The Wedge Connector was developed to satisfy the need to remotely couple lines larger than 4 inch IPS. A typical wedge connector is illustrated in Figure XII-8. The saddle is attached to the most permanent equipment and the wedge is attached to the more mobile equipment. The gasket is lowered by the crane onto the saddle's sealing surface; the wedge and the attached equipment are then lowered into the saddle where they will remain at rest until the nuts are tightened. Wedge connectors are designed to connect pipes with horizontal axes. The smaller wedge connectors utilize a spiral-wound stainless steel-asbestos gasket while the larger sizes require a more compressible gasket such as a tubular metallic "O" ring. Contact surfaces of the wedge connector should be re-lubricated with a suitable lubricant prior to each assembly.

D. SPECIAL TOOLS

Since a crane hook is not sufficiently versatile to perform all maintenance tasks, special tools are used in conjunction with it. Yokes are used to handle equipment which cannot be suspended from one point for structural, envelope, or clearance reasons. Such yokes are generally stored on racks within reach of the crane. Since few yokes are used to handle more than one equipment, let it suffice to say that each yoke is a "special" designed to fit only its intended equipment. Impact wrenches and grabbers are the more universal tools used with the crane to perform maintenance. A common electrical circuit serves all "hook-mounted" tooling. The electrical connectors of the grabber, impact wrench, or any other tool are the same so they will mate with the crane connector.

D. SPECIAL TOOLS (Continued)1. Impact Wrench (H-2-31103 and H-2-32324)

Electrically-driven reversible impact wrenches are employed to rotate the remote nuts and connector-operating screws. A bail on the impact wrench is designed so that when suspended on a crane hook, the wrench may be balanced with the socket axis either horizontal or vertical. The wrench attitude may be changed by resting the wrench on the floor and sliding the crane hook along the bail to the opposite suspension point. The electric motor drives an Ingersol Rand impact wrench head through a gear train. When transmitting low torques, the rotary hammer is engaged with the anvil lugs and the torque is transmitted directly through with no relative motion; but when the torque exceeds a preset value, the hammer and spring are repeatedly cocked and released each time delivering a sharp impact to the anvil lugs, thence to the nut via the socket. The impact wrench is prevented from rotating by a reaction bar alongside the socket. There are two types of impact wrenches - one has a 2-inch hexagonal socket and delivers approximately 500 ft.lb. of torque to the nut and is pictured in Figure XII-9. The other has a 3-inch hexagonal socket (for special occasions, it may be fitted with a 2-inch socket) and delivers a torque of about 600 ft.lb. It should be noted that the impact wrench torque is preset to one value and cannot be varied while in use. Impact wrenches may be seen suspended from the small crane hooks in Figure XII-2.

2. Grabber (CVI 74629)

The grabber is a clam-shell bucket device for handling small pieces of equipment that cannot be picked up with the crane hooks. The tool is powered by a reversible fractional-horsepower electric motor that rotates a threaded shaft which in turn opens or closes the bucket jaws. The lips of the jaws are used to grasp loose nuts and other small items. Pipes may be gripped in semicircular notches cut in the sides of the bucket jaws. A single pair of semicircular jaws are attached to one side of the bucket for handling vertical pipe. A grabber is illustrated in Figure XII-10.

3. Flushing Wand (H-2-33094)

The flushing wand is a device used for ridding apparatus of gross contamination prior to removal. The wand is a weighted (approximately 500 pounds) pipe with a remote connector nozzle at one end, a spray nozzle at the other, and lifting bails located to allow the crane operator several choices of wand

D. SPECIAL TOOLS (Continued)

attitude. In Figure XII-11 the wand is illustrated in a horizontal attitude spraying downward (the angle is 23° below the horizontal). Yoke D-63066-F is used with the crane hook to support the wand horizontally.

A flat, sharply-defined spray pattern with uniform distribution, minimum atomization, and maximum impact is characteristic of the spray nozzle which directs 25 gpm (water at 100 psi) against the apparatus being flushed. The nozzle forms a flat spray with a 40° spread. Since the wand is stainless steel, it may be used with most decontaminating solutions and may itself be decontaminated if necessary.

4. Jumper Cutter (CVI-12484 HWS-6335)

The jumper cutter is 50-ton alligator shear and is pictured in Figure XII-12. The primary function of the jumper cutter is to cut up contaminated jumpers prior to scrapping them; in this manner the volume of the scrap is reduced and burial is more efficient. Costly items such as remote connectors, valves, and instruments may be severed from the bulky jumpers, decontaminated individually, and reused. At times the jumper cutter is used in the cells to sever tangled jumpers and other equipment.

The jumper cutter is capable of cutting a 4 inch schedule 40S pipe and a structural 4 inch, 9.2 lbs./ft. tee simultaneously. The jaws, which open to 12 inches, are actuated by a four-bar toggle linkage which is powered by a ball screw driven by a 7-1/2 horsepower electric motor. The knives are 14 inches long with edges serrated to retain the victim material during cutting. The knives are fastened in the jaws by 2-inch remote nuts. Two fixed bails permit suspending the jumper cutter from a 10-ton crane hook with the jaws either horizontal or vertical.

The jumper cutter is powered by a 440 volt, 3-phase, electric motor supplied through the standard (impact wrench grabber) connector. The circuitry is such that only the "forward" momentary-contact pushbutton controls the cutter. Holding the button in the depressed position causes the jaws to cycle from open, to closed, to open again which takes about 45 seconds. A fifteen-second time delay following each cycle allows the operator to release the button before another cycle is begun. The cutter will continue to cycle as long as the button is depressed. If the button is released at any time during the cycle, the cutter will stop immediately; the jaws will open when the button is again depressed, regardless of the point in the cycle at which they were stopped.

D. SPECIAL TOOLS (Continued)5. Extension Hooks (H-2-57884)

Extension hooks are used to extend the reach of the crane and to permit hooking small bails. The hooks are for use with 10-ton crane hooks; lengths are 2 feet and 5 feet. The hook section is 1-1/4 inches deep by 1 inch wide (7-ton maximum based on a safety factor of 4 on ultimate tensile strength) with a throat of 1-1/4 inches.

E. PORTABLE CLOSED-CIRCUIT TELEVISION SYSTEM

A portable closed-circuit television system is available from Redox on a loan basis. This system may be used to view operations or apparatus from vantage points other than those afforded by the fixed optical aids. The television camera unit is a commercial unit (General Electric Model 4TE9B3) designed to withstand severe environmental conditions. The basic camera pictured in Figure XII-13 is approximately 5-1/2 inches in diameter and 11-3/4 inches long. The camera will accept any "C" mount lens and compensates automatically for light level variations. Several television monitors may be used with the camera, usually, however, a 12 inch (General Electric Model 4TH25B1) or a 14 inch (4TH26F3) is used.

Since this is a commercial system, neither radiation shielding nor remote aiming devices are provided; these items must be designed in accordance with the situation and provided by the user. Purex has a shielded enclosure with a bail which is rotated by a television antenna rotor to permit pan control. The camera is aimed downward at a mirror which "looks" horizontally; no tilt control is provided but the camera may be raised or lowered with the crane auxiliary hook. This enclosure is available on loan to the Waste Management Facilities.

F. DIVERSION BOXES

Diversion boxes are essentially piping "patch boards". Their function is to minimize duplication of piping and to allow the changing of line routings without the use of valves. The diversion boxes are concrete pits with pipes passing through the concrete and terminating in remote connector nozzles inside (see Figure XII-14). The nozzles are arranged so that all desired connections may be obtained with several jumper configurations. Mobile cranes are used to service the diversion boxes. One type of diversion box, known as a transfer box, which connects one common pipe to each of several others, one at a time, uses only one jumper and has the several nozzles arranged in a circle about the common nozzle as shown in Figure XII-15. All diversion box lines are capable of passing fluids under pressure;

F. DIVERSION BOXES (Continued)

this feature distinguishes diversion boxes from diverter stations which can only accomodate gravity flows. Leakage occurring within the diversion box is collected in a basin until there is sufficient quantity to return it to the processing operation.

Although one of the functions of diversion boxes is to eliminate valves, in some instances it has been necessary to utilize valves. Where valves are used, they are located in the jumpers so they may be removed from the diversion box remotely and either discarded and replaced or serviced. The valve stem extensions project upward through the concrete cover blocks and radiation shielding is provided around the penetration.

G. DIVERTER STATIONS

Diverter stations are similar to diversion boxes except that gravity flow is necessary. A typical diverter station is shown in Figure XII-16. Fluid flows into the diverter tank; when the fluid level reaches the height of the exit piping, it flows out through a short jumper and falls into the spout funnel. From the spout, the liquid flows out into the selected floor funnel. Selection of the floor funnel is accomplished manually. The spout is raised out of the funnel it is presently in, rotated until it is above the desired funnel, and lowered. The floor drain allows all leakage to collect in a sump from which it may be returned to the process operation.

H. REMOVAL AND REPAIR OF RADIOACTIVELY CONTAMINATED EQUIPMENT

Occasionally it is necessary to repair, replace, or maintain contaminated equipment located within a cell or vault. Wherever possible, the equipment is flushed or rinsed with decontamination solutions while still in location. On rare occasions, it is possible to perform the required "contact maintenance" after rinsing without removing the equipment, but usually it is necessary to remove the equipment for maintenance.

Often, due to the length of time an item would be out of service for decontamination and repair, the item, even though it can be repaired, must be replaced with new equipment. The nature of the equipment and the contaminant dictate the disposition of each particular piece of equipment. Employing chemical and physical decontamination methods, the radiation level of many items may be reduced sufficiently to permit the required maintenance. The remaining items must either be scrapped or, when the contaminating isotope(s) are relatively short-lived, allowed to "cool-off".

H. REMOVAL AND REPAIR OF RADIOACTIVELY CONTAMINATED EQUIPMENT (Continued)

Items to be scrapped are placed on an old, contaminated railroad flat car, often separated from the engine by several empty cars, and removed via the Hanford Railroad to a desert burial tunnel where it is abandoned - flat car and all. Equipment which is to "cool-off" is removed to a designated area where it will not be a hazard to personnel while the radioactive isotopes decay. At the end of the cooling-off period, maintenance may be performed and the equipment returned to service when needed.

Equipment which is to be chemically or physically decontaminated is sent via railroad to a decontamination facility, often the 221-T Building, where the required decontamination and repair may be performed.

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FIGURE XII-1
221-B Canyon Building
Sectional View

FIGURE NII-2

Main Crane and East Crane Maintenance Platform
221-B Building

FIGURE XII-3

214 AR Crane and Crane Maintenance Platform

FIGURE NII-4
Gantry Crane

FIGURE NII-5
20 Ton Lorain
Performing Work in Diversion Box

FIGURE XII-6
Pipe Connector

FIGURE XII-7
Electrical Connectors

FIGURE XII-8
Wedge Connector

FIGURE NII-9
Impact Wrench
(2 inch Socket)

FIGURE NII-10
Grabber

FIGURE XII-11
Flushing Wand

FIGURE XII-12
Jumper Cutter

FIGURE XII-13
Portable Television Camera

FIGURE XII-15
Plan View of Transfer Box

FIGURE XII-14
Diversion Box
(241-A-151)

FIGURE XII-16
Diverter Station

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PART VI

PROCESS CONTROL

CHAPTER XIII

INSTRUMENTATION

By

R. J. Merriman

HANFORD ENGINEERING SERVICES

UNCLASSIFIED

WASTE MANAGEMENT TECHNICAL MANUALCHAPTER XIIIINSTRUMENTATION

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CHAPTER XIIIINSTRUMENTATIONA. INTRODUCTION

Continuous processing employed in the Waste Management Program requires that automatic instrumentation measure and control a majority of the process variables encountered. These variables include flow, pressure, liquid level, weight factor, specific gravity, liquid-liquid interface position, speed, vibration, sound, pH, temperature and radiation.

Generally an instrument measuring and control system consists of several component elements integrated to function as a system. The integrated component elements are the primary element which "senses" the process variable; an element that receives the signal from the primary element, conditions or modifies this signal, and transmits the modified signal to a receiver element where it is indicated or recorded; the controlling element which automatically transmits varying signals to the final control element to keep the process variable at the desired operating condition; and the alarm element to warn the process operator of an abnormal condition.

The purpose of this chapter is to discuss in detail the various instruments used in the Waste Management Program to measure and control the many processes.

B. FLOW MEASUREMENT AND CONTROL

The following types of flow measuring and/or control systems are used in the Waste Management Program: (1) electronic transmitting rotameter, (2) pneumatic transmitting rotameter, (3) indicating rotameter, (4) magnetic flowmeter, (5) orifice meter, and (6) displacement meter. The choice of the system depends upon the solution to be measured, whether it is radioactive or non-radioactive, acid or caustic, aqueous or organic, contains solids or not; upon the accuracy of the measurement desired; and upon the flow rates and the range of flow likely to be encountered.

1. Rotameters

Rotameters make use of a constant differential head across a restriction of variable area to measure the flow rate of a fluid. The general flow equation is:

$$Q = CA\sqrt{2gH}$$
 where Q = flow rate, C = flow coefficient of discharge, A = area (variable), H = head difference across the annular restriction (constant), and g = acceleration due to gravity.

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B.1. Rotameters (Continued)

The stream being measured passes upward through a vertical, truncated conical metering tube having the maximum diameter at the top. A float inside the tube adjusts its vertical position as required by the flow rate, and in so doing changes the annular area between the tube and the maximum diameter of the float.

Rotameters are usually designed for a flow rangeability of 10 to 1, but up to about 20 to 1 can be obtained. Rotameters have given satisfactory operation in flow ranges from a minimum of 6 to 60 ml/min to a maximum of 10 to 100 gal/min. Rotameters are generally not recommended for ranges below 0.1 to 1.0 gal/min. For smaller flows, the magnetic flowmeter should be considered.

Volumetric flow rates are affected by the density and viscosity of the fluid being measured. A density correction can be applied if the viscosity is less than about 3.0 centipoise for flows up to 2 gal/min., and less than about 20.0 centipoise for flows from 2 to 20 gal/min.

$$F = \sqrt{\frac{(P_{f2} - P_{w2}) (P_{w1})}{(P_{f1} - P_{w1}) (P_{w2})}}$$

F = Correction Factor
(Multiply original calibration by factor
to obtain new flow rate)

P_{f1} = Density of original float

P_{f2} = Density of new float

P_{w1} = Density of original solution

P_{w2} = Density of new solution

The pressure drop across the rotameter is nominally 30 inches of water but can vary from about 0.1 inch to 50 inches depending upon size and service.

1.1 Electronic Transmitting Rotameters

A typical flow measurement and control system for use in a remotely operated separations facility is shown schematically in Figure XIII-1. The process solution line contains an electronic rotameter-transmitter and an air-operated control valve. An electrical conduit or jumper carries the signal wires from the rotameter through

B.1.1 Electronic Transmitting Rotameters (Continued)

the shielding wall to the amplifier-converter, located in a non-radioactive zone. It converts the electronic signal to a 3-15 psig air signal and is sent to a recorder-controller located on the instrument panelboard. The recorder-controller, in turn, sends a 3-15 psig air signal back through the shielding wall to operate the control valve.

1.1.1 Transmitters

A rotameter transmitter, especially designed for use in measuring the flow of a radioactive stream, is shown in Figure XIII-2. A float with an attached soft iron armature covered with a stainless steel tube assumes a vertical position in the tapered metering tube for a given flow rate. The transmitting coil, attached below the metering tube, forms an impedance bridge with a similar pair of inductance coils in the amplifier-converter. The float armature movement causes an impedance change that is detected by the amplifier-converter.

The stainless steel metering tube and coil housing are joined together by flanges and sealed with a Teflon "O" ring. The fluid enters at the bottom of the coil housing and passes through and around the coil housing (for flows greater than 0.25 gal/min), converges beneath the float, and then passes through the metering tube which is approximately 50 millimeters (mm) in active length. The tube has an enlarged section above the active length to allow purging of foreign matter which may cause the float to stick. The lower float stop is approximately 10 percent up the metering tube from the true zero so that the float portion will allow back flushing of the tube. All parts in contact with process solution are type 347 and 304L stainless steel or Teflon.

1.1.2 Amplifier-Converters

The amplifier-converter has a pair of induction coils and a soft iron armature (not stainless steel clad) similar to the rotameter. The armature is driven by a reversible motor controlled by the amplifier. Linkage attached to the upper part of the armature connects to a pneumatic transmitter to produce a 3-15 psig air signal proportional to flow.

The rotameter coils and the amplifier-converter are connected to form two parallel circuits. The outer leads are connected via a step-down transformer to a source of alternating current and the center lead of each coil is connected to the amplifier. The amplifier controls the rotation of the reversible servomotor. When the transmitter and receiver armatures are in corresponding positions in the coils, the impedance in each of the two circuits is equal, and no current flows through the center lead. However, as soon as the transmitter armature moves due to a change in flow rate, the impedance of the transmitter coils varies and causes a small current to flow in the center lead. The magnitude and phase relationship of this current is detected by the amplifier and energizes the reversing winding of the motor. The other winding (reference) of the

B.1.1.2 Amplifier-Converters (Continued)

motor is energized from a steady source of alternating current supplied through a capacitor to provide proper phase relationship. Depending on the direction of the error signal, the amplifier output current is always leading or lagging the current in the line winding by 90° , thus causing the servomotor to rotate in one direction or the other. Rotation of the servomotor is transmitted through a reduction gear and friction drive assembly to move the amplifier armature until it is again in a position corresponding to the transmitter armature. When this occurs, the error signal and amplifier output diminish to zero, the servomotor stops rotating, and the system is balanced.

The upper end of the armature in the amplifier-converter is connected through linkages to a pneumatic transmitter. The transmitter converts the mechanical input signal to a proportional 3-15 psig air signal, which is connected to a recorder-controller.

1.1.3 Recorder-Controllers

A miniature pneumatic recorder-controller is used for most flow measurements. It has a 3-15 psig bellows that receives the air signal from the amplifier-converter and, through linkages, operates a recording pen on a 4-inch, 0-100 percent, linear strip chart. A controller is usually attached to the recorder and a switching device is provided to allow transfer from "manual" to "automatic" control and vice versa without upsetting the flow control.

See Section B.6 for more information on the recorder and the various controller functions and see Section B.5 for information on control valves.

1.2 Pneumatic Transmitting Rotameters

The pneumatic transmitting rotameter is used only to measure the flow rate of certain "non-radioactive" process streams. A common control system consists of a pneumatic transmitting rotameter, a recorder-controller, and an air-operated control valve located in the process line. A 3-15 psig signal from the transmitter is received by the recorder-controller located on the instrument panelboard. The recorder-controller, in turn, sends a 3-15 psig air signal back through the shielding wall to operate the control valve.

A cascade control system consisting of pneumatic transmitting rotameters, master and slave recorder-controllers, ratio set point instrument, cascade subpanel and control valves, is shown schematically in Figure XIII-3. The function of the system is to maintain the flow rates of two streams according to a predetermined ratio.

The operation of the system is as follows: The set point of the master flow recorder controller (FRC) must be set for the desired operating conditions. Its 3-15 psig air control signal is directed to the control valve (DOV) located in the 1BX H₂O stream permitting flow through the pneumatic transmitting rotameter (FT) to the 1BX column. The flow transmitter's 3-15 psig output signal is transmitted to the master controller (see Figure XIII-4) and the ratio set point unit (SR).

B.1.2 Pneumatic Transmitting Rotameters (Continued)

The ratio unit contains a ratio relay which receives the linear input signal and produces an output signal that is a preset ratio of the input; a large dial for selecting and indicating the desired ratio; and a transfer station that consists of a transfer valve and a manual regulator. During normal operation, the transfer valve is placed in the "ratio set" position which permits the ratio relay to generate the output signal. When the transfer valve is placed in the "manual set" position, the manual regulator can be adjusted to generate the output signal.

The ratio set point output signal is transmitted to the slave flow recorder-controller (FRC) set point capsule, see Figure XIII-4, via the controller sub-panel described in Section B.6.3.4. The set point of the slave FRC is then adjusted automatically or manually by the ratio set point unit to maintain the proper flow ratio between the LBX H₂O and LBX chemical addition streams. The master flow recorder-controller transfer switch is described in Section B.6.3.4.

1.2.1 Transmitters

There are two general types of pneumatic transmitting rotameters. The first contains a glass metering tube which is fluted to guide the float and armature. The fluid enters horizontally at the bottom of the glass tube and leaves horizontally at the top. A stainless steel extension housing for the float armature is mounted on top of the glass tube with a magnetically-coupled pneumatic flow transmitter mounted around the extension housing. An armature is attached to the upper part of the float consisting of a stainless steel tube containing two cylindrical permanent magnets in the upper portion placed so that the north-seeking poles are adjacent. An additional pair of magnets is mounted around the outside of the stainless steel tube with their south-seeking poles adjacent to the north-seeking poles of the magnets inside the armatures. One manufacturer uses only one magnet on the armature and one on the follower. Thus, as the armature moves, the external magnets follow and, through a mechanical linkage system, operate a pneumatic transmitter to produce an air signal proportional to float position. The glass tube is usually calibrated in percent of maximum flow and the transmitter indicator reads in percent. The pneumatic 3-15 psig output signal is received by a panel-mounted recorder, recorder-controller or indicator.

The second type consists of a stainless steel metering tube with the fluid entering and leaving the bottom and top vertically. It is called a straight-through flow meter and is very compact. The transmitter is attached at about the middle of the metering tube. The operation is the same as described in the foregoing.

B.1.2.2 Recorders and Recorder-Controllers

A miniature pneumatic recorder-controller is used for most flow measurements. It has a 3-15 psig bellows that receives the air signal from the transmitter and, through linkages, operates a recording pen on a 4-inch, 0-100 percent, linear strip chart. A controller is usually attached to the recorder and a switching device is provided to allow transfer from "manual" to "automatic" control and vice versa without upsetting the flow control.

See Section B-6 for more information on the recorder and the various controller functions and Section B-5 for information on control valves.

1.3 Indicating Rotameters

1.3.1 Purge Rotameters for Dip Tubes

A small compact indicating rotameter, approximately six inches long, is used to measure the air flow to a dip tube for measuring weight factor, specific gravity, et cetera. It consists of a glass or plastic tapered metering tube and a ball float. The tube is calibrated in standard cubic feet per hour (SCFH) at 10 psig and 70 F. The range is usually 0.1 to 1.0 SCFH, 0.2 to 2.0 SCFH or 0.25-2.5 SCFH. A needle valve at the base of the metering tube is used for setting the desired flow rate. Accuracy is ± 3 percent of maximum flow.

1.3.2 Rotameters for Air, Water, and Chemical Flow

An indicating rotameter is located directly in the fluid to be measured and the flow rate is indicated by the float position opposite a calibration on the side of the glass tube or on a metal scale positioned vertically along the glass tube. The tubes are usually 130 mm or 250 mm in length and the calibration is usually in percent of maximum, but the calibration may be in actual flow units, gal/min, SCFM, et cetera, or in millimeters of float travel. If it is in mm float travel, a calibration curve would have to be provided. The body is usually stainless steel for chemical flow and brass or steel for water and air flow.

2. Magnetic Flowmeters

The "magnetic" flowmeter operates on the principle of Faraday's law of electro-magnetic induction - the voltage induced across any conductor as it moves at right angles through a magnetic field is proportional to the velocity of the conductor. The "magnetic" flowmeter is a modified form of an alternating current generator.

Figure XIII-5 illustrates the basic operating principle. Consider a segment of the moving fluid as a conductor of length "d", which is equal to meter pipe diameter. As the fluid conductor section moves

B.2. Magnetic Flowmeters (Continued)

transversely at velocity "V" through a uniform magnetic field "B", the voltage "E" induced across this section in the plane of the meter electrodes is proportional to the rate of fluid flow.

The "magnetic" flowmeter measures volumetric flow rate and is not affected by density, viscosity and fluid pressure. As long as the conductivity of the flowing fluid is above a certain minimum value, depending on meter size and cable length, changes in conductivity do not affect the flow measurement. The nominal minimum value of 80 micromhos per centimeter will be satisfactory for all meters. Some can go as low as 20 micromhos per centimeter. At 80 micromhos, the cable length between meter and amplifier can be up to 800 feet.

The "magnetic" flowmeter requires no "straightening" devices and may be connected directly at piping elbows and valves, or to a reducer from a larger or smaller diameter pipeline. The flowmeter has to be completely filled with the solution to be measured for accurate flow measurements. If the electrodes were covered with liquid but the upper portion of the pipe were filled with gas, the flow indicated would be the same as a completely filled pipe. The pressure drop through the meter is equivalent to an equal length of straight pipe of the same diameter.

The meter can measure flow in either direction by simply reversing the signal leads at the receiver or, if it is desired, the zero flow point could be elevated to 50% and flow measured in both directions. By adjustments at the receiver, a flow range change can be made over a 3,000 to 1 range.

The flowmeters are manufactured in the following sizes and are capable of operating over the range shown. Larger sizes can also be obtained.

<u>Size</u>	<u>Flow Range - Gal/Min</u>
1/10"	0 - 0.034 to 0 - 1.08
3/16"	0 - 0.137 to 0 - 4.1
1/2"	0 - 0.66 to 0 - 20.0
1"	0 - 2.9 to 0 - 80.0
2"	0 - 11.0 to 0 - 400.0

A typical flow system is very similar to an electronic rotameter system except that it uses a "magnetic" flowmeter instead of a rotameter. It consists of a process line incorporating the flowmeter and an air-operated control valve. An electrical conduit carries the signal and power via special cable through the shielding wall to an amplifier-converter located in a non-radioactive zone. It converts the electronic signal to a 3-15 psig air signal and is sent to a recorder-controller located on the instrument panelboard. The recorder-controller, in turn, sends 3-15 psig air signal back through the shielding wall to operate the control valve.

B.2.1 Flowmeter Transmitters

2.1.1 Special Radioactive-Service Flowmeter

A specially designed Fischer and Porter "magnetic" flowmeter is used to measure the flow of very radioactive streams that would cause a plugging problem if a "canyon type" rotameter were used.

The meter consists of a straight pipe section, approximately 10 to 20 inches in length, of "Inconel" coated with a liner of vitreous enamel 0.003 inches thick with two platinum electrodes fused into the liner. The liner provides the electrical insulation to prevent short-circuiting of the generated voltage. This liner should not be exposed to "caustic" or fluoride solutions. The meter is provided with either a butt weld fitting for welding directly into a process line, or with a standard 150 pound, type 316, stainless steel flange.

Two magnet coils, 180 degrees apart around the pipe, are wired in series and are fabricated of wire coated with a polyester film that has a very good resistance to gamma radiation. The signal wire and the wire for 120 volt, 60 Hz current to the magnet coils are insulated with linear polyethylene and go to a waterproof "Kovar" seal (an assembly of electrodes through a ceramic disc). From the "Kovar" seal, the signal and power cables are run together in a special shielded cable with linear polyethylene insulation. The coil, electrodes and a portion of the metering tube are covered with a 6-inch, Schedule 40, 304L stainless steel pipe to provide an acid-proof meter. The meter is potted with silicone rubber to fill all voids.

The reference calibration components that are normally in the meter were removed and placed in a box installed in an accessible location next to the amplifier-converter because these components could be damaged by radiation. However, it must be remembered that the calibration components are correct with only one meter and must be changed whenever the meter is changed.

See Figure XIII-6 for a schematic wiring diagram.

2.1.2 Standard Service Flowmeters

The "magnetic" flowmeter as obtained from the manufacturer is a standard line instrument and is very similar to the "special" described in foregoing Section except: (1) it cannot stand very high gamma exposure (10^6 R as compared to 10^9 R for the special meter, (2) the coil housing is not as resistant to chemical corrosion, and (3) it is not as rugged structurally. Since it is a production line instrument, the cost is about half of the special meter. Therefore, this type should be used wherever practical.

B.2.2 Amplifier-Converters

The amplifier-converter is an a-c, self-balancing potentiometer. The flow signal as developed across the meter electrodes is transmitted to the amplifier by a balanced line and is series-coupled through the dual secondary windings of a balancing transformer on the servomotor panel. A reference balancing signal is derived from a current transformer located in the calibration component block. The reference balancing signal goes through a servo-driven balancing network before being applied to the balancing transformer primary winding in phase opposition to the flow signal. The magnet coils and the reference calibration components are connected in series, and consequently are excited by the same current. Therefore, the amplitudes of the signal and reference voltage will increase or decrease proportionally with variations of line voltage. Since it is the ratio of signal to reference voltage which establishes the measurement criterion, no loss of accuracy will be experienced with a ± 10 percent variation of the line voltage or frequency.

The resultant error signal produced by the comparison of the flow and reference signals at the balancing transformer is amplified and applied to the control winding of a split-phase motor. The servomotor responds to the error signal by driving the balancing network slidewire potentiometer to a position which causes the signal output to be equal and opposite to that of the incoming flow signal. Thus, the servomotor is positioned by proportional feed back. The motor is mechanically joined to an indicating pointer to show the flow rate.

The motor is also connected through linkages to a pneumatic transmitter. The transmitter converts the mechanical input signal to a proportional 3-15 psig air signal, which is sent to a recorder-controller.

The output signal from the magnetic flowmeter electrodes is approximately 0.3 millivolts per ft/sec of fluid velocity. The flow range can be adjusted by two dials on the amplifier, from 0-1 ft/sec to 0-31 ft/sec. One dial increases the range by 10 ft/sec while the other dial is a ten-turn potentiometer which allows the velocity to be set to two decimal places. A full zero adjust allows the scale to be expanded from 1-31 ft/sec to any value from 1 to 62 ft/sec full scale. This also allows bi-directional flow to be measured by adjusting the zero to 50 percent for no flow.

2.3 Recorder-Controllers

A miniature pneumatic recorder-controller is used for most flow measurements. It has a 3-15 psig bellows that receives the air signal from the amplifier-converter and through linkages operates a recording pen on a 4-inch, 0-100 percent, linear strip chart. A controller is usually attached to the recorder, and a switching device is provided to allow transfer from "manual" to "automatic" control and vice versa without upsetting the flow control.

B.2.3 Recorder-Controllers (Continued)

See Section B.6 for more information on the recorder and the various controller functions and Section B.5 for control valves.

Sometimes the amplifier-converter is just an amplifier with recording provisions but may also have control functions. Such a recorder would have a 24-hour, 12-inch diameter, circular chart with a 4-5/8 inch calibrated length, 0-100 percent linear. If it has control functions, they would be the same as those described in Section B.6.

3. Orifice Meters

Orifice meters operate on the principle of a constant area flow restriction with variable head (pressure) loss. The relationship of flow rate and head loss is expressed in general form by the equation:

$Q = CA\sqrt{2gH}$ where Q = flow rate, C = flow coefficient of discharge, A = area (constant), H = head difference across the restriction (variable) and g = acceleration due to gravity. The difference in hydrostatic head created by the orifice is impressed across an instrument such as a manometer or a differential pressure transmitter.

The orifice system has a useful minimum to maximum flow range of about 3 to 1. The measurement of flow ratio beyond the range of a particular installation can be accomplished by either changing the size of the orifice or allowing a greater pressure drop across the orifice.

The orifice system is used primarily on air, steam, and water flow where all of the instruments including the orifice can be located in an accessible zone for maintenance.

Since air and steam are compressible fluids, the upstream orifice pressure should be fairly constant, otherwise a correction would have to be applied to the flow reading based on the known upstream pressure.

A typical orifice flow measuring system consists of: (1) an orifice plate mounted in a special flange on the process line, (2) high and low pressure taps at the flange, (3) valves in each line and by-pass valve between the two taps, (4) a differential pressure transmitter across the two taps below the valves, (5) a 3 - 15 psig air output signal from the transmitter to a recorder-controller located on a panelboard, and (6) a 3 - 15 psig signal from the controller to a control valve located in the process line. See Figure XIII-7.

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B.3.1 Orifice Plates

The device used to produce the variable head is usually a sharp-edge orifice made from a 1/8-inch thick plate. This orifice is usually mounted in a special orifice flange that has pressure taps located one inch upstream and downstream from the face of the orifice. If the pressure taps are not located at the orifice, they are located at 2-1/2 pipe diameters upstream and 8 pipe diameters downstream, and it is called a pipe tap installation.

The thickness of the orifice plate should not exceed $d/8$, $D/50$, or $(D-d)/8$, where d is orifice diameter and D is pipe diameter. If thicker plate is used, the outlet face of the orifice should be beveled so that a straightedge laid across the bevel will form an angle not less than 45° to the axis of the pipe. The upstream edge should be square and as sharp as possible. Any rounding should not exceed 0.025 percent of the orifice diameter. The orifice plate should be centered in the pipe so that its eccentricity is less than 3 percent of the pipe diameter.

Valves, pipe fittings, sharp bends, et cetera, set up swirls, eddy currents, or other irregular velocity distributions in the pipe and may cause substantial errors in flow measurement. These effects are dissipated after the fluid flows through a considerable length of straight pipe. The length of straight pipe required on the downstream side of a valve or fitting is a function of type of fitting and the ratio of orifice diameter d to pipe diameter D . The orifice should have five pipe diameters of straight pipe after a 90° elbow at a d/D of 0.1 and should have twenty pipe diameters at a d/D of 0.8. After a valve there should be fifteen pipe diameters of straight pipe with a d/D of 0.1 and fifty pipe diameters at d/D of 0.8.

3.2 Transmitters

Transmitters from several manufacturers are used throughout the Waste Management Program such as Fischer & Porter, Foxboro, Republic, et cetera. They all work on the force balance principle — the resultant force caused by a differential pressure applied to a lever is balanced by an air pressure which amplifies the pressure to a proportional 3-15 psig air signal. See Figure XIII-8. This type transmitter is also used for weight factor, specific gravity, interface and pressure measurement.

3.2.1 Linear Transmitters

The transmitter is connected across the high and low pressure taps at the orifice. These pressures are applied to opposite sides of a measuring diaphragm and the resulting differential pressure exerts a force on a lever. This lever transmits the force, which is exactly proportional to the differential pressure on the diaphragm, through a range adjustment fulcrum to move the lever towards or away from the flapper nozzle of an air relay. The air output pressure of the relay is transmitted to a recorder or indicator and to a feedback bellows. The force exerted by the feedback bellows is exactly proportional to the force applied to the force lever

B.3.2.1 Linear Transmitters (Continued)

(proportional to differential pressure). In operation, the movement of the force lever is continuously adjusting the flapper-nozzle to maintain a balance of forces.

The 3-15 psig output signal is proportional and linear in relation to the differential pressure across the orifice. Since the flow through an orifice is a function of the square root of the pressure drop, the output signal must be transmitted to a square root indicating or recording instrument. If the output signal is transmitted to an instrument with linear or uniform scale, a calibration curve must be provided.

3.2.2 Square Root Extractor

Square root extraction is frequently necessary to linearize flow measurements from differential pressure signals developed by a differential pressure type flow transmitter. The resulting linearized signals are proportional to the flow.

The Moore square root extractor, shown in Figure XIII-9, employs a geometric relationship as the operating principle — the cosine of an included angle is compared with the change in the angle. This relationship holds true for small angular displacements. Referring to Figure XIII-9, the signal whose square root is to be computed is the input pressure A. The value of T is the square root of A. That is:

$T = K\sqrt{A}$, where K is a constant. The device works on a motion-balance principle. Increasing input signal A moves the floating link to the left to restrict the pilot nozzle. The restricted nozzle increases the output pressure and moves the output feedback bellows upward until balance is restored. Since the length of the floating link is fixed, $\cos \theta$ equals $1 - X/L$. A plot of output displacement, $Y = \theta L$ (for small values of θ , in radians) versus input displacement X shows the relationship to be virtually an exact square root.

3.3 Recorder-Controllers and Indicators

The 3-15 psig air signal from the differential pressure transmitter is received by either a recorder or a pressure indicator located on the instrument panelboard. If the signal comes from a linear transmitter, the recorder chart and indicator scale is usually calibrated 0-100 or 0-10 square root so that they express percentage of maximum flow directly. If the chart or scale is 0-10, it would have to be multiplied by 10 to get actual percentage. If the signal is from a square root extractor, the chart or scale would be 0-100 percent linear and would express the flow directly as percentage of maximum flow.

B.3.3 Recorder-Controllers and Indicators (Continued)

A miniature recorder-controller is used for most flow measurements. It has 3-15 psig bellows that receives the air signal from the transmitter and through linkages operates a recording pen on a 4-inch strip chart. A controller is usually attached to the recorder and a switching device is provided to allow transfer from "manual" to "automatic" control and vice-versa without upsetting the flow control.

See Section B.6 for more information on the recorder and the various controller functions and Section B.5 for control valves.

A pressure gauge, calibrated 0-100 percent or 0-100 square root for 3-15 psig, may be used if only indication is required.

4. Displacement Meters

Inexpensive displacement meters are used to measure the volume of water transferred where rate measurement or control is not necessary.

The meter contains a nutating piston which is activated by the passage of a fixed volume of liquid. The nutation of the piston, through a gear train, actuates a counter and registers total flow. Usually a six digit counter is used and resets to zero only after a full register.

5. Valves

Control valves are used to regulate the flow of process solutions, air, water and steam at a given rate by "throttling" or full line flow by "on-off" operation.

The valve has a plug or trim that is raised or lowered within a seat ring to change the amount of flow area thus regulating the flow. There are three general types of plugs used: (1) a linear (parabolic) plug produces a constant change in flow rate for a unit change in valve plug travel providing the pressure drop across the valve remains constant. This type of plug is used in those cases where the pressure drop in the system is largely concentrated across the valve. (2) An equal percentage (ratio or logarithmic) plug produces an equal percentage in flow rate for a unit change in valve plug travel (above 2 percent) providing the pressure drop across the valve remains constant. At any position of the plug, when the travel is changed 10 percent, the flow changes approximately 50 percent. This plug is used in those cases where only a small fraction of the pressure drop is dissipated by the valve. At low flow rates, however, it is possible for practically all of the pressure drop to be concentrated at the valve if necessary. (3) Quick opening or "on-off" valves are usually the same size as the line. Some throttling can be done with this type plug but full flow is obtained at 25 percent of valve travel. See Figure XIII-10 for curves of valve characteristics.

B.5. Valves (Continued)

Control valves have a rangeability of approximately 50:1 based on the ratio of the maximum flow coefficient to the minimum flow coefficient, which is determined by the clearance between the valve plug and its seat. If this clearance becomes large, the rangeability will drop off. The flow coefficient (C_v) is the flow rate in gal/min of water at one psi drop across the valve. A flow range of 50:1 may seem to be an unnecessary requirement; however, it is necessary for a system where a decrease in flow greatly increases the pressure drop or the energy that must be absorbed by the valve. For example, assume the maximum flow is 10 gal/min at 9 psi pressure drop and the minimum flow is 0.5 gal/min at 49 psi pressure drop.

$$\text{Since: } C_v = \frac{\text{gal/min}}{\sqrt{\Delta P}}$$

$$\text{Then: } \frac{C_v \text{ Max}}{C_v \text{ Min}} = \frac{\frac{10}{\sqrt{9}}}{\frac{0.5}{\sqrt{49}}} = 46.7:1$$

A valve rangeability of 50:1 would just handle the above flow condition even though the actual flow ratio is only 20:1.

The general flow formulas are:

$$\text{Liquid: Flow rate in gal/min} = C_v \sqrt{\frac{\Delta P}{G}}$$

$$\text{Gas: } Q = 1360 C_v \sqrt{\frac{\Delta P}{(460 + ^\circ F)G}} \sqrt{\frac{P_1 + P_2}{2}}$$

$$\text{Steam: } W = 2.1 C_v \sqrt{\Delta P} \sqrt{P_1 + P_2}$$

Where C_v = the flow coefficient of valve defined as the flow rate in gal/min of water at 1 psi drop across the valve.

P_1 = Inlet pressure in psia

P_2 = Outlet pressure in psia

$\Delta P = (P_1 - P_2)$ pressure drop, psi

B.5. Valves (Continued)

Q = SCFH at 14.7 psia and 60 F

G = Specific Gravity

W = Pounds per hour saturated steam

The following plug sizes are available in both linear and equal percentage types. The listed C_v is based on Hammel Dahl data but other manufacturer types are approximately the same.

<u>Nominal Plug Size Inches</u>	<u>C_v For Fully Open Position</u>
1/4	1.6
3/8	2.5
1/2	4.0
3/4	6.3
1	12.0
1-1/4	18.0
1-1/2	28.0
2	48.0
2-1/2	72.0
3	100.0
4	160.0
6	360.0

For very small flows a "spline" type plug is used and consists of a 1/4-inch diameter rod with a groove of various tapers depending on size. This rod moves within a seat ring hole which must be a lap fit to give 50:1 rangeability. If the clearance is 0.001-0.002 inches, the rangeability is only 25:1. The splines come in sizes 1 through 15 but from a practical standpoint it is not recommended to use a spline smaller than No. 7.

<u>Spline No.</u>	<u>C_v For Fully Open Position</u>
1	0.63
2	0.40
3	0.25
4	0.16
5	0.10
6	0.063
7	0.040

Splines 1 through 5 come only as equal percentage and splines 6 through 15 come only as linear.

B.5.1 Diaphragm-Operated Valves

5.1.1 Radioactive Service

Diaphragm, air-operated control valves, especially designed for use in a radioactive area are shown in Figure XIII-11 and 12, and are the Hammel Dahl type and the Kieley-Mueller type which are similar in construction. The body is designed to allow complete drainage when the plug is off the seat ring and the valve is installed in a jumper to allow the liquid to return by gravity to a vessel. The valve has a single seat plug for tight shut-off with provision for easy removal of both the plug and seat. A welded, leaf-type stainless steel bellows is attached to the plug stem and is installed to permit the process solution to contact only the outside of the bellows, thus providing a washing action to prevent the bellows from fouling. Open construction between the auxiliary Teflon stem seal above the bellows seal and the diaphragm chamber allows the process solution to drain to the floor instead of backing up into a non-radioactive zone through the air line, if both seals should fail. The design of the Hammel Dahl diaphragm chamber allows the valve action to be changed from air-to-open to air-to-close by repositioning the spring adjustment nuts and moving the air connection from one side of the diaphragm to the other. The Kieley-Mueller valve is designed so that the diaphragm chamber must be removed and inverted in order to change the operation of the valve from normally closed to normally open. Most valves are the normally closed type, that is, on an air signal failure the valve will close. The diaphragm is fabricated of "Buna N" rubber with "nylon" inserts. This diaphragm can withstand a total gamma exposure of about $1 \times 10^9 R$ before failure. The life of the diaphragm can be improved somewhat by placing a lead shield around the chamber. If a valve is required to handle a much larger total exposure, the type described in Section B.5.2 should be used. Some of the other valves use neoprene with nylon inserts for the diaphragm and can withstand a total gamma exposure of about $1 \times 10^8 R$ before failure.

5.1.2 Non-Radioactive Service

Manufacturer's standard diaphragm-operated valves supplied by such companies as Fischer Governor, Foxboro, Honeywell, Keiley-Mueller, etc. are used to regulate the flow of non-radioactive streams. They are single- and double-seated valves designed for only one type of action, either air-to-open or air-to-close. The plug stem has a standard packing gland instead of a bellows seal — the packing is usually Teflon.

5.2 Piston-Operated Valves

An especially designed valve for very high gamma fields has been fabricated by the Fischer Governor Company and consists of a piston actuator instead of the diaphragm actuator. The piston actuator is

B.5.2 Piston-Operated Valves (Continued)

made without the use of plastics or organic materials and is capable of withstanding a very high gamma exposure in the magnitude of 1×10^{11} to 1×10^{12} R.

The valve body is of the angle type with the inlet vertical and the discharge horizontal. Two plug stem seals are provided: (1) the primary seal is a stainless steel convolution type bellows with the process solution on the outside of the bellows to provide a washing action, and (2) an auxiliary Teflon packing seal. The piston uses iron seal rings. An operating pressure greater than 40 psig is required for full-range operation of the piston. Since the controller output is a 3-15 psig air signal, an air relay must be installed to convert this signal to 9-45 psig.

5.3 Ball Valves

Ball valves are used in certain streams when positive shut-off is required. It consists of a stainless steel ball that rotates within an upstream and downstream Teflon seal ring. If used with high radioactive solutions, the seals are fabricated of linear polyethylene. The opening through the ball is equivalent to full line size and a ninety degree turn of the ball opens or closes the valve. It is normally used for on-off service and operated: (1) manually, (2) by an air-operated piston connected to the ball shaft, or (3) an electric motor connected to the ball shaft. If electric operated, micro switches operated by cams on the ball shaft are provided to limit the shaft rotation to ninety degrees each time the switch is energized. At times the switches get out of synchronization and then it is not known if the valve is open or closed. The ball valve can also be used for throttling service by the use of a "positioner" attached to the ball shaft which rotates the shaft proportionally for a 3-15 psig signal applied to the positioner. The positioner requires an air supply greater than 60 psig.

5.4 Solenoid Valves

Solenoid valves are installed in air signal lines to certain diaphragm or piston-operated control valves so that the valve can be opened or closed by an electrical signal from an alarm switch or relay. The alarm switch is operated by pressure, temperature, weight factor, flow, liquid level, power failure, etc.

A solenoid valve is a combination of two basic functional units, a solenoid (electro-magnet) with its plunger or core, and a valve containing a plug which is opened or closed by the magnetic plunger being drawn into the solenoid when the coil is energized. Most of the solenoids in service are three-way valves, that is, one port is connected to the diaphragm of an air-operated valve, the second port is connected to the

B.5.4 Solenoid Valves (Continued)

air supply, and the third port is a vent to remove air from the valve diaphragm when the air supply port of the solenoid valve is closed, thereby returning the control valve to its initial position. Two-way and four-way solenoid valves are also commonly used.

Solenoids must be installed with the direction of air flow through the valve as indicated by the arrows on the body. The process pressure must be on the top of the seat to assist in closing the valve when the plunger falls upon de-energizing the coil.

5.5 Pilot-Actuated Pressure Reducing Valves

A pressure reducing valve is used to reduce the pressure of air, water, steam, or any other process fluid to a fixed pressure lower than the supply pressure.

A pilot-actuated pressure reducing valve consists of a diaphragm-actuated main valve and a pilot valve to control the main valve by regulating the diaphragm pressure. The small pilot valve has a spring-loaded diaphragm. The spring tension can be adjusted by a screw. The pilot diaphragm is pressurized from the downstream (regulated) side of the main valve.

The pilot valve is normally open and is located in a small pilot line between the upstream (supply) pressure of the main valve and the top of the main valve diaphragm. The other side of this diaphragm is open to the downstream pressure. As supply pressure passes through the pilot, the main valve diaphragm is depressed, thus opening the main valve and allowing the process fluid to flow. When the desired downstream pressure is reached, the pilot valve closes the pilot line. A small bleed in the main valve diaphragm permits the pressure on both sides to equalize, restoring the main valve to its normal closed position. As fluid is drawn from the regulated pressure, the valve will open and modulate the flow to maintain a constant pressure. A pressure drop of at least 20 psi across the main valve is required to assure proper operation.

5.6 Safety Relief Valves

The basic function of the safety relief valve is protection of personnel, plant, and process equipment. In order to perform this function, the valve is designed to open automatically at a pre-determined set pressure, sized to provide full pressure relief of system, and to close tightly after operation.

The safety relief valves used are direct, spring-loaded pop type. The main parts of the valve are the valve body and trim, loading spring, and disc. The disc is the moving part of valve against which the spring load is applied. The spring tension can be adjusted by a screw.

B.5.6 Safety Relief Valves (Continued)

When the force per unit area on the valve disc overcomes the load set-up in the spring, the valve will pop open. The pop action of the valve is caused when the air, steam, or gas media is first liberated, resulting in a powerful expansion force. This force, added to the dynamic force of the media flowing from the valve orifice, is utilized to give definite pop valve action. The set pressure of the valve should not be greater than ten percent above the maximum allowable working pressure of the system.

6. Receiving and Controlling Instruments

6.1 Indicators

If the indicator is part of the transmitter, it is described in that Section. If an indicator is used on the panelboard, it is a 0-15 psig pressure gauge calibrated 0-100 percent for 3-15 psig. It is either the normal, round, bourdon-type gauge or a drum-type gauge consisting of a 3-15 psig bellows and a drum dial indicator mounted on a metal frame. The dial, calibrated 0-100 percent, revolves in response to the pressure signal until the approximate value on the dial coincides with a stationary index on the window through which the drum revolves.

6.2 Recorders

The recorder described herein is the standard miniature pneumatic strip chart recorder. All other recorders are described under the various operating systems. Fischer & Porter and Foxboro recorders are used extensively. Bristol and Taylor recorders are similar. The Foxboro instrument has a chart that rolls down and, if a controller, the control set pointer and valve pressure indicators are along the top. The Fischer & Porter instrument has a chart that rolls from right to left and, if a controller, the control set pointer and valve indicators are on the right side of the case. These recorders come with one, two or three pens but generally are two-pen recorders. Each recording pen is operated through linkages from a 3-15 psig bellows receiver. A 4-inch chart is operated by an electric motor and the chart speed is either 3/4 inch or 3/8 inch per hour.

6.3 Control Functions

The controller is attached to the rear of the recorder and has a control set pointer, valve pressure indicator and a "manual" to "automatic" transfer switch within the recorder case - all adjustable from the front of the recorder.

B.6.3 Control Functions (Continued)

In the "manual" position, the control pointer is set at the desired air pressure to the valve and the process control function assumes some reading for this valve setting. In the "automatic" position, the control pointer is set to the desired value of the process control function and the controller adjusts the valve output pressure to maintain this setting. The controller has one or more of three modes of operation, that is, proportional band, reset, or derivative. See Figure XIII-4.

Some controllers (slave) are reset by another controller (master) and require a cascade sub-panel or ratio unit (see Section B.6.3.4) through which a signal resets the control point of the slave controller by means of a 3-15 psig bellows attached to the set point.

6.3.1 Proportional Band

The proportional band setting determines the amount of process pen movement from the control set point, expressed as percent of chart, necessary to change the controller output pressure from 3-15 psig. This is usually adjustable from 0-200 or 0-500 percent.

Example: Assume a proportional band setting of 10 percent and the control pointer set at 50 percent controlling the flow of a system. The controller output will be 15 psig if the flow pen falls to 45 percent, and the output will be 3 psig if the flow pen goes to 55 percent. Whenever the controller set pointer and process pen coincide, the output is 9 psig regardless of percent of chart reading. The process pen can stabilize at any point within the proportional band setting, and not necessarily at the control point. The smaller the proportional band setting the closer the process pen will stabilize to the control set point. On any given application, however, the proportional band can be reduced only to a certain point below which the controller will cycle.

6.3.2 Reset

The reset function is proportional to the deviation of the process reading from the set point and is continuous only as long as any deviation exists. The reset function can be installed only in a controller that has the proportional band function. The reset rate is usually expressed in minutes and is the time it takes for the controller output pressure to stabilize after one upset. It is usually adjustable, 0.01 - 10 or 0.1 to 50 minutes. If the reset setting is too fast, the controller output will change faster than the process variable and cycling will result - the action will become more like an on-off type controller. If it is too slow, the controller will not recover fast enough and will behave like a straight proportional controller. If the process is oscillating, it may take several hours for the controller to stabilize at a 10 minute reset setting.

B.6.3.3 Rate or Derivative

A rate or derivative function is proportional to the rate of change of the setpoint and the process variable. Such control equipment can be installed only on controllers that have proportional band functions or proportional band and reset functions. It provides fast stabilization of the process after a load change. This function is usually used whenever there is a long dead time or transfer lag in a process system. It is expressed in minutes and is usually adjustable for 0.01 — 10 or 0.1 — 50 minutes.

6.3.4 Transfer Station and Cascade Sub-Panel

The transfer station is mounted on the interface of the recorder-controller air connection manifold. The station consists of a three-position transfer valve, manually adjustable pneumatic pressure regulator, and a pressure indicator. The pressure regulator is furnished when local set point is required and omitted for remote set point use. When the recorder-controller is used with remote set point, an external cascade sub-panel having a transfer valve and pressure regulator for local set point is usually used.

The shaft of the transfer valve and regulator extend through the case of the instrument and are accessible from the front of instrument. The transfer valve permits selection of "automatic" or "manual" operating mode. The intermediate "seal" position is used when switching the controller from "automatic" to "manual" or vice versa. The "manual" position of the transfer valve directs the output of the pressure regulator to the final control element and simultaneously isolates the controller output. When in the "seal" position, the controller signal is isolated and the final control element pressure is sealed in. This final control element pressure is indicated on the transfer station pressure indicator. When transferring from "automatic" to "manual", this sealed-in pressure is used to adjust the pressure regulator output, as indicated by the recorder-controller recording pen, to the same value as the final control element pressure. When transferring from "manual" to "automatic" the sealed-in pressure is used to adjust the pressure regulator output set pointer to the exact value indicated by the recording pen. In the "automatic" position, the controller output is connected to the final control element. The pressure regulator output then becomes the set point pressure and is disconnected from the final control element.

The cascade sub-panel is located beneath the "slave" controller and consists of a three-way, two-position air switch, pressure indicator and a pressure regulator. The switch positions are called: (1) "Local Set" or "Manual", and (2) "Remote Set", "Pneumatic Set", or "Auto". In position No. 1 the pressure regulator adjusts the set point of the "slave" controller. In position No. 2 the signal from the "master" controller adjusts the set point of the "slave" controller.

B.6.3.5 Ratio Unit

In order to maintain the flow rates of two streams according to a predetermined ratio, a flow system consisting of the following is used. A flow recorder-controller (master) controlling the stream sends a signal proportional to the flow through a ratio unit to the set point of the second flow recorder-controller (slave).

The ratio unit is a controller with fixed setting except for the proportional band adjustment. This proportional band adjustment moves along a dial calibrated 0.3 to 3.0 for linear flows, or 0.6 to 1.7 for square root functions, from an orifice transmitter. Thus, ratios may be established from 0.3 to 1 through 3 to 1 by setting the ratio lever to the desired value. This is a set point air signal adjustment and not a flow rate ratio; for a true flow ratio the flow calibration of the recorders must be taken into consideration. The 3-15 psig signal from the flow transmitter is multiplied by the ratio setting factor and this new signal goes to the set point of the slave controller. Thus, the ratio is based on the slave to master reading.

The ratio unit also has a transfer switch as described in Section B.6.3.4 combined in one unit. The selector switch has two positions called: (1) "Ratio Set", where the "master" signal goes through the ratio unit and then to the "slave" set point, and (2) "Manual Set", where the signal from the unit PRV goes to the "slave" set point. Example: Consider a "master" flow range of 0 - 10 gal/min for a 3-15 psig air signal. The flow reading is 50 percent at 5 gal/min with an air signal of 9 psig. The ratio unit is set at 0.6 so the signal to the "slave" set point is $(9-3)(0.6)=3.6+3=6.6$ psig. The "slave" flow range is 0 - 5 gal/min for 3 - 15 psig, so the control set point of the "slave" is 30 percent or 1.5 gal/min. This is a flow ratio of 1.5 to 5.

6.3.6 Reverse Acting Pneumatic Relay

In pneumatic valve control systems it is desirable at times to operate several valves with one pneumatic signal and to operate valves in the event of failure of the air supply (which in some instances will close and in other instances will open). This sometimes requires the reversal of air pressure from an increasing signal to a decreasing signal.

The reverse acting pneumatic relay will receive an increasing (3 to 15 psig) input and transmit a decreasing output (15 to 3 psig). It has three air ports; one port receives the 3 to 15 psig input, the second port receives a 20 psig air supply, and the third port is for the 15 to 3 psig output. There is a 1 psig change in the output for each psig change in the input.

The relay also functions as an air volume amplifier, receiving a small volume of air and transmitting a large volume of air for valve control. A screw adjustment is provided which permits setting the 15 psig output with a 3 psig input.

B.6.4 Manual Controllers

Manual controllers are used to provide 3-15 psig pressure to air-operated control valves. The controller is an adjustable pressure regulating valve with a vertical dial to indicate the output pressure. The dial is calibrated 3-15 psig or 0-100 percent.

6.5 Integrators

6.5.1 Indicators

The flow indicator integrator consists of a 3-15 psig bellows that receives the pneumatic output signal from a flow transmitter and converts this pneumatic input to a mechanical lever position representing the signal level. The output lever is in turn linked to the input mechanism of an integrator and to an indicator arm to provide a visual flow rate indication on the vertical scale of the instrument. The integrator is a mechanical device employing a synchronous motor to provide the source of timed power to operate a feeler mechanism. The feeler detects the rise of an integrator cam as it is positioned by the receiver bellows. The integrator shows the cumulative total flow on a six-digit counter.

6.5.2 Indicator-Controller

The flow indicator-controller integrator consists of two separate units mounted one above the other on the instrument panel. One unit is that described above in Section B.6.5.1 with one exception - the integrator is equipped with a cam (sometimes referred to as a star wheel) and a microswitch to provide electrical pulses which are used to actuate the second unit, an electronic pre-determining type counter.

The electronic counter is a six-digit unit consisting of an electro-magnetically operated set of geared digit wheels. When the coil of the magnet is energized, the armature and ratchet advance the units digit wheel by one-half step. When the coil is de-energized, the return spring advances the wheel a second half-step, thus completing the registration of one count. The count is transferred to the next higher digit wheel by lock teeth and transfer pinions. The counter is capable of indicating totalized flow and is equipped with a pre-determining counter. The set of pre-determining wheels operate a single-pole, double-throw switch by means of a trip mechanism. The pre-determining wheels can be preset for any desired value by raising the preset cover on the front of unit. When in operation, the pre-determining counter counts from zero up to the preset number or desired value at which point the switch trips and the pre-determining wheels return to zero. The switch is automatically restored to its untripped position when the counter is reset either manually or electrically. The unit speed is 10 counts per second.

B.6.6 Alarms

The majority of the visual and audible alarms in the Waste Management Program are activated electrically by pressure-actuated switches connected directly to an air-purged dip tube system, directly to process lines, or to the output signal from a pneumatic transmitter. The variables monitored are flow, pressure, weight factor, liquid-level and temperature.

6.6.1 Visual Alarm Units

The visual alarm unit consists of two lamps, plug-in relay, flasher and electrical circuitry interconnected with the remote pressure switch contacts. The components are installed within a metal enclosure the front of which is transparent plastic. Lettering engraved in the plastic shows the condition of the variable monitored. Should an abnormal condition exist, the equipment or process monitored is identified.

6.6.2 Audible Alarms

The audible alarm used is a horn. It is usually electrically paralleled with a number of visual alarm units.

6.6.3 Pressure Switches

The sensing element of pressure-actuated switches is a bourdon tube or diaphragm linked mechanically to a single pole double throw (SPDT) snap-acting switch. When the pressure overcomes the setting of the load spring, the switch contacts are activated to open or close an electrical circuit.

When an abnormal condition exists in the monitored system, the visual alarm is activated and begins flashing and the audible alarm is activated. The audible alarm may be silenced by pressing the "acknowledge" pushbutton. The alarm lights then change from flashing to steady-on.

C. WEIGHT FACTOR, SPECIFIC GRAVITY, PRESSURE AND LIQUID LEVEL MEASUREMENT AND CONTROL

1. Purge Dip Tube Systems

An air-purged dip tube system is used for the measurement of weight factor, specific gravity and pressure of process vessels in the Waste Management Program. The system utilizes a controlled stream of air through an open-ended tube to counterbalance the pressure or hydrostatic head of another fluid into which it is flowing. The back pressure in the line is measured by a sensing device such as a manometer, gauge or differential pressure transmitter. See Figure XIII-13.

C.1. Purge Dip Tube Systems (Continued)

The air purged system produces a reading that is proportional to liquid height and specific gravity which is called the weight factor; thus liquid level, in inches of water, equals the weight factor reading, in inches of water, divided by specific gravity. Specific gravity measurements are made across a fixed liquid height and equal the differential pressure, in inches of water, divided by the actual inches of vertical distance between the high and low pressure dip tubes. A reading of 20 inches of water divided by a 10 inch dip tube spacing gives a specific gravity reading of 2.0. There must be liquid covering both dip tubes or the specific gravity reading will be a weight factor reading. Differential pressure measurements, such as static pressures on columns, is identical to a weight factor installation.

1.1 Weight Factor

The sensing element consists of two 1/2-inch stainless steel pipes; one extends to a point 1/2-inch (approximately) from the tank bottom and is known as the high pressure dip tube, and the other, known as the low pressure dip tube, senses at the extreme top of the tank. A stream of air flows through each pipe, controlled by a purge rotameter (see Section B.1.3.1), at approximately one cubic foot per hour. A differential pressure transmitter, see Section B.3.2.1, is connected across the high and low pressure dip tubes. It transmits a 3 - 15 psig air signal to a receiving instrument such as a gauge, manometer or recorder-controller, see Section B.3.3. If the receiving instrument is a weight factor recorder-controller, its 3 - 15 psig air output signal is directed to either a control valve or to a slave flow recorder-controller to control the flow into or out of the vessel and thus maintain a constant weight factor. A special weight factor control system is shown schematically in Figure XIII-14 and described in Section I.4.

Weight factor alarm switches, see Section B.6.6.3, are connected either across the weight factor dip tubes or to the output of the weight factor transmitter. They are used to provide visual and audible alarms at high and low values and also to automatically shut down pumps, agitators, flows, etc. to prevent overflowing a vessel or damage to equipment.

1.2 Specific Gravity

The sensing element consists of two 1/2-inch stainless steel pipes, the high pressure tube is commonly the same as that used for the high pressure weight factor tube, and the low pressure dip tube is usually ten inches higher in elevation than the high pressure dip tube. The low pressure dip tube elevation above the high pressure dip tube can be less or greater than the ten inches indicated above, provided it is normally covered with the process solution. A stream of air flows through

C.1.2 Specific Gravity (Continued)

each pipe and is controlled by a purge rotameter, see Section B.1.3.1, at approximately one cubic foot per hour. A differential pressure transmitter, see Section B.3.2.1, is connected across the high and low pressure dip tubes. It transmits a 3 - 15 psig air signal to a receiving instrument such as a gauge, manometer or recorder-controller, see Section B.3.3. The transmitter is equipped with an additional adjustment that allows the zero reading to be suppressed in order to give greater accuracy and readability.

Example: If the specific gravity range of a solution in a vessel will normally be from 0.7 to 1.2, the zero of the transmitter can be suppressed so that 0 percent represents 0.7 and 100 percent represents 1.2 specific gravity. With a 10-inch dip tube spacing the transmitter would then have a range of 7 to 12 inches to produce a 3 to 15 psig output signal.

If the receiving instrument is a specific gravity recorder-controller, its 3 - 15 psig air output signal is directed to either a control valve or to a slave flow recorder-controller to control flows into a vessel and thus maintain a constant specific gravity.

1.3 Differential Pressure

Differential pressure is measured across an extraction column and is called static pressure. The sensing element consists of two 1/2-inch stainless steel pipes; the high pressure tube senses at a point near the bottom of the column and the other at a point two inches below the organic overflow line. The installation is exactly the same as the weight factor installation and the static pressure reading is in inches of water. See Figure XIII-15.

Differential pressure is also measured across various gas flow restrictions such as filters, towers, etc. to indicate plugging of the equipment. The sensing element is two 1/2-inch stainless steel pipes; one at the high pressure side of the restriction and the other at the low pressure side. A differential pressure transmitter, see Section B.3.3, is connected to the sensing elements. The transmitter's 3 - 15 psig output signal is received either by an indicator, recorder, or a recorder-controller. In some cases, a transmitter is not used and the differential pressure sensing elements are connected directly to a manometer or a differential gauge.

2. Pressure Gauges

2.1 Bourdon Tube Type

Standard bourdon tube-type dial gauges are used for visual pressure indication of process steam, air, and water in vessels and pipe lines. Combination pressure-vacuum gauges are used on the steam jet systems and spargers. These gauges indicate the steam pressure to the jet and also show

C.2.1 Bourdon Tube Type (Continued)

a vacuum in the line in the event of steam condensation after the jet is turned off. A vacuum is undesirable since radioactive solutions might be drawn to the operating gallery.

The bourdon tube is a curved (essentially circular in form) tube of elliptical cross section with one end sealed. Pressure applied to the open end tends to straighten the tube; conversely, vacuum causes the tube to curl up. The movement of the closed, free end of the bourdon tube is transmitted through a mechanical linkage which, in the conventional pressure gauge, is multiplied by a rack and pinion system to activate a pointer. The gauges are calibrated in pounds per square inch (psi) or inches of water.

2.2 Manometers

A manometer is an instrument for measuring the pressure exerted by a gas, vapor or liquid. The simplest form consists of a U-shaped glass tube partially filled with liquid and with provision for measuring the height of the liquid. When both ends of the tube are open to atmosphere, or when they are both under the same pressure (greater or less than atmospheric), the liquid is at the same height in each leg of the tube. When one leg of the tube is connected to a source of pressure, the liquid in that leg is forced downward and the liquid in the other leg rises until the difference in height corresponds exactly to the pressure applied. By measuring this difference in height of the liquid, the applied pressure can be determined. The measurement can be expressed in units of length, such as inches or millimeters, making sure the liquid used in the manometer is specified, or a scale can be provided so that the reading can be in pounds per square inch (psi) or any other units desired. Because the U-tube manometer has one leg at atmospheric pressure, the measurements show gauge pressure rather than absolute pressure. The measurement is actually differential pressure — the difference between the pressure applied to the two legs of the manometer.

Vacuum pressure is measured in the same way as positive pressure. One leg of the manometer tube is connected to the source of vacuum and the other leg open to the atmosphere.

The two types of manometers used in the Waste Management Program are the well type and the inclined type.

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C.2.2.1 Well Type Manometer

The fact that the reading of a manometer does not depend on the diameter of the manometer tube, and that the two legs do not have to be the same diameter makes possible the well type or single-tube manometer.

The well type manometer is essentially a U-tube manometer that has one leg of much greater cross sectional area than the other. In effect, the difference in level of the liquid in the well and the small tube is still being measured. However, the well is 200 or more times greater in area than the tube, and accordingly, the liquid in the tube changes its level 200 or more times as much as the liquid in the well. The change in the well liquid height is very minor and is corrected by the graduations on the scale. Thus, measurements are obtained by reading the change in level in the small tube. The well type manometer is used for weight factor and liquid level measurements which are usually read in inches of water.

2.2.2 Inclined Tube Manometers

The ventilation system of the canyon is so designed that the cells are maintained at a slight vacuum with respect to the operating gallery or deck level to prevent any radioactive gases from seeping into the operating gallery. The vacuum is measured by an inclined tube manometer having a range of 0-1 inch.

An inclined tube manometer is similar to the well type manometer except the small tube is inclined instead of vertical. Since vertical height controls the range of the manometer, the indicating liquid of an inclined manometer must travel a greater length in the tube to reach a given difference in vertical height. Therefore, the inclined manometer scale divisions are much farther apart and can be read much more easily and accurately.

3. Resin Column Pressure and Differential Pressure Measurement

The following instruments are used to measure and/or control the pressure in the resin column and the differential pressure across the resin bed: (1) pressure transducers, (2) signal converters, (3) differential pressure amplifier, (4) alarm, and (5) recorder. See Figure XIII-16.

3.1 Pressure Transducers

The diaphragm-type pressure transducer operates on the magnetic reluctance principle. The transducer is shown in simplified form in Figure XIII-17. A diaphragm of magnetically permeable stainless steel is clamped between two blocks and deflects when pressure is applied at

C.3.1 Pressure Transducers (Continued)

the pressure port. An "E" core and coil assembly is embedded in each block (with a small gap between the diaphragm and the "E" core) in a symmetrical arrangement, both coils having the same inductance when the diaphragm is in the undeflected position. Diaphragm deflection increases the gap in the magnetic flux path of one core, and decreases it in the other. The magnetic reluctance varies with the gap so that the effect of the diaphragm motion is a change in inductance of the two coils, one increasing and the other decreasing. The two coils, L_1 and L_2 , form two arms of a bridge circuit located in a carrier-demodulator unit described in the following section.

3.2 Carrier-Demodulation Converters

The solid-state carrier-demodulator instrument provides excitation to the bridge circuitry within the unit, including excitation of the two coils of the pressure transducer, which form two arms of the bridge. An amplifier and demodulator convert the bridge output to a 0 - 10 volt d-c signal.

3.2.1 Converters

The two signal converters in operation on the resin column convert the 0 - 10 volt d-c output signal from the carrier-demodulator to a d-c voltage compatible with other instruments of the system. Each converter utilizes six silicon transistors. Four transistors are connected as a stable dual-differential amplifier, and the remaining two transistors provide power amplification and a constant current output. One side of the differential amplifier is driven by the input signal through appropriate dividers; the other side is driven by feedback from the output stage.

The output stage provides a constant current source. It is also possible to obtain voltage outputs through internal loads in the output stage. The instrument is provided with potentiometer-type "zero" and "gain" adjustments.

3.3 Differential Pressure Amplifier

The function of the differential pressure amplifier is to provide an output signal proportional to the difference of two input signals. The signal converters, conditioning the two pressure transducer signals, provide the input to the differential pressure amplifier. The operation of the differential pressure amplifier is identical to that of the absolute pressure converters.

3.4 Alarms

The two alarms for the resin column monitor the absolute pressure in the area above the resin bed, and the differential pressure across the resin bed.

C.3.4 Alarms (Continued)

The alarms are electronic trip devices whose function is to actuate visual and audible alarms on high pressure/low differential pressure. Their action is similar to that of a relay and are used to sense a voltage level. When that voltage level exceeds the adjustable trip level, the single-pole, double-throw (SPDT) relay contacts in the device will switch.

The electronic trip receives a milliamp input signal from the converters, Section C.3.2.1. The device consists of a high gain, three-transistor amplifier and power supplies. The output of this amplifier is at approximately +12 volts until the input voltage exceeds that of the reference voltage, at which time the high gain causes the output to switch to zero volts. The reference voltage is set by a precision potentiometer powered by a zener diode reference supply.

3.5 Recorder

A miniature electronic two-pen recorder is used for recording absolute pressure and differential pressure measurements in the resin column system. The recorder is a self-balancing potentiometric instrument with built-in reference d-c power supply, servo-amplifier, and balancing motor components. The power supply, which furnishes power to the recorder-amplifier circuits and the balancing motor, and the servo-amplifier circuits are on printed circuit cards. Each servo-amplifier (two required) compares the process variable voltage with a local voltage generated by a slidewire circuit and, by means of an emitter-coupled difference amplifier, functions to produce sufficient voltage amplification to drive a two-phase balancing motor in a compensating direction. The balancing motor serves two major functions: (1) mechanically positions the slidewire to a condition of electrical null, and (2) mechanically positions the process indicator and recording pen. The recorder 4-inch strip chart and indicator scale is calibrated 0-100 linear. The strip chart speed is 7/8-inch per hour.

4. Conductivity Type Liquid Level Instruments

This type of system is used at the Tank Farm sluice pits for monitoring high water levels and liquid level in the underground waste storage tanks. See Figure XIII-18. The instruments of the system consist of the following:

- (1) Level sensing electrodes and electrode holder.
- (2) Indicating meter, and in some cases,
- (3) Alarm light and horn.

4.1 Sluice Pit Probe

The sensing electrodes are two solid stainless steel rods with Teflon insulation over their entire length except at the extreme

C.4.1 Sluice Pit Probe (Continued)

tips. The upper end of the rods are threaded to fit a pressure-tight electrode holder with electrode plugs. The electrode plugs provide electrical termination points for the system control wiring.

The sensing electrodes, supported within the electrode holder, are installed vertically in the sluice pits at a pre-determined elevation for level monitoring. When the conductive liquid in the sluice pit rises to the level of the sensing electrodes, an electronic relay is energized which may activate a visual and audible alarm on the Instrument Control Panel.

4.2 Underground Waste Tank Probe and Indicating Meters

The probes used to measure the level in the underground waste tanks are of two types.

The first consists of an electric, rubber-insulated cord which can be lowered through a nozzle into the tank by a small winch. The cord is connected to a stainless steel electrode at the lower end which makes contact with the solution in the tank. The cord is marked with metal markers, one foot apart, starting with zero at the winch when the electrode is touching the bottom of the tank.

The second type is similar except that the winch is insulated from the tank and a stainless steel measuring tape is used in place of the electric cord to indicate the depth of solution. An ohmmeter is connected across the cord or winch and the tank metal. A change in resistance indicates that the probe has contacted the liquid in the tank. The cord or tape markings then indicate the liquid level.

4.3 Alarms

The alarm light is one point or drop in a ten-unit annunciator. When the level sensing unit and electronic relay detect a high level in the sluice pit, the alarm light in the annunciator will begin to flash and a horn will be audible, indicating the abnormal condition. An acknowledge button which is part of the annunciator system silences the horn and changes the alarm light from flashing to steady-on. The alarm light will remain steady-on until the abnormal condition is corrected.

D. Interface Measurement

Two methods are utilized to obtain interface measurements between organic and aqueous phases in the solvent extraction tanks and columns: (1) An electronic float type system, and (2) the purged dip tube system. The electronic float system is used on the pulsed columns, because variation of pulse frequency would cause pressure variations in a purged dip tube system.

D.1 Electronic Float-Type System

A typical interface measurement and control system for use in a remotely-operated separations facility is shown schematically in Figure XIII-15. The vessel or column contains an electronic-float type transmitter assembly immersed in the process solution. The transmitter assembly also houses a resistance-type temperature bulb for measuring solution temperature. An electrical conduit or jumper carries the signal wires from the transmitter and the temperature bulb through the shielding wall to their respective amplifier-converters, located in a non-radioactive zone. For additional information on the temperature amplifier-converter see Section F.1.2.

The converter output is a 3 - 15 psig air signal and is received by a recorder-controller, which in turn sends a 3 - 15 psig air signal to a control valve to maintain the interface level constant.

1.1 Electronic Transmitter

The electronic transmitter utilized for interface measurement is a special instrument designed for applications in radioactive zones and is shown in Figure XIII-19. The transmitter consists of two separated chambers; the lower chamber contains the measuring float and is immersed directly in the process solution. The upper chamber contains the transmitting inductance coils. The float in the lower chamber is attached to a small-diameter, thin-walled, stainless steel tube that extends up through a larger stainless steel tube in the upper chamber. The larger diameter tube extends through the transmitting inductance coils. Contained within the small diameter tube, at its upper end, is a soft iron armature which is held in place by crimping the tube. The float assembly (float, connecting tube and armature) produces a linear motion in the vertical plane with changing interface levels. The float assembly must be weighted so that it will sink through the organic phase and float in the heavier aqueous phase. The float is calibrated so that it will float about 1/4 inch from the top of the float in an air-water interface and sink 1/4 inch from the bottom of the float in a 0.92 specific gravity organic-water interface. The transmitter inductance coils and similar inductance coils in the amplifier-converter are interconnected to form an inductance bridge.

1.2 Amplifier-Converter

The amplifier-converter for interface measurement is identical to that described in Section B.1.1.2.

1.3 Recorder-Controller - See Section B.6

2. Ultrasonic Detection (Resin Column)

A system utilizing ultrasonic techniques for measuring resin level in an ion exchange column is shown schematically in Figure XIII-20. The system consists of four basic components: (1) Transducer, (2) Scope, (3) Power Supply, and (4) Time Analog Unit.

D.2.1 Transducer

The transducer is a Branson Instruments, Inc. stainless steel clad probe. It is placed in the upper part of the resin tank, above the resin level but below the liquid level. A transmitted pulse will be reflected from the resin surface and return to generate an echo pulse in the transducer. The voltage analog of the time between transmitted pulse, plus an adjustable delay, and the echo pulse is received by the scope, and presents a visual indication on the cathode ray tube.

2.2 Scope

The function of the scope is to provide a pulse to the transducer, amplify the echo, and provide noise-free signals of the main bang and echos to the time analog converter. The scope also presents a visual display of the transmitted pulse (main bang) and the echo pulse. Some of the controls on the scope unit do not affect the time analog unit because the pulse height is not changed, but merely serves to control the visual display.

2.3 Time Analog Unit

The time analog unit converts the time between the gate and echo into a proportional voltage. This voltage is scaled with the material calibration dial on the unit and biased with the recorder zero dial. The gate can be delayed with respect to the main bang by the gate delay dial. If set too close to the main bang, adjustment of the damping or reject controls can cause faulty gating. The display of gating given on the scope is useful in correcting malfunction. The recorder zero of the time analog unit is not related to pulse time information but is used to generate a reference or bias for a recorder-output voltage.

3. Purged Dip Tube System

The purged dip tube system used for interface measurements is similar to that used for specific gravity measurements, see Section C.1.2, except the dip tube spacing for interface is usually greater.

This type of system cannot be used for bottom interface measurements on a pulse column due to the pressure variations created by the pulser.

4. Capacitance Probe

The liquid level of the waste cask is determined by the use of an electrical capacitance measurement. The level system consists of a capacitance probe, a pulse height to d-c converter, and a liquid level indicator.

This method for the conversion of capacitance to a pulse height or amplitude has been developed at Hanford. In essence, the method involves measuring the charge stored on an unknown capacitance by shunting the capacitor with one winding of a pulse transformer and measuring the output of the secondary

D.4 Capacitance Probe (Continued)

winding. This process is repeated by alternately charging and shunting the capacitor. The resulting output is a series of pulses whose amplitude is proportional to the unknown capacitance. The pulses are conditioned to develop a d-c voltage which is indicated on a voltmeter calibrated in liquid level units. A functional diagram is shown in Figure 21.

Measurement of the capacitance of the probe at the end of a long cable of high characteristic capacitance is accomplished as follows:

A pulse transformer is connected in series with one electrode of the capacitance probe C_x (see in Figure 21). The capacitor and cable are charged through resistor R_1 by power source E_0 , the cable is shorted periodically by the electronic switch S_1 , and the charge on the unknown capacitor C_x discharges through the pulse transformer T-1. A voltage proportional to the unknown capacitance is induced in the transformer secondary. A pulse height to d-c converter is then utilized to develop an analog d-c voltage for the level read-out.

All components of the capacitance measuring probe use radiation-resistant materials.

E. RADIATION MONITOR SYSTEMS

The Waste Management Program has two generalized applications for radiation monitoring instrumentation, (1) process control monitoring, and (2) environmental monitoring.

Process control monitoring is provided for measuring the radiation intensity of process streams and process vessels. This radiation information indicates: (1) the activity of the solutions inside a vessel, (2) permits the operator to "see" the solution enter and leave the vessel, and (3) indicates the effectiveness of the separation steps.

Environmental monitoring/health monitoring is provided throughout the building work areas for personnel protection. The radiation levels are continuously monitored by indicating and recording instruments. Should high radiation levels be detected, the system will activate audible and visual warning devices.

1. Geiger-Mueller Type

Two Geiger-Mueller type radiation detection systems are used to monitor the radiation level of the steam condensate to crib 216-B-55, and the process condensate to crib 216-B-12. Each Geiger-Mueller detector is mounted within a 3-inch diameter pipe well which is closed at the bottom end and is provided with a removable pipe cap at the upper end. One side of the pipe well at the upper end is slotted to accommodate the detector cables. The wells are approximately 4'-6" in length and are installed in their respective system condensate tanks.

E.1 Geiger-Mueller Type (Continued)

Each monitoring system consists of the following instruments: (1) a Geiger-Mueller counter tube, (2) a d-c power supply, (3) an amplifier-discriminator, (4) a count rate meter, and (5) a two-pen recorder which is used to record the radiation level of the two systems.

1.1 Geiger-Mueller Counter Tube

The Geiger-Mueller detector is a gas-filled, halogen quenched, beta-gamma counter tube which produces a large, easily counted, pulse for each ionizing event that enters and triggers the tube. Within the cylindrical metal tube, a fine wire anode is stretched along its axis. When a high voltage (500 to 2,000 volts) is impressed across the wire and the grounded metal tube wall, the radiation energies entering the counter tube will initiate the ionizing process and produce output pulses.

1.2 Power Supply

The high voltage d-c power supply for the system is rated 0 - 2100 volts at 30 milliamperes. The high voltage is developed by a voltage doubler circuit using a switched secondary high-voltage transformer, high-voltage silicon rectifier stacks, and oil-filled filter capacitors. The output of this supply is regulated by series pass tubes. The tubes are in turn controlled by a solid-state feedback amplifier with greater than 130 decibels of d-c gain. The variable voltage divider sampling string, which is switched to change output voltage, consists of stable low-temperature coefficient wirewound resistors. Output of the supply is available at both the front and rear panel through coaxial type connectors. Output polarity is controlled by a front panel switch to provide either positive or negative grounded operation. A zero-center panel meter monitors the output voltage. Calibration accuracy of the power supply unit is ± 0.25 percent or 100 millivolts (whichever is greater) with vernier at zero. Load regulation is 0.001 percent or 5 millivolts (whichever is greater) for a full-load change.

1.3 Amplifier-Discriminator

The function of the linear amplifier and discriminator is to accept pulses from the Geiger-Mueller counter tube and to provide amplification and amplitude discrimination of these pulses. The unit has three integrated controls that are accessible from the front of the unit: (1) course gain/ fixed sensitivity, (2) fine gain, and (3) discrimination. The output pulses of the amplifier are delivered directly to the discriminator section and must have an amplitude exceeding the level for which sensitivity is set in the discriminator. Any pulse above the discrimination level triggers the discriminator to produce an output pulse with a fixed amplitude and duration. This pulse is then received by the count rate meter. The d-c power required for operation of the amplifier-discriminator is available at each of the four plug-in module positions in the instrument cabinet.

E.1.4 Count Rate Meter

The count rate meter receives the positive output pulses from the discriminator, converts these pulses to a direct current proportional to the average count rate in counts per minute (CPM). This current, amplified, operates a 3-inch meter and records potentiometric outputs. This instrument offers the choice of linear or logarithmic presentation of the count rate. When the function switch is in the linear mode, a range switch selects one of eight full scale ranges from 500 to 1,000,000 CPM. With the function switch in the logarithmic mode, a three decade presentation between 10^3 and 10^6 CPM is obtained. The front panel controls and their functions are as follows:

1. Background Control - Single-turn potentiometer that allows the zero level of the front panel meter to be set above background which is below the region of interest.
2. Function Control - Two-position rotary switch to select the linear or logarithmic operating modes.
3. Volume Control - On-off switch and volume control adjusts the audio output for the built-in aural monitoring system.
4. Response Control - Six-position rotary switch which will function only in the linear mode. Switch selects one of five integrating time constants marked in seconds. The sixth position on the rotary switch is marked "Cal". When in this position, the count rate meter input is disconnected while the meter response is checked against an internal 3600 CPM signal. This "Cal" position will function in both linear and logarithmic modes.
5. Range Control - Eight-position rotary switch selects one of eight full-scale ranges marked in CPM. Range control switch functions in linear mode of operation only.
6. Potentiometer Expansion Control - Ten-turn precision potentiometer provides ten-times expansion of the count rate meter recorder outputs. The output toggle switch at the rear of unit must be in the 10 mv or 100 mv range to utilize this control.
7. Zero Adjustment Control - Single-turn potentiometer adjustable from the front of unit with a small screwdriver which sets the front panel meter or recorder to zero.

1.5 Radiation Recorder

The instrument is an electronic, self-balancing, potentiometer type strip chart recorder with two recording pens. The 4-inch strip chart and indicator scale are calibrated 0-100 linear. The strip chart is operated at 3/4 inches per hour by a synchronous motor. The 0-100 millivolt signal from the count rate meter is received by the recorder input conversion module. The input conversion module conditions the count rate meter signal and, through retransmitting circuitry, sends a 0-10 volt

E.1.5 Radiation Recorder (Continued)

d-c signal to the servo amplifier assembly. The components of the servo amplifier assembly consist of an operational amplifier and other circuit components to amplify the difference between the input signal and a d-c feedback voltage. The operational amplifier also provides power to drive a torque motor clockwise or counter-clockwise.

The torque motor has a permanent magnet field stator and a one coil armature for bi-directional rotation of its output shaft. Also attached to the output shaft is a potentiometer which provides a servo system feedback voltage variation of 10 volts d-c. The torque motor drives the recording pen through linkages.

When the input signal to the operational amplifier increases, a momentary difference occurs in the ratio of input signal to the feedback voltage. This error signal is amplified by the operational amplifier to rotate the torque motor and the attached potentiometer clockwise. The increased feedback voltage is also applied to a summing junction. Upscale motor rotation (clockwise) will bring the motor into a position that restores the balance between the feedback voltage and the input signal.

2. Gamma Spectrometer System

The gamma spectrometer system is used to measure cesium 137 breakthrough on the ion-exchange column effluent line. Similar systems monitor additional process streams, such as LAP, LCP, etc.

Each isotope has a gamma spectrum, and usually one or more descriptive peaks that can be used to identify the radioactive substances carried in a process stream.

2. Gamma Spectrometer System (Continued)

By calibrating the spectrometer spread in pulse height, 0 - 1 Mev for example, a scan can be made to show what isotopes are present. Then by utilizing the pulse height analyzer in the system, a given peak can be selected and monitored continuously. The gamma-ray energy peak of 0.667 Mev is used for cesium 137; with the pulse height set to monitor between 0.647 and 0.687 Mev.

The gamma spectrometer system consists of the following components:

1. Monitor probe encasement assembly.
2. Detector assembly.
3. High-voltage power supply.
4. Linear amplifier.
5. Pulse height analyzer.
6. Baseline sweep.
7. Count rate meter.
8. Recorder.
9. Nuclear instrument modular bin.

2.1 Monitor Probe Encasement Assembly

The monitor probe encasement assembly (see Figure XIII-22) is a collimating column that penetrates the concrete wall separating the radioactive process cell and a non-radioactive zone. It consists of a 3-inch, schedule 40S, stainless steel pipe approximately 9'6" long, extending from the non-radioactive zone into the radioactive zone at an angle of 20 degrees from the horizontal. The pipe end that penetrates the radioactive zone is sealed by a 1/4-inch thick steel plate welded to the pipe, and is as close as possible to the process line being monitored. A hinged door at the other end of the pipe is shielded with lead and has provisions for the routing of the radiation detector electrical cable. Within the 3-inch pipe is a 2-1/2 inch, Schedule 40, carbon steel pipe whose length depends on the number of

E.2.1 Monitor Probe Encasement Assembly (Continued)

lead shields or plugs required in the length of 3-inch pipe. Each lead shield has a hole through its length on the centerline to form a collimating column. The lead shield closest to the stream to be monitored has the smaller diameter hole and, in each plug thereafter, the hole size increases a fractional amount. The detector assembly described in the following Section is inserted between the shielding door and the final plug.

2.2 Detector Assembly

The detector assembly consists of scintillation crystal, photomultiplier tube, and preamplifier. The approximate dimensions of the assembly are 3 inches in diameter by 10-1/2 inches long.

An americium doped sodium iodide (thallium-activated) crystal is used for gamma ray detection of cesium 137. It is approximately 1-3/4 inches in diameter by 2 inches thick. The photomultiplier tube is an 11 stage, head-on, flat-surface type with an S-11 response.

The preamplifier accepts the output signal from the crystal and photomultiplier combination and transforms the signal into a pulse that can be amplified. It has a 3-12 adjustable gain control.

2.3 High-Voltage Power Supply

The high-voltage power supply for the system is a regulated d-c source delivering from 1 to 2,012 volts at up to 10 milliamperes. It is possible to select any voltage over the range of 1 to 2,012 volts by three, step switches and a unit volts vernier potentiometer. Output regulation is 0.0025 percent of voltage setting or 2 millivolts (whichever is greater) at any setting for a 100 percent load change or a 10 percent a-c line voltage variation. Calibration accuracy of the power supply is less than 0.25 percent from 250-2,012 volts.

2.4 Linear Amplifier

The double RC clipped linear amplifier accepts the input pulses from the preamplifier (Section E.2.2), shapes these pulses, and increases their amplitude. The instrument is equipped with "course" and "fine" gain controls, adjustable 20 to 1,000. This linear amplifier furnishes power to the preamplifier.

2.5 Pulse Height Analyzer

The pulse height analyzer accepts input pulses from the linear amplifier. The instrument trigger circuit performs two important functions: (1) it establishes a pulse amplitude threshold level, permitting discrimination against noise pulses, and (2) it produces output pulses of fixed amplitude and width for reliable operation of the count rate meter, Section E-2.7. The pulse height analyzer controls are accessible from the front

E.2.5 Pulse Height Analyzer (Continued)

of unit and consist of an "E" discriminator (a 10-turn precision potentiometer) that may be varied continuously over a range of 300 millivolts to 10 volts; a " ΔE " discriminator (a 10-turn precision potentiometer) continuously variable over a range of 0-10 volts; an integral-differential toggle switch which selects the pulse height analysis mode; and a baseline sweep control to permit a choice of either front panel baseline control or remote baseline control.

2.6 Baseline Sweep

The baseline sweep instrument in the gamma spectrometer system permits a recorder plot of all or part of an energy spectrum by continuously sweeping the window (the acceptance region whose edges are defined by the upper and lower trigger levels) of the pulse height analyzer through the region of interest.

The controls for the instrument are accessible from the front and consist of the following:

1. Upper limit control - potentiometer to select upper or starting voltage across a 0-10 volt baseline.
2. Lower limit control - potentiometer to select lower or ending voltage across a 0-10 volt baseline.
3. Sweep time control - four-position selector switch to select sweep times of 2, 5, 10 or 20 minutes over the full 10-volt sweep range.
4. Recycle-manual control - two-position switch to select automatic recycle or manual operation.
5. Start control - pushbutton to initiate sweep operation.

When the upper and lower limit voltages and the sweep time are selected, the instrument will continuously drive the threshold setting of the pulse height analyzer, to which it is electrically connected, from the upper to lower setting. In the automatic recycling mode, the sweep voltage, upon reaching the lower level setting, will return to the starting value. After a pause the sweep cycle will be repeated. The range of the sweep is from 0 to 10 volts which matches the dynamic range of the pulse height analyzer. With the sweep limits set for the full ten-volt range, the sweep time will be as selected by the sweep time control. The length of the sweep period is reduced proportionately as the range of the sweep is reduced. The meter located at the front of instrument reads sweep position at all times.

E.2.7 Count Rate Meter

The linear count rate meter integrates the input pulses from the pulse height analyzer, Section E.2.5, and shows the integrated count rate in terms of counts per second (CPS) on the 2-1/2 inch meter of the instrument. It has thirteen linear ranges with full-scale values from 10 to 100,000 CPS. The instrument has the following controls:

1. Signal selector control - four-position selector switch which selects polarity of the signal to be counted. It also selects one of two calibration frequencies.
2. Time constant control - selects desired integration time constant of 0.5, 2, 10 and 40 seconds.
3. Range switches - primary range switch selects 10, 100, 1,000 and 10,000 CPS full-scale reading. The secondary range switch selects the multiplier factor to which the meter scale is multiplied.
4. Zero suppression control - 10-turn precision potentiometer can provide zero suppression up to 100 percent of full scale.
5. Recorder output control - the output voltage level to the recorder may be adjusted over a range of plus 20 millivolts.

2.8 Recorder

The recorder is a null-balance, servo-operated potentiometric strip chart recorder with the following basic functions: (1) display, (2) feedback generating, (3) error-detecting, and (4) amplifying.

The voltage to be measured is connected to the recorder in opposition to an internally generated feedback voltage. The difference between the voltage to be measured and the feedback voltage is applied as the input to the amplifier. The amplifier output drives the servomotor which, in turn, drives a potentiometer which changes the internally generated voltage until the difference voltage is very small. The servomotor then stops and the pen records the value of voltage measured. Very little current is drawn from the voltage source because it is balanced by the internal feedback voltage. In addition to these basic functions, the recorder requires damping. With a sudden change in the input signal, the error voltage may be sufficient to run the servomotor at full speed. But when the error voltage reaches zero, the servomotor inertia prevents a sudden reduction to zero speed. Without damping, the recorder would overshoot the proper balance point and go into steady oscillation, first overshooting on one side of the balance point and then the other. The damping system develops a voltage proportional to the speed and feeds it into the amplifier so that the servomotor torque generator stops exactly when the feedback voltage equals the voltage to be measured.

E.2.8 Recorder (Continued)

The recorder reference power supply is a highly accurate d-c voltage source. The unit consists of a voltage-regulator circuit with a temperature-compensated zener diode reference element. The accuracy of the recorder is ± 0.25 percent full scale or ± 5 microvolts - whichever is greater. The chart speed for spectra analysis can be selected from one of seven basic speeds: 1, 6, or 10 inches per hour and 1, 6, 10, or 30 inches per minutes and, by the installation of change gears, the 1-inch per hour and 1-inch per minute speeds can be doubled and quadrupled. Normal chart speed is 1 inch per hour; but, when a scan is run the chart speed is 1 inch per minute. The response time for full-scale pen travel is 5.0 seconds.

2.9 Nuclear Instrument Modular Bin

The instrument modular bin provides power and mounting space for the instruments described in Sections E.2.4, 2.5, 2.6 and 2.7. The bin conforms to the adopted standards of the Atomic Energy Commission Committee on Nuclear Instrument Modules as described in Report TID-20893(Rev.).

3. Ionization Chambers

There are two types of ionization chambers used: (1) process type and (2) environmental/health monitoring type. The principle of operation is the same for both types.

The ionization chamber is simply a cylindrical container housing an insulated center "collector electrode" or anode, and a concentric "high-voltage electrode" near the outer shell. The container is filled with a gas, such as dry air or argon, at atmospheric pressure. When gamma rays enter the container, some of their energy is expended in ionizing the gas. These ions are attracted to the electrode of opposite charge and cause a minute electric current to flow from one electrode to the other through a sensitive external readout circuit.

3.1 Process Type Chambers

Process type ionization chambers for monitoring in-cell process vessels are 5-inch diameter, 27-inch long steel cylinders, filled with argon gas. The chambers are located in a 6-inch steel pipe embedded in the concrete cell wall. A "window" covered with a steel plate is provided in the concrete opposite each chamber so that the chamber "sees" predominately only the vessel which it is intended to monitor.

The ionization chamber is connected electrically to a picoammeter, described in Section E.3.3, which provides the chamber with regulated power as well as the circuitry for measuring the chamber output currents.

3.2 Environmental/Health Monitoring Chambers

The environmental type ionization chambers are 5-inch diameter, 19-inch long, paper-reinforced, phenolic cylinders, filled with dry air. A description of the chamber is as follows: Refer to Figure XIII-23.

E.3.2 Environmental/Health Monitoring Chambers (Continued)

The chamber anode consists of a polystyrene tube with a conductive spray paint coating over its entire surface except for a 1/2-inch insulation barrier at the open end. The anode structure is attached to the head plate with epoxy cement. Since the head plate is at ground potential, it provides isolation between the anode current path and the cathode polarizing potential and, therefore, acts as an anode guard ring.

A 1/4-inch female pipe thread opening is provided in the center of the head plate for insertion of a low-level radioactive source to obtain a minimum chamber output current for certain radiation monitoring system requirements. The insertion or removal of this source does not affect the chamber seal due to the sealed anode structure. Since the source can be inserted in the center of the chamber volume, providing 4π geometry, a minimum source intensity can be used to provide any given background current.

The cathode consists of a conductive spray coating on the inside of the cylindrical shell. As in the case of the anode structure, a 3/8-inch insulating barrier is provided at the open end to prevent the polarizing voltage shorting to ground. Because the shell is constructed of an insulating material, there is no shock hazard when the assembled chamber is placed in an active circuit.

A simulated high radiation level monitoring system check circuit is incorporated in the chamber. The circuit provides a means for checking all the cables and connections to the ion chamber for proper makeup and to determine that the system will function in a high radiation level. The check circuit is actuated by placing a permanent magnet on the outside surface of the chamber near a magnetically-actuated reed switch. The most effective position of the external magnet is marked on the outside of the chamber by a painted yellow rectangle. Any magnet that will produce a magnetic field strength of 80 gauss at a point 1/2 inch inside the chamber surface will actuate the reed switch.

The chamber has a gamma sensitivity of 3.33×10^{-10} amperes per Roentgen per hour and has less than 10 percent loss of saturation in a field of 1,000 R/hr when operated at a polarizing voltage of 250 volts d-c.

The environmental ionization chamber is connected electrically to a picoammeter, described in Section E.3.3, which provides the chamber with regulated power as well as the circuitry for measuring the chamber currents.

3.3 Picoammeters

Picoammeters are used to measure small electric currents generated in the ionization chambers described in Sections E.3.1 and E.3.2. The current produced by a chamber is proportional to the radiation intensity. Picoammeters discussed below are the Keithley Model 410 and Model 410-C.

E.3.3 Picoammeters (Continued)

The Keithley Model 410 is a line-operated, vacuum-tube, electrometer designed for measuring small currents. The total range is from 1×10^{-3} to 3×10^{-13} amperes. This range is divided into twenty overlapping full-scale current ranges in amperes as follows:

10×10^{-4}	10×10^{-9}
3×10^{-4}	3×10^{-9}
10×10^{-5}	10×10^{-10}
3×10^{-5}	3×10^{-10}
10×10^{-6}	10×10^{-11}
3×10^{-6}	3×10^{-11}
10×10^{-7}	10×10^{-12}
3×10^{-7}	3×10^{-12}
10×10^{-8}	10×10^{-13}
3×10^{-8}	3×10^{-13}

The above ranges are selected and read from the front panel. The major panel controls are the range switch (amperes full scale) and the zero adjust knob. Minor controls are the zero check, used to short circuit the input to permit setting the zero point; meter polarity switch for providing up-scale readings for current flows in either direction; and an on-off power switch. An illuminated meter, calibrated 0 to 10 and 0 to 3 is located on the panel.

An output of up to 5 volts and 5 ma is provided from a connector located on the back of the chassis for driving recorders. Most ionization chambers require an extremely well regulated polarizing voltage. A connection on the back of the chassis provides a +216 d-c voltage suitable for this purpose.

The Keithley Model 410 C is identical to the Model 410, except that the panel meter is provided with contacts which can be set to close at any predetermined pointer deflection. The delicate meter contacts operated a relay within the chassis, and the relay contacts (SPDT) are available for external switching functions through a connector on the back of the chassis.

3.4 Recorders

3.4.1 Process Cell Radiation Recorder

The process cell radiation recorder is a Leeds & Northrup "micromax" potentiometric-type, multipoint recorder.

It is approximately twenty-four years old, but this four-point recorder has been reconditioned to record the radiation intensity in the process cells as detected by the ionization chambers described in Section E.3.1.

3.4.2 Environmental Radiation Recorder

The instrument is a potentiometric type, multipoint recorder utilizing an automatic null-balance measuring system. The essential parts of the system

E.3.4.2 Environmental Radiation Recorder (Continued)

are: (1) the null-balance measuring circuit, (2) the null detector-amplifier, (3) the balancing motor and linkage, and (4) the display system.

The measuring circuit consists of an adjustable, calibrated emf connected to oppose the emf being measured. If the two voltages are not equal, an "error" or unbalance current flows and is detected by the input circuit of the amplifier.

After amplification, the error signal is applied to a reversible balancing motor which adjusts the calibrated emf through a mechanical linkage. The system is sensitive to the direction of error current so that the motor always adjusts the calibrated emf in the proper direction to reduce the magnitude of the error current. The motor continues to drive until the error current is so small that the amplified signal will no longer produce motor rotation, but this occurs when the error is substantially zero and the calibrated emf differs by only a negligible amount from the emf being measured. A null or balance condition then exists. While adjusting the calibrated emf, the motor also drives the display system.

The recorder measuring circuit is supplied by a-c power, rectified and regulated by a zener diode circuit.

Additional pertinent information is noted below:

Strip Chart	9-7/8 inches width. Calibrated 0-100 linear.
Indicator Scale	9-7/8 inches length. Calibrated 0-100 linear.
Chart Speed	2 inches per hour.
Number of Points	Most recorders have 8 points.
Printing Speed	3 seconds per point.
Response Time	1 second full scale.
Accuracy	± 0.3 percent of scale span.

F. TEMPERATURE MEASUREMENT AND CONTROL

The following types of temperature measuring and/or control systems are used in the Waste Management Program.

1. Resistance thermometers
2. Filled-system thermometers
3. Filled-system temperature indicating alarm switches
4. Thermocouples.

Resistance type thermometers are used predominately for temperature measurements, usually to monitor the process vessel liquids.

1. Resistance Thermometer Systems

A resistance temperature measuring system comprises a resistance-type primary element, an amplifier-converter, and a pneumatic recorder. Sometimes the pneumatic recorder is equipped with a controller to perform control functions. Other systems consist of the primary element and an electronic recorder only.

1.1 Resistance Element

The resistance thermometer depends upon the inherent characteristic of metals to change in electrical resistance when they undergo a change in temperature. The sensitive element of the thermometer is a nickel or platinum wire wound on an insulating spool and housed in a metal sheath. Nickel wire is used for low temperature ranges (32-248F) and platinum wire is used for high temperature ranges (32-1000F). The sheathed element is approximately 3/8 inch in diameter and is inserted in a well which is immersed in the media whose temperature is to be measured. The temperature-sensitive nickel or platinum wire forms one arm of a Wheatstone bridge circuit. The other three arms of the bridge, located within a resistance to pneumatic converter or recorder instrument, contain resistances which have an extremely low temperature coefficient of resistance.

An extensive test program was performed at Hanford prior to the Waste Management Program to determine the service life of resistance-type temperature elements in a high radiation environment. Temperature elements, as received from several manufacturers, were subjected to an accumulated gamma radiation exposure of 8×10^9 Roentgens (R). The results of the test indicated that a Leeds & Northrup (L&N) temperature element, type 8181, nickel thermohm with rubber-insulated wire encased within a metallic lead jacket would function indefinitely. The other elements failed after a gamma exposure of 1×10^9 R due to radiolytic decomposition of water vapor which leaked into the element due to an inadequate waterproof seal around the electrical wires at the element.

The L&N type 8181, nickel thermohm with a resistance of 100 ohms at 68F has a response time of 20 seconds and a limit of error of ± 0.5 F in the temperature range 32 to 248F, and is used to measure the temperature of process vessel liquids. For higher temperature measurements a platinum thermohm, 25 ohms at 32F, is used. The response time of the platinum element is approximately 15 seconds and has a limit of error of ± 1.5 F in the range of 32 to 248F and ± 3 F in the range 248 to 1000F.

Standard conversion tables for Leeds & Northrup nickel and platinum thermohms are shown in Tables XIII-1, XIII-2, XIII-3 and XIII-4, on the following pages 1350, 1350(a) and 1350(b).

TABLE XIII-1

NICKEL THERMOHMS
Degrees Fahrenheit

Deg. F	Ohms	Deg. F	Ohms	Deg. F	Ohms	Deg. F	Ohms	Deg. F	Ohms	Deg. F	Ohms	Deg. F	Ohms
		0	87.696	50	96.708	100	106.34	150	116.64	200	127.64	250	139.39
		1	87.872	51	96.896	101	106.54	151	116.85	201	127.87	251	139.63
		2	88.047	52	97.085	102	106.74	152	117.06	202	128.10	252	139.87
		3	88.223	53	97.273	103	106.94	153	117.28	203	128.32	253	140.12
		4	88.399	54	97.462	104	107.13	154	117.49	204	128.55	254	140.36
		5	88.574	55	97.650	105	107.33	155	117.70	205	128.78	255	140.60
		6	88.750	56	97.839	106	107.53	156	117.91	206	129.01	256	140.85
		7	88.926	57	98.027	107	107.73	157	118.12	207	129.23	257	141.09
		8	89.101	58	98.216	108	107.93	158	118.34	208	129.46	258	141.33
		9	89.277	59	98.404	109	108.13	159	118.56	209	129.69	259	141.57
40	80.890	10	89.453	60	98.592	110	108.34	160	118.78	210	129.92	260	141.82
39	81.057	11	89.628	61	98.781	111	108.54	161	119.00	211	130.15		
38	81.224	12	89.804	62	98.969	112	108.74	162	119.21	212	130.37		
37	81.392	13	89.980	63	99.158	113	108.94	163	119.43	213	130.60		
36	81.559	14	90.155	64	99.346	114	109.14	164	119.65	214	130.84		
35	81.726	15	90.335	65	99.535	115	109.34	165	119.86	215	131.07		
34	81.894	16	90.514	66	99.723	116	109.55	166	120.08	216	131.30		
33	82.061	17	90.694	67	99.911	117	109.75	167	120.30	217	131.54		
32	82.228	18	90.873	68	100.10	118	109.95	168	120.52	218	131.77		
31	82.396	19	91.053	69	100.29	119	110.15	169	120.73	219	132.01		
30	82.563	20	91.232	70	100.48	120	110.35	170	120.95	220	132.24		
29	82.730	21	91.412	71	100.67	121	110.55	171	121.17	221	132.48		
28	82.898	22	91.591	72	100.87	122	110.76	172	121.38	222	132.71		
27	83.065	23	91.771	73	101.06	123	110.97	173	121.60	223	132.95		
26	83.232	24	91.950	74	101.25	124	111.18	174	121.82	224	133.18		
25	83.400	25	92.130	75	101.44	125	111.39	175	122.04	225	133.41		
24	83.567	26	92.309	76	101.63	126	111.60	176	122.25	226	133.65		
23	83.734	27	92.489	77	101.83	127	111.81	177	122.47	227	133.88		
22	83.902	28	92.668	78	102.02	128	112.02	178	122.69	228	134.12		
21	84.074	29	92.848	79	102.21	129	112.23	179	122.92	229	134.35		
20	84.246	30	93.027	80	102.40	130	112.44	180	123.14	230	134.59		
19	84.418	31	93.207	81	102.60	131	112.64	181	123.36	231	134.83		
18	84.589	32	93.386	82	102.79	132	112.85	182	123.59	232	135.07		
17	84.761	33	93.571	83	102.98	133	113.06	183	123.81	233	135.31		
16	84.933	34	93.755	84	103.17	134	113.27	184	124.03	234	135.55		
15	85.104	35	93.940	85	103.36	135	113.48	185	124.26	235	135.79		
14	85.276	36	94.124	86	103.56	136	113.69	186	124.48	236	136.03		
13	85.448	37	94.309	87	103.76	137	113.90	187	124.70	237	136.27		
12	85.620	38	94.493	88	103.96	138	114.11	188	124.93	238	136.51		
11	85.791	39	94.678	89	104.16	139	114.32	189	125.15	239	136.75		
10	85.963	40	94.863	90	104.36	140	114.52	190	125.37	240	136.98		
9	86.135	41	95.047	91	104.55	141	114.73	191	125.60	241	137.22		
8	86.306	42	95.232	92	104.75	142	114.94	192	125.82	242	137.46		
7	86.478	43	95.416	93	104.95	143	115.15	193	126.04	243	137.70		
6	86.650	44	95.601	94	105.15	144	115.37	194	126.27	244	137.94		
5	86.822	45	95.785	95	105.35	145	115.58	195	126.50	245	138.18		
4	86.993	46	95.970	96	105.55	146	115.79	196	126.73	246	138.42		
3	87.169	47	96.154	97	105.75	147	116.00	197	126.96	247	138.66		
2	87.345	48	96.339	98	105.94	148	116.21	198	127.18	248	138.90		
1	87.520	49	96.524	99	106.14	149	116.43	199	127.41	249	139.15		
0	87.696	50	96.708	100	106.34	150	116.64	200	127.64	250	139.39		

TABLE XIII-2

25 OHM PLATINUM THERMOHMS
Degrees Fahrenheit

Deg. F	Ohms	Deg. F	Ohms	Deg. F	Ohms	Deg. F	Ohms
		0	23.236	350	42.149	700	59.947
		10	23.792	360	42.672	710	60.439
-330	4.123	20	24.347	370	43.195	720	60.930
320	4.734	30	24.901	380	43.717	730	61.420
310	5.344	40	25.455	390	44.238	740	61.910
-300	5.950	50	26.007	400	44.758	750	62.398
290	6.553	60	26.558	410	45.277	760	62.885
280	7.154	70	27.108	420	45.796	770	63.372
270	7.752	80	27.658	430	46.314	780	63.859
260	8.348	90	28.206	440	46.830	790	64.343
-250	8.941	100	28.753	450	47.346	800	64.827
240	9.533	110	29.299	460	47.862	810	65.310
230	10.122	120	29.846	470	48.376	820	65.793
220	10.709	130	30.391	480	48.889	830	66.274
210	11.295	140	30.935	490	49.401	840	66.754
-200	11.878	150	31.479	500	49.913	850	67.233
190	12.459	160	32.020	510	50.423	860	67.712
180	13.039	170	32.561	520	50.932	870	68.189
170	13.618	180	33.101	530	51.440	880	68.666
160	14.194	190	33.641	540	51.948	890	69.142
-150	14.769	200	34.179	550	52.454	900	69.617
140	15.343	210	34.716	560	52.960	910	70.092
130	15.915	220	35.253	570	53.465	920	70.564
120	16.485	230	35.790	580	53.970	930	71.036
110	17.054	240	36.325	590	54.473	940	71.507
-100	17.623	250	36.858	600	54.975	950	71.978
90	18.189	260	37.391	610	55.476	960	72.447
80	18.754	270	37.924	620	55.977	970	72.915
70	19.319	280	38.455	630	56.476	980	73.383
60	19.882	290	38.985	640	56.974	990	73.850
-50	20.443	300	39.515	650	57.471	1000	74.316
40	21.004	310	40.043	660	57.968		
30	21.564	320	40.571	670	58.464		
20	22.123	330	41.098	680	58.959		
-10	22.680	340	41.625	690	59.453		
0	23.236	350	42.149	700	59.947		

TABLE XIII-4
25-OHM PLATINUM THERMOHM
Degrees Centigrade

Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms
-200	4.245	0	25.012	200	44.342	400	62.496								
-195	4.795	5	25.510	205	44.810	405	62.934								
-190	5.344	10	26.007	210	45.277	410	63.372								
-185	5.889	15	26.503	215	45.745	415	63.810								
-180	6.432	20	26.998	220	46.211	420	64.246								
-175	6.973	25	27.493	225	46.676	425	64.682								
-170	7.513	30	27.987	230	47.140	430	65.117								
-165	8.050	35	28.480	235	47.605	435	65.551								
-160	8.585	40	28.972	240	48.068	440	65.985								
-155	9.119	45	29.465	245	48.530	445	66.418								
-150	9.651	50	29.956	250	48.991	450	66.850								
-145	10.181	55	30.446	255	49.452	455	67.281								
-140	10.709	60	30.935	260	49.913	460	67.712								
-135	11.237	65	31.424	265	50.372	465	68.142								
-130	11.762	70	31.912	270	50.830	470	68.571								
-125	12.285	75	32.399	275	51.288	475	68.999								
-120	12.807	80	32.885	280	51.746	480	69.427								
-115	13.329	85	33.372	285	52.202	485	69.855								
-110	13.849	90	33.857	290	52.657	490	70.281								
-105	14.367	95	34.341	295	53.112	495	70.705								
-100	14.884	100	34.824	300	53.567	500	71.130								
-95	15.400	105	35.307	305	54.020	505	71.554								
-90	15.915	110	35.790	310	54.473	510	71.978								
-85	16.428	115	36.271	315	54.924	515	72.400								
-80	16.940	120	36.751	320	55.375	520	72.822								
-75	17.452	125	37.231	325	55.826	525	73.243								
-70	17.962	130	37.711	330	56.276	530	73.663								
-65	18.471	135	38.189	335	56.725	535	74.083								
-60	18.980	140	38.667	340	57.173	540	74.502								
-55	19.488	145	39.144	345	57.621										
-50	19.994	150	39.621	350	58.068										
-45	20.499	155	40.096	355	58.514										
-40	21.004	160	40.571	360	58.959										
-35	21.508	165	41.045	365	59.403										
-30	22.011	170	41.519	370	59.848										
-25	22.513	175	41.991	375	60.291										
-20	23.014	180	42.463	380	60.733										
-15	23.515	185	42.934	385	61.175										
-10	24.016	190	43.404	390	61.616										
-5	24.514	195	43.874	395	62.057										
0	25.012	200	44.342	400	62.496										

TABLE XIII-3
NICKEL THERMOHM
Degrees Centigrade

Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms	Deg. C	Ohms
-40	80.880	10	96.708	60	114.52	110	134.59	170	152.64	230	170.79	290	188.94	350	207.09
-39	81.191	11	97.047	61	114.90	111	135.02	171	153.02	231	171.14	291	189.28	351	208.38
-38	81.492	12	97.386	62	115.28	112	135.45	172	153.35	232	172.29	292	190.57	352	209.67
-37	81.793	13	97.725	63	115.66	113	135.88	173	153.68	233	173.43	293	191.76	353	210.96
-36	82.094	14	98.064	64	116.04	114	136.31	174	154.01	234	174.57	294	192.95	354	212.25
-35	82.396	15	98.404	65	116.43	115	136.75	175	154.34	235	175.71	295	194.14	355	213.54
-34	82.697	16	98.743	66	116.81	116	137.18	176	154.67	236	176.85	296	195.33	356	214.83
-33	82.998	17	99.082	67	117.19	117	137.61	177	155.00	237	177.99	297	196.52	357	216.12
-32	83.299	18	99.421	68	117.57	118	138.04	178	155.33	238	179.13	298	197.71	358	217.41
-31	83.600	19	99.760	69	117.95	119	138.47	179	155.66	239	180.27	299	198.90	359	218.70
-30	83.902	20	100.10	70	118.34	120	138.90	180	156.00	240	181.41	300	200.09	360	219.99
-29	84.211	21	100.45	71	118.73	121	139.34	181	156.33	241	182.55	301	201.28	361	221.28
-28	84.520	22	100.79	72	119.12	122	139.78	182	156.66	242	183.69	302	202.47	362	222.57
-27	84.829	23	101.14	73	119.51	123	140.21	183	156.99	243	184.83	303	203.66	363	223.86
-26	85.138	24	101.49	74	119.90	124	140.65	184	157.32	244	185.97	304	204.85	364	225.15
-25	85.448	25	101.83	75	120.30	125	141.09	185	157.65	245	187.11	305	206.04	365	226.44
-24	85.757	26	102.18	76	120.69	126	141.53	186	157.98	246	188.25	306	207.23	366	227.73
-23	86.066	27	102.52	77	121.08	127	141.96	187	158.31	247	189.39	307	208.42	367	229.02
-22	86.375	28	102.87	78	121.47	128	142.40	188	158.64	248	190.53	308	209.61	368	230.31
-21	86.684	29	103.22	79	121.86	129	142.84	189	158.97	249	191.67	309	210.80	369	231.60
-20	86.993	30	103.56	80	122.25	130	143.27	190	159.30	250	192.81	310	211.99	370	232.89
-19	87.309	31	103.92	81	122.65	131	143.72	191	159.63	251	193.95	311	213.18	371	234.18
-18	87.625	32	104.28	82	123.05	132	144.17	192	160.00	252	195.09	312	214.37	372	235.47
-17	87.941	33	104.63	83	123.45	133	144.62	193	160.33	253	196.23	313	215.56	373	236.76
-16	88.257	34	104.99	84	123.85	134	145.07	194	160.66	254	197.37	314	216.75	374	238.05
-15	88.574	35	105.35	85	124.26	135	145.52	195	161.00	255	198.51	315	217.94	375	239.34
-14	88.890	36	105.71	86	124.66	136	145.97	196	161.33	256	199.65	316	219.13	376	240.63
-13	89.206	37	106.06	87	125.06	137	146.42	197	161.66	257	200.79	317	220.32	377	241.92
-12	89.522	38	106.42	88	125.46	138	146.87	198	161.99	258	201.93	318	221.51	378	243.21
-11	89.838	39	106.78	89	125.86	139	147.32	199	162.32	259	203.07	319	222.70	379	244.50
-10	90.155	40	107.13	90	126.27	140	147.77								
-9	90.478	41	107.49	91	126.68										
-8	90.801	42	107.85	92	127.09										
-7	91.124	43	108.22	93	127.50										
-6	91.447	44	108.58	94	127.91										
-5	91.771	45	108.94	95	128.32										
-4	92.094	46	109.30	96	128.73										
-3	92.417	47	109.67	97	129.14										
-2	92.740	48	110.03	98	129.55										
-1	93.063	49	110.39	99	129.96										
0	93.386	50	110.76	100	130.37										

F.1.2 Amplifier-Converter

The resistance thermometer leads are usually connected to a resistance to pneumatic converter consisting of a d-c power supply, Wheatstone bridge, amplifier and a current to air pressure transducer. The final output from the converter is a 3-15 psig air signal, proportional to the measured temperature, and is received by a pneumatic recorder or recorder-controller.

1.3 Recorder-Controller

The recorder for temperature measurement is usually a single-pen recorder, but there are some two-pen recorders in use. The recorder 4-inch strip charts and indicator scales are calibrated for several ranges (0-100 C, 0-150 C). The strip chart is operated by a synchronous motor at speeds of 3/4 inch or 1 inch per hour. Each recorder pen is operated through linkages by a 3-15 psig receiver bellows.

Some recorders are equipped with controller functions. See Section B.6.3 for description.

1.3.1 Electronic Recorder

The recorder for temperature measurement is a four-pen recorder. The recorder 7-1/8 inch strip chart and indicator scale are calibrated for a range of 0-100 C. The strip chart is operated by a synchronous motor at a speed of 1 inch per hour. The recorder is complete with a Wheatstone bridge excited by a zener regulated d-c power supply, a slide-wire contact, photoelectric chopper, amplifier and a two-phase balancing motor.

When the resistance of the sensitive element in one arm of a Wheatstone bridge changes, the bridge is unbalanced and an error signal is developed between the slide-wire contact and the sensitive element inputs to the amplifier. The error signal is converted to an a-c voltage by a photoelectric chopper and amplified. The amplifier output drives a two-phase balancing motor whose direction of rotation depends on the polarity of the error signal. The balancing motor moves the contact on the slide-wire until the bridge is rebalanced and no error signal exists. The recorder pen and slide-wire contact are positioned simultaneously to indicate the temperature.

1.3.2 Existing Leeds & Northrup Recorder

This instrument (approximately twenty-four years old) is a multipoint strip chart recorder with a single recording pen. The recorder is capable of recording the temperature of four, independent, temperature-sensitive elements through an automatic selector switch. The multipoint instrument makes use of the Wheatstone bridge method to determine the resistance change of the temperature-sensitive elements utilizing a galvanometer balancing unit.

F.1.3.2 Existing Leeds & Northrup Recorder (Continued)

The galvanometer deflection is determined by the balancing unit, which in turn rotates the slide-wire until the bridge circuit is rebalanced. The recording pen is moved across a calibrated temperature scale by means of a mechanical linkage.

1.4 Alarm Switch

The alarm switch is a pressure-actuated switch whose primary function is to trigger visual and audible alarm devices. The pressure-sensitive element is a Bourdon tube or a diaphragm which is mechanically linked to the switch contacts. When the pressure sensed by the sensitive element overcomes the setting of the load spring, a SPDT snap-action switch is activated to open or close an electrical circuit. The temperature alarm switches in the Waste Management Program are usually connected to the pneumatic output signal from a transmitter or a controller, and have a pressure range of 0-15 psig.

2. Filled-System Thermometers

The filled-system thermometer is used for temperature measurement of process streams and vessels where a record is not required. The system consists of a sensitive measuring element or bulb containing a gas or fluid which changes in physical characteristics (either volumetric or pressure) with temperature. This change is communicated to a Bourdon tube, located within the case of a dial indicator, through a capillary tube. The Bourdon tube responds to the signal from the sensitive measuring element to provide motion in relation to the temperature which is transmitted by mechanical linkages to a dial indicator pointer to provide temperature indication.

Some filled-system thermometers, in addition to providing temperature indication, are equipped to perform an alarm function. They have one or more SPDT electrical snap-action switches to provide high/low limit adjustable trip points. The trip points may be adjusted from the front of the dial indicator to open or close an electrical circuit at a pre-determined temperature limit.

3. Thermocouple Systems

A temperature measuring system using a thermocouple for the primary element usually consists of the element and an electronic multipoint recorder. Thermocouples are used in the tank farm installations and other systems where temperatures exceed the limits of a resistance type element.

3.1 Element

The thermocouple temperature sensing element is based on the thermoelectric effect of dissimilar metallic junctions. The heat liberated or absorbed by the junctions results in a change of the thermal electromotive force.

F.3.1 Element (Continued)

The majority of the thermocouple elements are of the iron-constantan type and have a usual temperature range of (-)300 to 1400 F. The upper temperature limit is dependent upon the size of the thermocouple wire. Two other common thermocouple types are chromel-alumel, temperature range (-)300 to 2300 F; and copper-constantan, temperature range (-)300 to 700 F.

The thermocouple measuring junction is usually formed by twisting together and welding the ends of the two dissimilar conductors. The junctions are formed to provide the required spacing between the wires to permit easy insertion of ceramic insulators. Protecting tubes of stainless steel are used for most of the thermocouple installations to prevent contamination of the thermocouple and provide mechanical protection and support. Thermocouples with magnesium oxide insulation and encased within a stainless steel sheath are used in high gamma radiation fields. The protecting tube must be immersed in the process stream to a sufficient depth to minimize heat transfer along the length of tube. A thermocouple connection head or a quick-disconnect plug and jack are used to provide a positive connection between the thermocouple and the thermocouple extension wire.

The response time of thermocouples is from 0.1 to 10 seconds and is dependent upon the time constant of the protecting tube. The limits of error for thermocouples, as recommended by the Instrument Society of America (ISA), are given in Table XIII-3.

TABLE XIII-3

LIMITS OF ERROR FOR THERMOCOUPLES

<u>Type</u>	<u>Temp. Range °F</u>	<u>Limits of Error</u>	
		<u>Standard</u>	<u>Special</u>
Copper-Constantan	-300 to -75	--	+ 1%
	-150 to -75	+ 2%	+ 1%
	-75 to +200	± 1-1/2 F	± 3/4 F
	200 to 700	± 3/4%	± 3/8%
Iron-Constantan	0 to 530	± 4 F	± 2 F
	530 to 1400	± 3/4%	± 3/8%
Chromel-Alumel	0 to 530	± 4 F	--
	530 to 2300	± 3/4%	--

The millivolt signal generated by the thermocouple is received by a multipoint potentiometric recorder as described in the following Section.

3.2 Recorder

The instrument employed for recording thermocouple temperature measurements is a multipoint recorder with an automatically-balanced d-c potentiometer measuring circuit. The measuring circuit current is supplied from an a-c line,

F.3.2 Recorder (Continued)

rectified and regulated by a zener-diode circuit. Any unbalance of the measuring circuit is amplified, and a reversing motor is utilized to restore the balance.

The instrument is equipped with an automatic reference junction compensator and five individually adjustable, dual, SPDT, alarm contacts. The recorder is capable of recording the temperature of sixteen independent thermocouple elements through an automatic selector switch at a speed of two seconds per point. The recorder strip chart has a calibrated width of 9-7/8 inches, and a speed of 3/4 inch per hour. The recorder accuracy is ± 0.3 percent full span.

G. pH MEASUREMENT

The pH measurement system employs special electrodes that develop an emf proportional to the hydrogen-ion concentration in the solution into which they are immersed. By definition:

$$\text{pH} = \log \frac{1}{\text{hydrogen-ion concentration in moles/liter}}$$

The hydrogen-ion concentration of a solution is determined electrometrically by measuring the difference in potential between an electrode which has a fixed voltage (calomel reference electrode) and an electrode in which the voltage varies with the solution pH (glass electrode). The pH system consists of the sampling air jet, a flow chamber with pH electrodes, a pH analyzer, and an electronic recorder. Refer to Figure XIII-24.

1. pH Electrodes

The glass electrode consists of a glass tube closed at the bottom by a membrane of special pH sensitive glass. In contact with the inner wall of the glass membrane is a constant pH solution in which is immersed an internal metallic element. When the glass electrode is immersed in the sample solution, a surface potential is developed on the pH sensitive membrane of the electrode which is proportional to the active hydrogen-ion concentration of the sample. The potential developed by the glass electrode is compared with the constant-potential calomel reference electrode. The calomel electrode is contained within a glass tube and consists of mercury and mercurous chloride in contact with saturated potassium chloride as an electrolyte. The electrolyte is permitted to flow slowly through a porous palladium junction sealed in the immersion end of the electrode, and into the sample solution. This flow of the electrolyte from the electrode to the sample solution completes the electrical circuit of the pH measurement system. The glass and reference electrodes can tolerate a total gamma exposure of 5×10^8 Roentgen; at this point they will break due to pressure build-up by radiolysis.

G.1 pH Electrodes (Continued)

The thermocompensator is a well-type platinum resistance-temperature detector that is tip sensitive and has a response time of less than three seconds. When immersed in the sample solution, the thermocompensator corrects automatically the pH amplifier circuit for the effects of temperature variations in the sample solution. The three pH elements described above are placed side by side in a Hanford-designed, in-line flow chamber and connected by shielded cable to the pH analyzer.

2. pH Analyzer

The analyzer is an electroanalytical instrument equipped with an amplifier circuit board, two power supply circuit boards, and a potentiometric and current output board; all furnished as plug-in units. A special multi-conductor electrical cable connects the analyzer with the electrodes. The analyzer measures the electrochemical properties of the process streams for the degree of acidity or alkalinity, and indicates on a panel meter the H-ion concentration in pH units. Also, the analyzer provides an output signal that drives a special potentiometric recorder.

3. Recorder

The recorder is a null-balance, servo-operated potentiometric recorder having two independent measuring circuits and pens and a common strip chart.

The potentiometer circuit is the conventional slide-wire type, but has continuous standardization by means of a highly accurate silicon (zener) diode reference. The unknown input voltage is balanced against a known voltage from the voltage reference. Balance is achieved when the two opposing voltages are equal and no current flows in the balancing circuit.

A slide-wire equipped with a moving contact is used to vary the known voltage. The unbalanced or error signal is amplified sufficiently to drive the servo motor (rebalancing motor). Because the motor is mechanically linked to the slide-wire contact as well as the pen, the position of the contact is proportional to the measured variable.

The recorder range is 0-14 pH units. It has zero and span adjustment knobs accessible from the front of instrument. The normal span is 2 pH, and by using the zero adjustment it can be adjusted from 0-2 pH to 10-12 pH.

The recorder has an accuracy of $\pm 1/4$ percent of full scale and a response time of four seconds full scale. Recorder strip chart calibrated width is 10-3/4 inches and the chart speed is 2 inches per hour.

4. Buffer and Rinse Tanks

In order to calibrate the pH system periodically, each station has its own small capacity buffer and rinse tanks. To transfer buffer solution to the flow chamber, the three-position selector switch (SS) must be manually turned

G.4 Buffer and Rinse Tanks (Continued)

to position 3. This will energize the time-delay relay coil K-TDR and the canyon and operating gallery buffer solenoid valves. When the transfer of buffer solution is completed, the selector switch is returned to the "off" or No. 2 position which de-energizes the time delay relay coil; de-energizes the buffer solenoid valve in the operating gallery; the buffer solenoid valve in the canyon area will remain energized until the K-TDR contacts are timed out (5-180 second delay on de-energization of relay coil). To rinse the flow chamber with demineralized water, the selector switch must be placed in the No. 1 position, which will energize solenoid valve EV-Water in the canyon area.

H. MISCELLANEOUS INSTRUMENTATION

1. Cell Microphones

All process tanks are equipped with contact microphones. The operator may ascertain, to some degree, conditions within a tank by listening to loud speakers connected to these microphones. Thus, it is possible to determine the proper operation of agitators and pumps and to determine whether jets are gassing or pumping liquids.

The amplifiers are located in the operating gallery opposite the panelboards. Some amplifiers handle more than one microphone and the required switches are located on the panelboard. Loudspeakers, one for each amplifier, are located at the top of the panelboard. The sound volume is controlled by gain controls located on the amplifier and on the panelboard.

2. Tachometers

All centrifuges are equipped with electric tachometers to indicate the speed of rotation. The tachometer consists of: (1) a small a-c generator mounted on the centrifuge shaft with voltage output proportional to speed, and (2) a panel-mounted indicator with control functions.

An automatic control attached to the centrifuge tachometers prevents inadvertent reversal of the centrifuge in case of prolonged "plugging". When a centrifuge is plugged, the power phases to the motor are reversed so that the motor torque is applied in the reverse direction. This causes the speed to decrease rapidly, but if the plug control is held in too long the centrifuge will reverse its direction of rotation resulting in serious damage to the centrifuge. To forestall that possibility, a panel-mounted indicator with a locking coil d-c meter-relay device is used. It has an adjustable control-action pointer, load relays (with d-c power supply), and rectification components to make it compatible with the tachometer a-c generator. In operation, the pointer is set at approximately zero RPM. Should the speed of the centrifuge motor, during "plugging", decrease to near zero RPM, the control-action is initiated and the motor is shut down. The indicating meter is a dual-range unit calibrated in revolutions per minute (RPM). The outer scale range is 0-2000 RPM

H.2. Tachometers (Continued)

and the inner scale range is 0-1000 RPM. The indicating accuracy is ± 2 percent full scale. A two-position, electrical selector switch is mounted near the panel-mounted indicator to select the proper indicator scale range.

3. Ammeters

Indicating ammeters are used to provide a visual indication at the instrument panel of the current drawn by electric motors used to drive pumps, agitators, and centrifuges. The ammeters assist in the detection of abnormal operating conditions manifested by changing current demand. The a-c ammeters used are the iron-vane, repulsion type. It consists of two vanes or iron pieces placed within a coil. One of the vanes is stationary and the other is movable and mounted on a shaft with an attached pointer. When the alternating current passes through the coil the vanes become magnetized and a force or torque is created which repels the vanes. This causes the movable vane to rotate and move the pointer shaft. The ammeter size is approximately 3-1/2 inches square and has a graduated scale calibrated in amperes. The ammeter accuracy is ± 2.0 percent of full scale reading.

4. Selector Switches

4.1 Electric Switches

An electric selector switch is a manually-operated pilot device used to control (usually by actuating a remote magnetic device) and to indicate the condition of one or more electrical circuits. It is fundamentally a contact "making" and "breaking" device with one or more sets of movable and stationary contacts depending upon the number of selector switch positions required and the number of electrical circuits to be controlled.

The contact arrangements are referred to as normally open (N.O.) or normally closed (N.C.). A normally open position is one where the stationary and movable contacts are separated prior to actuation. When the actuator control shaft is positioned, the contacts join and close a circuit. Normally closed refers to the condition where the movable and stationary contacts are touching prior to actuation. When the actuator control shaft is positioned, the contacts separate, breaking the circuit. Cams attached to the actuator control shaft are used to make or break electrical circuits for each selector switch position.

There are two types of selector switch contacts — momentary and maintained. Momentary contacts return to their original position as soon as the actuator is released. Maintained contacts remain in the position in which they are actuated.

H.4.2 Air Switches

An air switch is basically a plug-type selector valve with a minimum of three ports. Most switches are of the two-position, three-port type and are used to open and close a diaphragm-operated valve.

The inlet port is connected to an air supply header, the outlet port is connected to the controlled device, and a vent port is open to the atmosphere. The switch selector handle, attached to the valve plug, controls flow direction by positioning passes within the valve plug over the inlet and outlet ports. The nameplate provided shows the internal function of the switch. Some of the nameplate legends used are: "On-Off", "Automatic-Manual", and "Load-Unload". When the selector handle is placed in the "On" position, the inlet and outlet ports are connected and the vent port is closed. When the handle is in the "Off" position, the outlet and vent ports are connected and the inlet port is closed.

Air switches are also available as two-position, four-port; three-position, four-port; and four-position, five-port. They are used in control systems where more than one device is to be controlled from a single air switch.

I. SPECIAL CONTROL SYSTEMS

1. Concentrator Safety Interlocks

Concentrators E-5-2, E-20-2, and E-23-3 located in Building 221-B process cells 5, 20, and 23 respectively, are equipped with safety devices and electrical interlocks designed to shut down the steam flow to the concentrator tube bundles whenever one or more of the following occur:

1. High steam pressure to tube bundles
2. Low pressure in the tube bundles (for air pressurization)
3. Low weight factor in concentrator, and
4. High temperature in concentrator

The safety devices eliminate the possibility of an explosion, when red oil is formed in the concentrator, by limiting the solution temperature and the pressure in the concentrator.

A typical tube bundle control system is shown in Figure XIII-25 and the tube bundle safety interlocks are on Figure XIII-26.

The concentrators E-5-2 and E-20-2 are each equipped with one tube bundle system but the concentrator E-23-3 has a two-tube bundle system.

The operation of a one-tube bundle system is as follows: System start-up is initiated by depressing PB-1 which energizes relay K-1, solenoid valve EV-STM (operating steam valve DOV-1) and solenoid valve EV-COND (opening condensate valve DOV-3) to permit steam flow to tube bundle. At the same time, solenoid valve EV-AIR is de-energized (closing air valve DOV-2). PB-1 must be held depressed until pressure switch PS-2 (Lo) contact closes to place system in the automatic mode.

I.1 Concentrator Safety Interlocks (Continued)

Automatic shutdown of the system will occur in the event any of the following conditions occur.

1. High pressure steam to the tube bundles - The monitoring pressure switch, PS-1 (Hi), dual contacts will open, deactivating the system and activating a visual and audible annunciation system, PA-1 (Hi).
2. Low pressure in the tube bundles - The monitoring pressure switch, PS-2 (Lo), dual contacts will open, deactivating the system and activating a visual and audible annunciator system, PA-2 (Lo). This also admits air to the tube bundle to prevent any solution leaking from bundle to condensate header.
3. Low weight factor in concentrator - The monitoring pressure switch WFAS-2 (Lo), contact will open, deactivating the system.
4. High temperature in concentrator - The monitoring pressure switch, TAS-1 (Hi), dual contacts will open, deactivating the system and activating a visual and audible annunciator system, TA-1 (Hi).

When any one of the above shutdown conditions occur, the following takes place to deactivate the tube bundle system. Relay K-1 is de-energized, solenoid valve EV-STM is de-energized closing steam valve DOV-1, solenoid valve EV-COND is de-energized closing steam condensate valve DOV-3, solenoid valve EV-AIR is energized opening air valve DOV-2, thus pressurizing the tube bundle with air.

To add raw water to concentrator tube bundle, it will be necessary to hold pushbutton PB-1 in until pressure to tube bundle is approximately 10 psig which will energize solenoid valve EV-COND opening steam condensate valve DOV-3, and open raw water header block valve upstream from raw water pressure reducing valve PRV-3.

To restart the steam flow to tube bundle, pushbutton PB-1 must be depressed momentarily until pressure to tube bundle is approximately 10 psig.

2. Ammonia, Carbon Dioxide, and Nitrogen System

The control system used for the addition of ammonia or carbon dioxide to tank TK-21-1 is shown schematically in Figure XIII-27.

The measuring components are identical for both systems and consist of a flow orifice FE-1, differential pressure transmitter FT-1, and a flow indicating integrator controller FIQC-1.

I.2 Ammonia, Carbon Dioxide, and Nitrogen System (Continued)

The operation of the ammonia or carbon dioxide addition system is as follows:

The desired quantity to be added must be preset on the pre-determining counter which is one unit of the FIQC instrument (see Section B.6.5.2). Manual switch MS-1 must be in the operating position. The system is then started by momentarily depressing pushbutton PB-1 to close the flow alarm switch FAS-1, which seals in the control circuit. Relay K-1 and time delay relay TDR are then energized permitting DOV-1 to be positioned via manual controller MC-1, solenoid valve EV-3 is energized opening DOV-3. When the desired flow quantity, preset on the pre-determining counter, has been added to the system, the SPDT switch in the counter opens automatically and will cause the following to take place.

Relay K-1 is de-energized, flow alarm FA-1 will indicate a visual and audible alarm condition, EV-1 is de-energized closing DOV-1, time delay relay coil TDR is de-energized but its contact will remain closed for a preset timed period (three minute maximum delay before opening) which will energize the solenoid valve EV-3 allowing a nitrogen purge of the system. After the timed nitrogen purge, all relays and valves in the system will automatically return to their normal condition.

3. Vent Systems

The instrument controls for vent systems No. 1 and No. 2 serving Cell 22, Building 221-B, are shown schematically in Figure XIII-28 and Figure XIII-29 respectively. The controls for both systems are identical except for the additional pressure switch PS-22-4-2 in vent system No. 1.

The operation of vent system No. 1 is as follows:

The set point of differential pressure recorder controller DPRC-22-4 must be set for the desired operating conditions to maintain the correct differential pressure between the process cell and the air tunnel. The system start-up is initiated by placing selector switch SS-22-4 in the automatic position. This de-energizes solenoid valve EV-22-4-1, permitting diaphragm-operated valve DOV-22-4-1 to open and respond to the DPRC-22-4 control signals. The opening of DOV-22-4-1 allows the 100 psig steam supply to motivate the variable jet J-22-4. The jet is then varied or throttled automatically via DPRC-22-4 and DOV-22-4-1 to maintain the correct differential pressure between the process cell and the air tunnel. If the steam supply pressure to the jet is lost or drops to a low value, pressure switch PS-22-4-1 contacts will close at its preset trip setting.

I.3 Vent Systems (Continued)

energizing EV-22-4-1 and closing DOV-22-4-1, energizing EV-22-4-2 to permit DPRC-22-4 to automatically control DOV-22-4-2 in the 100 psig air supply line. At this time jet J-22-4 is motivated by air and is varied automatically via DPRC-22-4 and DOV-22-4-2. Should the steam supply pressure return to normal, the system jet J-22-4 will again be motivated by steam automatically. When selector switch SS-22-4 is placed in position 3 (the air position), jet J-22-4 is motivated by air. The pressure switch PS-22-4-2 is used as a permissive switch for the vent system of Cell 5, Building 221-B. Cell 5 vent instrument controls are inoperative until Cell 22 jet J-22-4 is operating. At this time PS-22-4-2 contacts close permitting the Cell 5 vent system to function. The cell 22 vent system may be shut down by placing selector switch SS-22-4 in the "off" position.

4. Weight Factor Control System - Cell 18

The weight factor control system for tank TK-18-3 is shown schematically in Figure XIII-14 and operates as follows:

The setpoint of the weight factor recorder controller WFRC-18-3 must be set for the desired operating conditions. During normal operation, solenoid valve EV-18-3-2 is de-energized and the control signal from WFRC-18-3 is as shown in Figure XIII-14. When in this operating mode, it is possible to transfer automatically the process solutions from tanks TK-13-1, TK-17-2 or TK-21-1 (located in cells 13, 17 and 21 respectively) after first depressing the appropriate pushbutton at the pushbutton station. Each pushbutton depressed will open the contacts of the preceding pushbutton operated; therefore, it is not possible to transfer the process solution from two or more vessels at the same time. To shut down the process solution transfer operation, the "All Systems Off" pushbutton must be depressed.

The chemical addition line to tank TK-18-3 is made up of three streams manifolded together. To add ammonium carbonate from one stream, it is necessary for solenoid valve EV-18-3-2 to remain de-energized, solenoid valve EV-18-3-5 must be energized via PB-18-3-5 to allow the WFRC-18-3 to control automatically DOV-18-3-3. The two remaining streams in the weight factor system utilize a cascade control system to control automatically their flow rate according to a predetermined ratio. The cascade control instruments include the weight factor recorder controller WFRC-18-3, flow recorder controller FRC-18-3-3, flow recorder controller FRC-18-3-1, FRC-18-3-3 cascade subpanel, and the setpoint or ratio instrument SP-18-3.

To activate the cascade control system, solenoid valve EV-18-3-2 must be energized via PB-18-3-2 at the pushbutton station. The WFRC-18-3 (master controller) control signal is then directed to the setpoint capsule in FRC-18-3-3 (slave controller - see Figure XIII-14) via the FRC-18-3-3 cascade subpanel. Refer to Section B.6.3.4 for description of the cascade subpanel. The output signal of the flow transmitter FT-18-3-2, measuring the demineralized water stream, is received by FRC-18-3-3 and the setpoint or ratio instrument SP-18-3.

I.4 Weight Factor Control System - Cell 18 (Continued)

The function of the FRC-18-3-3 "slave" controller is to record and control automatically the demineralized water flow rate which is dependent upon the "master" controller WFRC-18-3. The SP-18-3 instrument contains a ratio relay which receives the linear input signal and produces an output signal that is a preset ratio of the input signal, a large dial for selecting and indicating the desired ratio, and a transfer station consisting of a transfer valve and a manual regulator. During normal operating conditions the transfer valve control knob is placed in the "ratio set" position which permits the ratio relay to generate the output signal. When the transfer valve is placed in the "manual set" position, the manual regulator can be adjusted to generate the output signal. The output signal of the SP-18-3 is directed to the setpoint capsule of FRC-18-3-1. The setpoint of FRC-18-3-1 is then adjusted automatically or manually by the SP-18-3 instrument to maintain the proper flow ratio in the chemical addition line (from chemical make-up tank TK-18-3C) and the demineralized water line.

5. Pulser Drive Equipment

Piston-type pulsers are installed in Cells 27, 28, 29, and 30 for columns T-27-1, T-28-1, T-29-1, and T-30-1. The following is a brief description of the electrical power and control equipment installed to drive these pulsers at variable speeds. See Figure XIII-30 for schematic diagram.

Five complete and separate drive units are installed, one for each pulser and one standby unit. The standby drive may be used to power any one of the pulser motors in the event of failure or during maintenance of a normal drive. The control system is arranged so that not more than one pulser can be driven from the standby drive at any particular time.

Each individual drive consists of a 15 HP, 440 volt, a-c motor connected to a 9 KW alternator through a eddy-current coupling (electrically-controlled clutch) so that the speed and frequency of the alternator may be varied. A feedback voltage from a tachometer generator on the output side of the clutch maintains the speed constant for any control setting.

Two motor generator sets are provided to furnish field excitation for the alternators. Each consists of a 7-1/2 HP motor driving two, 2 KW, 120 volt, d-c generators. One motor generator set is capable of supplying the field current for four alternators. The 15 HP drive motors cannot be started until either one of the two motor-generator sets are running. The second motor generator is provided as a spare unit, but it is necessary to manually switch the d-c output to the exciter bus.

Each of the four 15 HP pulser-drive, induction motors can be fed from its normal alternator supply or from the standby alternator. The change-over is affected by a selector switch on the instrument panel. If any

I.5 Pulser Drive Equipment (Continued)

one pulser motor is being driven from the standby alternator, no other pulser can be started with its selector switch in the standby position. The pulser motors drive the pulsers through a gear reduction unit.

The start-stop pushbuttons and indicator lights for the main drive motors and exciter motors, the selector switches, the pulser motor ammeters, the pulse rate controls, and the pulse rate indicators are located on the instrument panels. The control equipment and contactors are located in a cabinet adjacent to the main drive motors, alternators, and the exciter sets in the electrical gallery.

Each pulse control (PUC) is simply a 1,000 ohm potentiometer and the pulse indicator (PUI) is a frequency meter calibrated 0 to 100 pulses per minute. The speed control devices are packaged, solid-state, electronic units (one for each drive) located in the control cabinet, and sensitivity and maximum speed adjustments are incorporated in each of these units.

FIGURE XIII-1
Typical In-Cell Rotameter Flow System

UNCLASSIFIED

1371

ISO-100

FIGURE XIII-2
Electronic Rotameter

UNCLASSIFIED

FIGURE XIII-4

Fisher Porter Controller Schematic

FIGURE XIII-5
Magnetic Flowmeter

FIGURE XIII-7
Typical Orifice Flow System

FIGURE XIII-6

"Special" Magnetic Flowmeter, Electrical Schematic

FIGURE XIII-8
Differential Pressure Transmitter
(Flow, Weight Factor, Specific Gravity and Pressure)

FIGURE XIII-9
Square Root Extractor

FIGURE XIII-10
Typical Control Valve Trim Characteristics

FIGURE XIII-11

In-Cell Control Valve (Hammel-Dahl Type)

FIGURE XIII-12

In-Cell Control Valve (Kieley-Muller Type)

FIGURE XIII-13

Purge Dip Tube Systems
(Weight Factor, Specific Gravity and Pressure)

FIGURE XIII-14
Tank 18-3 Weight Factor Control System

FIGURE XIII-15

Typical Column Interface, Pressure and Specific Gravity Systems

FIGURE XIII-16

Resin Column Pressure Systems

UNCLASSIFIED

FIGURE XIII-17

Variable Reluctance Pressure Transducer

FIGURE XIII-18

Conductivity Type Level System

FIGURE XIII-19
Electronic Interface Float

FIGURE XIII-20

Ultrasonic Probe Resin Level Detector

FIGURE XIII-21

Capacitance Measurement Functional Diagram

UNCLASSIFIED

FIGURE XIII-22
Monitor Probe Encasement Assembly

VIEW B-B

FIGURE XIII-23

Ionization Chamber

UNCLASSIFIED

FIGURE XIII-25
Tube Bundle Control System

FIGURE XIII-26

Concentrator Safety Interlocks

FIGURE XIII-27

Ammonia, Carbon Dioxide and Nitrogen Purge System

UNCLASSIFIED

1391

ISO-100

FIGURE XIII-28
Vent System No. 1

UNCLASSIFIED

FIGURE XIII-29
Vent System No. 2

UNCLASSIFIED

1393

ISO-100

FIGURE XIII-30
Pulser Control System

UNCLASSIFIED

PART VI, Cont.
PROCESS CONTROL
CHAPTER XIV

SAMPLING AND ANALYTICAL METHODS

By

A. H. Case

Separations Chemistry Laboratory

PART VI: PROCESS CONTROL, Cont.CHAPTER XIVSAMPLING AND ANALYTICAL METHODS

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PART VI: PROCESS CONTROL, CONT.CHAPTER XIVSAMPLING AND ANALYTICAL METHODS

Information required for control of the operation of B Plant processes will be furnished by in-line instrumentation and by laboratory analysis of samples taken from the various tanks and streams. The variations in composition of feed material and the complexity and variety of the processes put heavy demands on the laboratory for versatility and reliability. Adequate methods and equipment used with painstaking workmanship are necessary to insure that the information supplied by the laboratory is valid and timely. To make the laboratory results meaningful, it is essential that the samples delivered to the laboratory be representative of the tank or stream from which they are taken. The sampling equipment has been designed with this in mind but strict adherence to established sampling procedures is required.

A. SAMPLING1. Sampling Installation and Equipment

The installed sampling equipment consists of shielded boxes containing the sample risers and the necessary piping to circulate the desired process solution through the risers by air jet. A portion of the sample is taken from the sample riser in a plastic pipet on the end of a shielded "trombone." The pipet, ordinarily containing 0.5 milliliters of sample, is transferred to a lead-lined, stainless steel container called a "doorstop" and delivered to the laboratory. "Trombones" and "doorstops" are prepared for use by the laboratory, including decontamination when necessary. The sampling installation and equipment are shown in prints 43062-25, 43062-26, H-2-32654, H-2-32655, H-2-2337, H-3-1398, H-3-1514, and H-2-32514.

2. Sampling Procedure

Procure a trombone and doorstop from the laboratory and check to be sure the doorstop is equipped with a plastic insert and a neoprene gasket on the plug. Follow these steps in obtaining a sample.

- 1) Slowly turn on the air jet to the sampler and check that the sampler is circulating properly. Sample circulation can normally be confirmed by measuring the fluctuating radiation levels on the front side of the sample port. Do not loosen the riser cap while the sample is circulating.
- 2) Remove the doorstop handle and lift the doorstop plug. Attach the syringe to the trombone.

- 3) After the sampler has circulated for 15 minutes, shut off the air jet valve slowly. Remove the riser cap from the sampler, swinging the cap away from the port. With the syringe attached and holding the trombone at an angle, insert the trombone into the port riser, then lower the trombone until it strikes the stop. The sample pipet is now in the sampling position.
- 4) Slowly draw out the syringe plunger 1.5 - 2.0 ml. Then raise the trombone one inch and slowly press the syringe back to zero. (This forces out the excess sample and empties the tip of the pipet.) Raise the trombone three to four inches and wait five to ten seconds to allow dripping of excess sample solution before continuing.
- 5) Lift the trombone out of the riser and pass the pipet near the chamber of the survey instrument while transferring the sample from the port to the doorstep. A significant reading on the instrument will indicate that a sample has been obtained.
- 6) If the survey instrument indicates that no sample was obtained, repeat steps 3, 4, and 5.
- 7) After a sample is obtained, replace the sample port cap and remove the syringe from the trombone.
- 8) With the trombone tip positioned in the doorstep, turn the assembly slowly to the right while pressing down slightly to engage the pipet in its hole in the bottom of the doorstep well. When the tip engages, the trombone assembly will not turn easily in either direction.
- 9) Unscrew the pipet by turning the trombone handle counter-clockwise until the pipet is disengaged from the trombone shaft.
- 10) Remove the plastic trombone from the handle and discard in the receptacle for hot waste.
- 11) The sample port should be promptly restored to normal condition by making a water flush of the riser and then replacing the riser cap.
- 12) Perform a contamination survey and any clean-up which is found to be necessary.
- 13) Attach a sample tag containing all pertinent information to the doorstep and deliver the sample to the laboratory.

This procedure covers the operation of the sampling equipment in use at present in B-Plant. Other types of sampling equipment are planned for the future and procedures for their use will be written as needed.

B. ANALYTICAL METHODS

Following are short descriptions of the general analytical methods used in analyzing B-Plant samples. Where necessary, the methods are preceded by chemical or physical separations to eliminate extraneous materials which would interfere in the analysis.

As plant needs change or as better procedures are developed, other methods may be added or substituted.

1. Counting Methods

Available instrumentation makes it possible to measure the concentration of a radioactive isotope by determining the alpha, beta, or gamma emission rate and using the proper calculations involving specific activity of the isotope, instrument geometry, etc.

- 1) Alpha - Alpha emitters must be separated from gross quantities of extraneous solids which could cause low results by absorption. Often two or more alpha emitters can be determined in each others presence by an alpha energy analysis. In some cases a separation is necessary.
- 2) Beta - A beta emitter can be determined by counting only after separating from all other beta emitters.
- 3) Gamma - In most cases rather complex mixtures of gamma emitters can be analyzed for one or all of the components by a gamma energy analysis. Exceptions would be samples containing isotopes with similar gamma energies or a great disparity in the activity of the isotopes of interest. In these cases a separation is necessary.

Gamma counting can be applied to many non-radioactive isotopes through activation analysis. In this technique, the same is subjected to a controlled exposure in a neutron flux, converting the element of interest to a radioactive species which is determined by gamma energy analysis. Comparison with a standard of known concentration which is given identical treatment makes quantitative results possible.

2. Colorimetric - Spectrophotometric Methods

In many cases the desired constituent of a sample may have a color or can be converted to a compound having a color which is characteristic. The absorbance of the solution for light of a definite

wavelength can be measured on a spectrophotometer and the concentration of the component of interest read from a calibration curve. The wavelength of maximum absorbance may be in the visible, ultraviolet, or infrared portion of the spectrum.

3. Titration Methods

For application of a titrimetric method, the chemical process involved must consist of a single, rapid, stoichiometric reaction between the substance being determined and the standard solution used as a titrant. The point of equivalence is detected by an indicator which shows a marked change in some property (color, potential of an electrode system, etc.) of the titration system. From the concentration of the titrant and the volume required to reach the equivalence point, the concentration of the desired substance may be calculated.

Titrimetric methods may be classified as acid-base titrations, complexometric titrations and oxidation-reduction titrations.

4. Emission Spectrographic Methods

When excited to incandescence the ions of most of the metals and several of the non-metals emit light in wavelength patterns which are characteristic and distinctive for the various ions. In the emission spectrograph the sample is vaporized in an electric arc between two graphite electrodes. The light from the arc is resolved into its various wavelengths by means of a prism or diffraction grating and is focused on a photographic plate. After development, the lines on the plate serve to identify the components of the sample as well as indicate the quantity present.

Although in many cases the results may be considered only semi-quantitative, the method is particularly valuable in determining minor impurities in the parts per million range.

5. Flame Photometry and Atomic Absorption

The principle of flame photometry is identical with that of emission spectrography. In this case the sample, in solution, is aspirated into a flame. The intensity of the resultant light of a characteristic wavelength is measured with a photodetector and suitable electronics. When referred to a calibration curve, this intensity indicates the concentration of the elements sought.

Atomic absorption is based on the fact that most of the atoms of an element present in a flame are not heated to incandescence and emit no light. They are, however, in an excited state where they absorb light of the same characteristic wavelength.

In atomic absorption, monochromatic light of the proper wavelength is passed through the flame into which the sample is aspirated. A suitable detector and instrumentation measures the absorption of light and this is converted into concentration by means of a calibration curve.

6. X-Ray Fluorescence

This method may be applied to all except the lightest elements of the periodic table, present in amounts from a few percent to one hundred percent. It is not particularly good for trace amounts.

The primary X-rays from an X-ray tube are allowed to strike the sample, producing a secondary or fluorescent radiation, also in the X-ray portion of the spectrum. This fluorescent radiation with wavelengths characteristic of the emitting elements passes through a collimating slit onto a crystal spectrometer (goniometer) and thence into a detector. The intensity from a given element is affected by the amount of that element present in an almost linear manner.

7. Fluorimetry

Several substances (e.g., uranium) have the property of fluorescence. This is similar to X-ray fluorescence except that the impinging rays are in the ultraviolet and the secondary emission is in the ultraviolet or visible portion of the spectrum. With the proper instrumentation this provides a sensitive method for determining very low concentrations of uranium.

8. Gas Chromatography

Gas chromatography consists of the separation of the components of a mixture of gases or vapors by passage through a column containing a stationary liquid phase on a solid support such as firebrick or celite. The emergence of each component from the column is indicated by a suitable detector and is registered as a peak on a strip chart. By comparison with standards, the components may be identified by the position of the peak (retention time) and quantity may be determined by the area under the peak.

9. Miscellaneous Methods

The following analyses and tests do not fit into any general category but are designed to furnish specific needed information.

- 9.1 pH - By glass electrode - pH meter. (Electrodes are now available which are sensitive only to certain ions, e.g., Na^+ , Ca^{++} , F^- , Cl^- , etc. These may find some application in B-Plant control.)

- 9.2 Percent Solids - Volume percent undissolved solids is determined visually on a sample allowed to reach equilibrium at a definite temperature and then centrifuged.
- 9.3 Carbonate - Potentiometric titration. The carbonate break is determined on an automatic titrator.
- 9.4 Ammonia - Ammonia is determined by a Kjeldahl distillation method.
- 9.5 Tests for Tartaric, Citric, and Hydroxyacetic Acids - These are qualitative tests to ensure that the correct acid was used in making up process reagents.
- 9.6 Specific Gravity - This is defined as the ratio of the weight of a substance to the weight of an equal volume of water. There are several standard methods for measuring specific gravity, e.g., pycnometer and hydrometer.

The following tables show the primary samples and the analyses to be performed. These samples and analyses are based on conceptual flowsheets and operating requirements as seen at the time this chapter was written. Operating experience, altered requirements, and development of improved methods of analysis will no doubt result in additions, deletions, and substitutions in these tables.

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TABLE XIV-1

CENTRIFUGING AND LEACHING FACILITY

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
PAW Tk-11-12	H ⁺	0.5M	Titration with complexing
	% Solids	--	Visual estimate after centrifugation
	Sr-90	--	Chem. Sep. followed by beta counting
	Pm-147	--	Chem. Sep. followed by beta counting
	Ce-144, ZrNb-95, Ru-103, 106, Sb-125, Ce-137	--	Gamma energy analysis
	Pu, Np, Am	Low	Chem. Sep. followed by alpha count (and alpha energy analysis if necessary)
Leached PAW Tk-12-1	Zr	0.005M	Colorimetric
	H ⁺	0.5M	Titration with complexing
	Sr-90	--	Chem. Sep. followed by beta counting
	Pm-147	--	Chem. Sep. followed by beta counting
	Ce-144, ZrNb-95, Ru-103, 106, Cs-137	--	Gamma energy analysis
	Am, Np, Pu	Low	Chem. Sep. followed by alpha count (and alpha energy analysis if necessary)
	Fe	0.18M	Colorimetric
	Na	0.65M	Flame photometer
	Al	0.05M	Colorimetric
	U	0.01M	Chem. Sep.; Fluorimetric determination
	Zr	0.003M	Colorimetric
	Isotopic Sr (89, 90, inert)	--	
	Total Metallic Impurities	--	Emission Spectrograph
	Sulfate	0.14M	
	Nitrate	1.3M	Colorimetric

TABLE XIV-2ANALYTICAL REQUIREMENTS FOR PRECIPITATION

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
PAS Tk-31-3	H ⁺	0.1M	Titration with complexing
	Sr-90	20 Ci/gal	Chem. Sep. followed by beta counting
	Ce-144	--	Gamma energy analysis
	Pm-147	10 Ci/gal	Chem. Sep. followed by beta counting
	Am, Np, Pu	Low	Chem. Sep. followed by alpha counting
	Na	0.4M	Flame photometry
	Al	0.6M	Colorimetric
	Fe	0.4M	Colorimetric
	Ca	0.03M	Atomic Absorption
	Mg	0.01M	Atomic Absorption
	Mn	0.01M	Atomic Absorption
	Isotopic Sr (89, 90, inert)	--	
Supernates and Washes Tk-32-1	pH	1	Glass electrode- meter
	Sr-90	0.2 Ci/gal	Chem. Sep. followed by beta counting
	Pm-147	0.5 Ci/gal	Chem. Sep. followed by beta counting
	Fission Products	--	Gamma energy analysis
	Am, Pu, Np	Low	Chem. Sep. followed by alpha count

TABLE XIV-2 (Cont.)

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
Dissolved Cake Tk-31-1	H ⁺	1M	Titration with complexing
	Sr-90	200 Ci/gal	Chem. Sep. followed by beta counting
	Pm-147	100 Ci/gal	Chem. Sep. followed by beta counting
	Ce-144	--	Gamma energy analy- sis
Crude Feed Tk-33-1	H ⁺	1M	Titration with complexing
	Sr-90	200 Ci/gal	Chem. Sep. followed by beta counting
	Pm-147	100 Ci/gal	Chem. Sep. followed by beta counting
	Am, Np, Pu	low	Chem. Sep. followed by alpha counting
	Fission Products	--	Gamma energy analysis
	Na	0.1M	Flame photometry
	Al	0.1M	Colorimetric
	Fe	0.2M	Colorimetric
	Ca	0.3M	Atomic Absorption
	Mg	0.1M	Atomic Absorption
	Mn	0.01M	Atomic Absorption
	Pb	0.01M	Colorimetric or atomic absorption
	U	0.01M	Fluorimetric after chemical separation
	Isotopic Sr	--	

TABLE XIV-3

ANALYTICAL REQUIREMENTS FOR SOLVENT EXTRACTION

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
1AF Tk-29-2	pH	4	Glass electrode-meter
	Sr-90	--	Chem. Sep. followed by beta counting
	Pm-147		Chem. Sep. followed by beta counting
	RuRh-106, ZrNb-95, Ce-144, Cs-137	--	Gamma energy analysis
	Am, Np, Pu	Low	Chem. Sep. followed by alpha counting
	Na	1.3 - 1.4M	Flame Photometry
	Al	0.04-0.1M	Colorimetric
	Fe	0.1-0.15M	Colorimetric
	Ca	0.001-0.1M	Atomic Absorption
	Mg	0.001-0.01M	Atomic Absorption
	U	0.01-0.02M	Fluorimetric determination after chem. sep.
	Zr	0.001M	Colorimetric
	Isotopic Sr	--	
1AX Tk-28-3	Y-91	--	Gamma energy analysis
	D2EHPA	0.3M	
	TBP	0.2M	
1AW (In-Line Sample)	Pm-147	0.5-2 Ci/gal	Chem. Sep. followed by beta counting
	Sr-90	1 Ci/gal	Chem. Sep. followed by beta counting
	Fission Products	--	Gamma energy analysis
	pH	4	Glass electrode - meter

TABLE XIV-3 (Cont.)

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
1AW Tk-30-2	Pm-147	0.5-2 Ci/gal	Chem. Sep. followed by beta counting
	Sr-90	1 Ci/gal	Chem. Sep. followed by beta counting
	Fission Products	--	Gamma energy analysis
	pH	4	Glass electrode - meter
1BP (in-line sample)	pH	2.2	Glass electrode - meter
	Sr-90	--	Chem. Sep. followed by beta counting
	Pm-147	0.1-0.2 Ci/gal	Chem. Sep. followed by beta counting
	Ce-144	--	Gamma energy analysis
	Na	0.002-0.01M	Flame photometry
	Ca	0.001-0.01M	Atomic absorption
	Mg	0.001M	Atomic absorption
Conc. 1BP Tk-5-1	HNO ₃	0.12-0.5M	Titration with complexing
	Sr-90	--	Chem. Sep. followed by beta counting
	Na	0.1-0.2M	Flame photometry
	Ca	0.01-0.1M	Atomic absorption
	Mg	0.01M	Atomic absorption
	Isotopic Sr	--	Atomic absorption
	Ce-144	--	Gamma Energy analy- sis
	Sr-80/Sr-90	--	
	Fe	0.0001-0.01M	Colorimetric
	Al	0.0001-0.01M	Colorimetric
	Pb	0.01M	Colorimetric or atomic absorption

TABLE XIV-3 (Cont.)

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
1CP-Pm (in-line sample)	Pm-147	--	Chem. sep. followed by beta counting
	HNO ₃	2M	Titration with com- plexing
	Ce-144	--	Gamma energy analysis
	Persulfate	0.2M	
1CW Tk-26-3	Ce-144	--	Gamma energy analysis
Ce Prod. Tk-27-3	HNO ₃	2M	Titration with com- plexing
	Pm-147	--	Chem. Sep. followed by beta counting
	Ce-144	--	Gamma energy analysis
	Al	Trace	Colorimetric
	Fe	Trace	Colorimetric
	Ag	Trace	Colorimetric or atomic absorption
	Na	Trace	Flame photometry
	Isotopic Ce	--	
Pm Ex-W Tk-26-2W	Pm-147	--	Chem. Sep. followed by beta counting
	Fission Products	--	Gamma energy analysis
	pH	3.5	Glass electrode - meter
Pm Prod. Tk-26-2P	Pm-147	400 Ci/gal	Chem. Sep. followed by beta counting
	HNO ₃	1M	Titration with com- plexing
	Ce-144, Y-91	--	Gamma energy analysis
	Sr-90	--	Chem. Sep. followed by beta counting
1OW Tk-26-1	Sr-90	--	Chem. Sep. followed by beta counting
	Pm-147	--	Chem. Sep. followed by beta counting
	Ce-144, ZrNb-95 Y-91	--	Gamma Energy analysis

TABLE XIV-3 (Cont.)

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
CONC. Pm Prod. TK-36-4	HNO ₃	0.5M	Titration with complexing
	Pm-147	10 ³ -10 ⁴ Ci/gal	Chem. Sep. followed by beta counting
	Am-241	1 x 10 ¹¹ c/m/gal	Chem. Sep. followed by alpha counting
	Y-91	--	Chem. Sep. followed by gamma energy analysis
	Ce-144	--	Gamma energy analysis
	Pm-148/Pm-147	--	
	Total Rare earths	0.5M	
	Al	Trace	Colorimetric
	Fe	Trace	Colorimetric
	Ca	Trace	Atomic absorption
	Ag		Atomic or colorimetric
	TMI	--	Emission spectrograph

TABLE XIV-4

STRONTIUM PURIFICATION

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
Sr-1AF Tk-29-2-Sr	pH	4.9	Glass electrode - meter
	Sr-90	PAW-600 Ci/gal PAS-100 Ci/gal	Chem. Sep. followed by beta counting
	Na	PAW 1.8M PAS 3.2M	Flame photometry
	Ca	0.01-0.04M	Atomic absorption
	Ce-144	--	Gamma energy analysis
	Ba	Trace	Atomic absorption
	Mg	Trace	Atomic absorption
	Fe	Trace	Colorimetric
	Al	Trace	Colorimetric
	Sr-90	2-5 Ci/gal	Chem. Sep. followed by beta counting
Sr-1AW (In-line sample)	Fission products	--	Gamma energy analysis
	pH	5	Glass electrode - meter
	Sr-90	2-5 Ci/gal	Chem. Sep. followed by beta counting
Sr-1AW Tk-30-2-Sr	Fission products	--	Gamma energy analysis
	pH	5	Glass electrode - meter
	Sr-90	PAW 700 Ci/gal PAS 500 Ci/gal	Chem. Sep. followed by beta counting
Sr-1BP (In-line Sample)	Ce-144	--	Gamma energy analysis
	Citric acid	1M	
	Citric acid	0.05M	
Sr-PROD. Tk-5-1-Sr	HNO ₃	1M	
	Sr-90	10 ³ Ci/gal	Chem. Sep. followed by beta counting
	Fission products	--	Gamma energy
Sr-10W Tk-27-3 or 27-1	Sr-90	1 Ci/gal	Chem. Sep. followed by beta counting
	Y-91	--	Gamma energy analysis

TABLE XIV-5

ANALYTICAL REQUIREMENTS FOR ION EXCHANGE

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
PSN 105-C RSN 101-BX	Na	4M	Flame photometry
	Al	0.8M (RSN)	Colorimetric
	Pb	Trace	Colorimetric or atomic absorption
	pH	PSN 10	Glass electrode - meter
	Cs-134, Cs-137	--	Gamma energy analysis
	NO ₃ ⁻	PSN 1M RSN 5M	Colorimetric
	NO ₂ ⁻	PSN 2M RSN 0.4M	Colorimetric
	CO ₃ ⁻²	PSN 1M	
	SO ₄ ⁻²	PSN 0.1M RSN 0.03M	
	Isotopic Cs		
1XF Tk-17-2	Na	4M	Flame photometry
	pH	PSN 10 RSN 12	Glass electrode - meter
	Cs-134, Cs-137	--	Gamma energy analysis
1XW Tk-18-1	Cs-137	--	Gamma energy analysis
1XW Tk-19-1	Cs-137	--	Gamma energy analysis
	NH ₄ ⁺	8M	
	CO ₃ ⁻²	3M	
	Na	0.01M	Flame photometry
Cs Prod. Tk-20-1	Cs-137	--	Gamma energy analysis
Tk-14-2 Tk-17-1	Na	0.3M	Flame photometry
	Rb	0.01M	Chem. Sep. Followed by atomic absorption
	Isotopic Cs	--	
	TMI	--	Emission spectro- graph
	Total Cs	0.05	Atomic absorption

TABLE XIV-6

AQUEOUS AND ORGANIC MAKE-UP

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
Solvent Tk-M0154	D2EHPA	0.3M	Gas chromatography
	TBP	0.2M	Gas chromatography
	SpGr.	0.8	Hydrometer
Bisulfate Tk-101	NaHSO ₄	6M	
Carbonate	Na ₂ CO ₃	2M	
ISS Butt Tk-H301	HC ₂ H ₃ O ₃ (Hydroxy- acetic acid)	2.5M	Qualitative test
	pH	2.4	Glass electrode-meter
Sr-1SS Butt Tk-H301	Citric acid	2.08M	Qualitative test
	pH	3.4	Glass electrode-meter
Tartaric Acid Tk-H302	H ₂ C ₄ H ₄ O ₆	2M	Qualitative test
1BX-Butt Tk-H312	HNO ₃	0.3M	
Sr-1BX Butt Tk-H-312	Citric Acid	3.14M	
Lead Carrier H-401	Pb(NO ₃) ₂	1M	Indirect dichromate titration
Sugar sol'n H-403	Sugar	1.4M	Specific gravity
1CX-1 27-1A 27-1B	HNO ₃	2M	
	Persulfate	0.5M	
1CX-2 27-1C 27-1D	HNO ₃	2M	
	Ag ⁺	0.04M	Thiocyanate titration
1CX 27-1A 27-1B 271-C 27-1D	(During processing of sludge and during Sr purification) HNO ₃	2M	NaOH titration
Ce Strip ^(a) 27-3-A	HNO ₃	2M	NaOH titration
Ce Strip ^(b) 27-3-B	NaNO ₂	3M	KMnO ₄ titration
Sr 105-2 27-3-A	HNO ₃	2M	

TABLE XIV-7

ANALYTICAL REQUIREMENTS FOR B-PLANT WASTE HANDLING

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
HIW (Hi-level Waste) Tk's 25-1, 25-2	Caustic ratio	--	Titration
	Sr-90	1 Ci/gal	Chem. Sep. followed by beta counting
	Pm-147	2 Ci/gal	Chem. Sep. followed by beta counting
	Fission products	--	Gamma energy analysis
	Pu, Np, Am	Low	Chem. Sep. followed by alpha counting
LIW Tk-24-1	HNO ₃	0.1M	
	Cs-137	0.0001 Ci/gal	Chem. Sep. followed by gamma energy analysis
	Sr-90	0.0001 Ci/gal	Chem. Sep. followed by beta counting
	pH	10-11	Glass electrode - meter
LIW Tk-23-1	Sr-90	0.01 Ci/gal	Chem. Sep. followed by beta counting
	Pm-147	0.02 Ci/gal	Chem. Sep. followed by beta counting
	Fission products	--	Gamma energy analysis
	Pu, Np, Am	Low	Chem. Sep. followed by alpha counting
	Cs-137	0.01 Ci/gal	Gamma energy analysis
	NH ₄ ⁺	Trace	Qualitative test
	Gross beta	0.001 Ci/gal	Beta counting
RET. Basin	Fission products	--	Gamma energy analysis

TABLE XIV-8

ANALYTICAL REQUIREMENTS FOR STORED FISSION PRODUCTS

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
CRUDE Sr Tk's 6-1, 6-2, 7-1, 7-2, 8-1, 8-2	HNO ₃	0.1M	Titration with com- plexing
	Sr-90	10 ³ Ci/gal	Chem. Sep. followed by beta counting
	Na	0.2M	Flame photometry
	Ca	0.01M	Atomic absorption
	Mg	0.001M	Atomic absorption
	Isotopic Sr	--	
	Fission products	--	Gamma energy analysis
	Sr-89/Sr-90	--	
	Fe	Trace	Colorimetric
	Al	Trace	Colorimetric
	Ba	Trace	Atomic absorption
Sr Prod Tk-36-1	HNO ₃	1M	Titration with com- plexing
	Sr-90	10 ³ Ci/gal	Chem. Sep. followed by beta counting
	Sr Total	0.15M	
	Ca	0.005M	Atomic absorption
	Ba	0.003M	Atomic absorption
	Mg	0.002M	Atomic absorption
	Pb	0.004M	Atomic absorption
	Fe	0.002M	Colorimetric
	Al	0.002M	Colorimetric
	Zr	0.002M	Colorimetric
	Sr-89/Sr-90	0.05	
	Ce-144, Ru-106, ZrNb-95, Y-91	--	Gamma energy analysis
	Isotopic Sr	--	
	Na	0.2M	Flame photometry
	Citric Acid	Trace	

TABLE XIV-8 (Cont.)

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
Pr PC Tk's 37-1, 37-2, 37-3	HNO ₃	0.5M	Titration with com- plexing
	Pm-147	10 ⁴ Ci/gal	Chem. Sep. followed by beta counting
	Am-241	10 ¹¹ c/m/gal	Chem. Sep. followed by beta counting
	Y-91	--	Chem. Sep. followed by gamma energy analysis
	Ce-144	--	Gamma energy analysis
	Pm-148/Pm-147	10 ⁻⁴ -10 ⁻⁷	
	TRE	0.5-1.0M	
	TMI	--	Emission spectro- graph
	HNO ₃	0.5M	Titration with com- plexing
	Pm-147	10 ³ Ci/gal	Chem. Sep. followed by beta counting
Pm PS (From Sludge)	Am-241	10 ¹¹ c/m/gal	Chem. Sep. followed by alpha counting
	Fission products	--	Gamma energy analysis
	TRE	1M	
	TMI	--	Emission spectro- graph
	Pm-148/Pm-147	10 ⁻⁷	

TABLE XIV-9

ANALYTICAL REQUIREMENTS FOR 244-AR VAULT

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
PAS Tk-004	H ⁺	0.1M	Titration with complexing
	Sr-90	20 Ci/gal	Chem. Sep. followed by beta counting
	Ce-144, Cs-137	--	Gamma energy analysis
	Pm-147	10 Ci/gal	Chem. Sep. followed by beta counting
	Am, Np, Pu	Low	Chem. Sep. followed by alpha counting
	U	0.02M	Fluorimetric determination after chemical separation
	Na	0.4M	Flame photometer
	Al	0.6M	Colorimetric
	Fe	0.4M	Colorimetric
	Ca	0.03M	Atomic absorption
	Isotopic Sr	--	
Sludge Slurry Tk-002	pH	10	Glass electrode - meter
	% Solids	10-20	Visual estimate after centrifugation
	% Insolubles	1	
PAW Tk-001	Cs-137	--	Gamma energy analysis
	H ⁺	0.5M	Titration with complexing
	% Solids	1	Visual estimate after centrifugation
	Sr-90	45 Ci/gal	Chem. Sep. followed by beta counting
	Pm-147	180 Ci/gal	Chem. Sep. followed by beta counting
NHW Tk-003	Ce-144, Cs-137	--	Gamma energy analysis
	Sr-90	1 Ci/gal	Chem. Sep. followed by beta counting
	Pm-147	2 Ci/gal	Chem. Sep. followed by beta counting
	Cs-137, Ce-144, ZrNb-95, Ru-106	--	Gamma energy analysis
	pH	10-12	Glass electrode - meter

TABLE XIV-10

ANALYTICAL REQUIREMENTS FOR IN-TANK SOLIDIFICATION FACILITY

<u>Sample</u>	<u>Analysis</u>	<u>Estimated Concentration</u>	<u>Method</u>
ITS-F 103-BY	SpGr.	1.3	Hydrometer
	% Solids	5-10	Visual estimate after centrifugation
	Cs-137	--	Gamma energy analysis
	Viscosity	2	
	Sr-90	0.5 $\mu\text{Ci/gal}$	Chem. Sep. followed by beta counting
	Na	8M	Flame photometry
	OH ⁻	1M	Colorimetric
	NH ₄ ⁺	1M	
	Reducing normality	0 to trace	
Condensate	Cs-137	--	Gamma energy analysis
	Sr-90	10 ⁻⁴ $\mu\text{Ci/gal}$	Chem. Sep. followed by beta counting
	pH	9	Glass electrode - meter
	Na	0.2M	Flame photometry
	Pu	10 ⁵ c/m/gal	Chem. Sep. followed by alpha counting
	Organic	--	Qualitative check
Salt Cake 101-BY 102-BY	Cs-137	500 $\mu\text{Ci/gal}$	Gamma energy analysis
	Sr-90	1 $\mu\text{Ci/gal}$	Chem. Sep. followed by beta counting
	Melting Point	--	
	% Solids		Visual estimate after centrifugation
	Na	15-23M	Flame photometry
	SpG	1.7	

PART VII
SAFETY
CHAPTER XV
GENERAL SAFETY
AND
HAZARDS OTHER THAN RADIATION

By

W. W. Roos

Personnel Protection Operation

PART VII: SAFETY (Cont.)

CHAPTER XVI

RADIATION INTENSITIES AND SHIELDING

By

H. H. Van Tuyl

PACIFIC NORTHWEST LABORATORY

PART VII: SAFETY, Cont.CHAPTER XVI: RADIATION INTENSITIES AND SHIELDINGTABLE OF CONTENTS

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PART VII: SAFETY (Cont.)

CHAPTER XVI

RADIATION INTENSITIES AND SHIELDING

by H. H. Van Tuyl, BNW

A. INTRODUCTION

Large amounts of fission products and other radioactive materials must be handled in Waste Management without undue danger to the operator either from excessive exposure to the ionizing radiations or from taking the materials internally. This chapter deals with protection from external radiation, while Chapter XV deals with internal deposition of radioactive materials.

Fission products emit beta and gamma radiations. Beta radiation consists of high energy electrons. Light shielding is adequate for protection from beta radiation since it travels only a short distance through matter. Gamma radiation consists of high energy electromagnetic radiation. Massive shielding is often required for gamma radiation, especially if its energy is very high.

B. UNITS AND CONVERSION FACTORS1. Basic Constants and Conversion Factors

<u>Name</u>	<u>Symbol</u>	<u>Value</u>
Avogadro's number	$= N_A$	$= 6.02252 \times 10^{23}$ atoms/mole (carbon-12 scale)
Barn	$= b$	$= 10^{-24} \text{ cm}^2$
Curie	$= \text{Ci}$	$= 3.7 \times 10^{10} \text{ dis/s}$ $= 2.22 \times 10^{12} \text{ dis/m}$
Electron Charge	$= e$	$= 1.60210 \times 10^{-19}$ Coulomb $= 4.80298 \times 10^{-10}$ $\text{cm}^{3/2} \text{ g}^{1/2} \text{ s}^{-1} \text{ (e.s.u.)}$
Electron Radium (Classical	$= r_e$	$= 2.81777 \times 10^{-13} \text{ cm}$

Electron Rest Energy	= $mc^2 = 0.511006 \text{ MeV}$
Electron Rest Mass	= $m = 9.1091 \times 10^{-28} \text{ g}$
Energy Absorbed Per Rad	= 100 erg/g
Energy Absorbed Per Roentgen	= $87.7 \text{ erg/g in air}$ = $96.5 \text{ erg/g in water or soft tissue}$
Energy of One Atomic Mass Unit	= 931.478 MeV
Energy of One MeV	= $1.60210 \times 10^{-6} \text{ erg}$
Fine Structure Constant	= 7.29720×10^{-3} = $1/137.0388$
Natural Logarithm of 2	= $\ln 2 = 0.693147$
Planck's constant	= $h = 6.6256 \times 10^{-27} \text{ erg sec.}$
Seconds in One Day	= 8.64×10^4
Seconds in One Year	= 3.1557×10^7
Velocity of Light	= $c = 2.997925 \times 10^{10} \text{ cm/s}$
Watt	= $w = 10^7 \text{ erg/s}$

2. Activity Units

2.1 Curies

Quantities of radioactive material are most commonly expressed in curies. Originally the curie was the disintegration rate of radon-222 in equilibrium with one gram of radium, but it has since been standardized as 3.700×10^{10} disintegrations per second (or 2.22×10^{12} disintegrations per minute). As defined the unit refers to total decay rate of a specific nuclide, regardless of decay mechanism. By extension, it is applied to the partial decay rate by a particular process. Then the unit is qualified as, for example, in alpha curie or beta curie. These are not necessarily the same as total curies. For example, americium-242 decays by beta emission and electron capture. In 100 curies of americium-242 there are approximately 810 beta curies and 190 electron capture curies.

A further extension is made when the term "gamma curie" is used as a measure of the quantity of a radionuclide. Few, if any, nuclides decay with the emission of exactly one gamma photon per disintegration. Some, such as cobalt-60, emit more than one photon per disintegration. Other nuclides, such as tellurium-125m, emit photons in being transformed to the stable or ground state of the same element. Thus, gamma curies do not necessarily relate in a simple manner to beta curies or the total number of decays. Two usages of the term "gamma curie" are common at Hanford. The first is based on the total number of gammas, while the second is based on the number of gammas of a particular energy. For dose rate purposes, only the photons which escape the atom (i.e., those which are not internally converted) should be considered. Beta curies and gamma curies should not be added together to obtain total curies. Gamma curies should be reserved for use when considering gamma detection or gamma dose rates and shielding.

An example of some differences in curie notation can be given for cerium-144 in equilibrium with its short-lived praseodymium-144 daughter. A low energy photon occurs in 13 percent of the cerium-144 disintegrations, and a 2.2 MeV photon occurs in 0.8 percent of the praseodymium-144 disintegrations, and a 2.2 MeV photon occurs in 0.8 percent of the Pr-144 disintegrations. Thus, 1000 curies of Ce-144, 2000 curies of Ce-Pr-144, 1000 beta curies of Ce-144, 2000 beta curies of Ce-Pr-144, 130 gamma curies of Ce-144, and 8 curies of 2.2 MeV gamma from Ce-Pr-144 are all expressions defining about the same amount of radiation. Any of these units is acceptable provided it is adequately defined by the user.

2.2 Watts

The curie refers to the rate of disintegration without regard to energy, while the watt refers to the rate of energy released without regard to the number of atoms or rate of disintegrations. Therefore, the watt is the logical unit to use if heating is being considered. Simple application of basic conversion factors yields the equation

$$\text{watts} = \text{curies} \times \text{energy in MeV} \times 5.93 \times 10^{-3} \quad (1)$$

Consistency must be maintained between the curie and energy values. For example, if total curies are used, then the average energy per disintegration should be used. If gamma curies are used, then the average energy per photon should be used. If curies of a certain energy gamma are used, then the energy of that gamma should be used. For beta particles, the average energy should be used instead of the maximum beta energy. Conversion from maximum to average beta energy will be discussed later.

2.3 Weight

Quantities of fission products are sometimes expressed in grams of total element or in tons of uranium equivalent. These terms are not sufficiently definitive to be used by themselves in calculating dose rates. The data and methods of Chapter II can often be used to convert these indefinite quantities into values for the activity of a specific nuclide. If the weight of a nuclide is given and its half life is known, the activity can be calculated:

$$Ci = \frac{1.3058 \times 10^8 \times \text{weight (grams)}}{\text{half life (days)} \times \text{atomic weight}} \quad (2)$$

$$Ci = \frac{3.5752 \times 10^5 \times \text{weight (grams)}}{\text{half life (years)} \times \text{atomic weight}}$$

3. Dose Rate Units

3.1 Roentgen

The original dose rate unit, the roentgen, is the amount of X or gamma radiation which, in 0.001293 g of air, will produce in air ions carrying one esu of quantity of electricity of either sign. This corresponds to an energy absorption per gram of about 87.7 ergs in air or 96.5 ergs in water. Both of these values have been revised in recent years from lower values that were previously used. The value in water is higher than that in air simply because water has a higher energy absorption coefficient. The quantity of ionizing radiation incident on a detector is often calculated as a flux, ϕ , usually expressed as photons or particles per $\text{cm}^2 \cdot \text{sec}$. Dose rate units, however, are related to the effect of the radiation on its surroundings, rather than numbers of photons or particles. A photon flux can be converted to a dose rate by simple application of conversion factors to yield the equation

$$D = 6.576 \times 10^{-5} \phi E \mu_E / \rho \quad (3)$$

where D is in R/hr, E is in MeV, and μ_E / ρ is the energy absorption coefficient for air in cm^2/g . The energy absorption coefficient for air varies substantially with energy, as shown in Figure XVI-1. An empirical equation, good to about one percent over the range 0.01 to 10 MeV, is as follows:

$$\mu_E / \rho = \frac{5.0518 \times 10^{-6} E^{-3} - 4.0145 \times 10^{-3} + 0.52224 E + 0.074214 E^2}{1 + 12.7525 E + 7.67493 E^2} \quad (4)$$

The flux is not necessarily calculated as such, but may be implicitly included in an equation to yield dose rates. For example,

the flux at a distance r from a point source is simply the source strength in photons per second divided by the surface area of a sphere of radius r . Because of this relationship, the dose rate from a point source is inversely proportional to the square of the distance from the source. At one foot from a point source containing C curies of material, the dose rate is given by the equation

$$D = 208 C E \mu_E / \rho \quad (5)$$

Thus far all expressions for dose rate have involved explicit use of the energy absorption coefficient for air. Between 0.06 and 2 MeV this quantity is constant within about 20 percent. Using a value of $0.0288 \text{ cm}^2/\text{g}$ (or $3.72 \times 10^{-5} \text{ cm}^{-1}$) results in the following simplified point source conversion factor:

$$D = 6 C E \quad (6)$$

This simplified equation is adequate for most dose rate calculations, but more accuracy may be obtained by explicit inclusion of the energy absorption coefficient for air.

FIGURE XVI-1

Energy Absorption Coefficient for Air

3.2 Rep and Rad

The Roentgen applies only to X or gamma radiation, but a similar concept is used to define dose rates from beta radiation. The Rep (Roentgen equivalent physical) is the quantity of ionizing radiation which will cause the absorption in tissue of the same amount of energy that is absorbed by one Roentgen, or about 96.5 ergs per gram. A newer unit, the rad represents 100 ergs absorbed per gram of material. The rad and Rep are often used interchangeably (in spite of the 3.5 percent error), while the Roentgen is reserved specifically for X and gamma radiation.

3.3 Rem

The Rep and rad are proper dose rate units for neutrons as well as for beta or gamma radiation. However, the biological tolerance for neutrons on an energy absorption basis is less than that for beta and gamma radiation. Thus, the Rem (Roentgen equivalent man) has been defined as the quantity of ionizing radiation which causes damage in man equivalent to one Roentgen. For fast neutrons the dose rate in Rem is about ten times the dose rate in Rep.

C. GAMMA AND X RADIATION

1. Nature and Sources

1.1 Gamma Ray

A gamma ray is a high energy electromagnetic photon resulting from nuclear rearrangements. The energy range of greatest interest in waste management is from 0.01 to 3 MeV. Gamma rays occur when an excited nuclear state de-excites to a lower energy state of the same nuclide. The simplest case, typified by 2.6 min. barium-137m, is the de-excitation of a metastable nuclear state to the ground state. In other cases, such as 58-day tellurium-125m, the metastable state may de-excite to an unstable state (i.e., less than one second half life), which then de-excites to a lower state. Thus, two or more photons may be emitted in de-exciting a single excited state of an atom. Although metastable excited states show gamma decay clearly, they are not the most important sources of gamma radiation. Most fission product gammas arise when beta decay populates an unstable excited state of the daughter nuclide. This unstable state will then de-excite by emission of one or more gamma rays until the nucleus reaches the ground state. Gamma rays also occur when an excited nucleus is formed in other ways, such as electron capture, alpha decay, fission, and other nuclear reactions.

1.2 X-Rays

Characteristic X-rays are different from gamma rays only in their mode of formation and range of energies. While gamma rays originate in the nucleus, X-rays originate in the extranuclear electron shells. When a K shell electron is ionized, an electron from a higher shell or from outside the atom will fill the vacancy. This filling is accompanied by the emission of quantized electromagnetic radiation (called K X-rays when the K shell is being filled) equal in energy to the difference between the initial and final energy states of the electron. The K X-ray group consists of several photon energies since electrons in several energy levels are available for filling the K shell. For convenience, the $K\alpha_1$ X-ray energy is often taken to represent all of the K X-ray group. X-rays have energies below 0.15 MeV, while most gamma rays of interest have energies of over 0.5 MeV.

1.3 Bremsstrahlung

Both gamma rays and characteristic X-rays are emitted as monoenergetic radiation, or as a mixture of several monoenergetic radiations. Bremsstrahlung, or continuous X radiation, is emitted with energies varying from zero up to a finite high energy cutoff. This radiation occurs when a charged particle is accelerated or decelerated. The high energy cutoff is the maximum energy available for accelerating the charged particle, or the maximum energy of the charged particle being decelerated. In beta decay the radiation due to acceleration when an electron leaves the nucleus is called inner or internal bremsstrahlung, and the radiation due to deceleration of the electron is called external bremsstrahlung. In electron capture, inner bremsstrahlung is emitted, but there is no external particle to cause external bremsstrahlung. Most of the bremsstrahlung energy is concentrated in the lower energy radiations. From a shielding standpoint, bremsstrahlung is the same as gamma radiation, except that the spectrum is divided into energy groups and the total number of photons within each group is treated as a single gamma with an energy equal to the average energy of the group. Since bremsstrahlung production is intimately related to beta radiation, the calculation of bremsstrahlung spectra is described in the section on beta radiation.

1.4 Internal Conversion

During emission of a gamma or X-ray, internal photoelectric absorption may occur, in which the photon energy is absorbed by an extra-nuclear electron of the same atom. The kinetic energy of the emitted electron is equal to the initial photon energy less the binding energy of the electron. This binding energy is approxi-

mately equal to the energy of the X-ray for the shell from which the electron was ejected. The secondary X-ray, emitted when an electron drops into the site vacated in the conversion process, may also be internally converted. Thus, the radiation observed from gamma or X-ray transitions in a given nuclide may consist partly of monoenergetic electrons and X-rays, and fewer primary photons than expected.

The fraction of X-rays which escape internal conversion is called the fluorescent yield, ω . Values of the K shell fluorescent yield (Table XVI-1) are given approximately by

$$\omega_K = 1 - \frac{4}{F_K} \quad (7)$$

for values of Z above 40. The L shell fluorescent yield is lower than the K shell fluorescent yield on an atomic number basis, but about the same on an X-ray energy basis.

TABLE XVI-1

INTERNAL CONVERSION OF CHARACTERISTIC X-RAYS

<u>Atomic Number</u>	<u>X-Ray Energy, KeV</u>	<u>Fluorescent Yield, ω</u>
10	0.9	0.01
15	2.0	0.07
20	3.7	0.17
25	5.9	0.30
30	8.6	0.49
35	12	0.63
40	16	0.74
45	20	0.81
50	25	0.85
55	31	0.87
60	37	0.89
65	45	0.907
70	52	0.919
75	61	0.931
80	71	0.944
85	81	0.956
90	94	0.976

The extent of internal conversion of gammas is dependent on both the energy and the type of transition (i.e., spin and parity change). Conversion is very common below 0.2 MeV, and usually negligible above 1 MeV. A notable exception is the $0^+ \rightarrow 0^+$ transition, typified by yttrium-90, which can de-excite only by internal conversion. According to most representations of the decay scheme, the de-excitation of the 1.752 MeV excited state formed by yttrium-90 decay looks like a gamma photon, but in reality no photon is emitted since only conversion electrons are allowed. The only photons from strontium-yttrium-90 decay are X-rays, bremsstrahlung, and annihilation radiation.

The extent of internal conversion has been determined experimentally for many nuclides. The result is often given as α which is the ratio of gamma conversion electrons to escaping primary photons for a specific gamma transition. Another common expression is α_K , which is the ratio of K shell conversion electrons to escaping primary photons. In this latter case, the contribution of L and higher shells should also be included in determining the number of gamma photons which leave the nucleus. Care must be exercised to see whether gamma data have already been corrected for internal conversion before applying the appropriate corrections. Many tabulations of data contain part of the gamma data corrected for internal conversion, and part of it uncorrected, with no clear indication of which is which.

A common example of the importance of internal conversion is the decay of cesium-137, which results in gamma transitions in 95 percent of the disintegrations. Ten percent of these transitions are by internal conversion instead of photon emission, so that only 85 percent of the decays give rise to gamma photons outside of the atom.

2. Attenuation Processes

2.1 Attenuation Coefficient

The most important quantity characterizing the attenuation of gamma radiation is the attenuation coefficient, μ . This quantity, which depends on the photon energy E and on the atomic number Z of the medium, may be defined as the probability per unit path length that a photon will undergo an interaction. In a thin layer, dt , within a slab shield there will occur a reduction of the intensity I of the gamma ray beam due to absorption or scattering. The resulting fractional reduction of the beam intensity, $-dI/I$, is proportional to the attenuation coefficient, μ , and to the layer thickness, dt ; i.e.,

$$-dI/I = \mu dt. \quad (8)$$

Integrating this equation with an incident beam intensity I_0 , and constant μ throughout the slab (homogeneous medium) gives

$$I(t) = I_0 e^{-\mu t}. \quad (9)$$

This is the basic equation for gamma or X-ray attenuation, but modifications must be made for geometry considerations and secondary radiations. The attenuation coefficient has a dimension of inverse length, and thus varies as the absorber density. This density dependence is commonly removed by use of the "mass attenuation coefficient," μ/ρ , instead of the linear attenuation coefficient. If μ is in cm^{-1} and ρ is in g/cm^3 , the mass attenuation coefficient will be expressed in the customary units of cm^2/g . Values of mass attenuation coefficients for several elements and mixtures are listed in Table XVI-2. More complete tabulations are given by Hubbell and Berger.

TABLE XVI-2
GAMMA RAY MASS ATTENUATION COEFFICIENTS

Energy, MeV	Mass Attenuation Coefficient, cm^2/g						Concrete*
	Oxygen Z = 8	Iron Z = 26	Tin Z = 50	Lead Z = 82	Uranium Z = 92	Water	
0.01	5.54	179.	145.	137.	239.	4.96	23.2
0.015	1.63	57.7	46.1	114.	85.7	1.49	7.06
0.02	0.747	25.0	20.7	90.	88.8	0.705	3.01
0.03	0.332	7.91	41.9	30.6	51.5	0.335	1.00
0.04	0.230	3.46	19.5	14.3	25.2	0.243	0.495
0.05	0.195	1.80	10.5	7.96	14.5	0.211	0.326
0.06	0.179	1.11	6.48	4.72	9.11	0.196	0.254
0.08	0.162	0.554	2.95	2.12	4.42	0.178	0.193
0.1	0.151	0.347	1.63	5.56	2.51	0.167	0.167
0.15	0.134	0.185	0.595	1.93	2.56	0.149	0.139
0.2	0.123	0.139	0.314	0.950	1.21	0.136	0.125
0.3	0.107	0.106	0.157	0.381	0.485	0.118	0.106
0.4	0.0953	0.0921	0.111	0.220	0.273	0.106	0.0961
0.5	0.0870	0.0830	0.0907	0.153	0.185	0.0966	0.0877
0.6	0.0806	0.0763	0.0790	0.119	0.141	0.0896	0.0811
0.8	0.0708	0.0665	0.0653	0.0853	0.0969	0.0786	0.0712
1	0.0636	0.0596	0.0572	0.0689	0.0760	0.0706	0.0640
1.5	0.0518	0.0486	0.0459	0.0510	0.0543	0.0575	0.0521
2	0.0445	0.0425	0.0407	0.0451	0.0475	0.0493	0.0449
3	0.0359	0.0361	0.0367	0.0417	0.0436	0.0396	0.0366
4	0.0311	0.0332	0.0357	0.0416	0.0435	0.0340	0.0319
5	0.0279	0.0316	0.0357	0.0424	0.0442	0.0302	0.0288
6	0.0255	0.0307	0.0360	0.0435	0.0452	0.0276	0.0268
8	0.0226	0.0299	0.0371	0.0460	0.0479	0.0242	0.0242
10	0.0208	0.0298	0.0387	0.0491	0.0512	0.0220	0.0227

* Concrete: 1% H, 0.1% C, 52.9% O, 1.6% Na, 0.2% Mg, 3.4% Al, 33.7% Si, 1.3% K, 4.4% Ca, 1.4% Fe by weight.

For shielding purposes, the most important components of the attenuation coefficient are photoelectric absorption, Compton scattering, and electron-positron pair production. Typical values of these components are shown in Figure XVI-2, along with the total attenuation coefficient.

FIGURE XVI-2

Components of the Mass Absorption Coefficient for Lead

2.2 Photoelectric Absorption

In photoelectric absorption, also called the atomic photoeffect, a photon disappears and an electron is ejected from an atom. The electron carries away all the energy of the absorbed photon, minus the energy with which the electron was bound to the atom. The K-shell electrons, which are the most tightly bound, are the most important for this effect. However, if the photon energy drops below the binding energy of a given shell, an electron from that shell cannot be ejected. Hence, a plot of the absorption coefficient versus photon energy exhibits characteristic "absorption edges." Absorption coefficient for common shield materials are shown in Figures XVI-3 and XVI-4. As a crude approximation, the photoelectric attenuation coefficient varies as the 3.5 power of the atomic number, and inversely as the cube of the photon energy. The contribution due to L and higher shells increases with atomic number from zero for hydrogen to about 25 percent of the total photoelectric attenuation coefficient for uranium.

2.3 Compton Scattering

In Compton scattering, a photon collides with an electron, loses some of its energy, and is deflected from its original direction of travel. The relationship between scattering angle and energy loss is given by

$$E' = \frac{E}{1 + (E/mc^2)(1 - \cos \theta)} \quad (10)$$

where E and E' are the energies of the photon before and after the scattering, and θ is the photon deflection angle. Klein and Nishina developed an equation for the scattering probability as a function of scattering angle. Integration of this equation over all angles of scattering gives the total scattering probability, which is the Compton attenuation coefficient. Minor corrections to the Klein-Nishina theory are necessary because of electron binding effects, emission of an additional scattered photon, and certain radiation corrections. However, the Klein-Nishina equation closely approximates the actual Compton scattering probability.

Compton scattering varies with the charge to mass ration, Z/A, and is thus roughly independent of atomic number. Hydrogen is a notable exception because of its unusually high charge to mass ratio.

2.4 Pair Production

In electron-positron pair production, a photon disappears in the field of a charged particle, and an electron-positron pair appears. Pair production requires a photon of at least 1.022 MeV ($2mc^2$) for production in the field of the nucleus, and 2.044 MeV ($4mc^2$) for

FIGURE XVI-3
Mass Absorption Coefficients for Common Shield Materials
(Lead, Iron, Water)

FIGURE XVI-4

Mass Absorption Coefficients for Common Shield Materials
(Lead Glass, Magnetite Concrete, Normal Concrete)

production in the field of an electron. Pair production occurs chiefly in the field of the nucleus, especially for high atomic number materials. The attenuation coefficient due to pair production varies approximately as the square of the atomic number.

2.5 Other Processes

In Rayleigh scattering, photons are scattered by bound atomic electrons so that the atom is neither ionized nor excited. This effect is usually disregarded in shielding calculations since little energy is lost, and scattering is either at a small angle or a small fraction of the total attenuation probability.

At higher energies (usually above 5 MeV) a photonuclear effect occurs which is similar to the photoelectric effect, but a nucleon (usually a neutron) is emitted instead of an electron. The photonuclear threshold is sufficiently high to make this process of little or no concern in Waste Management.

3. Buildup of Secondary Radiation

Each attenuation process results in some secondary photons. The photoelectric effect produces X-rays, Compton scattering produces the scattered photons, and pair production results in the 0.511 MeV radiations due to the eventual annihilation of the positron. These secondary radiations result in a higher dose rate than predicted according to the simple exponential law. This increase is usually included by use of a "buildup factor," which is the ratio of the actual dose rate to the dose rate expected in accordance with the simple exponential law. (This definition actually applies only to a dose rate buildup factor, which is the one most commonly used in shielding calculations.) The buildup factor is dependent on the gamma energy, shield material, and shield and source geometry.

The calculation of buildup factors, even for simple situations, is a formidable task since the source and shield geometries, probable energy distribution, and direction of gamma rays must be considered, and the gammas may be scattered several times before finally being removed by photoelectric capture. Factors for a few simple idealized cases, and a few different elements have been calculated by different workers, but the data currently accepted as best were calculated by Nuclear Development associates using a National Bureau of Standards, SEAC computer. Although the project required several man-years of effort, and a large amount of machine time, the results of interest to most shielding problems are quire meager in number. Some of these data, dose buildup factors for a point isotropic source in an infinite shielding medium, are presented in Table XVI-3.

TABLE XVI-3

DOSE BUILDUP FACTORS, POINT ISOTROPIC SOURCE

<u>Water</u>					
<u>μt</u>	<u>0.5 MeV</u>	<u>1.0 MeV</u>	<u>2.0 MeV</u>	<u>3.0 MeV</u>	<u>4.0 MeV</u>
1	2.52	2.13	1.83	1.69	1.58
2	5.14	3.71	2.77	2.42	2.17
4	14.3	7.68	4.88	3.91	3.34
7	38.8	16.2	8.46	6.23	5.13
10	77.6	27.1	12.4	8.63	6.94
15	178	50.4	19.5	12.8	9.97
20	334	82.2	27.7	17.0	12.9
<u>Aluminum</u>					
1	2.37	2.02	1.75	1.64	1.53
2	4.24	3.31	2.61	2.32	2.08
4	9.47	6.57	4.62	3.78	3.22
7	21.5	13.1	8.05	6.14	5.01
10	38.9	21.2	11.9	8.65	6.88
15	80.8	37.9	18.7	13.0	10.1
20	141	58.5	26.3	17.7	13.4
<u>Iron</u>					
1	1.98	1.87	1.76	1.55	1.45
2	3.09	2.89	2.43	2.15	1.94
4	5.98	5.39	4.13	3.51	3.03
7	11.7	10.2	7.25	5.85	4.91
10	19.2	16.2	10.9	8.51	7.11
15	35.4	28.3	17.6	13.5	11.2
20	55.6	42.7	25.1	19.1	16.0
<u>Tin</u>					
1	1.56	1.64	1.57	1.46	1.38
2	2.08	2.30	2.17	1.96	1.81
4	3.09	3.74	3.53	3.13	2.82
7	4.57	6.17	5.87	5.28	4.82
10	6.04	8.85	8.53	7.91	7.41
15	8.64	13.7	13.6	13.3	13.2
20	----	18.8	19.3	20.1	21.2

TABLE XVI-3 (Continued)

<u>Tungsten</u>					
<u>μt</u>	<u>0.5 MeV</u>	<u>1.0 MeV</u>	<u>2.0 MeV</u>	<u>3.0 MeV</u>	<u>4.0 MeV</u>
1	1.28	1.44	1.42	1.36	1.29
2	1.50	1.83	1.85	1.74	1.62
4	1.84	2.57	2.72	2.59	2.41
7	2.24	3.62	4.09	4.00	4.03
10	2.61	4.64	5.27	5.92	6.27
15	3.12	6.25	8.07	9.66	12.0
20	----	(7.35)	(10.6)	14.1	20.9
<u>Lead</u>					
1	1.24	1.37	1.39	1.34	1.27
2	1.42	1.69	1.76	1.68	1.56
4	1.69	2.26	2.51	2.43	2.25
7	2.00	3.02	3.66	3.75	3.61
10	2.27	3.74	4.84	5.30	5.44
15	2.65	4.81	6.87	8.44	9.80
20	(2.73)	5.86	9.00	12.3	16.3
<u>Uranium</u>					
1	1.17	1.31	1.33	1.29	1.24
2	1.30	1.56	1.64	1.58	1.50
4	1.48	1.98	2.23	2.21	2.09
7	1.67	2.50	3.09	3.27	3.21
10	1.85	2.97	3.95	4.51	4.66
15	2.08	3.67	5.36	6.97	8.01
20	----	----	(6.48)	9.88	12.7

The first problem with these data is application to other shielding materials. This can be accomplished adequately by using graphs of B versus Z at the various energies and μt values for which data are available. Extension of the data to other μt and energy values is possible in various ways. One convenient way is to plot B versus μt at different energies. From this the dose buildup factor can be interpolated for any energy and μt value for the absorber chosen.

Another method of obtaining the buildup factors at different values of μt and E was developed by Taylor, who represented buildup factors as a sum of two exponentials. A modification of his method gives the equation

$$B = Ae^{\alpha\mu t} - (A-1)e^{(\alpha-0.10)\mu t} \quad (11)$$

Values of the constants in this equation are chosen to fit the data of Goldstein and Wilkins. After these constants have been determined

for a given absorber, energy, and range of μt values, the calculation of buildup factors is simplified for these conditions since no graphical interpolation is required. When B is expressed in this form it can be applied to an exponential attenuation equation by simply modifying the exponent. Values of these constants for water, concrete, iron and lead are shown in Figures XVI-5 to XVI-8 and in Table XVI-4.

TABLE XVI-4
CONSTANTS FOR EXPONENTIAL REPRESENTATION
OF BUILDUP FACTORS

<u>Energy, MeV</u>	<u>α</u>	<u>A</u>	<u>Max. Error, %</u>
<u>Water</u>			
0.255	0.205	23.5	29
0.5	0.160	18.7	25
1.0	0.105	12.7	11.4
2.0	0.063	9.35	4.9
3.0	0.046	7.84	2.3
4.0	0.040	6.65	1.7
<u>Iron</u>			
0.5	0.092	10.7	7.5
1.0	0.0835	9.7	7.4
2.0	0.067	7.8	5.8
3.0	0.063	6.33	3.7
4.0	0.064	5.15	3.4
<u>Lead</u>			
0.5	0	3.1	3.3
1.0	0.0175	4.5	3.3
2.0	0.0425	4.35	1.4
3.0	0.0675	3.6	2.1
4.0	0.095	2.7	1.5
<u>Normal Concrete</u>			
0.5	0.125	14.8	12.9
1.0	0.092	11.6	9.4
2.0	0.064	8.8	6.3
3.0	0.052	7.32	3.3
4.0	0.046	6.16	2.2

FIGURE XVI-5
Constants for Exponential Representation of Build-Up
Factors for Water

FIGURE XVI-6
Constants for Exponential Representation of Build-Up
Factors for Normal Concrete

FIGURE XVI-7

Constants for Exponential Representation of Build-Up Factors for Iron

FIGURE XVI-8

Constants for Exponential Representation of Build-Up Factors for Lead

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The range of values covered by Nuclear Development Associates is adequate for most normal shielding problems, but several situations occur in which data outside this range are required. For example, shielding of bremsstrahlung from Pm-147 and shielding of gammas and X-rays from transuranic elements requires buildup factors for lower energy radiations. The calculations have, therefore, been extended by a modified "straight ahead" approximation that is much simpler (and less accurate) than the "moments" method used by Nuclear Development Associates. The two methods agreed within 30 percent over the range covered by the moments method. Results for iron and lead are shown in Figures XVI-9 and XVI-10.

FIGURE XVI-9

Build-Up Factors for Iron

FIGURE XVI-10
Build-Up Factors for Lead

After a maximum near 0.5 MeV the iron values decrease with decreasing energy because of the increasing importance of photo-electric absorption. A similar effect is seen with lead, but the maximum occurs at a higher energy. Another effect is seen with lead at energies slightly above the 88 keV X-ray absorption edge. The X-ray buildup factor becomes important, approaching the exponential of the difference in mean free paths for the primary photon and the X-ray. Below the X-ray absorption edge the buildup factor is again low, and decreases with decreasing energy. Selected low energy buildup factor data are shown in Table XVI-5.

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TABLE XVI-5

COMPTON BUILDUP FACTORS AT LOW ENERGIES

μt	0.01 MeV	0.02 MeV	0.05 MeV	0.1 MeV	0.2 MeV
<u>Aluminum</u>					
1	1.007	1.058	2.06	2.82	2.71
2	1.014	1.113	3.19	5.64	5.35
4	1.027	1.212	4.87	12.9	13.2
7	1.043	1.34	9.39	40.6	45.3
10	1.058	1.45	14.3	91.0	117.
15	1.078	1.59	24.0	245.	345.
20	1.095	1.72	34.8	457.	718.
<u>Iron</u>					
1	1.001	1.007	1.086	1.35	1.71
2	1.002	1.013	1.16	1.67	2.63
4	1.004	1.024	1.27	2.28	4.88
7	1.006	1.037	1.39	3.07	9.25
10	1.008	1.047	1.48	3.83	14.8
15	1.011	1.060	1.60	5.04	24.2
20	1.013	1.070	1.70	6.25	37.3
<u>Tin</u>					
1	1.002	1.009	1.013	1.054	1.20
2	1.003	1.017	1.023	1.093	1.35
4	1.006	1.031	1.038	1.15	1.58
7	1.009	1.048	1.054	1.20	1.87
10	1.012	1.062	1.065	1.25	2.11
15	1.016	1.080	1.078	1.30	2.46
20	1.020	1.094	1.089	1.35	2.76
<u>Tungsten</u>					
1	1.001	1.003	1.030	1.019	1.073
2	1.001	1.006	1.054	1.033	1.121
4	1.002	1.012	1.090	1.052	1.19
7	1.004	1.018	1.13	1.073	1.26
10	1.005	1.023	1.16	1.090	1.32
15	1.006	1.030	1.19	1.12	1.39
20	1.008	1.035	1.22	1.15	1.45
<u>Lead</u>					
1	1.000	1.002	1.022	1.018	1.055
2	1.001	1.005	1.039	1.033	1.091
4	1.002	1.009	1.066	1.062	1.14
7	1.003	1.013	1.093	1.10	1.20
10	1.004	1.017	1.11	1.14	1.23
15	1.005	1.022	1.14	1.22	1.29
20	1.006	1.026	1.16	1.30	1.33
<u>Uranium</u>					
1	1.000	1.002	1.016	1.058	1.042
2	1.001	1.004	1.029	1.10	1.069
4	1.001	1.006	1.048	1.16	1.11
7	1.002	1.010	1.069	1.23	1.15
10	1.003	1.013	1.083	1.28	1.18
15	1.004	1.017	1.10	1.34	1.23
20	1.004	1.020	1.12	1.39	1.28

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Application of buildup factors to homogeneous shields composed of different elements involves assignment of an effective atomic number to the shield. This is accomplished by determining the value of μ for the mixture, and comparing the shape of the μ versus E curve with similar curves for the elements. The atomic number of the element giving the best fit is assigned as the effective atomic number of the mixture. Buildup factors for this atomic number are then used for the composite shield.

For laminated shields where the lighter shield is on the outside, the buildup factor for the lighter shield is usually used, even though this may overestimate shielding requirements. Where the heavier shield is on the outside and μt is greater than one, the buildup factor for the heavier material only is used. For other cases the buildup factors may be weighted in accordance with the μt values in each material, or the shield may be treated as described for homogeneous shields.

The buildup factors were calculated for a point source in an infinite shield, but the error to be expected in applying these to a finite shield is usually small, especially for thick shields, high atomic numbers, and a shield perpendicular to the line between the source and detector. For angles of penetration up to about 30° the thickness of the shield is usually taken as the actual thickness traversed by straight line radiation (up to about 15 percent more shielding than the slab thickness). At greater angles either the thickness of shielding or buildup factors should be adjusted to correct for the lowered effectiveness. In most cases it is adequate to assume no greater than a 30° angle of penetration, even though the actual angle exceeds this value.

4. Geometry Effects

4.1 Symbols.

The following symbols will be used in the discussion of geometry:

- B Integrated buildup factor
- C Total gamma curies of specified energy in entire source
- D Dose rate at detector, R/hr
- D_0 Unshielded dose rate at one foot from point source (Equation 5, R/hr)
- E Photon energy in MeV
- a Distance from detector to nearest point of source, feet

- b μt value for shield, or sum of μt values for layered shield
- b' $\mu_s r$ value for source (used only for three dimensional sources
such as cylinders and spheres)
- h Height of cylinder, feet
- r Radius of disc, cylinder, or sphere, feet
- s Length of line source, feet
- t Perpendicular thickness of slab shield, feet
- μ Absorption coefficient for external shield, feet⁻¹
- μ Absorption coefficient for source, feet⁻¹

$$\exp(b) = e^b \quad (\text{exponential of } b)$$

$$E_n(b) = b^{(n-1)} \int_b^{\infty} \frac{e^{-x}}{x^n} dx \quad (\text{exponential integral})$$

$$F(\theta, b) = \int_0^{\theta} e^{-b \sec \psi} d\psi \quad (\text{secant integral})$$

Values of exponential and secant integrals have been either tabulated or plotted in several books on radiation shielding. A few values are included in Figures XVI-11 and XVI-12. For large values of b , and $n \geq 1$, $E_n(b)$ may be evaluated by

$$\frac{e^{-b}}{b+n} < E_n(b) \leq \frac{e^{-b}}{b+n-1}$$

4.2 Point Sources

All of the previous discussion has assumed a point source of radiation. Even though this condition is never actually met, it is by far the most used and the easiest to calculate. Other simple finite geometries are the line, plane disc, cylinder, and sphere. Calculations for some of these geometries are possible by integration of formulas for point sources to yield relatively simple analytical expressions. Most other geometries yield expressions which are best evaluated by computers rather than manual methods. Solid figures, such as the cylinder and sphere, involve consideration of shielding within the source (self-shielding) as well as the effects of distance on dose rate. The most important simple geometries are discussed below, but more extensive compilations of both exact and approximate methods for other geometries have been published.

FIGURE XVI-11
Exponential Integral Functions

FIGURE XVI-12
Secant Integral Functions

The elementary formula for dose rate from a point source of radiation is the basis for all of the other formulas in this section:

$$D = \frac{B D_o}{a^2} e^{-b} \quad (12)$$

The buildup factor, B, given by Equation 11 may be substituted to obtain the following equation:

$$D = \frac{D_o}{a^2} [A e^{-b(1-\alpha)} - (A-1) e^{-b(1.1-\alpha)}] \quad (13)$$

This equation is particularly valuable when evaluating buildup for sources other than point sources. For a point source the buildup factor is evaluated for a constant shield thickness, but for other sources the shield thickness varies as different points of the source are considered. This variation of buildup factor can be included by using a simple point attenuation kernel for integration, and evaluating the result by first substituting $b(1-\alpha)$ for b , and then substituting $b(1.1-\alpha)$ for b . A combination of the two results, using the appropriate constant multiplier for each, will properly account for buildup, corrected for variation in shield thickness with location in the source.

4.3 Line Sources

The line source approximates liquids in tubing or pipes, ion exchange, or solvent extraction columns, or in general any cylinder where the radius is small compared to the distance between the source and detector. If self-shielding is important, the line source approximation should not be used.

Three cases can be profitably distinguished with the line source and slab shield: I. A line parallel to the shield; II. A line perpendicular to the shield but not passing through the detector; and III. A line perpendicular to the shield and passing through the detector. In the first case, a simplification can be made by considering only a line beginning at the perpendicular from the detector to the line of the source, and extending in one direction. Other arrangements with this can be handled by addition or subtraction of the appropriate line sources.

$$\text{Case I.} \quad D = \frac{B D_o}{as} F(\tan^{-1} \frac{s}{a}, b) \quad (14)$$

$$\text{Case II.} \quad D = \frac{B D_o}{sc} [F(\tan^{-1} \frac{c}{d}, b) - F(\tan^{-1} \frac{c}{d+s}, b)] \quad (15)$$

where c is the perpendicular distance from the detector to the line of the source, and

$$d = \sqrt{a^2 - c^2}$$

$$\text{Case III.} \quad D = \frac{B D_o e^{-b}}{a(a+s)} \quad (16)$$

It is possible to approximate the radiation from a line source by considering the slab shield thickness to be constant. For Case I, this gives

$$D = \frac{B D_o}{as} (e^{-b}) (\tan^{-1} \frac{s}{a}). \quad (17)$$

This approximation gives a dose rate about a factor of $(1 + 0.05b)$ too high at an angle of 30° for b up to 20, but the error is smaller at smaller angles. For sources which end a distance c from the perpendicular from the source to the slab, b should be replaced by

$\frac{ba}{\sqrt{a^2 - c^2}}$ to compensate for the increased thickness of shielding. For closer approximations, the line source may be divided into a series of line sources, each of which subtends a rather small angle at the detector.

For Case II, the constant slab thickness approximation gives

$$D = \frac{B D_o}{sc} (e^{-b}) (\tan^{-1} \frac{c}{d} - \tan^{-1} \frac{c}{d+s}) \quad (18)$$

where c and d are defined for this case in the solution given above, and b may be replaced by $\frac{ab}{d}$.

4.4 Disc Sources

The disc source approximates contamination on flat surfaces, or cylinders of small height where self-shielding in the source is negligible. For a disc source observed on the axis of the disc (the line perpendicular to the disc and passing through the center of the disc), and with the slab parallel to the disc, a simple analytical expression is possible.

$$D = \frac{2 B D_o}{r^2} [E_1(b) - E_1(\frac{b}{a} \sqrt{a^2 + r^2})] \quad (19)$$

When the shielding is considered to be constant (for example, at small angles or at angles over 30°),

$$D = \frac{B D_o}{r^2} e^{-b} \log(\frac{a^2 + r^2}{a^2}) \quad (20)$$

This approximation yields an error of about a factor of $(1 + 0.1b)$ for an angle of 30° .

When the detector is not on the axis of the disc, or when the shield is not parallel to the disc source, evaluation is much more difficult.

4.5 Cylindrical Sources

Cylindrical sources are probably the most common actual sources encountered in shielding calculations. Here not only the distance from volume elements of the source to the detector and the actual thickness of slab shielding, but also the shielding of the source itself should be considered. Since the limits of the triple integration are not simple expressions, exact solutions are not possible. An exact solution is possible for a truncated cone viewed on the axis of the cone, and this solution can be used to give upper and lower limits for the simple case of a cylinder with the axis perpendicular to the shield. The dose rate from a cylinder is less than that from a truncated cone with the top of the cone equal to the base of the cylinder,

$$D < \frac{2B D_0}{r h b'} [E_2(b) - \cos \theta E_2(b \sec \theta) - E_2(k) + \cos \theta E_2(k \sec \theta)] \quad (21)$$

$$\text{where } \tan \theta = \frac{r}{a} \text{ and } k = \frac{1}{r}(rb + h b') = b + \frac{h}{r} b'$$

The dose rate is more than that from a truncated cone with the base equal to the base of the cylinder,

$$D > \frac{2 B D_0}{r h b'} [E_2(b) - \cos \theta E_2(b \sec \theta) - E_2(k) + \cos \theta E_2(k \sec \theta)] \quad (22)$$

$$\text{where } \tan \theta = \frac{r}{a+h} \text{ and } k = \frac{1}{r}(rb + h b').$$

For other orientations of a cylinder on end, or for the cylinder axis parallel to the shield, the calculations are even more complicated.

4.6 Spherical Sources

The first two integrations for a spherical source and slab shield can be readily performed, but the final integration is more difficult:

$$D = \frac{1.5 B D_0}{r^2 b'} \int_0^\theta [1 - \exp(-2b' \sqrt{1 - \csc^2 \theta \sin^2 \psi})] e^{-b \sec \psi} \sin \psi d\psi \quad (23)$$

$$\text{where } \sin \theta = \frac{r}{a+r}.$$

This final integration can be performed graphically or numerically. Another possibility is to replace part of the expression by a simple approximation. Since the first exponent varies from $-2b'$ to 0, using a constant value of $-2b'$ will give a conservative estimate of the dose rate. Using this approximation and integrating gives:

$$D < \frac{1.5 B D_0}{r^2 b'} (1 - e^{-2b'}) [E_2(b) - \cos \theta E_2(b \sec \theta)] \quad (24)$$

Another approximation, especially useful and accurate for small values of b' , involves integration of the first exponential by approximating a term of $\sec \psi e^{-b \sec \psi}$ as e^{-b} . This approximation is conservative for values of b above 1 for θ up to 30° , and for even smaller values of b at smaller angles. This integration yields:

$$D = \frac{3 B D_0 e^{-b}}{8(b')^3 (a + r)^2} [2(b')^2 - 1 + (2b' + 1) e^{-2b'}] \quad (25)$$

A more convenient approximation is obtained by regarding $\sec \psi$ as 1, and the entire first exponential as 0. In the integrated equation, the function $(1 - \cos \theta)$ may be approximated adequately as $1/2 \sin^2 \theta$ for small angles. Using all of these approximations gives:

$$D = \frac{3 B D_0 e^{-b}}{4 (a + r)^2 b'} \quad (26)$$

This differs from the formula for a point source at the center of the sphere only by a factor of $0.75/b'$ and from equation 25 by the b' term. It differs from equation 25 by only 30% at $b' = 1$, 13% at $b' = 2$, and less at higher values of b' . It agrees with equation 24 at $b = 20$, b' above 1.5 within 25% for $\theta = 10^\circ$, a factor of 2 for $\theta = 20^\circ$, and a factor of 3 for $\theta = 30^\circ$. The agreement is much better at smaller values of b (e.g., 35% at $b = 5$, $\theta = 30^\circ$). Therefore, although this formula is extremely simple, it is quite accurate for a wide range of shielding conditions.

5. Approximate Methods For Calculating Dose Rates and Shield Thickness

Preliminary evaluation does not require detailed shielding calculations, but adequate accuracy is provided by techniques for obtaining quick, order-of-magnitude estimates of dose rates and shield thicknesses. These methods are based on point source geometry with buildup factors included in the calculations.

5.1 Unshielded Dose Rate

The unshielded dose rate may be obtained from Equation 12, using either Equation 5 or 6 to evaluate D_0 depending on the accuracy desired. A nomogram for obtaining unshielded dose rates by Equations 5 and 12 is shown in Figure XVI-13. A straight edge can be laid across columns A and B at the known values of source strength (gamma curies) and gamma ray energy, respectively, and the intersection point on reference column C determined. By laying the straight edge between this reference point and column D at the known distance to the detector, the intersection point on column E determines the unshielded dose rate at the detector in mR/hr. If the source strength falls outside the range of the scale in column A, it may be brought into range by dividing by some power of 10, represented by 10^N on the nomogram. The resultant dose rate obtained from the nomogram must then be multiplied by the same power of 10 to yield the correct dose rate.

5.2 Shielded Dose Rate

The attenuation of the dose rate in passing through a shield of thickness t is given by the attenuation factor, $Be^{-\mu t}$. Values of attenuation factors for point sources and slab shields with several common shielding materials are shown in Figures XVI-14 to XVI-19. This attenuation factor must then be multiplied by the dose rate at the detector calculated without any intervening shielding.

5.3 Shield Thickness

If an estimate of required shield thickness is desired, the desired dose rate after shielding is divided by the dose rate from Figure XVI-13 to determine the required attenuation factor. An estimate of shielding requirements can then be obtained from the graphs in Figures XVI-14 to XVI-19 by reading the shield thickness corresponding to the required attenuation factor and gamma energy level. Conversely, if the shield thickness is known, the figures can be used to determine the attenuation factor of the shield. By multiplying the attenuation factor by the unshielded dose rate obtained from Figure XVI-13, an estimate of shielded dose rate at a detector can be obtained.

These figures have been used to calculate dose rates as a function of shield thickness for several fission products of interest and lead shields, as shown in Figures XVI-20 and XVI-21. The dose rate obtained from these curves must be multiplied by the source strength in kilocuries and divided by the square of the distance in feet between source and detector.

FIGURE XVI-13
Unshielded Dose Rate From Point Source

FIGURE XVI-14

Attenuation Factors for Water, Density 1.0

FIGURE XVI-15

Attenuation Factors for Normal Concrete, Density 2.3

FIGURE XVI-16

Attenuation Factors for Magnetite Concrete, Density 3.5

FIGURE XVI-17

Attenuation Factors for Iron, Density 7.85

FIGURE XVI-18

Attenuation Factors for Lead, Density 11.2

FIGURE XVI-19

Attenuation Factors for Lead Glass, Density 6.2

FIGURE XVI-20
Dose Rate from One Kilocurie Point Sources
Shielded with Lead (Sr-Y-90, Cs-Ba-137, Ce-Pr-144)

FIGURE XVI-21
Dose Rate from One Kilocurie Point Sources
Shielded With Lead (Zr-Nb-95, Ru-103, Ru-Rh-106, Ba-La-140)

6. Scattered Radiation and Sky Shine

Gamma radiation travels in a straight line, but interaction with a scatterer causes secondary radiation to be emitted in all directions. The effect of scattered radiation along the path of the primary gamma causes buildup, as previously discussed. Radiation from Compton scattering at greater angles has lower energies and lower scattering probabilities, but is still present. Thus, radiation which impinges on a shield at a steep angle of incidence can "turn the corner" to proceed through the shield normal to its surface as scattered radiation. Therefore, as previously mentioned, shield thicknesses should be considered as no greater than 15 per cent more than the perpendicular thickness of the shield.

Radiation can also scatter or reflect from walls or even from air to go around shadow shields or labyrinths designed to shield out direct line radiation. As a crude approximation, each 90° turn that the radiation makes will be accompanied by a tenfold decrease in dose rate. The increased path length for the scattered radiation will also improve attenuation by the inverse square law. An accurate treatment of scattered radiation is much too complex for inclusion in this manual, but may be obtained from several of the sources listed in the bibliography.

7. ISOSHL D Computer Code

Most shielding calculations are either laborious or approximate. Hand calculations are prohibitively time-consuming, except for the rather simple geometries described previously, and repetitive calculations for even these simple geometries is time-consuming. Computer program ISOSHL D was developed to fill the need for a convenient semirigorous calculational method to handle the majority of these problems.

The program was designed to include most of the basic data required for these calculations. The data, contained in libraries chained to the code, include attenuation coefficients, gamma ray decay energies and probabilities, maximum beta energies and probabilities, fission product data, and buildup factor data. For most problems the user need only supply 1) the geometry and material composition of the source and 2) the geometry and materials of the shield. Optional modes of data entry are available for solving special problems.

The solution of radioisotope shielding problems often requires consideration of the amount and distribution of bremsstrahlung produced by the slowing down and stopping of beta particles. Indeed, problems are often encountered in which a mixed emission of beta and gamma rays must be treated. Therefore, a revised version

of the code (ISOSHL-D-II) has the added capability of solving shielding problems for which bremsstrahlung may contribute all or part of the penetrating radiation. Bremsstrahlung is produced only in the source region; i.e., the beta particles are completely stopped by the material in that source region.

The point kernel integration technique is used to perform the attenuation calculation so that the dose at the exposure point is the contribution from a large number of individual point sources. A numerical integration is carried out over the source volume to obtain the total dose.

The code obtains solutions for any combination of the variables listed below:

Shield and Source Geometry

1. Point
2. Line
3. Sphere
4. Sphere with slab shields
5. Truncated cone
6. Disc
7. Cylinder
8. Cylinder with slab shields
9. Cylinder end
10. Rectangular solid
11. Infinite slab and plane
12. Exponential source distribution where applicable

Isotope Selection from Calculated Fission Products

1. Noble gases
2. Halogens
3. Volatile solids
4. All except the above 3
5. All fission products
6. Individual isotopes by individual specification

Source Type

1. Calculated source strength from known fuel irradiation exposure (see Note).
2. Specify curies of isotopes in library--both fission products and activation products.
3. Source strength in photons of specific energies for source volume.

Note: If Source Type 1 is specified, the irradiation history of the fuel must be described by supplying:

1. Initial conversion ratio
2. Fuel exposure time
3. Fast fission in U-238 per thermal fission
4. Reactor power history
5. Cooling time
6. Proper choice of above variables also approximates fuel irradiation in a fast reactor.

Shield Region Geometry and Materials

1. Number of regions - up to five
2. Material in each region - choice of 20 materials in library
3. Material density in each region - five materials allowed in a region
4. Region and material for which buildup is most important.

D. BETA RADIATION

1. Nature and Sources

Most of the primary fission products are unstable with respect to beta decay since they contain an excess of neutrons. A high energy electron called a beta particle is emitted from the nucleus, thus converting a neutron to a proton, and bringing the nuclide closer to stability. Simultaneously with the beta particle, a neutrino is emitted. The sum of the energies of the beta particle and neutrino is equal to the total decay energy available for that particular beta transition. The amount of energy given to either particle may vary from zero to the maximum available energy, thus yielding beta particles with a continuous spectrum of energy values. The neutrino can be neglected since it is extremely penetrating and escapes without interacting with the surroundings. It is of no practical concern except for its role in causing the continuum of beta particle energies. The beta particle, however, is important because of biological, radiolytic, and heating effects.

A few nuclides in spent reactor fuels can decay by converting a proton to a neutron. This can be accomplished by positron emission, which is very similar to beta decay except for the charge on the electron. After leaving the nucleus, the positron is annihilated by an electron to yield two photons of 0.511 MeV gamma radiation. The maximum kinetic energy of the positron is 1.022 MeV less than the decay energy available. If the maximum decay energy available is less than 1.022 MeV, positron emission is impossible, but a proton can capture an extranuclear electron and thus be converted to a neutron. Usually a K shell electron is captured, giving this process the name of electron capture or K capture. It is unlikely that either positron emission or electron capture will be of any real concern in Waste Management.

1.1 Beta Spectra

Two types of beta transitions based on spin and parity changes are of greatest interest in the study of fission product beta spectra. The "allowed" transitions involve a spin change of 0 or 1, and no parity change (0 or 1, no); while the "unique first forbidden" transitions involve a spin change of 2 and a change of parity (2, yes). Spectra for transitions of these types can be calculated, but spectra for most other transitions cannot be simply and accurately predicted as yet.

The shape of the energy spectrum of beta particles is dependent on several factors, especially the decay energy, atomic number of the nucleus, and transition type. Typical beta spectra calculated for $Z = 50$ are shown in Figure XVI-22. The shape of the energy spectrum of beta particles is used to determine the average energy of beta particles for use in heat calculations, and to determine the energy distribution of bremsstrahlung.

The relative number of betas, $P(E)$, of kinetic energy E from and emitter of atomic number Z and maximum kinetic energy E_0 is given for an allowed transition by:

$$P(E) = K p W F(Z, W) (E_0 - E)^2 \quad (27)$$

where K is an arbitrary constant, W is the beta total energy in rest mass units, p is the beta momentum, $W^2 - 1$, and $F(Z, W)$ is the Fermi differential function. Values of the Fermi function have been tabulated by the National Bureau of Standards as $p^2 F(Z, W)$ where their Z is for the product nucleus. A screening correction such as the one calculated by Reitz should be applied to the NBS values. Since the correction usually is quite small, only an approximate evaluation of it is required.

Distributions for unique first forbidden transitions are given by:

$$P(E) = K p W F(Z, W) (E_0 - E)^2 p^2 + (W_0 - W)^2 \quad (28)$$

The average beta energy is approximately one-third of the maximum beta energy, but it varies from about 25 to 50 percent of the maximum energy, depending on the atomic number, energy, and transition type. For some purposes the approximate average energy is adequate, but more accurate values may be obtained easily. The ratio of average to maximum beta energy is shown in Figure XVI-23 for allowed transitions, and in Figure XVI-24 for unique first forbidden transitions. The average beta energy determined from these curves can then be used in calculating heat generation by beta decay.

FIGURE XVI-22

Typical Beta Spectra for $Z = 50$

FIGURE XVI-23

Average Beta Energy for Allowed Transitions

FIGURE XVI-24

Average Beta Energy for Unique First Forbidden Transitions

1.2 Bremsstrahlung

An electron that is accelerated or decelerated emits part of its energy as electromagnetic radiation. Radiation emitted when a beta particle leaves a nucleus is called internal bremsstrahlung; when a beta particle is absorbed, the radiation is called external bremsstrahlung. In either case the spectral distribution is from zero to the maximum beta energy, but most of the energy is in the less energetic radiations. Even though all beta emitting nuclides produce bremsstrahlung, substantial interest in this process as applied to beta emitters has developed only recently. The nuclear gamma radiation from most radionuclides overshadows bremsstrahlung radiation. The importance of bremsstrahlung radiation in handling beta emitters was first widely recognized when highly purified strontium sources were prepared and used in thermoelectric generators, and shielding had to be provided for the bremsstrahlung radiation. Since that time the necessity of shielding for bremsstrahlung from other beta emitters has also been recognized.

The energy emitted as inner bremsstrahlung depends only on the beta energy and is small even for very energetic electrons. For the 1.5 MeV beta of Y-91 this accounts for only about 0.16 percent of the total beta energy.

External bremsstrahlung increases with increasing beta energy and increasing atomic number (Z) of the absorber. The ratio of energy loss by radiation to that by ionization for a monoenergetic electron is approximately

$$\frac{(dE/dX)_{\text{rad}}}{(dE/dX)_{\text{ion}}} = ZE/800 \quad (29)$$

where E is the kinetic energy of the electron in MeV. Although this approximation is rather inaccurate for low energy electrons, it is usually adequate because the low penetration of bremsstrahlung from low energy electrons usually does not make great accuracy imperative. Application of this formula to beta emission requires division of the beta spectrum into several energy groups and calculation of the total bremsstrahlung energy resulting from each group. This gives only the total amount of bremsstrahlung and not the energy spectrum. For each energy group of betas, the maximum bremsstrahlung energy is equal to the maximum energy of betas in that group.

An approximate bremsstrahlung spectrum $S(k)$, for photons of energy k may be evaluated as the product of three factors, summed over all beta energies from k to E_0 . The factors are 1) the fraction of the total beta energy at energy E, 2) the fraction of this energy which is lost by radiation, and 3) the fraction of this radiated energy which has energy k. The total energy of bremsstrahlung of energy k per Δk photon energy interval per unit beta energy is thus given by:

$$S(k) = \sum_{E=k}^{E_0} \frac{E P(E)}{\sum E P(E)} \frac{ZE}{ZE + 800} \frac{1}{1.25E} \left[4\left(1 - \frac{k}{E}\right) + 3\frac{k}{E} \ln \frac{k}{E} \right] \Delta k \quad (30)$$

where $\sum E P(E)$ is from $E = 0$ to $E = E_0$.

More accurate evaluations of both internal and external bremsstrahlung spectra are possible with computer code BREMRAD, or with the methods and equations given in several of the references. Results of these more accurate calculations for strontium-yttrium-90 and for promethium-147 are shown in Figures XVI-25 and XVI-26, respectively.

2. Beta Dose Rates and Shielding

For most applications to beta particles the problems of dose rate and shielding need to be considered together since even the source itself provides significant attenuation of the betas. Calculations with betas are generally much less important than with gamma rays because of the much lower penetrating power of the betas, but they may become important at Hanford since pure beta emitters are being isolated.

FIGURE XVI-25

Bremsstrahlung Spectra from Sr-Y-90 Betas
stopped in Strontium Oxide

FIGURE XVI-26

Bremsstrahlung Spectra from Pm-147 Betas
stopped in Promethium Oxide

Beta particles passing through matter interact with electrons in the matter to lose their energy by ionization. The energy loss per unit weight of absorber is reasonably independent of atomic number, since the number of electrons per unit mass determines the stopping power, and this varies as Z/A . Because of the large number of collisions between beta particles and the electrons of the absorber, the range of betas with a given energy and absorber is virtually constant. The range shown in Figure XVI-27 is specifically for aluminum, but is useable for any absorber by inclusion of corrections for the number of electrons per unit mass. Even without this correction the range curve is a good approximation. This range curve is useful in both dose rate and shielding calculations since it can be used to determine the energy lost by an electron or beta particle in passing through a given thickness of matter.

FIGURE XVI-27

Range of Beta Particles in Aluminum

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Beta particles above about 0.5 MeV undergo about 15 collisions per cm of air, and cause about 60 ion pairs per cm, which corresponds to an energy loss of about 2 KeV per cm. The ionization loss per cm increases as the beta energy decreases. An approximate value of the specific energy loss (energy loss per path length) may be obtained by dividing the beta energy by the total range, but this is somewhat in error because of the higher ionization at lower energies. This value, together with the geometry, can be used to determine the dose rate. For point source geometry, and neglecting shielding, the dose rate is approximately

$$\text{rads/hr at one foot} = 1.8 \times 10^5 \times \text{energy} \times \text{curies/range} \quad (31)$$

where the energy is in MeV and the range is in mg/cm^2 . This formula actually applies to monoenergetic electrons rather than to the spectrum of beta energies, but is a reasonable approximation.

An example of shielding calculation is the amount of steel required to completely shield a strontium-yttrium-90 source. The maximum beta energy is 2.27 MeV, which corresponds to 1.37 g/cm^2 of aluminum. Because of the Z/A correction this is equal to about 1.41 g/cm^2 of steel. If the density of steel is taken as 7.8 g/cm^3 , this is 0.18 cm, or 0.071 inches. Thus, slightly more than 1/16 inch of steel will completely shield the beta radiation from strontium-yttrium-90. Shielding for bremsstrahlung must be handled the same as for gamma radiation.

An example of dose rate calculations is the dose rate one foot from one curie of strontium-90 and its yttrium daughter, with the source being weightless but enclosed in 1 mm of glass. The weight of shielding is $0.1 \text{ cm} \times 2.6 \text{ g/cm}^3 = 260 \text{ mg/cm}^2$ of glass, plus $30.5 \text{ cm} \times 1.29 \text{ mg/cm}^3 = 39.4 \text{ mg/cm}^2$ of air. This shielding will absorb all beta particles of energy below about 0.63 MeV, and will reduce the yttrium-90 maximum beta energy from 2.27 MeV to about 1.8 MeV, with a residual range of the beta being about 1070 mg/cm^2 . Because of the absorbers the strontium-90 beta will not contribute to the dose rate at one foot. Since the average energy of yttrium-90 betas is about 0.88 MeV, slightly less than half of these betas are absorbed. The spectrum of beta energies one foot from the source is essentially from 0 to 1.8 MeV with a distribution similar to the yttrium-90 beta distribution from 0.63 to 2.27 MeV. The average energy of this spectrum is about 0.7 MeV, with a range of 260 mg/cm^2 . Using these values, and a source strength of 0.6 Curies to allow for absorption, the dose rate is approximately 300 rads/hr. The source self-shielding and geometry factors should usually be included in a practical problem, but are omitted here for simplicity.

E. ALPHA RADIATION

Many nuclides, particularly above mass 200, are unstable with respect to emission of a helium nucleus, or alpha particle. The energy liberated in alpha decay is usually between 5 and 7 MeV, with most of the energy going to the alpha particle. Some energy also appears as recoil energy of the emitting nuclide. The alpha emitting nuclides most likely to be encountered in Waste Management are uranium-235, uranium-238, plutonium-238, plutonium-239, plutonium-240, neptunium-237, americium-241, curium-242, and curium-244. The alpha particles have a very short range and are of little concern in shielding, except for their role in producing neutrons as discussed below. Gamma radiation or X-rays accompany the decay of most alpha emitters. These radiations are treated the same as gamma or X-rays from beta emitters.

F. NEUTRONS

Fast neutrons are emitted in the process of spontaneous fission, which occurs with several heavy nuclides such as plutonium-238, plutonium-240, curium-242, and curium-244. The neutron generation rate due to spontaneous fission depends only on the amount of the fissioning nuclide present, and is not affected by the chemical form or composition.

Another source of fast neutrons is the reaction of alpha particles with light elements by an α, n reaction. Beryllium yields a particularly high number of neutrons in this way, but other elements also produce a significant number of neutrons. Table XVI-6 lists the expected dose rates due to α, n neutrons with several different light elements mixed with selected alpha emitters. The dose rate from α, n neutrons thus depends on the type and amount of light elements associated with the alpha emitters.

TABLE XVI-6
NEUTRON DOSE RATES FROM ALPHA EMITTERS

Light Element	Relative Effectiveness	Dose Rate, mrem/hr at one foot per gram				
		Po ²¹⁰	Pu ²³⁸	Am ²⁴¹	Cm ²⁴²	Cm ²⁴⁴
Be	1200	112,000	500	100	200,000	4200
C	1.7	140	0.7	0.14	260	5.6
O	1.0	88	0.4	0.08	160	3.4
F	100	8,800	40	8.0	16,000	340
Al	12	1,100	5.0	1.0	2,000	42
Spontaneous Fission		-----	0.03	---	190	100

Neutrons from α, n reactions generally have a higher energy and a smaller energy spread than do neutrons from spontaneous fission. However, attenuation of neutrons of the two types is roughly comparable.

Fast neutrons are very penetrating in most materials, but they are slowed down or moderated by light elements, especially hydrogen. After moderation, they may be stopped by many materials. Figure XVI-28 shows the attenuation of neutron dose rates by water and by lithium hydride shields as a function of shield thickness.

FIGURE XVI-28

Attenuation of Dose Rate From Fast Neutrons

The expected neutron dose rate at one foot from one gram of selected alpha emitter oxides is shown in Table XVI-7 for different thicknesses of water shielding. The neutron dose rates are directly proportional to the weight of alpha emitter and inversely proportional to the square of the distance from the source to the dose point, at least for distances over one foot.

TABLE XVI-7
NEUTRON ATTENUATION BY WATER SHIELDING

Shield Thickness, Inches	Dose Rate, mrem/hr at One Foot Per Gram				
	Po ²¹⁰	Pu ²³⁸	Am ²⁴¹	Cm ²⁴²	Cm ²⁴⁴
0	88	0.43	0.08	350	103
4	33	0.16	0.030	133	39
8	7.8	0.038	0.0071	31	9.1
12	2.2	0.011	0.0020	8.7	2.6
16	0.67	0.003	0.0006	2.7	0.78
20	0.22	0.001	0.0002	0.9	0.26

When neutrons are absorbed penetrating gammas sometimes result. These gammas may be more difficult to shield than the original neutrons. The effect of secondary gammas has been included in the above discussion, but may be altered if additional elements are present in the moderator.

Neutron dose rates will probably be of no importance in Waste Management unless alpha emitters are recovered in a concentrated form.

G. NUCLEAR DATA

Dose rate and shielding calculations require an accurate knowledge of the penetrating radiations associated with the source material. Chapter II contains information for obtaining the activities in mixed fission products in terms of total curies, but does not provide information on beta or gamma energies and abundances. Translation from total curies to individual beta and gamma energies and abundances requires a knowledge of the decay schemes involved. Table XVI-8 contains such data for principal fission products, and Table XVI-9 contains data for selected alpha emitting nuclides. The gamma data have been corrected for internal conversion, and conversion electrons (if appreciable) have been included with the beta particles. Bremsstrahlung radiations are not included in the table.

Most of the data were derived from Nuclear Data Sheets and the Journal of Nuclear Data, updated where applicable by the 9th edition of the KAPL Chart of the Nuclides. Some more recent decay scheme investigations are also included.

TABLE XVI-8

SIMPLIFIED DECAY SCHEMES OF FISSION PRODUCTS

Nuclide	Half Life	Particles			Photons	
		Max. E, MeV	Avg. E, MeV	Abund., %	E, MeV	Abund., %
Se 79	6.5×10^4 y	0.160*	0.060	100	--	
Kr 85	10.6 y	0.672*	0.252	99.6	0.514	0.42
		0.15	0.041	0.42		
Rb 86	18.7 d	1.777*	0.723	91	1.084	9
		0.696	0.1232	9		
Sr 89	50.6 d	1.463*	0.582	100	0.913	0.01
Sr 90	28 y	0.544*	0.201	100	--	
Y 90	64 h	2.27*	0.942	100	0.511 pair	0.0045
		0.52*	0.191	0.017	0.016 Kx	0.011
		1.74 ce	1.74	0.017		
Y 91	59 d	1.54*	0.615	99.7	1.208	0.3
		0.33	0.097	0.3		
Zr 93	9.5×10^5 y	0.063*	0.024	75	--	
		0.034*	0.013	25		
Nb 93m	3.7 y	0.026 ce	0.026	88	0.017 Kx	9
		0.010 ce	0.012	12		
Zr 95	65 d	1.13*	0.437	0.4	0.760	43
(Nb 95m)	(90 h)	0.885*	0.335	2	0.726	55
		0.396	0.120	55	0.235	0.8
		0.360	0.107	43	0.017 Kx	0.7
Nb 95	35 d	0.93*	0.352	1	0.768	99
		0.16	0.044	99		
		0.748 ce	0.748	0.2		
Tc 99	2.1×10^5 y	0.292*	0.107	100	--	
Ru 103	40 d	0.71	0.234	3	0.610	7
(Rh 103m)	(57m)	0.39	0.117	1	0.498	89
		0.212	0.059	89	0.362	0.3
		0.10	0.026	7	0.297	0.4
		0.475 ce	0.475	0.6	0.040	0.25
		0.037 ce	0.037	91		
Ru 106	1.0 y	0.0394	0.010	100	2.9 M	0.012
(Rh 106)	(30 s)	3.54	1.51	78	2.4 M	0.026
		3.0	1.26	8	2.0 M	0.09
		2.4	0.977	11	1.6 M	0.27
		2.0	0.792	2	1.1 M	2.4
		1.5	0.564	0.5	0.9 M	0.7
		1.3	0.477	0.2	0.624	9.9
		1.2	0.434	0.4	0.612	1
		1.0	0.351	0.09	0.513	20.5
Pd 107	7×10^6 y	0.035*	0.014	100	--	
Cd 109	453 d	0.085 ce	0.085	52	0.088	4
(Ag 109m)	(40 s)	0.062 ce	0.062	44	0.022 Kx	100
					0.003 Ix	10

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TABLE XVI-8 (Cont.)

Nuclide	Half Life	Particles			Photons	
		Max. E., MeV	Avg. E., MeV	Abund., %	E., MeV	Abund., %
Ag 110 m (Ag 110)	260 d (24 s)	2.87	1.19	2	1.5 M	18
		0.53	0.166	33	1.384	24
		0.085	0.022	65	0.937	34
					0.885	72
					0.76 M	32
Ag 111	7.5 d				0.69 M	35
					0.656	93
		1.05	0.370	92.7	0.342	6
		0.79*	0.292	1.1	0.247	1
		0.69	0.226	6.2		
Cd 115 m	43 d	1.63*	0.644	96.7	1.30	1
		0.687*	0.252	2	1.14	0.03
		0.335	0.098	1	0.935	2.3
		0.20	0.055	0.3	0.485	0.3
Sn 123 m	129 d	1.42*	0.551	98	1.08	2
		0.34	0.100	2		
Sb 124	60 d	2.313	0.932	23	2.09 M	6.3
		1.59	0.601	5	1.69	48
		1.016	0.355	1.5	1.4 M	10
		0.954	0.330	5	1.0 M	4
		0.621	0.199	51	0.72 M	14
		0.225	0.063	11	0.645	7.2
		0.051	0.013	2	0.603	96
Sn 125	9.6 d	2.33*	0.953	95	1.97	1.2
		1.3*	0.50	1.3	1.068	3.9
		0.47	0.144	1.5	0.904	0.9
		0.37	0.109	2.1	0.811	1.0
					0.468	0.5
Sb 125	2.7 y	0.612*	0.223	13.4	0.668	1.6
		0.437	0.133	5.8	0.633	11
		0.295	0.085	40.4	0.60 M	24
		0.233	0.065	1	0.43 M	41
		0.124	0.033	30.7	0.35 M	2
		0.118	0.031	6.0	0.205 M	0.5
		0.09	0.024	1.9	0.174 M	7.1
Te 125 m	58 d	0.105 ce	0.105	47	0.1096	0.3
		0.078 ce	0.078	53	0.0353	7.5
		0.030 ce	0.030	13	0.027 Kx	114
Sn 126 (Sb 126 m)	2x10 ⁵ y (19 m)	0.4	0.12	100	0.695	1
		1.9	0.74	1	0.665	1
					0.415	1
Sb 126	12.5 d	1.9	0.74	100	0.695	100
					0.665	100
					0.415	100
Te 127 m (Te 127)	105 d (9.3 h)	0.73*	0.268	1.5	0.665	0.013
		0.695	0.226	97.5	0.418	0.83
		0.27	0.077	1	0.360	0.12
		0.054	0.014	0.013	0.21 M	0.1
		0.084 ce	0.084	56	0.089	0.1
		0.057 ce	0.057	42	0.059	0.5
					0.027 Kx	37

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TABLE XVI-8 (Cont.)

Nuclide	Half Life	Particles			Photons	
		Max. E., MeV	Avg. E., MeV	Abund., %	E., MeV	Abund., %
Te 129 m (Te 129)	33 d (67 m)	1.59	0.601	5	1.12	1
		1.453	0.542	76	0.72	1
		0.99	0.343	15	0.475	16
		0.7	0.23	3	0.211	2
		0.3	0.09	1	0.106	0.3
		0.101 ce	0.101	47	0.027	25
		0.074 ce	0.074	48	0.027 Kx	41
I 129	1.6x10 ⁷ y	0.150*	0.055	100	0.040	10
		0.035 ce	0.035	17	0.030 Kx	64
		0.005 ce	0.005	73		
I 131	8.05 d	0.81*	0.298	0.7	0.724	2.8
		0.606	0.193	87.5	0.638	9.1
		0.33	0.096	9.1	0.364	80
		0.25	0.070	2.8	0.284	5.2
					0.2 M	2
					0.08	2
Xe 131 m	12 d	0.159 ce	0.159	35	0.164	2
		0.129 ce	0.129	63	0.030 Kx	55
Cs 134	2.1 y	1.453*	0.561	0.2	1.57	0.1
		0.892*	0.329	1.5	1.365	5
		0.658	0.211	61	1.0 M	8
		0.410	0.122	9	0.800 M	83
		0.282	0.080	0.5	0.605	98
		0.086	0.022	27	0.566 M	25
					0.475	4
Cs 135	2x10 ⁶ y	0.210*	0.076	100	--	
Cs 136	13 d	0.657	0.211	7.4	1.255	21
		0.341	0.099	92.6	1.065	84
					0.830	100
					0.337	59
					0.2 M	67
Cs 137 (Ba 137 m)	30 y (2.6 m)	1.18*	0.446	5	0.6616	85
		0.514*	0.165	95	0.032 Kx	9
		0.625 ce	0.625	10		
Ba 140	12.8 d	1.01	0.349	60	0.537	25
		0.9*	0.33	5	0.43 M	6
		0.6	0.19	10	0.304	4
		0.48	0.15	25	0.16 M	9
		0.025 ce	0.025	77	0.030	16
La 140	40 h	2.20	0.873	7	2.9	0.1
		1.71	0.653	10	2.52	6
		1.38	0.506	45	1.597	94
		1.10	0.387	26	0.9 M	15
		0.83	0.276	12	0.8 M	28
					0.45 M	43
					0.329	20
Ce 141	32.5 d	0.580	0.183	30	0.145	48
		0.435	0.131	70	0.036 Kx	17
		0.138 ce	0.138	3		
		0.103 ce	0.103	19		

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TABLE XVI-8 (Cont.)

Nuclide	Half Life	Particles			Photons	
		Max., E., MeV	Avg. E, MeV	Abund., %	E, MeV	Abund., %
Pr 143	13.8 d	0.933	0.318	100	--	
Ce 144	285 d	2.98	1.222	97.7	2.18	0.8
(Pr 144)	(17 m)	2.29*	0.918	1.3	1.49	0.25
		0.80	0.263	1	0.691	1.6
		0.32	0.092	76	0.134	10.5
		0.24	0.067	4	0.100	0.1
		0.186	0.051	20	0.080	2
Pm 146	5.53 y	0.78	0.256	33	0.74 M	58
		0.145	0.039	2	0.633	2
					0.589	0.6
					0.454	65
Nd 147	11.1 d	0.82	0.271	65	0.65 M	2.3
		0.50	0.153	2	0.532	25
		0.38	0.112	28	0.43 M	6
		0.22	0.061	5	0.3 M	7
					0.14 M	2
					0.091	27
Pm 147	2.62 y	0.225	0.0605	100	0.121	0.004
		0.104	0.027	0.01		
Pm 148 m	41 d	2.48*	1.002	3.8	1.465	2.4
(Pm 148)	(5.4 d)	1.93	0.741	1	0.95 M	41
		1.02	0.350	3.5	0.727	36
		0.69	0.221	24	0.630	87
		0.50	0.152	18	0.605 M	14
		0.40	0.118	52	0.551	94
					0.4 M	46
Sm 151	90 y	0.0759	0.020	98.4	0.0216	0.08
		0.0543	0.014	1.6	0.007 Lx	0.5
		0.020 ce	0.020	0.5		
		0.014 ce	0.014	1.0		
Eu 152	12.4 y	1.484	0.542	6	1.409	25
		1.05	0.359	1	1.25 M	8
		0.70	0.224	12	1.10 M	28
		0.38	0.111	3	0.96 M	18
		0.20	0.055	2	0.779	13
					0.45 M	7
					0.3 M	31
					0.122	30
Eu 154	16 y	1.855	0.701	10	1.61	2
		0.87	0.288	24	1.276	38
		0.58	0.180	38	1.00 M	30
		0.26	0.073	28	0.874	15
					0.724	20
					0.593	6
					0.248	6
					0.123	31

TABLE XVI-8 (Cont.)

Nuclide	Half Life	Particles			Photons	
		Max., E., MeV	Avg. E., Me	Abund., %	E., MeV	Abund., %
Eu 155	1.8 y	0.247	0.069	15	0.1053	21
		0.185	0.050	10	0.0865	33
		0.158	0.043	32	0.0600	1.7
		0.140	0.037	43	0.10453	0.8
		0.097 ce	0.097	0.8	0.0265	1
		0.078 ce	0.078	2	0.0188	0.03
		0.055 ce	0.055	8		
		0.036 ce	0.036	13	0.043 Kx	32
		0.010 ce	0.010	40	0.007 Lx	10
Eu 156	15 d	2.447	0.069	32	2.18 M	5.3
		1.21	0.419	11	2.05 M	11.5
		0.48	0.145	34	1.90 M	5
		0.30	0.085	23	1.25 M	33
					1.0 M	13
					0.86 M	2
					0.812	9.5
					0.65 M	11
Tb 160	72.4 d	1.72	0.640	0.4	1.27 M	13
		0.86	0.284	31	1.18 M	18
		0.56	0.172	36	0.966 M	35
		0.46	0.138	19	0.879	31
		0.26	0.073	14	0.75 M	3
					0.36 M	2
					0.30 M	27
					0.20 M	9
Tb 161	6.9 d	0.584	0.182	10	0.300	0.1
		0.509	0.155	64	0.10 M	0.4
		0.452	0.135	26	0.074 M	10
		0.215	0.059	0.1	0.057 M	5
					0.049	19
					0.026	21
					0.046 Kx	26

Nuclide identification and half lives in parenthesis refer to short-lived daughters included in equilibrium with long-lived parent.

- * Beta with unique first forbidden shape. Others have allowed shape.
- ce Conversion electron instead of beta particle.
- M Multiple gammas near the listed photon energy.
- Kx K x-rays from internal conversion or K capture.
- Lx L x-rays from internal conversion or L capture.
- Pair Annihilation radiation resulting from internal conversion by positron-electron pair creation.

TABLE XVI-9

PROPERTIES OF SELECTED ALPHA EMITTERS

	Po ²¹⁰	Pu ²³⁸	Am ²⁴¹	Cm ²⁴²	Cm ²⁴⁴
Half Life, years	0.379	89	458	0.446	18
Specific Activity, Ci/g	4500	17	3.24	3320	81
α Energy, MeV	5.30	5.49	5.48	6.10	5.79
Spont. Fission Half Life	---	4.9×10^{10}	2×10^{14} y	7.2×10^6	1.4×10^7
Neutron Generation, n/g-sec					
Spont. Fission	---	3.4×10^3	---	2.3×10^7	1.2×10^7
α, n as Oxide	1.1×10^7	5.4×10^4	1.0×10^4	2.0×10^7	4.2×10^5
Selected Gammas*	0.803 (1.2-3)	0.013 (28) 0.044 (0.038) 0.760 (5-5) 0.875 (2-5)	0.013 (90) 0.060 (36) 0.618 (1.1-4) 0.661 (7.0-4) 0.688 (1.0-4) 0.721 (2.8-4)	0.013 (26) 0.562 (1.8-4) 0.605 (1.4-4) 0.89 (2.5-5) 1.01 (1.0-5)	0.013 (23) 0.100 (1.5-3) 0.150 (1.3-3) 0.610 (2.5-5) 0.820 (6.5-5) 0.863 (8.3-6)

*First value is energy in MeV. Value in parentheses is photons per 100 decays. Values such as (1.2-3) and (5-5) represent a number and a power of ten; i.e., 1.2×10^{-3} and 5×10^{-5} respectively. Spontaneous fission and fission product gammas are not included in the tabulation.

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PART VII, Continued

SAFETY

CHAPTER XVII

HEALTH PROTECTION FROM RADIATION

By

W. N. Koop

Personnel Protection Operation

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PART VII: SAFETY, Cont.CHAPTER XVIIHEALTH PROTECTION FROM RADIATION

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CHAPTER XVII - HEALTH PROTECTION FROM RADIATION

This chapter presents key features of radiation safety programs established to protect not only employees but people located beyond areas of Waste Management operations from the hazardous radiations resulting from those operations. These programs are summarized in the ARHCO Manual of Radiation Protection Standards and Controls. Since the standards and controls are frequently reviewed and revised, they should be considered prime reference sources.

There is no discussion in this chapter on biological effects of radiation nor upon the consequences of losing control of either radiation exposure or of contamination. Other sources of information are available on these pertinent subjects. Furthermore, facility design is not discussed here, since the subject is treated extensively in other portions of this manual. It must be acknowledged however, that facility design plays a major role in achieving effective radiation protection. Design engineers have followed approved radiological criteria in Waste Management facilities with consequent reductions in radiation exposure and improvement in contamination control. The presence of radiation protection personnel on the design council assures that radiation protection principles will be consistently applied in subsequent facility modifications.

A. NATURE OF RADIATIONS

Materials processed in Waste Management operations are radioactive. The radiations produced are from atomic nuclei as they change spontaneously from an unstable condition to a more stable form by the process of radioactive decay. Nearly all the beta and gamma radiations in these facilities are from the decay of fission products. Where alpha radiation is found, the source is the decaying atoms of uranium or of transuranic elements. Alpha and beta radiations consist of high velocity charged particles in contrast to gamma radiation that consists of electromagnetic waves of the same general type as light and radio waves but characterized by extremely short wave lengths.

1. Alpha Particles

An alpha particle, with 2 protons and 2 neutrons, has a mass of four, a positive charge of two, and is structurally identical to the helium nucleus. Because of the charge and large mass, even high velocity alpha particles (5 MeV) have only a range of about 3.5 cm in air or 0.004 cm in tissue. A thin sheet of paper, a film of water, or the outer layer of skin will completely stop alpha particles. Because of this limited penetration, bodily damage from external alpha radiation is negligible. However, because alpha particles produce an extremely dense path of ionization before being stopped (one alpha particle may produce 150,000 ion pairs), it is vitally important to prevent alpha emitters from entering the body. Significant internal exposure is sustained from relatively small depositions of any alpha emitting material.

2. Beta Particles

Beta particles are electrons emitted from decaying radioactive atoms. They have energies up to 12 MeV or speeds almost to that of light. Particles of more than 2 MeV are rare, however, in waste management facilities where the prime sources of beta radiation are aged fission products. The distance a 2 MeV beta particle travels is limited to less than 700 cm in air, .9 cm in water or tissue, and .08 cm in lead. Because such a particle penetrates to the germinal layer of the skin, external exposure from beta radiation can be significant. Furthermore, beta particles can cause external exposure indirectly by bremsstrahlung or secondary photon radiation (X-rays) produced by deceleration of the electrons passing through matter. However, the prevention of beta emitters entry into the body tends to dominate protection efforts.

3. Gamma Rays

Gamma rays are a form of electromagnetic radiation that have wave lengths of about one-millionth that of light. They are emitted from the nucleus of some atoms undergoing radioactive decay in packets or photons of discrete energies. Energy is lost exponentially as it traverses through matter and so the rays are not considered to have a definite limit or range. Gamma rays are very penetrating, much more so than either alpha or beta radiations. Since Chapter XVI deals more completely with the attenuation of gamma radiation, only a brief example will be cited here. The intensity of a 2 MeV gamma ray beam is reduced to 0.2 MeV after passing through 1.8 inches of lead or 2.7 inches of steel or 19 inches of water. The same reduction of intensity for this energy gamma ray would require 1300 feet of air. Within waste management facilities the presence of gamma radiation is the prime source of external exposure.

B. OCCUPATIONAL PROTECTION

An effective program of radiation control is based on the limits of radiation exposure suggested by recognized knowledgeable bodies. The permissible radiation exposure limit is the quantity of radiation which under any combination of circumstances is not expected to cause appreciable bodily injury to the average normal individual at any time during his lifetime.

1. Definition of Terms

1.1 Roentgen

A roentgen (R) is the quantity of X or gamma radiation such that the associated corpuscular emission per 0.001293 gram of air produces in air, ions carrying one electrostatic unit of quantity of electricity of either sign. (NOTE: 0.001293 gram is the mass of one cubic centimeter of dry atmospheric air at 0°C and 760 mm Hg pressure.) This unit of dose corresponds to the absorption of about 83.8 ergs/gram of air.

1.2 Rad

The term rad is an acronym for radiation absorbed dose. A rad is 100 ergs of absorbed energy per gram of absorbing material. The rad is a measure of the energy imparted to matter (i.e. retained by matter) by ionizing radiation per unit mass of irradiated material at the place of interest.

1.3 Rem

A rem (roentgen equivalent man) is that quantity of any ionizing radiation such that the energy imparted to a biological system (cell tissue, organ or organism) per gram of living matter by the ionizing materials present in the region of interest has the same biological effectiveness as an absorbed dose of one rad of X-radiation (about 0.4 MeV) in the same region. The use of the rem permits adding exposures from mixed radiations by recognizing the relative biological effectiveness of the various radiations. The list below is used for this purpose.

X-rays or gamma rays	1R $\rightarrow$ 1 rad = 1 rem
beta particles	1 rad = 1 rem
alpha particles	1 rad = 20 rem

1.4 Curie

A curie (Ci) is defined as that quantity of a radioactive material disintegrating at the rate of 3.7×10^{10} atoms per second and is the unit used in measuring radioactivity of these materials. Since the curie is a relatively large unit, the millicurie (mCi = 0.001 Ci) and the microcurie (μ Ci = 10^{-6} Ci) are often used. The curie is based on the number of nuclear disintegrations and not on the number of radiations emitted. For example, some radionuclides emit two or more gamma photons for each nuclear disintegration and hence the decay scheme or the exact mode of decay must be known if accurate values of activity are to be calculated from experimental data. Furthermore, due to counting efficiencies being much less than 100 percent, conventional measuring instruments do not count all radiations emitted, so corrections need to be applied to the counts recorded.

2. Exposure Limits in Controlled Areas

The program to control radiation exposure is designed to conform to the intent of AEC Manual Chapters 0230, 0524 and 0525. Limits of exposure are established in the ARHCO Manual of Radiation Standards and Controls and are summarized below.

<u>Type of Exposure</u>	<u>Period of Time</u>	<u>Dose (rem)</u>
Whole body, head and trunk, blood forming organs, gonads, lens of the eye	Lifetime accumulation	5 (N-18)*
	Calendar year	12
	Calendar quarter	3
Bone, thyroid, skin	Calendar year	30
	Calendar quarter	10
Other single organ	Calendar year	15
	Calendar quarter	5
Skin of hands, forearms, feet and ankles	Calendar year	75
	Calendar quarter	25

*Where N is the age in years.

The above standard limits exposure sustained from radiation sources both internal and external of the body. In a rigorous evaluation of sustained exposure against these limits, external dose and internal dose are additive. In many routine protection programs in the nuclear industry, exposures from external sources up to the limit are allowed, while avoiding significant depositions of radionuclides (internal dose). This practice is followed in the Waste Management facilities where depositions of radionuclides can usually be prevented but where accurate determinations of dose from radionuclide depositions can be very difficult. In contrast, external exposure can be measured with adequate accuracy and relative ease. Routine control, therefore, involves careful measuring of external exposure and preventing bodily entry of radioactive materials through wounds, ingestion or inhalation.

The measurement of external radiation exposure is achieved primarily by the use of individually assigned beta-gamma film badge dosimeters. These dosimeters are processed rapidly and the results promptly made available to management. The film badge dosimeter measurement is supplemented, as required, by measurements made with other individually assigned dosimeters, (i.e., film finger rings and "pencils") and by measurements made with fixed and portable instruments that are discussed later in this chapter.

Bioassay programs and whole body counter examinations are used to assess radiation exposure from internally deposited radionuclides. The frequency and type of measurement are established on the basis of the exposure potential of the individual's work assignment, and is dependent upon the physical and biological properties of the materials with which he works.

Radiation exposure records for each worker are maintained in individual folders. All results obtained from the external and internal exposure

measurement program are periodically transferred to these folders, along with the evaluations and interpretations of these results. In addition to the routine information, any unusual incident in which the individual may have been involved or any unusual exposure he may have received is investigated, documented and placed in the individual's record file. References to the medical treatment or work restrictions which are occasionally required as a consequence of an incident are also retained in this file.

3. Radiation Zones and Radiation Work Procedures

A Radiation Zone is established where significant radiation exposure can be received. The following criteria are applied in establishing Radiation Zones:

- 1) Where there is a persistent radiation dose rate in excess of 1 mrem/hour, or
- 2) A potential radiation dose rate in excess of 50 mrem/hour, or
- 3) Smearable surface contamination is likely to be present in amounts exceeding 200 c/m beta-gamma contamination per 100 square centimeters or 500 d/m alpha contamination per 100 square centimeters, or
- 4) Fixed surface contamination exceeds 1000 c/m beta-gamma or 500 d/m alpha contamination from plutonium or 2000 d/m alpha from natural uranium, per 100 square centimeters, or
- 5) Where airborne contamination potentially can exceed the 40-hour occupational maximum permissible concentration.

In posting Radiation Zones, no distinction is made as to the nature of the hazard (i.e., external radiation, surface contamination or airborne contamination) which is present, nor any radiation protection controls which may be required. However, any entry to a Radiation Zone and the performance of all work in the zone is in accordance with a "Radiation Procedure" established for the location and work where whole body dose rates greater than 25 rem/hour can be encountered. Access is often controlled on a physical basis by lock and interlock systems in addition to administrative access control.

Radiation Procedures detail the requirements for protective clothing, respiratory equipment, personnel monitoring devices, surveillance of work by Radiation Monitoring, the locking out of process equipment, etc. There are many different Radiation Procedures used and while

some authorize work for only one shift most of them are prepared for use over an extended period. Radiation Procedures require approvals of operating management, radiation monitoring supervision and supervision of service groups involved. The radiation monitoring group participates in the preparation of Radiation Procedures, but it is clearly understood that the responsibility for achieving a high degree of radiation safety rests with operating management.

4. Radiation Protection Instrumentation

Much effort has been directed toward the development of versatile, rugged and accurate instruments for use in the radiation protection program. The principal portable instruments used for beta-gamma dose rate monitoring are the CP and Juno. Geiger-Mueller (GM) instruments are used for beta-gamma contamination surveys. Alpha contamination surveys are made with several kinds of proportional counters. Some of the proportional counters have scintillation detectors and others have gas-filled ionization detectors. Portable instruments are distributed from a Battelle Northwest facility in the 300 Area where they are calibrated and serviced at intervals of one to four weeks depending on the type of instrument.

Instruments and instrument systems used in routine control activities such as remote area monitors, hand and shoe counters, air samplers, and semi-portable contamination detectors are assigned permanently to a Waste Management Facility. The routine performance checks and maintenance are carried out by personnel in the facility.

Hand and shoe counters are placed in several convenient locations and portable contamination survey instruments are available at the exits of many radiation zones. Dose rate monitoring instruments are also available where operating personnel can make effective use of them.

Fixed instruments for measuring gamma radiation intensities are installed in locations where there is a potential for abnormal radiation doses. Dose rates from these remote instruments are transmitted and recorded in centralized locations. Two types of alarms are provided for most of these fixed instruments. One is an "intermediate" alarm with a trip setting at a few hundred mrem/hour and the second trip point is at a dose rate level where radiation is an immediate hazard to personnel in the vicinity. The strip chart recorders are routinely checked by Radiation Monitoring personnel.

The concentration of radioactive material in building air is monitored by sampling and analyses. Fixed filter paper holders (sampling heads) on the building vacuum system are located in many work locations. Room air is drawn through filter paper at controlled rates. The filter papers are collected periodically, counted in the laboratory and the air concentration of radioactive material computed.

5. Radioactive Contamination of Air and Water

The concentrations of radionuclides in air and water concern internal exposure, and a list of maximum permissible concentrations provides a guide in establishing controls to achieve the occupational protection program objective of keeping internal exposure at insignificant levels. The tables below list the radionuclides encountered in Waste Management processes. Table XVII-1 A lists the maximum permissible concentrations in air and water for radiation workers (MPC for a 40-hour week).

The plant drinking water is routinely sampled and analyzed, and concentrations of radionuclides are found to be insignificant compared to the maximum permissible concentrations in water as shown in Table XVII-1 B. Where the potential air concentration of any radionuclide approaches the values shown in Table XVII-1, column 1, a radiation zone must be established and respiratory protection becomes a requirement for occupants.

These tables are displayed here to indicate the basis for the controls used in keeping the internal exposure of radiation workers at insignificant levels and to show the relative hazard of the different radionuclides encountered. Furthermore, the concentrations applicable to occupationally involved personnel as shown in A can be readily compared to the permissible concentrations in B that apply to the non-occupational population. Further reference to the values in B are made under the discussion of the Environmental Protection Program.

6. Radiation Occurrences

The radiation protection program is based on control, and each time control is lost, an investigation is required. The established criteria for classifying the loss of control conditions are shown below.

6.1 Type A

- 1) A single radiation exposure to an employee exceeding 25 rems whole body, 150 rems skin of the whole body, or 375 rems hands, forearms, feet or ankles, or the summation of exposure during a calendar year exceeding 25 rems whole body.
- 2) A release of radioactive material off-site may result in any member of the general population receiving an exposure exceeding limits stated in AEC Manual Chapter 0524.

TABLE XVII-1

MAXIMUM PERMISSIBLE CONCENTRATION OF SELECTED RADIONUCLIDES IN AIR AND WATER

(From RL-AEC Manual Chapter 0524 Appendix)

Element (Atomic Number)	Isotope		Table A		Table B	
			Air (mc/ml)	Water (mc/ml)	Air (mc/ml)	Water (mc/ml)
Americium (95)	Am-241	S	6×10^{-12}	1×10^{-4}	2×10^{-13}	4×10^{-6}
		I	1×10^{-10}	8×10^{-4}	4×10^{-12}	2×10^{-5}
	Am-243	S	6×10^{-12}	1×10^{-4}	2×10^{-13}	4×10^{-6}
		I	1×10^{-10}	8×10^{-4}	4×10^{-12}	3×10^{-5}
Barium (56)	Ba-140	S	1×10^{-7}	8×10^{-4}	4×10^{-9}	3×10^{-5}
		I	4×10^{-8}	7×10^{-4}	1×10^{-9}	2×10^{-5}
Cerium (58)	Ce-141	S	4×10^{-7}	3×10^{-3}	2×10^{-8}	9×10^{-5}
		I	2×10^{-7}	3×10^{-3}	5×10^{-9}	9×10^{-5}
	Ce-144	S	1×10^{-8}	3×10^{-4}	3×10^{-10}	1×10^{-5}
		I	6×10^{-9}	3×10^{-4}	2×10^{-10}	1×10^{-5}
Cesium (55)	Cs-137	S	6×10^{-8}	4×10^{-4}	2×10^{-9}	2×10^{-5}
		I	1×10^{-8}	1×10^{-3}	5×10^{-10}	4×10^{-5}
Curium (96)	Cm-242	S	1×10^{-10}	7×10^{-4}	4×10^{-12}	2×10^{-5}
		I	2×10^{-10}	7×10^{-4}	6×10^{-12}	3×10^{-5}
	Cm-244	S	9×10^{-12}	2×10^{-4}	3×10^{-13}	7×10^{-6}
		I	1×10^{-10}	8×10^{-4}	3×10^{-12}	3×10^{-5}
Iodine (53)	I-131	S	9×10^{-9}	6×10^{-5}	1×10^{-10}	3×10^{-7}
		I	3×10^{-7}	2×10^{-3}	1×10^{-8}	6×10^{-5}
Lanthanum (57)	La-140	S	2×10^{-7}	7×10^{-4}	5×10^{-9}	2×10^{-5}
		I	1×10^{-7}	7×10^{-4}	4×10^{-9}	2×10^{-5}
Neodymium (60)	Nd-147	S	4×10^{-7}	2×10^{-3}	1×10^{-8}	6×10^{-5}
		I	2×10^{-7}	2×10^{-3}	8×10^{-9}	6×10^{-5}
Niobium (41)	Nd-95	S	5×10^{-7}	3×10^{-3}	2×10^{-8}	1×10^{-4}
		I	1×10^{-7}	3×10^{-3}	3×10^{-9}	1×10^{-4}
Plutonium (94)	Pu-238	S	2×10^{-12}	1×10^{-4}	7×10^{-14}	5×10^{-6}
		I	3×10^{-11}	8×10^{-4}	1×10^{-12}	3×10^{-5}
	Pu-239	S	2×10^{-12}	1×10^{-4}	6×10^{-14}	5×10^{-6}
		I	4×10^{-11}	8×10^{-4}	1×10^{-12}	3×10^{-5}
	Pu-240	S	2×10^{-12}	1×10^{-4}	6×10^{-14}	5×10^{-5}
		I	4×10^{-11}	8×10^{-4}	1×10^{-12}	3×10^{-5}
	Pu-241	S	9×10^{-11}	7×10^{-3}	3×10^{-12}	2×10^{-4}
		I	4×10^{-8}	4×10^{-2}	1×10^{-9}	1×10^{-3}
	Pu-242	S	2×10^{-12}	1×10^{-4}	6×10^{-14}	5×10^{-6}
		I	4×10^{-11}	9×10^{-4}	1×10^{-12}	3×10^{-5}

TABLE XVII-1, Continued

Element (Atomic Number)	Isotope		Table A		Table B	
			Air (mc/ml)	Water (mc/ml)	Air (mc/ml)	Water (mc/ml)
Praseodymium (59)	Pr-143	S	3×10^{-7}	1×10^{-3}	1×10^{-8}	5×10^{-5}
		I	2×10^{-7}	1×10^{-3}	6×10^{-9}	5×10^{-5}
Promethium (61)	Pm-147	S	6×10^{-8}	6×10^{-3}	2×10^{-9}	2×10^{-4}
		I	1×10^{-7}	8×10^{-3}	3×10^{-9}	2×10^{-4}
Rhodium (45)	Rh-103m	S	8×10^{-5}	4×10^{-1}	3×10^{-6}	1×10^{-2}
		I	6×10^{-5}	3×10^{-1}	2×10^{-6}	1×10^{-2}
	Rh-105	S	8×10^{-7}	4×10^{-3}	3×10^{-8}	1×10^{-4}
		I	5×10^{-7}	3×10^{-3}	2×10^{-8}	1×10^{-4}
Ruthenium (44)	Ru-103	S	5×10^{-7}	2×10^{-3}	2×10^{-8}	8×10^{-5}
		I	8×10^{-8}	2×10^{-3}	3×10^{-9}	8×10^{-5}
	Ru-106	S	8×10^{-8}	4×10^{-4}	3×10^{-9}	1×10^{-5}
		I	6×10^{-9}	3×10^{-4}	2×10^{-10}	1×10^{-5}
Strontium (38)	Sr-89	S	3×10^{-8}	3×10^{-4}	3×10^{-10}	3×10^{-6}
		I	4×10^{-8}	8×10^{-4}	1×10^{-9}	3×10^{-5}
	Sr-90	S	3×10^{-10}	4×10^{-6}	3×10^{-11}	3×10^{-7}
		I	5×10^{-9}	1×10^{-3}	2×10^{-10}	4×10^{-5}
Tellurium (52)	Te-129	S	5×10^{-6}	2×10^{-2}	2×10^{-7}	6×10^{-4}
		I	4×10^{-6}	2×10^{-2}	1×10^{-7}	8×10^{-4}
Uranium	U-235	S	5×10^{-10}	8×10^{-4}	2×10^{-11}	3×10^{-5}
		I	1×10^{-10}	8×10^{-4}	4×10^{-11}	3×10^{-5}
	U-238	S	7×10^{-11}	1×10^{-3}	3×10^{-12}	4×10^{-5}
		I	1×10^{-10}	1×10^{-3}	5×10^{-12}	4×10^{-5}
	U natural	S	7×10^{-11}	5×10^{-4}	3×10^{-12}	2×10^{-5}
		I	6×10^{-11}	5×10^{-4}	2×10^{-12}	2×10^{-5}
Xenon (54)	Xe-133		1×10^{-5}		3×10^{-7}	
	Xe-135		4×10^{-5}		1×10^{-7}	
Yttrium (39)	Y-90	S	1×10^{-7}	6×10^{-4}	4×10^{-9}	2×10^{-5}
		I	1×10^{-7}	6×10^{-4}	3×10^{-9}	2×10^{-5}
	Y-91m	S	2×10^{-5}	1×10^{-1}	8×10^{-7}	3×10^{-3}
		I	2×10^{-5}	1×10^{-1}	6×10^{-7}	3×10^{-3}
	Y-91	S	4×10^{-8}	8×10^{-4}	1×10^{-9}	3×10^{-5}
		I	3×10^{-8}	8×10^{-4}	1×10^{-9}	3×10^{-5}
Zirconium (40)	Zr-95	S	1×10^{-7}	2×10^{-3}	4×10^{-9}	6×10^{-5}
		I	3×10^{-8}	2×10^{-3}	1×10^{-9}	6×10^{-5}

- 3) An unplanned release of radioactive material which exceeds, in 24 hours, 5000 times the continuous non-occupational MPC_a or MPC_w shown in AEC Manual Chapter 0526 at the point of release.
- 4) An accident or radiation exposure which gives rise to an inquiry by members of the public or press or which is believed to have public information significance.

Type A radiation occurrences are investigated by a committee established by the Richland Office of the AEC (RL-AEC) and formal reports are issued.

6.2 Type B

- 1) A radiation exposure in a calendar quarter exceeding 3 rems whole body, 10 rems skin of the whole body, 25 rems hands, forearms, feet or ankles.
- 2) An employee's accumulated whole body exposure exceeds $5(N-18)$ rems, where N is the age in years.
- 3) An internal deposition of radioactive material where, on the basis of a preliminary internal dosimetry measurement, the exposure received over a period of one year will exceed the annual occupational exposure limits.

Type B radiation occurrences are usually investigated by a committee established by the manager of the facility involved. The Richland office of the AEC must approve of the committeemen selected. A formal report is also issued.

6.3 Type C

- 1) Conditions existing where exposure meeting the criteria in A or B above were narrowly averted.
- 2) Internal deposition of radioactive materials where the estimated exposure received over the period of a year will exceed five percent of the annual occupational exposure limits.
- 3) An unplanned single exposure exceeding 1 rem to the whole body, 6 rems to the skin of the whole body, or 15 rems to the hands, forearms, feet or ankles.
- 4) Measurable deposition occurred in five or more persons but the limit set forth in item 2) above was not exceeded.

- 5) Radioactive materials may have been released to the atmosphere or to open roads at a rate exceeding 100 times established release controls.
- 6) A formal investigation report is considered necessary by the Personnel Protection Operation to provide an adequate radiation protection record.

A Type C occurrence is investigated by a committee chosen by the manager of the facility involved and a report compiled on a pre-printed form. This report includes an orderly presentation of the pertinent facts of the occurrence, a statement of conclusions of the investigators as to causes and a list of actions to be taken to minimize consequences and to prevent recurrence.

C. ENVIRONMENTAL PROTECTION

The purpose of the Hanford Environmental Protection Program is to prevent significant radiation exposure of people off-site as a consequence of plant operations. This purpose is accomplished by controlling the off-plant release of radioactive materials. In the operation of the Waste Management Facility it is necessary to conform to the interest of those AEC Manual Chapters pertaining to the protection of individuals and population groups in uncontrolled areas. The maximum permissible dose for both external and external exposure to people off-site is stated in RL-AEC Manual Chapter 0524 Appendix II and is shown below.

<u>Type of Exposure</u>	<u>Dose (rem/year)</u>	
	<u>Based on maximum exposure of individuals</u>	<u>Based on the average exposure of a suitable sample of the exposed population</u>
Whole body, or gonads	0.5	0.17
Thyroid, bone, or GI tract	1.5	0.5

In addition to limits for total radiation exposure, AEC Manual Chapter 0524 also sets limits for radioactive isotopic concentrations in air and water (see Table XVII-1B). The limits for total radiation exposure and for radioactivity concentration in air and water are applicable to the operation of the total AEC facilities at Hanford. Radioactive Waste Disposal Guides, RL AEC Manual Chapter 0510 and RL Manual Appendix 0510, were developed to govern the waste disposal practices for the operation of single or multiple facilities at Hanford within these established limits. The major portion of the Environmental Protection Program is concerned with operating within the requirements of the Waste Disposal

Guides. Serious loss of off-site radiation exposure control would most likely occur with the uncontrolled release of radioactive liquid and gaseous effluents from the operation of the Waste Management facilities.

1. Radioactive Liquid Wastes

This section summarizes key features of the Radioactive Waste Disposal Guides and their impact on Waste Management Operations. Details of waste disposal controls are presented in references 25 and 27.

- 1) "Radioactive liquid wastes discharged into or onto the ground should be limited to the lowest practical amount". This guide is directly related to objective number four of the Waste Management Program, "Reduce to a minimum the amount of radioactive waste dispersed to the environs".
- 2) "The capability of quantitatively measuring actual releases of radioactive liquid wastes to the ground should be maintained". "Representative measurements should be made and documented for all radioactive liquid wastes discharged to ground, along with identification of the radionuclides so disposed". Operation within these guides is assured by sampling, analysis and volume measurement of the streams discharged to the ground. Samples are analyzed for total radioactivity as well as for long-lived radioisotopes of concern (e.g., Sr-90, Cs-137).
- 3) "Continuous instrument monitoring should be provided for all effluent streams having the capability of exceeding the release guides. An alarm should be used in conjunction with instrument monitoring to signal release rates in excess of operating controls". Following this guide has become an important environmental safeguard. Alternate disposal methods or retention procedures can often be initiated promptly upon detection of abnormal levels of radioactive materials in liquid effluent streams.
- 4) "Each waste stream should be evaluated to determine compatibility with the proposed disposal facility and to assure adequate fission product retention. The effect of combining wastes should be evaluated before using a common disposal facility. Whenever practical, low activity wastes should not be discharged with higher activity wastes". "Characteristics of wastes, affecting the use-continuity of the disposal site, including radioactive and non-

radioactive materials, physical and chemical composition, volume flow rate should be defined. Permissible variations of each characteristic of the waste should also be defined". Special consideration should be given to liquid wastes which are immiscible with water". These guides have several obvious environmental protection points but in addition provide bases for practical methods of administering disposals.

- 5) "The number of subsurface liquid disposal sites for materials with biological significance and long half-lives should be kept to a minimum and should be identified. Liquid wastes exceeding 100 $\mu\text{Ci/ml}$ (high level), of relatively long lived radionuclides, should be contained and not discharged into the ground". The disposal in subsurface facilities is restricted, in practice, to those effluent streams containing less than 100 microcuries of spectrum activity or 2 microcuries of strontium-90 per milliliter of wastes. In this context, "spectrum activity" signifies fission products having concentration ratios approximating those present in Hanford fuels three to twelve months after reactor discharge.
- 6) "Liquid wastes discharged to large open ponds should be essentially free of radioactive materials. Concentrations of 5×10^{-5} $\mu\text{Ci/ml}$ (low level) should not be routinely exceeded". "Other than cooling water, disposal of liquid radioactive wastes should be subsurface facilities only". "Leaking radioactive liquids to open pools or ponds can lead to serious contamination spreads by wind borne residues from evaporation and/or filtration. The problem becomes complicated by pond-edge vegetation concentrating radioactive materials and by subsequent feeding of animals, particularly water fowl, on this vegetation. Even in the design of new or modified cooling water effluent lines, consideration is given to subsurface disposal, since experience has shown these streams become contaminated even when the probability appears to be very low.
- 7) "Liquids should not be discharged to facilities intended for the disposal of radioactive solid waste". The leaching of the solid waste by the liquids could mean loss of control of radioactive materials entering ground water.
- 8) "Surveillance over the movement of radioactive materials from underground disposal facilities should be maintained by monitoring the ground water from adjacent wells. Additional control measures, or termination of disposal should be effected when analysis of well water shows that radio-

nuclides such as cobalt-60, cesium-137 and strontium-90 intended for long-term retention by the soil are approaching one-tenth of their maximum permissible concentration as indicated in Table XVII-1 B." This surveillance is carried out primarily by Battelle Northwest Laboratory personnel who advise on the additional control measures to be taken.

2. Gaseous Radioactive Wastes

The Radioactive Waste Disposal Guides include the following definition: "Gaseous radioactive wastes are radioactive particulates, mists, and/or gases, contained in effluents released to the environment", (atmosphere). Key guides on these wastes are presented with comments on their application in Waste Management operations.

- 1) "Radioactive wastes released to the atmosphere should be minimized to the fullest extent technically and economically feasible". Here again is guidance on making efforts to achieve minimum releases rather than only striving to remain under prescribed levels of environmental pollution.
- 2) "Gaseous effluents should be filtered or otherwise controlled so on-site concentrations do not exceed the Standard in Table XVII-1 B." A double filtration system is maintained in Waste Management facilities that adequately controls the atmospheric concentrations under nearly all operating conditions.
- 3) "The guide for total release of iodine-131 from all 200 Area facilities is 500 curies per calendar quarter". The guides for effluent release from each stack in the 200 Areas are:

<u>Radionuclide</u>	<u>Release Guide (Ci/week)</u>	
	<u>200-ft. Stack</u>	<u>Short Stack or Vent</u>
Strontium-90	1	1×10^{-1}
Iodine-131	20	3
Plutonium (total)	1×10^{-2}	1×10^{-3}
Uranium (natural)	4×10^{-2}	4×10^{-3}
Total of others (except tritium, carbon-14 and noble gases)	20	2

*The policy is to strive to keep routine release at or below 10 percent of these values.

The ARHCO release limits are ten percent of the listed values and prompt corrective measures become necessary whenever data indicate ten percent value is likely to be exceeded. For design of effluent disposal equipment, the ten percent values are considered as the maximum permissible emission rates.

- 4) "Additional release guides should be developed when and where other radionuclides become present in concentrations that release might contribute significant exposure to individuals in uncontrolled areas". This guide would become pertinent upon consideration of handling different radioactive wastes than those under consideration at the time of this writing.
- 5) "Continuous instrument monitoring should be provided for gaseous effluent streams having a significant probability of exceeding the release guide rates of emission. An alarm should be used in conjunction with instrument monitoring to signal releases in excess of operational controls". This type of instrumentation is in place and operating. Corrective measures need to be taken upon sounding of the alarm.
- 6) "Continuous sampling capability should be provided for gaseous effluent streams having a significant probability of exceeding one percent of a release guide value". "The capability of quantitatively measuring any radionuclide having a significant probability of being in a gaseous effluent in concentrations of one percent of release guide value or in concentrations that release might contribute significant exposure to individuals in uncontrolled areas". The sampling and analytical program meets the intent of these guides and reports the quantity of radioactive materials released to the atmosphere from the disposal of gaseous wastes to the RL AEC.

3. Other Aspects of Contamination Control

The most likely ways losses of off-plant radiation exposure control would be sustained are through releases of radioactive liquid or gaseous wastes. However, there are other ways control might be lost that are worthy of brief review.

3.1 Solid Waste

The disposal of solid radioactive wastes by burial has little direct relationship to possible significant radiation exposure of people off-site, since contamination control precautions taken for protection of the plant site and personnel adequately prevent loss

of control off-site. However, due to the quantity of radioactive material deposited in 200 Area burial grounds and cribs, control measures will be necessary at the disposal locations of both solid and liquid waste for many generations. These control measures include limitations on access and on use of the land. The integrity of a terminated disposal site needs to be maintained to provide control of vegetation and animals, soil stabilization, adequate back-fill, and visibility of site boundary markers. Portions of the Radioactive Waste Disposal Guides (RL AEC Manual Chapter 0510) pertain directly to solid wastes and the traditional solid waste disposal methods follow the guidance provided.

3.2 Containers, Vehicles, and Personnel

The loss of control of radioactive materials from Waste Management facilities could result from undetected contamination on the surfaces of containers, vehicles, and personnel transported off-site. In general, the occupational protection procedures supply adequate directions for contamination control within the plant and prevent transport of contamination off-site. Guidance on the packaging, shipping, receiving, and transferring of radioactive material is given in RL AEC Manual Chapter 0550, Part III, Chapter 2 Appendix. This guidance is based primarily on regulations promulgated by the Interstate Commerce Commission (ICC), Title 49, Code of Federal Regulations, Parts 71-73. The ICC regulations form the basis for all other domestic regulations concerning radioactive materials in transport. Radiation procedures at individual facilities and provisions of the ARHCO Manual of Radiation Protection Standards and Controls follow the guidance of RL AEC Manual Chapter 0550 for intercontractor shipments and off-site shipments as well as providing rules for shipment between ARHCO facilities.

3.3 Explosion, Fire, Enemy Action, Earthquake

Explosion, fire, enemy action, earthquake, etc could result in the loss of control of radioactive materials from Waste Management facilities. Although radiation exposures to personnel resulting from such catastrophic events are not regulated by the same limits as radiation exposure from operational events, effort needs to be made to minimize the probability of occurrence and/or reduce the severity of the potential consequences. Safeguards were taken in the design of Waste Management facilities that were specifically directed toward prevention of serious spreads of contamination even from these events. Furthermore, operating procedures need periodic review to assure adequate off-site radiation control under any circumstance.

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PART VII, Continued

SAFETY

CHAPTER XVIII

DECONTAMINATION OF SURFACES

By

N. P. Nisick

Personnel Protection Operation

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PART VII: SAFETY, Cont.CHAPTER XVIIIDECONTAMINATION OF SURFACES

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PART VII: SAFETY, Cont.CHAPTER XVIIIDECONTAMINATION OF SURFACES

Decontamination is employed at B-Plant for the removal of all or part of the residual radioactive contamination from operating equipment and areas to improve working time limits and to control the spread of contamination. This chapter presents a summary of information concerning decontamination methods. The ability to decontaminate a surface is determined by the material the surface is made of, protective coatings (if any), chemical composition of the contaminant, the length of time the surface has been contaminated, and the amount of physical effort used in decontamination.

A. GENERAL1. Introduction

The need requiring the removal of radioactive contamination from equipment or areas varies widely. The amounts and concentrations of radioactivity within B-Plant cover a wide range and include some of the highest concentrations on site. The bulk of the radioactivity entering the plant is acid fission product salt waste originally generated at the Purex Plant. This fission product waste will pass successively through feed treatment, solvent extraction, and concentrating vessels with the more noxious fractions going to in-canyon tank storage and the less noxious but more voluminous fractions going to ITS (in-tank solidification) at one of the 200-E Area tank farms.

Because of the nearly universal use of stainless steel in the construction of all B-Plant process equipment, decontamination of process equipment is largely a matter of removing contamination from stainless steel. This particular material has received considerable study, and considerable success has been realized. The structural and support components of the plant are fabricated almost entirely of mild steel or reinforced concrete. These materials if not covered with a protective coating are extremely difficult, if not impossible, to decontaminate. In the processing areas, all non-stainless steel components have been painted. This permits the use of reagents for decontamination that might otherwise react with the unprotected surface.

Decontamination techniques developed to date have proven highly successful for many specific needs, but may not be the optimum techniques for all new B-Plant application. The following sections describe reagents and techniques which have been used successfully for decontamination. Continued experience and study of decontamination should lead to even better reagents and techniques.

2. Terminology

The procedure of decontamination has given rise to the use of some special terminology. The term "decontamination" is used to designate the removal of radioactive material from solid surfaces.

"Contamination" or "contaminants" are the radioactive materials present on the solid surface. Decontamination methods and techniques are the means utilized to remove the radioactive material. They may be generally classified as (a) physical--total or partial removal of the contaminate surface; (b) chemical--reaction with the radioactive material or the larger mass of the associated non-radioactive materials to convert them to a soluble or extractable condition; and (c) physicochemical--suspension by surface-active agents.

3. Principles of Decontamination

A review of decontamination techniques reveals many conflicting and varied decontamination procedures. One can conclude that no "cut and dried" methods for decontamination exist and no reagent is universal for decontamination. In most cases the best decontamination agent for a specific problem must be developed empirically. However, the lack of exact knowledge does not call for a random approach to decontamination.

The mechanisms governing surface contamination and decontamination are not yet too well understood. However, laboratory tests and decontamination of process equipment indicate some of the principles of contamination-decontamination to be as follows:(3)

- a. The art of good decontamination requires the control of radioactivity at all times. Planning and the subsequent use of a well-thought-out decontamination procedure is helpful no matter how small the job.
- b. Surfaces contacted by "spills" should be flushed or scrubbed before the activity has had a chance to go to dryness. This applies also to the interior of process vessels.
- c. Removal of a thin film or layer of the contaminated surface is necessary for achievement of maximum decontamination in the shortest period of time.
- d. Complexing, chelating, and metathesizing agents are of little value after the activity has gone to dryness.
- e. Successive use of several reagents over short periods of time (one to two hours) appears to produce better decontamination than the use of a single reagent over an extended period of time (twelve to sixteen hours). It appears that one reagent may prepare a contaminated surface for attack or removal of radioactivity by a second reagent that follows.

- f. Good agitation (in many instances good old "elbow grease") is necessary for the successful use of any reagent. Stagnant or static surface films produce little or no decontamination.
- g. The efficiency of a given reagent usually increases as the temperature increases; however, the maximum practical temperature may be limited by corrosion or boiling.
- h. Dry-solids contaminants such as dusts should not ordinarily be placed into solution to expedite removal. Vacuum cleaning or flushing with a reagent that does not appreciably dissolve or convert dry solids into the ionic form is much more desirable.
- i. In general, surfaces may be protected from radioactive contaminants by reduction of the surface free energy (used here as analogous to ease of wetting). Coating exposed surfaces with relatively non-wetting membranes such as paint or non-polar plastics is always desirable.
- j. Strippable coatings or other inert membranes where such application is feasible presents the easiest and perhaps the most successful method for decontamination at this time.

4. Factors Influencing Decontamination

The following are some of the factors affecting decontamination procedures in B-Plant.

- a. The inactive anions and cations in the B-Plant process solutions do not normally form insoluble compounds. Hence, any deposits formed by exceeding the saturation point should be removable with water flushes.
- b. B-Plant incorporates design for confining process materials within the interior or processing equipment.
- c. The employment of some continuous-flow equipment in the B-Plant process necessitates some mechanical complexity with the associated possibility of occasional need for equipment replacement and adjustment.

5. Provisions for Application of Decontamination Procedures

5.1 Protective Coatings

Structural elements in the plant have been either protected with a chemically resistant coating such as "Amercoat" or constructed on stainless steel. Thus, all exposed concrete within the cells has been protected with "Amercoat". Structural steel elements and certain equipment fabri-

cated from carbon steel have been protected with "Amercoat". This type of construction facilitates removal of the gross radioactivity by simple water flushing.

5.2 Materials of Construction

Process equipment normally wetted by process solutions has been fabricated almost entirely from stainless steel. Some important but relatively small elements utilize alloys such as Stellite or fluorocarbon plastics. All of these materials have exceptionally good resistance to chemical attack and are readily decontaminable.

5.3 Design Features Facilitating Decontamination

All equipment normally in contact with process solutions is designed to be fully drainable and flushable. The process equipment also incorporates seals on all pump and agitator shafts, which, in conjunction with the vacuum vent system, effectively confine radioactive material to the interiors of process equipment.

B. STAINLESS STEEL

The process equipment components (tanks, lines, pumps, etc.) of the B-Plant are fabricated almost entirely from the 300 series stainless steels. The specific type employed has been chosen on the basis of corrosion resistance and the type of fabrication required. The decontamination of stainless steel is consequently of prime interest. Since the problem of decontamination is solved by an empirical approach, discrimination between the types of 300 series stainless steel is not justifiable.

The contamination of stainless steel can be placed in four categories: (a) alpha contaminants on internal surfaces, (b) alpha contaminants on external surfaces, (c) beta and/or gamma contaminants on interior surfaces, and (d) beta and/or gamma contaminants on exterior surfaces. The recommended procedures for removal are based on empirical 200 Area results. In general, the least corrosive effective decontaminant should be used so that attack upon the equipment may be maintained at a minimum.

Internal surfaces should be first in the sequence of decontamination because of the greater freedom and control associated with this operation and because these surfaces contain large amounts of easily removable contamination. To produce results of the greatest value, decontamination flushes should be routed from areas of low radioactivity into areas of high radioactivity. Decontaminants that are combined with process streams for disposal must be compatible with the process solutions so that normal plant production is not interrupted. Cribbable decontaminating solutions must not contain reagents at the time of cribbing that have an adverse affect on the removal of radioactive material by the soil. (5)

1. Alpha Contamination

1.1 Internal

Alpha (notably U and Pu) contamination inside process vessels assumes relative little importance and only where the fission-product beta and gamma activities associated with it have reached comparatively low levels. Little U and Pu will normally be associated with the material being processed.

Nitric acid is the preferred decontamination reagent, as the chemistry of the principal alpha contaminants favors solution in this medium. Sixty per-cent acid is the most effective, although lesser concentrations have been used successfully. Normally a temperature of 25 to 50°C is adequate. Generally, physical and chemical principles indicate that higher temperatures would be more effective although there is very little practical decontamination experience to support this.

1.2 External

The problem of decontaminating external surfaces is complicated by the possibility of extending the contamination to otherwise clean areas. Therefore, caution must be exercised since the need for decontaminating surfaces adjacent to those originally contaminated may be increased by unrestricted and uncontrolled flushing.

The following precautions should be observed in decontaminating external surfaces:

- (a) The redistribution of existing contamination should be limited to the smallest possible area.
- (b) Normally the surface should not be flooded with water or other decontaminating agents.
- (c) The surrounding surfaces which might be wetted during the decontamination treatment should be protected.
- (d) Contaminated materials such as tools, rags, swabs, or gloves should not be placed in uncontaminated areas. Disposable containers such as bags or boxes should be used for storing all cleaning supplies.

The choice of decontamination reagents is based on factors such as the original surface finish, necessity for preserving the finish, and limitations of drainage facilities for solvents or highly radioactive chemical agents. The materials listed below have been found to be useful for room temperature application:

- (a) Nitric 15% to 57%
- (b) Oxalic 5% Nitric 3%
- (c) Caustic 25%
- (d) Permanganate-bisulfite. The sequence of operations consists of scrubbing the surface with saturated KMnO_4 solution, removing the KMnO_4 by wiping, scrubbing the surface with 10% NaHSO_3 solution, and flushing the surface with water.
- (e) Organic solvents; e.g. Stoddard Solvent, CCl_4 .
- (f) Abrasives; e.g. Bon Ami
- (g) Detergents; e.g. Tide
- (h) Proprietary reagents; Turco 4306-B, 4502, 4518

2. Beta and Gamma Contamination

2.1 Internal

Since most of the surfaces are contaminated with beta and/or gamma contaminants, it is general practice to use nitric acid for the first flush. Although beta and/or gamma contaminants are not completely removed by nitric acid, it is believed that it is useful in removing the major portion of non-radioactive materials constituting the film in which the radioactivity is bound.

Oxidizing, reducing, and complexing agents have been used successfully. A solution of sodium tartrate in sodium hydroxide has been found to be effective. The concentrations of sodium hydroxide and sodium tartrate are not well defined, but 50 to 20 percent NaOH and 1.25 to 10 percent $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ have been recommended. The addition of hydrogen peroxide to the alkaline tartrate improves its efficiency.(8) Oxalic acid, citric acid, and nitric acid give approximately equal decontamination results. HNO_3 is often preferred because it is the cheapest and most readily available agent.

The use of mixtures of nitric acid and sodium fluoride to remove the final contamination is often necessary. A mixture of 3 percent fluoride and 20 percent nitric used at room temperature has been found to be an effective reagent. It decontaminates rapidly without excessive corrosion of stainless steel equipment. The degree of corrosion and of decontamination is not necessarily related.(9) Although some surface corrosion may be necessary for the removal of tightly bound contaminants, corrosion is not always accompanied by good decontamination. At higher temperatures, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (ANN) is added for corrosion control.

Experience at Hanford has shown that a basic solution of permanganate (1.5% KMnO_4 , 0.5% NaOH) is very effective for the removal of fission product contamination, especially of rutherfium.(2) The rutherfium is believed to be oxidized to a soluble ruthenate, probably RuO_2 which is soluble in a basic solution.(6)

For successful internal decontamination, frequent changes of decontamination solutions are more beneficial than extended contact time. It has been found that the most rapid dissolution of radioactive contaminants in the decontamination solutions occurs in from 12 minutes to 2 hours, depending upon the solution used.(7)(8) Considerations governing the frequency of solution change include the cost of the disposal of the solution. Adequate agitation is a prime requisite of successful internal decontamination and elevated temperatures usually add to the effectiveness of the flushing solution.

In addition to these liquid decontaminants, live steam seems to assist materially in the decontaminating process. The mechanism of decontamination with steam is not fully understood. It is conjectured that it penetrates the minute recesses inaccessible to liquids. It is also believed that it acts by the exertion of some abrasive action.

2.2 External

The plant areas in which external beta and gamma contamination is of potential concern coincide with those in which beta-gamma internal contamination levels are high. This problem is the most difficult of the four discussed because (a) the flush solution is not confined by equipment, and (b) precautionary measures to restrict the spread of contamination by the decontamination agents cannot be employed nearly as effectively as with alpha contamination because the range of the gamma rays often prohibits the approach of personnel to the contaminated surfaces. The decontaminating agents recommended for the removal of internal contamination (under B 2.1 above) can also be employed for the removal of external contamination. To assist in carrying the contamination from the decontaminated areas, sump, or drain, the entire area undergoing decontamination should be liberally flushed with water as a concluding treatment.

The method of applying external decontaminating agents will vary widely with the amount of radioactivity present in the area to be decontaminated. If the radiation level is sufficiently low to permit entry of personnel, the solutions may be applied manually by mop or preferably by brush or broom. This application may be followed by steam cleaning and water flushing or water flushing alone.(2)

If the radiation level does not permit entry by personnel, the decontamination solutions may be applied from the closest point of vantage by means of a pump or jet and a spray nozzle. Repeated applications of the decon-

tamination solutions followed by water flushes or steam cleaning and water flushing usually reduces the radiation sufficiently to permit eventual entry by personnel.

3. Procedure for Decontamination

The general procedure for internal decontamination usually starts with a nitric acid flush to remove any process solutions present. Decontamination itself is then accomplished by successive flushes with suitable decontaminating agents kept in the vessels with agitation, generally at elevated temperatures for the proper period of time.

External decontamination is accomplished by application of a suitable reagent by the most effective means available. Abrasive action applied either manually or by some other means, such as high pressure water, usually assists in contamination removal. The contamination loosened from the surface should be flushed away with water.

In order to select a suitable decontamination reagent, a gamma scan of the contamination may be used to determine the specific fission products present.

C. OTHER MATERIALS OF CONSTRUCTION

1. Iron and Carbon Steel

Iron and carbon steel have been employed for machine and structural elements (e.g. electric motors, jumper braces) which are not normally wetted by process solutions. As installed, these elements are protected by a chemically resistant coating, "Amercoat". The type of contamination expected on these surfaces follows the pattern given in Section C of this chapter. Experience with decontamination of unprotected iron or steel has been generally disappointing. Complete removal of the contaminated piece usually is the most practical solution to the problem.

Nitric acid, although effective in decontaminating stainless steels, is not effective in the decontamination of unprotected iron and steel. The degree of readsorption of the highly diluted, radioactive elements by the freshly formed, unoxidized metallic surface appears to create a practical obstacle which limits the decontamination. In addition to the ineffectiveness of acidic solutions, their use increases the difficulty of successfully removing the contamination with subsequent decontaminating agents because of the surface-etching effect of the acid.

Alkaline solutions (sodium carbonate, alkaline permanganate) and detergents have been found the most effective of the agents tried.(2)

2. Concrete

Concrete, in the absence of a protective surface coating, retains contaminants to a high degree. Chemical or physicochemical reagents have not been effective in removing either chemically fixed or physically adsorbed radioactivity. B-Plant has been designed and constructed on the basis that concrete surfaces will always be protected by a chemically resistant coating (Amercoat). In the event of contamination which penetrates through the concrete base material, only two courses appear practical: (a) physical removal of the contaminated surface, or (b) shielding of the contaminated concrete surface to permit necessary maintenance work in the immediate area of contamination.

Experience has indicated that spots of gross contamination imbedded in unprotected concrete may be reduced somewhat by repeated alternate treatments with sodium carbonate paste (or solution) and dilute (3 to 5 percent) nitric acid. The effervescing action produced by the two reagents helps to lift some of the contamination out of the concrete so that it can be flushed away with water. However, because of the destructive action of the nitric acid on the concrete, part of the remaining contamination is usually forced deeper into the concrete, thus making complete removal of the contamination practically impossible.

3. Glass

Glass finds its greatest application in the construction of laboratory equipment. Accordingly, the type of contamination may vary widely. A five percent solution of NH_4HF_2 has been effective in decontaminating glass at ORNL. Etching does not result if the time of contact is kept to a minimum (a few minutes).⁽⁴⁾

Nitric acid in concentrations of 20 to 60 percent is also used effectively for decontaminating laboratory glassware. The more concentrated solutions are used for soaking the equipment while the less concentrated are usually used for swabbing. Laboratory cleaning solution (95 percent sulfuric acid saturated with sodium dichromate) is another effective agent for decontaminating glassware.

4. Wood

Wood is utilized primarily for structural or equipment items, such as office fittings and furniture, not normally subject to contamination. Occasional temporary requirements may result in the introduction of wood into process or laboratory areas. Decontamination of wood is extremely difficult because of its porous, absorbent structure.⁽⁴⁾ Protection from fixation of activity is dependent upon the applied protective coating. In the event that contamination penetrates the protective coating, either partial or complete removal of the wood appears to be the most practical and economical procedure.

D. PROTECTIVE COATINGS

Protective coatings employed in B-Plant for application to steel and concrete surfaces are Amercoat No. 33, 55, and 74. These coatings provide a protective film that is smooth, chemically resistant to process and decontaminating solutions, and not readily wetted by them.

Since the protective films are the only barrier to essentially permanent contamination of the base materials, it is important to use a decontaminant which will inflict the minimum damage to the coating. Highly reactive materials such as nitric acid or caustic soda should be used as sparingly as possible and only in dilute solutions. The following agents, listed in order of preference, are recommended:

- a. Water
- b. Detergent solutions
- c. Complexing agents, oxalates, citrates, tartrates
- d. Alkaline permanganate-oxalic acid. This requires direct manual application of 1-1/2 percent KMnO_4 -1/2 percent NaOH solution for a 5 to 10 minute period followed by an application of 1 to 2 percent NaOH solution and, in turn, by a water flush. Manual application of 5 percent oxalic acid followed by a water flush completes the procedure.

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TABLE II-36 (Continued)

Weight, Grams Per Ton of Uranium

Element	1.5 y	2 y	3.5 y	5 y	7.5 y	10 y	20 y
Ge	.0079	.0079	.0079	.0079	.0079	.0079	.0079
As	.0025	.0025	.0025	.0025	.0025	.0025	.0025
Se	1.656	1.656	1.656	1.656	1.656	1.656	1.656
Br	.6353	.6353	.6353	.6353	.6353	.6353	.6353
Kr	11.28	11.23	11.07	10.92	10.75	10.54	10.06
Rb	11.61	11.66	11.82	11.96	12.13	12.35	12.82
Sr	30.57	30.34	29.66	29.02	28.19	27.02	23.70
Y	15.79	15.78	15.78	15.78	15.78	15.78	15.78
Zr	114.00	114.21	114.87	115.52	116.35	117.52	120.84
Nb	.0501	.0072	.0001	.0001	.0001	.0002	.0003
Mo	98.69	98.77	98.78	98.78	98.78	98.78	98.78
Tc	24.81	24.81	24.81	24.81	24.81	24.81	24.81
Ru	49.60	49.29	48.80	48.63	48.55	48.53	48.53
Rh	13.43	13.43	13.44	13.44	13.44	13.44	13.44
Pd	11.04	11.35	11.84	12.01	12.08	12.10	12.10
Ag	.5791	.5791	.5791	.5791	.5791	.5791	.5791
Cd	.4890	.4890	.4890	.4890	.4890	.4890	.4890
In	.0669	.0669	.0669	.0669	.0669	.0669	.0669
Sn	1.009	1.009	1.009	1.009	1.009	1.009	1.009
Sb	.3623	.3395	.2859	.2493	.2181	.1931	.1732
Te	13.58	13.60	13.65	13.69	13.73	13.75	13.77
I	6.766	6.769	6.771	6.771	6.771	6.771	6.771
Xe	142.64	142.64	142.64	142.64	142.64	142.64	142.64
Cs	76.47	76.07	74.90	73.79	72.39	70.41	64.77
Ba	38.32	38.72	39.89	41.00	42.40	44.38	50.02
La	35.60	35.60	35.60	35.60	35.60	35.60	35.60
Ce	74.78	72.25	68.92	68.05	67.79	67.74	67.73
Pr	32.38	32.38	32.38	32.38	32.38	32.38	32.38
Nd	110.37	112.90	116.23	117.11	117.37	117.42	117.42
Pm	7.784	6.819	4.586	3.083	1.817	.8214	.0583
Sm	15.99	16.95	19.17	20.65	21.00	22.87	23.53
Eu	1.302	1.295	1.284	1.284	1.292	1.313	1.397
Gd	.5177	.5302	.5567	.5724	.5843	.5932	.6040
Tb	.0179	.0179	.0179	.0179	.0179	.0179	.0179
Dy	.0028	.0028	.0028	.0028	.0028	.0028	.0028
RE	278.75	278.75	278.75	278.75	278.75	278.75	278.75
Np	3.420	3.420	3.422	3.424	3.429	3.436	3.469
Am	.3291	.4283	.7095	.9684	1.282	1.691	2.648

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TABLE II-37

COMPOSITION OF IRRADIATED 0.947% ENRICHED URANIUM

1000 MWd/T, 10 MW/T

Element	Discharge	Weight, Grams Per Ton of Uranium			
		90 d	120 d	180 d	270 d
Ge	.0088	.0088	.0088	.0088	.0088
As	.0035	.0028	.0028	.0028	.0028
Se	1.848	1.849	1.849	1.849	1.849
Br	.7088	.7088	.7088	.7088	.7088
Kr	12.78	12.74	12.73	12.70	12.67
Rb	12.69	12.73	12.74	12.76	12.80
Sr	43.94	37.30	36.36	35.28	34.60
Y	21.23	19.27	18.84	18.26	17.83
Zr	129.32	127.92	127.59	127.11	126.76
Nb	5.688	5.027	4.040	2.405	1.002
Mo	89.07	98.63	101.32	105.09	107.96
Tc	25.59	26.69	26.69	26.69	26.69
Ru	64.27	58.17	57.42	56.56	55.94
Rh	7.973	13.39	13.98	14.54	14.78
Pd	10.08	10.76	10.92	11.22	11.60
Ag	.7201	.6950	.6950	.6949	.6949
Cd	.5367	.5572	.5570	.5568	.5567
In	.0678	.0724	.0726	.0728	.0729
Sn	1.153	1.135	1.134	1.133	1.132
Sb	.5720	.4827	.4772	.4662	.4501
Te	17.34	15.26	15.20	15.13	15.10
I	8.445	7.316	7.396	7.475	7.517
Xe	158.93	159.17	159.17	159.17	159.17
Cs	83.19	86.00	85.92	85.76	85.53
Ba	48.11	41.52	41.56	41.70	41.94
La	40.47	39.58	39.57	39.57	39.57
Ce	112.21	101.13	98.50	94.71	90.70
Pr	28.51	33.98	34.92	35.71	35.97
Nd	95.27	106.51	108.23	111.25	115.00
Pm	10.95	11.90	11.65	11.15	10.44
Sm	13.21	14.34	14.60	15.10	15.80
Eu	1.566	1.500	1.496	1.490	1.483
Gd	.4251	.5416	.5466	.5542	.5641
Tb	.0213	.0208	.0207	.0207	.0207
Dy	.0026	.0031	.0032	.0032	.0032
RE	302.64	309.51	309.54	309.56	309.55
Np	31.28	3.840	3.840	3.840	3.840
Am	.0214	.0917	.1149	.1611	.2296
Cm*	.7923	.5661	.4985	.3864	.2636

*Curium values are in milligrams

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TABLE II-37 (Continued)
Weight, Grams Per Ton of Uranium

Element	1 y	2 y	5 y	10 y	20 y
Ge	.0088	.0088	.0088	.0088	.0088
As	.0028	.0028	.0028	.0028	.0028
Se	1.849	1.849	1.849	1.849	1.849
Br	.7088	.7088	.7088	.7088	.7088
Kr	12.64	12.51	12.16	11.73	11.21
Rb	12.83	12.96	13.30	13.73	14.25
Sr	34.31	33.73	32.26	30.04	26.35
Y	17.64	17.54	17.54	17.54	17.54
Zr	126.66	127.01	128.48	130.70	134.39
Nb	.3760	.0079	.0001	.0002	.0004
Mo	109.16	109.85	109.87	109.87	109.87
Tc	26.69	26.69	26.68	26.68	26.68
Ru	55.55	54.68	53.93	53.83	53.83
Rh	14.83	14.84	14.84	14.84	14.84
Pd	11.94	12.80	13.55	13.65	13.65
Ag	.6949	.6949	.6948	.6948	.6948
Cd	.5567	.5568	.5568	.5568	.5568
In	.0729	.0729	.0729	.0729	.0729
Sn	1.132	1.131	1.131	1.131	1.131
Sb	.4338	.3792	.2776	.2142	.1917
Te	15.11	15.14	15.24	15.30	15.33
I	7.534	7.549	7.550	7.550	7.550
Xe	159.17	159.17	159.17	159.17	159.17
Cs	85.28	84.36	81.82	78.05	71.77
Ba	42.18	43.10	45.65	49.41	55.69
La	39.57	39.57	39.57	39.57	39.57
Ce	87.49	80.32	75.67	75.33	75.32
Pr	36.01	36.02	36.02	36.02	36.02
Nd	118.17	125.33	129.98	130.32	130.33
Pm	9.745	7.480	3.382	.9010	.0639
Sm	16.50	18.75	22.82	25.25	25.99
Eu	1.476	1.458	1.444	1.473	1.557
Gd	.5737	.6032	.6486	.6718	.6849
Tb	.0207	.0207	.0207	.0207	.0207
Dy	.0032	.0032	.0032	.0032	.0032
RE	309.56	309.56	309.56	309.56	309.56
Np	3.840	3.842	3.846	3.858	3.902
Am	.3011	.5659	1.278	2.232	3.495
Cm*	.1761	.0378	.0010	.0006	.0005

*Curium values are in milligrams

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TABLE II-38
COMPOSITION OF IRRADIATED 0.947% ENRICHED URANIUM
1200 MWd/T, 10 MW/T

Element	Weight, Grams Per Ton of Uranium				
	Discharge	90 d	120 d	180 d	270 d
Ge	.0107	.0107	.0107	.0107	.0107
As	.0040	.0034	.0034	.0034	.0034
Se	2.203	2.203	2.203	2.203	2.203
Br	.8439	.8439	.8439	.8439	.8439
Kr	15.21	15.16	15.15	15.12	15.08
Rb	15.09	15.14	15.16	15.18	15.22
Sr	51.12	44.02	43.01	41.85	41.11
Y	24.96	22.75	22.28	21.64	21.16
Zr	154.25	152.59	152.21	151.67	151.29
Nb	6.858	5.614	4.484	2.653	1.100
Mo	108.20	119.31	122.31	126.47	129.63
Tc	31.07	32.17	32.17	32.17	32.17
Ru	77.09	70.38	69.54	68.56	67.82
Rh	10.51	16.37	17.01	17.62	17.88
Pd	12.96	13.80	14.00	14.38	14.86
Ag	.9665	.9385	.9385	.9385	.9384
Cd	.6896	.7127	.7125	.7123	.7122
In	.0834	.0883	.0886	.0888	.0889
Sn	1.411	1.392	1.391	1.390	1.388
Sb	.6864	.5927	.5859	.5725	.5528
Te	20.52	18.39	18.30	18.23	18.20
I	9.954	8.860	8.947	9.032	9.079
Xe	190.99	191.25	191.25	191.25	191.25
Cs	100.49	103.25	103.16	102.96	102.67
Ba	56.41	49.83	49.89	50.07	50.36
La	48.33	47.43	47.42	47.42	47.42
Ce	132.73	120.14	117.19	112.86	108.20
Pr	35.03	41.07	42.05	42.88	43.16
Nd	116.03	128.24	130.25	133.76	138.14
Pm	13.23	14.03	13.73	13.14	12.31
Sm	16.27	17.57	17.87	18.46	19.29
Eu	1.949	1.871	1.867	1.860	1.852
Gd	.5743	.7070	.7126	.7212	.7326
Tb	.0278	.0272	.0272	.0272	.0271
Dy	.0036	.0042	.0042	.0042	.0043
RE	364.17	371.09	371.12	371.13	371.14
Np	32.05	4.680	4.680	4.680	4.680
Am	.0415	.1539	.1911	.2649	.3744
Cm*	1.857	1.317	1.159	.8987	.6134

*Curium values are in milligrams.

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TABLE II-38 (Continued)
Weight, Grams Per Ton of Uranium

Element	1 y	2 y	5 y	10 y	20 y
Ge	.0107	.0107	.0107	.0107	.0107
As	.0034	.0034	.0034	.0034	.0034
Se	2.203	2.203	2.203	2.203	2.203
Br	.8439	.8439	.8439	.8439	.8439
Kr	15.04	14.89	14.49	13.98	13.35
Rb	15.27	15.42	15.81	16.32	16.95
Sr	40.78	40.10	38.36	35.72	31.32
Y	20.96	20.85	20.85	20.85	20.85
Zr	151.18	151.62	153.36	156.00	160.39
Nb	.4125	.0086	.0001	.0002	.0005
Mo	130.95	131.71	131.73	131.73	131.73
Tc	32.17	32.17	32.17	32.16	32.16
Ru	67.33	66.23	65.28	65.15	65.15
Rh	17.93	17.94	17.94	17.94	17.94
Pd	15.29	16.38	17.33	17.46	17.47
Ag	.9384	.9383	.9393	.9383	.9383
Cd	.7122	.7123	.7123	.7123	.7123
In	.0890	.0890	.0890	.0890	.0890
Sn	1.388	1.387	1.387	1.387	1.386
Sb	.5328	.4659	.3416	.2640	.2365
Te	18.21	18.25	18.38	18.46	18.49
I	9.098	9.115	9.117	9.117	9.117
Xe	191.25	191.25	191.25	191.25	191.25
Cs	102.37	101.26	98.17	93.64	86.10
Ba	50.66	51.77	54.85	59.39	66.93
La	47.42	47.42	47.42	47.42	47.42
Ce	104.46	96.09	90.66	90.26	90.25
Pr	43.20	43.21	43.21	43.21	43.21
Nd	141.85	150.20	155.64	156.04	156.04
Pm	11.49	8.816	3.986	1.062	.0754
Sm	20.11	22.77	27.56	30.43	31.32
Eu	1.844	1.822	1.803	1.831	1.918
Gd	.7436	.7774	.8303	.8588	.8771
Tb	.0271	.0271	.0271	.0271	.0271
Dy	.0043	.0043	.0043	.0043	.0043
RE	371.14	371.14	371.14	371.14	371.14
Np	4.680	4.682	4.688	4.710	4.779
Am	.4887	.9123	2.052	3.576	5.595
Cm*	.4098	.0881	.0025	.0015	.0013

*Curium values are in milligrams

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TABLE II-39
COMPOSITION OF IRRADIATED 0.947% ENRICHED URANIUM
2200 MWd/T, 11 MW/T

		Weight, Grams Per Ton of Uranium				
Element	Discharge	90 d	120 d	180 d	270 d	1 y
Ge	.0206	.0206	.0206	.0206	.0206	.0206
As	.0071	.0065	.0065	.0065	.0065	.0065
Se	3.849	3.849	3.849	3.849	3.849	3.849
Br	1.464	1.464	1.464	1.464	1.464	1.464
Kr	26.41	26.33	26.31	26.23	26.19	26.12
Rb	26.13	26.21	26.23	26.28	26.34	26.42
Sr	82.33	74.25	73.08	71.72	70.80	70.32
Y	41.23	38.31	37.71	36.91	36.32	36.07
Zr	272.46	269.68	269.10	268.32	267.81	267.73
Nb	10.54	7.387	5.822	3.393	1.394	.5206
Mo	208.33	224.07	227.98	233.35	237.37	239.04
Tc	58.81	60.02	60.02	60.02	60.02	60.02
Ru	146.76	137.18	135.83	134.14	132.62	131.50
Rh	24.62	32.32	33.16	33.96	34.30	34.37
Pd	33.68	35.55	36.05	36.95	38.14	39.18
Ag	2.831	2.784	2.783	2.783	2.783	2.783
Cd	1.816	1.857	1.857	1.856	1.856	1.856
In	.1684	.1754	.1758	.1761	.1763	.1764
Sn	2.914	2.887	2.886	2.883	2.881	2.880
Sb	1.367	1.241	1.227	1.199	1.158	1.117
Te	37.03	34.53	34.43	34.35	34.32	34.34
I	18.03	16.87	16.99	17.10	17.16	17.19
Xe	352.34	352.75	352.75	352.75	352.75	352.75
Cs	187.06	189.78	189.57	189.16	188.56	187.93
Ba	98.34	91.47	91.63	92.03	92.63	93.26
La	87.24	86.25	86.25	86.24	86.24	86.24
Ce	228.89	210.93	206.63	200.05	192.69	186.70
Pr	69.17	76.61	77.75	78.70	79.02	79.07
Nd	221.21	237.86	241.06	246.70	253.74	259.69
Pm	22.77	22.98	22.48	21.51	20.14	18.80
Sm	33.83	35.93	36.44	37.41	38.77	40.11
Eu	4.718	4.581	4.572	4.559	4.541	4.525
Gd	1.643	1.876	1.886	1.902	1.923	1.944
Tb	.0763	.0748	.0747	.0746	.0745	.0744
Dy	.0110	.0126	.0126	.0128	.0129	.0129
RE	669.56	677.10	677.16	677.16	677.15	677.17
Np	44.27	12.34	12.34	12.34	12.34	12.34
Am	.2915	.7297	.8745	1.162	1.589	2.034

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TABLE II-39 (Continued)

Weight, Grams Per Ton of Uranium

Element	1.5 y	2 y	3.5 y	5 y	7.5 y	10 y	20 y
Ge	.0206	.0206	.0206	.0206	.0206	.0206	.0206
As	.0065	.0065	.0065	.0065	.0065	.0065	.0065
Se	3.849	3.849	3.849	3.849	3.849	3.849	3.849
Br	1.464	1.464	1.464	1.464	1.464	1.464	1.464
Kr	25.99	25.86	25.50	25.18	24.80	24.31	23.23
Rb	26.55	26.67	27.03	27.36	27.74	28.23	29.31
Sr	69.73	69.20	67.66	66.19	64.30	61.65	54.09
Y	35.96	35.94	35.94	35.94	35.94	35.94	35.94
Zr	268.06	268.55	270.07	271.55	273.43	276.09	283.65
Nb	.0756	.0109	.0002	.0002	.0003	.0004	.0008
Mo	239.88	240.00	240.02	240.02	240.02	240.02	240.02
Tc	60.02	60.02	60.02	60.02	60.02	60.02	60.02
Ru	129.93	128.84	127.13	126.52	126.28	126.20	126.20
Rh	34.38	34.38	34.38	34.38	34.38	34.38	34.38
Pd	40.73	41.83	43.54	44.14	44.39	44.46	44.47
Ag	2.783	2.783	2.783	2.783	2.783	2.783	2.783
Cd	1.857	1.857	1.857	1.857	1.857	1.857	1.857
In	.1764	.1764	.1764	.1764	.1764	.1764	.1764
Sn	2.878	2.878	2.878	2.878	2.878	2.878	2.877
Sb	1.044	.9796	.8281	.7248	.6365	.5658	.5096
Te	34.38	34.46	34.60	34.70	34.79	34.87	34.92
I	17.21	17.22	17.22	17.22	17.22	17.22	17.22
Xe	352.75	352.75	352.75	352.75	352.75	352.75	352.75
Cs	186.76	185.64	182.50	179.59	176.01	171.08	157.18
Ba	94.43	95.55	98.69	101.59	105.17	110.11	124.02
La	86.24	86.24	86.24	86.24	86.24	86.24	86.24
Ce	178.51	173.26	166.35	164.53	163.98	163.88	163.87
Pr	79.07	79.07	79.07	79.07	79.07	79.07	79.07
Nd	267.88	273.13	280.04	281.86	282.41	282.51	282.52
Pm	16.47	14.43	9.703	6.524	3.844	1.738	.1233
Sm	42.43	44.47	49.17	52.32	54.97	57.03	58.51
Eu	4.498	4.477	4.434	4.414	4.406	4.414	4.487
Gd	1.978	2.008	2.074	2.118	2.157	2.194	2.266
Tb	.0744	.0744	.0744	.0744	.0744	.0744	.0744
Dy	.0129	.0129	.0129	.0129	.0129	.0129	.0129
RE	677.16	677.17	677.17	677.16	677.16	677.16	677.17
Np	12.34	12.34	12.35	12.37	12.39	12.46	12.73
Am	2.869	3.682	5.993	8.118	10.69	14.06	21.92

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TABLE II-40
COMPOSITION OF IRRADIATED 1.25% ENRICHED URANIUM
2200 MWd/T, 11 MW/T

Weight, Grams Per Ton of Uranium						
Element	Discharge	90 d	120 d	180 d	270 d	1 y
Ge	.0199	.0199	.0199	.0199	.0199	.0199
As	.0070	.0063	.0063	.0063	.0063	.0063
Se	3.968	3.968	3.968	3.968	3.968	3.968
Br	1.516	1.516	1.516	1.516	1.516	1.516
Kr	27.36	27.28	27.25	27.21	27.14	27.06
Rb	27.22	27.31	27.33	27.38	27.45	27.52
Sr	85.91	77.36	76.13	74.68	73.71	73.21
Y	42.95	39.95	39.34	38.51	37.89	37.64
Zr	278.52	276.02	275.49	274.77	274.30	274.23
Nb	10.71	7.518	5.926	3.454	1.420	.5300
Mo	208.72	224.76	228.73	234.20	238.30	240.00
Tc	59.02	60.22	60.22	60.22	60.22	60.22
Ru	139.67	130.92	129.74	128.28	127.03	126.14
Rh	23.91	31.16	31.96	32.70	33.02	33.09
Pd	27.68	29.18	29.57	30.28	31.21	32.04
Ag	2.012	1.977	1.977	1.976	1.976	1.976
Cd	1.452	1.482	1.482	1.481	1.481	1.481
In	.1568	.1629	.1632	.1635	.1637	.1637
Sn	2.676	2.652	2.651	2.649	2.647	2.646
Sb	1.238	1.119	1.106	1.081	1.044	1.007
Te	36.30	33.87	33.77	33.69	33.66	33.68
I	17.60	16.46	16.57	16.68	16.74	16.77
Xe	346.55	346.85	346.85	346.85	346.85	346.85
Cs	190.30	193.08	192.88	192.48	191.91	191.31
Ba	98.60	91.63	91.78	92.16	92.74	93.34
La	87.73	86.73	86.73	86.73	86.73	86.73
Ce	230.92	212.83	208.49	201.80	194.32	188.22
Pr	69.41	76.70	77.83	78.78	79.10	79.15
Nd	222.91	239.91	243.18	248.92	256.08	262.14
Pm	23.42	23.62	23.11	22.11	20.71	19.32
Sm	32.46	34.58	35.10	36.10	37.49	38.87
Eu	4.124	4.020	4.012	4.001	3.986	3.972
Gd	1.320	1.504	1.513	1.528	1.547	1.566
Tb	.0577	.0567	.0566	.0566	.0565	.0565
Dy	.0081	.0091	.0092	.0092	.0093	.0093
RE	672.36	679.96	680.03	680.03	680.03	680.03
Np	40.96	12.34	12.34	12.34	12.34	12.34
Am	.2333	.5926	.7113	.9396	1.297	1.662

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TABLE II-40 (Continued)
Weight, Grams Per Ton of Uranium

Element	1.5 y	2 y	3.5 y	5 y	7 y	10 y	20 y
Ge	.0199	.0199	.0199	.0199	.0199	.0199	.0199
As	.0063	.0063	.0063	.0063	.0063	.0063	.0063
Se	3.968	3.968	3.968	3.968	3.968	3.968	3.968
Br	1.516	1.516	1.516	1.516	1.516	1.516	1.516
Kr	26.93	26.79	26.42	26.08	25.68	25.17	24.06
Rb	27.66	27.79	28.16	28.50	28.90	29.41	30.52
Sr	72.59	72.04	70.45	68.91	66.95	64.18	56.31
Y	37.52	37.50	37.50	37.50	37.50	37.50	37.50
Zr	274.58	275.09	276.68	278.22	280.18	282.95	290.82
Nb	.0770	.0111	.0002	.0002	.0003	.0004	.0008
Mo	240.85	240.97	241.00	241.00	241.00	241.00	241.00
Tc	60.22	60.22	60.22	60.22	60.22	60.22	60.22
Ru	124.90	124.04	122.69	122.21	122.02	121.96	121.95
Rh	33.10	33.10	33.10	33.10	33.10	33.10	33.10
Pd	33.26	34.12	35.47	35.95	36.14	36.20	36.21
Ag	1.976	1.976	1.976	1.976	1.976	1.976	1.976
Cd	1.481	1.481	1.482	1.482	1.482	1.482	1.482
In	.1637	.1637	.1637	.1637	.1637	.1637	.1637
Sn	2.645	2.644	2.644	2.644	2.644	2.644	2.644
Sb	.9412	.8829	.7461	.6529	.5732	.5094	.4586
Te	33.73	33.78	33.91	34.00	34.09	34.15	34.20
I	16.79	16.80	16.80	16.80	16.80	16.80	16.80
Xe	346.85	346.85	346.85	346.85	346.85	346.85	346.85
Cs	190.19	189.10	186.05	183.21	179.68	174.79	160.96
Ba	94.46	95.54	98.59	101.43	104.96	109.85	123.68
La	86.73	86.73	86.73	86.73	86.73	86.73	86.73
Ce	179.88	174.54	167.51	165.66	165.10	165.00	164.99
Pr	79.15	79.15	79.15	79.15	79.15	79.15	79.15
Nd	270.47	275.81	282.84	284.70	285.25	285.36	285.36
Pm	16.93	14.83	9.973	6.706	3.951	1.786	.1268
Sm	41.26	43.35	48.18	51.42	54.14	56.25	57.76
Eu	3.949	3.931	3.898	3.887	3.888	3.909	4.015
Gd	1.598	1.625	1.684	1.722	1.754	1.785	1.840
Tb	.0565	.0565	.0565	.0565	.0565	.0565	.0565
Dy	.0093	.0093	.0093	.0093	.0093	.0093	.0093
RE	680.03	680.03	680.03	680.04	680.03	680.03	680.03
Np	12.34	12.34	12.35	12.36	12.40	12.43	12.65
Am	2.348	3.015	4.909	6.652	8.763	11.52	17.97

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TABLE II-41
COMPOSITION OF IRRADIATED 2.1% ENRICHED URANIUM

2100 MWd/T, 10.6 MW/T						
Weight, Grams Per Ton of Uranium						
Element	Discharge	90 d	120 d	180 d	270 d	1 y
Ge	.0182	.0182	.0182	.0182	.0182	.0182
As	.0065	.0058	.0058	.0058	.0058	.0058
Se	3.907	3.908	3.908	3.908	3.908	3.908
Br	1.501	1.501	1.501	1.501	1.501	1.501
Kr	27.09	27.01	26.98	26.94	26.87	26.79
Rb	27.11	27.19	27.22	27.26	27.33	27.41
Sr	85.83	77.08	75.82	74.35	73.36	72.86
Y	42.81	39.86	39.25	38.42	37.80	37.55
Zr	271.92	269.83	269.37	268.73	268.31	268.27
Nb	10.45	7.367	5.809	3.388	1.393	.5201
Mo	199.11	214.83	218.73	224.08	228.10	229.77
Tc	56.50	57.66	57.66	57.66	57.66	57.66
Ru	125.57	118.08	117.12	115.98	115.08	114.47
Rh	22.13	28.60	29.30	29.97	30.25	30.31
Pd	19.85	20.87	21.13	21.60	22.22	22.77
Ag	1.025	1.005	1.005	1.004	1.004	1.004
Cd	1.014	1.029	1.029	1.029	1.029	1.029
In	.1386	.1434	.1437	.1439	.1441	.1441
Sn	2.295	2.276	2.275	2.274	2.272	2.271
Sb	1.044	.9364	.9257	.9045	.8737	.8426
Te	33.83	31.57	31.48	31.41	31.38	31.39
I	16.35	15.29	15.39	15.49	15.54	15.57
Xe	318.78	318.97	318.97	318.97	318.97	318.97
Cs	190.09	192.81	192.64	192.29	191.78	191.26
Ba	94.31	87.47	87.60	87.93	88.44	88.97
La	84.16	83.19	83.19	83.19	83.19	83.19
Ce	222.47	205.00	200.78	194.29	187.00	181.06
Pr	66.36	73.19	74.28	75.19	75.50	75.54
Nd	214.03	230.73	233.90	239.49	246.47	252.37
Pm	23.36	23.57	23.06	22.07	20.67	19.29
Sm	29.26	31.28	31.80	32.79	34.18	35.56
Eu	3.228	3.164	3.158	3.148	3.136	3.124
Gd	.8973	1.020	1.028	1.041	1.059	1.077
Tb	.0351	.0346	.0346	.0346	.0346	.0346
Dy	.0045	.0050	.0050	.0050	.0050	.0051
RE	643.80	651.18	651.24	651.25	651.25	651.25
Np	32.38	12.34	12.34	12.34	12.34	12.34
Am	.0657	.1707	.2055	.2744	.3768	.4836
Cm*	2.645	1.849	1.628	1.262	.8615	.5752

* Curium values are in milligrams.

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TABLE II-41 (Continued)
Weight, Grams Per Ton of Uranium

Element	1.5 y	2 y	3.5 y	5 y	7.5 y	10 y	20 y
Ge	.0182	.0182	.0182	.0182	.0182	.0182	.0182
As	.0058	.0058	.0058	.0058	.0058	.0058	.0058
Se	3.908	3.908	3.908	3.908	3.908	3.908	3.908
Br	1.501	1.501	1.501	1.501	1.501	1.501	1.501
Kr	26.66	26.52	26.15	25.82	25.42	24.91	23.80
Rb	27.54	27.68	28.05	28.38	28.78	29.29	30.40
Sr	72.24	71.69	70.10	68.57	66.62	63.87	56.03
Y	37.42	37.41	37.40	37.40	37.40	37.40	37.40
Zr	268.62	269.12	270.71	272.24	274.20	276.95	284.79
Nb	.0756	.0109	.0002	.0002	.0003	.0004	.0008
Mo	230.61	230.73	230.75	230.75	230.75	230.75	230.75
Tc	57.66	57.66	57.66	57.66	57.66	57.66	57.66
Ru	113.64	113.07	112.17	111.85	111.72	111.69	111.68
Rh	30.32	30.33	30.33	30.33	30.33	30.33	30.33
Pd	23.59	24.16	25.06	25.37	25.50	25.54	25.55
Ag	1.004	1.004	1.004	1.004	1.004	1.004	1.004
Cd	1.029	1.029	1.029	1.029	1.029	1.029	1.029
In	.1441	.1441	.1441	.1441	.1441	.1441	.1441
Sn	2.270	2.270	2.269	2.269	2.269	2.269	2.269
Sb	.7875	.7387	.6240	.5459	.4791	.4256	.3831
Te	31.42	31.47	31.58	31.66	31.72	31.78	31.83
I	15.59	15.59	15.59	15.59	15.59	15.59	15.59
Xe	318.97	318.97	318.97	318.97	318.97	318.97	318.97
Cs	190.27	189.29	186.51	183.89	180.59	175.99	162.88
Ba	89.96	90.93	93.71	96.33	99.62	104.23	117.34
La	83.19	83.19	83.19	83.19	83.19	83.19	83.19
Ce	172.94	167.74	160.89	159.07	158.53	158.43	158.42
Pr	75.55	75.55	75.55	75.55	75.55	75.55	75.55
Nd	260	265.69	272.54	274.36	274.90	275.00	275.01
Pm	16.90	14.81	9.956	6.695	3.944	1.783	.1266
Sm	37.93	40.02	44.83	48.06	50.77	52.86	54.31
Eu	3.106	3.093	3.074	3.076	3.094	3.137	3.311
Gd	1.106	1.130	1.183	1.215	1.240	1.261	1.292
Tb	.0346	.0346	.0346	.0346	.0346	.0346	.0346
Dy	.0051	.0051	.0051	.0051	.0051	.0051	.0051
RE	651.25	651.25	651.25	651.25	651.25	651.25	651.25
Np	12.34	12.34	12.34	12.35	12.35	12.37	12.43
Am	.6842	.8793	1.433	1.944	2.561	3.367	5.256
Cm*	.2658	.1235	.0140	.0033	.0021	.0020	.0017

*Curium values are in milligrams

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TABLE II-42
LONG LIVED FISSION PRODUCTS

MWd/T	MW/T	U-235, %	Unit	Se-79	Zr-93	Tc-99	Pd-107	Sn-126	I-129	Cs-135
640	8.17	Natural	Grams	0.117	16.5	17.6	1.38	0.383	3.89	5.40
			Millicuries	7.58	67.2	304	0.658	10.9	0.674	7.15
			Microwatts	2.70	5.61	151	0.039	1.29	0.320	2.46
750	10	Natural	Grams	0.135	19.0	20.2	1.48	0.434	4.43	5.30
			Millicuries	8.70	76.7	347	0.709	12.3	0.768	7.02
			Microwatts	3.10	6.44	173	0.042	1.46	0.364	2.41
900	10	Natural	Grams	0.160	22.5	24.1	1.93	0.525	5.32	6.36
			Millicuries	10.3	91.2	414	0.919	14.9	0.922	8.42
			Microwatts	3.68	7.66	206	0.054	1.77	0.437	2.89
900	9.7	0.947	Grams	0.166	23.3	24.8	1.80	0.432	5.44	8.04
			Millicuries	10.7	94.9	427	0.859	15.1	0.943	10.6
			Microwatts	3.81	7.93	212	0.051	1.79	0.447	3.66
1000	10	0.947	Grams	0.185	25.9	26.7	2.09	0.600	6.06	8.69
			Millicuries	12.0	106	459	0.996	17.0	1.05	11.5
			Microwatts	4.25	8.81	228	0.059	2.02	0.497	3.96
1200	10	0.947	Grams	0.220	30.9	32.2	2.73	0.730	7.31	10.4
			Millicuries	14.3	126	553	1.30	20.7	1.27	13.8
			Microwatts	5.07	10.5	276	0.077	2.45	0.601	4.75
2200	11	0.947	Grams	0.385	54.6	60.0	7.54	1.43	13.9	19.3
			Millicuries	24.9	221	1032	3.60	40.6	2.41	25.6
			Microwatts	8.86	18.6	514	0.213	4.82	1.14	8.79
2200	11	1.25	Grams	0.397	56.0	60.2	5.71	1.36	13.6	23.0
			Millicuries	25.7	227	1036	2.72	38.5	2.35	30.5
			Microwatts	9.12	19.0	516	0.161	4.56	1.11	10.5
2100	10.6	2.1	Grams	0.391	54.9	57.7	3.48	1.21	12.5	31.2
			Millicuries	25.3	224	992	1.66	34.4	2.17	41.3
			Microwatts	8.98	18.7	494	0.099	4.08	1.03	14.2

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FIGURE II-2
Total Neutron Cross Section of Pu-239

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FIGURE II-5
Methods of Forming Transuranic Nuclides

FIGURE II-6Cumulative Yields from U-235 Thermal Fission

FIGURE II-7
Average Energy for Allowed Beta Spectra

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FIGURE IV-42

Cerium Distribution as a Function
of Time and Persulfate Concentration
(Source of Data: HW-78987)

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FIGURE IV-43

Cerium Distribution as a Function
of Time and Acid Concentration
(Source of Data: HW-78987)

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FIGURE IV-44

Cerium Distribution as a Function
of Time and Radiation Field
(Source of Data: HW-78987)

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FIGURE IV-45

FIGURE IV-46

Cerium Distribution as a Function of Contact Time
 (Comparison of NPH and SOLTROL-170 as Diluents)
 (Source of Data: HW-84101)

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FIGURE IV-47

Stripping Studies for Ce(IV)
(Hot Cell)

(Source of Data: BNWL-187)

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3.5 Chemical Flowsheets

Detailed chemical flowsheets are presented in Figures IV-48, IV-49 and IV-50 for the primary extraction of strontium, rare earths, and americium from the three major Purex waste streams: PAW, ZAW (current waste derived from zirconium-clad fuels), and PAS (acidified stored sludge). Feeds for the processes are prepared in head-end steps involving centrifugation and leaching of the PAW and ZAW and PbSO_4 scavenging of the PAS.

The feeds are first adjusted with hydroxyacetic acid for pH control and HEDTA and tartaric acid to complex unwanted fission products and inert impurities. Approximately 10 to 20% excess HEDTA is added over that required to form 1 to 1 complexes with iron, aluminum, chromium, nickel, and lead. The tartaric acid addition is based on the apparent improvement in rare earth extraction kinetics described in Section 3.2.3. Tartaric acid alone is a reasonably effective complexant for most of the impurities (with the notable exception of lead) and it, citric acid, or other as yet unspecified complexants, may be substituted for HEDTA for certain applications.

The feed is adjusted to $\text{pH } 4.0 \pm 0.1$ by the addition of NaOH and digested at cell temperature for several hours or at 60 to 90 C for about 30 min to assure complete complexing of the impurities. Digestion may not be required with all feeds, but pilot plant experience has shown that more reproducible performance and less trouble with solids and solid-induced instability are obtained with digested feeds.

A solvent composition of 0.3M D2EHPA was chosen as a compromise to provide adequate strontium extraction in the 1A Column while allowing strontium and rare earths to be stripped with a minimum amount of dilute acid in the 1B Column and 1C Column, respectively. The solvent is partially neutralized to minimize sodium transfer in the 1A Column and thus to improve pH control. The addition of 0.2M TBP prevents "third phase" formation in the solvent washing procedure and also improves the strontium distribution ratio as discussed in Section C 2.5.2).

The LSS contains sufficient hydroxyacetic acid to be capable of quantitatively removing extracted sodium from the LAP, according to the criteria discussed in Section C 3.3. The LSS optionally contains a small amount of HEDTA to improve decontamination from nickel and other strongly complexed impurities which may have extracted in minor quantities in the 1A Column. Finally, the LSS pH is adjusted to 2.4 to avoid scrubbing significant quantities of strontium from the solvent.

The 1EX stream is supplied with about a 2-fold excess of HNO_3 over that required to stoichiometrically exchange with the strontium and sodium entering the 1B Column. Insufficient HNO_3 will result in exceeding the desired maximum pH of 2.2 and may lead to excessive strontium losses and

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column instability while excessive HNO_3 will lower the decontamination from calcium and rare earths. The LBP is routed to the LBP concentrator and interim crude strontium storage.

The LCX stream composition will vary depending on whether or not cerium is to be separated from the other rare earths. When cerium separation is desired, the LCX must be supplied as two separate streams -- one containing the persulfate and the other the silver catalyst. Premature mixing can result in destruction of the persulfate by silver-catalyzed reactions with water and HNO_3 . The proposed concentrations of 0.4M $\text{Na}_2\text{S}_2\text{O}_8$ and 0.005M AgNO_3 were chosen from the results of pilot plant tests designed to minimize reagent costs. The combined LCX in all three flowsheets contains 2M HNO_3 , sufficient to quantitatively strip the promethium and other rare earths while leaving most of the yttrium in the solvent. A LCX stream is specified for the PAW and ZAW flowsheets. This stream can either be fully acid-form solvent or, for simplicity, the same as the LAX. The flow ratio in the scrub section is not critical but was chosen at a relatively high O/A ratio for improved dispersion characteristics.

The LCP stream from current wastes will be routed to a batch contactor for re-extraction of the rare earths away from silver and the sulfate formed by reduction of the persulfate. A description of this process is presented in Section C 5.

The LCM from the PAW and ZAW flowsheet contains the Ce(IV) extracted in the LC Column and most of the yttrium entering the process. The cerium is removed in a batch contactor with 2M HNO_3 containing 0.05M NaNO_2 . Again, most of the yttrium will remain in the solvent. The cerium product is routed to a concentrator (not shown) where the volume is reduced about ten-fold and the excess HNO_3 is destroyed by sugar treatment. The concentrated cerium is then routed to FPCE or to underground storage. The stripped solvent is sent to a batch solvent wash, described in Section C 5.

All solvent extraction operations should be carried out at elevated temperature for optimum extraction efficiency and improved column stability. The expected cell ambient temperature of 35°C should be adequate for all columns with the possible exception of the LA Column which may require operation at higher temperatures to obtain the required extraction of Pm-147.

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FIGURE IV-48

D2EHPA Extraction of Current Acid Waste (PAW) - Conceptual Flowsheet

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FIGURE IV-49

D2EHPA Extraction of Zirflex Acid Waste - Conceptual Flowsheet

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FIGURE IV-50

D2EHPA Extraction of Acid Sludge Waste - Conceptual Flowsheet

4. Solvent Extraction Purification of Strontium Fraction

4.1 Introduction

The strontium fraction obtained from current acid waste by the mainline D2EHPA extraction process described in Section C 3 is scheduled to be sent to the privately-owned Fission Products Containment and Encapsulation (FPCE) plant at Hanford for fabrication into strontium titanate sources. However, before fabrication into such sources can be undertaken, the strontium fraction must be purified further from inert and radioactive contaminants. This is accomplished by the D2EHPA solvent extraction process described in this section.

This D2EHPA extraction process can also be used to purify the strontium fraction obtained from sludge wastes. However, because of the low Sr-90 isotopic content of the Redox sludges and a portion of the Purex sludges, it is anticipated that only about 30% of the sludge strontium product would be purified by further D2EHPA extraction. The remainder will be packaged in Waste Management containers for storage according to the scheme discussed in Section F of this chapter and in Chapter VII.

4.2 Feed Material and Impurities

Feed stock for the D2EHPA purification cycle will be prepared from the crude-strontium fractions obtained from processing PAW and stored sludge. These crude strontium fractions are estimated (from Figures IV-48 and 50) to have the composition shown in Table IV-17.

TABLE IV-17
COMPOSITION OF IMPURE STRONTIUM FRACTIONS

<u>Component</u>	<u>Composition (M) of</u> <u>Strontium Fraction From</u>	
	<u>PAW</u>	<u>Stored Sludge</u>
Na	0.10	0.04
Ca	0.0048	0.05
Sr	0.058	0.13
Rare Earths	<0.004	<0.006
HNO ₃	0.16	0.17

As this manual was written there was still some uncertainty about the expected calcium concentration of the strontium fraction recovered from stored sludge. Actual operating experience will resolve this difficulty. Trace quantities of lead, aluminum, nickel, iron, and chromium are also expected to be present in the crude strontium fractions.

4.3 Purification Process

4.3.1 Process Concept

The accompanying schematic (Figure IV-51) illustrates the D2EHPA extraction process for purification of the Sr-90 fraction:

FIGURE IV-51

D2EHPA Purification of the Sr-90 Fraction

Crude strontium feed is butted with DTPA (diethylenetriaminepentacetic acid), acetic acid, and caustic prior to introduction to the 1A Column. DTPA is used to complex most metal ions present, including the rare earths, to prevent their extraction by the solvent. Strontium and calcium are extracted by the D2EHPA extractant in the 1A Column. A highly buffered feed to the 1A Column is necessary to provide the pH control necessary for proper extraction of strontium. Hence, acetate is used as a buffer with caustic providing the pH adjustment necessary to maintain a feed pH of 4.9. A hydroxyacetic acid scrub is used in the 1S Column to strip sodium from the solvent. The reduction in sodium content in the solvent from the 1S Column facilitates pH control and improves the decontamination from calcium and cerium that can be achieved in the 1B Column by minimizing hydrogen ion exchange there.

Strontium and sodium are stripped from the solvent with 1M citric acid in the 1B Column. Conditions are adjusted so that nearly all of the calcium present remains in the organic phase. The strontium product from the 1B Column is concentrated while H_2O_2 and HNO_3 are added to destroy citric acid. Finally, the concentrated and purified strontium product is sent to storage for eventual use in a Fission Product Program or to storage on zeolite.

The waste from the 1A Column is sent to waste concentration while the solvent from the 1B Column is routed to solvent treatment facilities for removal of cations present (principally calcium).

The D2EHPA extraction process was originally developed⁽³³⁾ for use in the Hanford Strontium Semiworks to recover and purify Sr-90 from Purex Plant crude Sr-90 concentrate as produced by $PbSO_4$ carrier precipitation from Purex Plant LWW solution. The process has been used very extensively since the original development; this Strontium Semiworks experience is reviewed in Section D 7.

4.3.2 1A Column

The function of the 1A Column in the strontium purification process is to provide for essentially complete extraction of strontium while rejecting, as completely as possible, Ce-144, other rare earths, and inert contaminants to the aqueous waste. This is accomplished by control of feed pH and by selection of a suitable complexing agent (DTPA) to add to the extraction column feed.

Data which illustrate the effectiveness of DTPA over several other complexants in suppressing extraction of Ce-144 are presented in Table IV-18 and Figure IV-52^(33b). At approximately equal concentrations, EDTA and DTPA have about the same effect on the strontium E_a^0 , but DTPA complexes cerium more strongly than EDTA, in agreement with the stability constants presented in Table IV-67. Data in Table IV-18 also predict that DTPA would strongly suppress extraction of iron, lead, etc.; this expectation is borne out by Strontium Semiworks experience.

TABLE IV-18
COMPARISON OF COMPLEXING AGENTS
(Source of Data: HW-42966, Section 3)

Conditions: Purex plant crude concentrate^(a) made 0.45M sodium acetate and 0.1 to 0.20M complexant, adjusted to pH 4.3 with NaOH, and contacted 10 min. at 25°C with one-tenth volume of 0.45M D2EHPA, 0.2M TBP, solvent.

Type	Complexing Agent		Feed, Vol. pH	Feed, Vol. %					Eq.
	M	Eq. M ^(b)		Fe	Sr	Ce	Ce	Eq.	
DTPA	0.15	0.07	4.6	—	15	—	0.05	—	—
EDTA	0.15	0.11	4.4	0.0002	16	100	0.10	0.15	—
HEPES	0.20	0.12	4.6	0.005	23	1400	12	1.1	—
Citric Acid	0.20	0.12	4.6	0.04	14	1800	250	400	—
EDTA + Ascorbic	0.20	0.12	4.6	1.5	15	2600	150	110	—

(a) 1.0M HNO_3 + 0.002M $Si(NO_3)_4$ + 0.001M $Cr(NO_3)_3$ + 0.002M RE³⁺ and 0.001M Co , 1M Pb , Zn , and Fe .

(b) M = total complexant; total M complexant = 0.01M EDTA + 0.01M DTPA + 0.01M HEPES + 0.01M Citric Acid.

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FIGURE IV-52

Comparison of DTPA and EDTA as Complexing Agents
for Cerium and Strontium
(Source of Data: HW-72666)

Data in Figure IV-52 indicate that operation of the extraction column with high pH (pH 4.5) feeds is desirable to minimize contamination of the Sr-90 product with Ce-144. However, complexing of strontium by either EDTA or DTPA begins to occur at about pH 4 and increases at higher pH's. The choice of a suitable feed pH must thus be a compromise between the need for satisfactory extraction of strontium and maximum decontamination from Ce-144. A feed pH of 4.9 is considered optimum.

Neither DTPA nor EDTA complexes calcium efficiently in the pH range of interest. Hence, essentially all of the inert calcium in the strontium fraction is extracted with the strontium.

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DTPA forms 1:1 complexes with most metal ions. Hence, the amount of DTPA added to the impure Sr-90 fraction is calculated to be sufficient to form 1:1 complexes with the rare earths and to make the final feed about 0.07M "free" (uncomplexed) DTPA. Higher concentrations of complexant are uneconomical and result in decreased distribution ratios for all feed components (33b).

Complexing of cerium by DTPA is adversely affected by radiolysis. Laboratory studies (33b) indicate cerium decontamination in the extraction column would be completely lost after feeds containing DTPA had been irradiated to a total exposure of about 8×10^7 rad (about 2 days standing).

4.3.3 1S Column

In the extraction column, because of the high pH and the concentration of sodium ions in the 1AF stream, considerable sodium extracts even though the sodium E_a^0 is smaller than either the strontium or calcium E_a^0 . The primary function of the 1S Column in the Sr-90 purification process is the same, therefore, as in the mainline D2EHPA process (Section C. 3.3.1), namely, to remove the bulk of the coextracted sodium prior to stripping of strontium. Removal of most of the sodium at this point not only gives a purer strontium product but makes control of pH in the 1B Column much easier.

Proper scrub column operation requires adequate pH control to ensure maximum scrubbing of sodium without excessive losses of strontium. A small flow of hydroxyacetic acid adjusted to pH 2.6 provides the required buffer capacity. Citric acid should be a suitable alternate. A small amount of DTPA is added to the scrub to provide additional decontamination from Ce-144 and other trivalent contaminants. Sodium equilibrium data for hydroxyacetate scrub systems are presented in Section C. 3.3.2.

Sodium scrubbing has not been studied in detail on a laboratory scale. It has, however, been extensively tested and satisfactorily demonstrated on a plant scale, both in the Strontium Semiworks and in cold pilot plant studies (33c, 59).

4.3.4 1B Column

Strontium and sodium not removed in the scrub column are stripped from the organic phase into an aqueous 1M citric acid solution in the 1B Column while calcium and rare earths are left in the organic phase. Precise control of pH is required to obtain good calcium and rare earth decontamination factors. Because of their lack of buffer capacity, dilute HNO_3 solutions cannot be used to obtain this control within desired strontium solvent loadings and flow rates; however, satisfactory buffer capacity is provided by several organic polycarboxylic acids.

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Distribution ratios of strontium, calcium, and cerium between 0.37M D2EHPA-0.2M TBP-Shell Spray Base and aqueous solutions of citric and tartaric acids as a function of equilibrium aqueous phase pH are given in Table IV-19(33b).

TABLE IV-19
1B COLUMN DISTRIBUTION RATIOS
(Source of Data: HW-72666, Section 3)

Conditions: Citric or tartaric acid solutions containing either 0.01M $\text{Sr}(\text{NO}_3)_2$, 0.0005M $\text{Ce}(\text{NO}_3)_3$, or 0.05M $\text{Ca}(\text{NO}_3)_2$ were adjusted to the desired pH with NaOH and contacted 10 min. at 25 C with an equal volume of 0.37M D2EHPA, 0.2M TBP, Shell Spray Base.

A. Citric Acid

Initial Aqueous Phase Composition		Strontium		Cerium		Calcium	
Citrate, M	Na ⁺ , M	Equil. pH	E _a ^o	Equil. pH	E _a ^o	Equil. pH	E _a ^o
0.833	0.588	3.2	2.3	2.9	57	2.8	29
0.870	0.460	2.9	1.1	2.7	53	2.7	15
0.909	0.321	2.6	0.48	2.4	46	2.3	6.6
0.952	0.168	2.1	0.15	2.0	33	1.9	2.5
0.976	0.086	1.8	0.034	1.7	15	1.6	1.2
0.988	0.044	1.7	0.030	--	--	1.5	0.67
1.00	0.00	--	--	1.2	4.4	1.0	0.2
1.88	0.963	2.5	0.28	2.5	8.7	--	--
1.92	0.456	2.0	0.083	2.0	7.4	--	--
1.94	0.148	1.6	0.02	1.4	4.4	--	--
2.48	1.62	2.6	0.22	2.6	4.4	--	--
2.71	0.939	2.0	0.07	2.1	3.2	--	--
2.74	0.41	1.6	0.02	1.5	2.4	--	--

B. Tartaric Acid

Tartrate, M	Na ⁺ , M						
0.833	0.588	2.9	0.7	2.8	32	2.8	21
0.870	0.460	2.7	0.38	2.6	42	2.6	9.6
0.909	0.321	2.4	0.17	2.3	23	2.3	4.5
0.952	0.168	2.0	0.055	1.9	12	1.9	1.6
0.976	0.086	1.7	0.022	1.7	6.6	1.6	0.79
0.988	0.044	1.6	0.011	--	--	1.4	0.45
1.00	0.00	--	--	1.2	2.0	--	--

Cerium distribution ratios decrease as citrate concentration increases because of formation of cerium citrate complexes in the aqueous phase. Strontium distribution ratios also decrease as citrate concentration increases but to a lesser extent. One molar citric acid was chosen for use in the 1B Column since this concentration supplies sufficient buffer capacity and provides adequate separation of strontium from calcium and cerium.

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Tartaric and maleic acids were also considered as alternate stripping agents. In the final evaluation these reagents showed no promise over citric acid. Maleic acid formed an insoluble strontium salt, and tartaric acid, during radiolytic decomposition, formed porous solid compounds of about the same volume as the starting solution⁽⁷⁷⁾.

Titration curves for 1M tartaric acids are shown in Figure IV-53^(33b). These can be used to estimate the effect of hydrogen-cation exchange in the 1B Column on the equilibrium aqueous phase pH.

FIGURE IV-53

Variation in pH as a Function of Neutralization
of Citric and Tartaric Acids
(Source of Data: HW-72666, Section 3)

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4.3.5 Concentration of Strontium Product

The purified strontium product (LBP) solution obtained from the D2EHPA purification process is too dilute for storage and must be concentrated. To avoid process problems caused by citric acid radiolytic degradation products, it is necessary to destroy citric acid in the LBP solution and convert to a nitrate media prior to storage. These radiolytic products have not been identified but include tars as well as other objectionable solids when radiolysis proceeds far enough. Furthermore, in one Strontium Semiworks run, addition of HNO_3 to a strontium - citric acid solution which had undergone extensive radiolysis resulted in formation of unmanageable foams and gels⁽⁷⁷⁾.

Citric acid in HNO_3 solutions can be readily and rapidly destroyed by reaction with H_2O_2 . This was first demonstrated on a laboratory scale by Buckingham⁽³¹⁾ and subsequently on a plant scale in the Strontium Semiworks. The end products of the reaction between citric acid and H_2O_2 are undoubtedly water and carbon dioxide, but neither the reaction mechanism nor the reaction stoichiometry have been defined rigorously. Buckingham's experiments indicated that destruction of a mole of citric acid in 1 to 2M HNO_3 required from 5 to 10 moles of H_2O_2 . In the Strontium Semiworks, the combination of radiolysis and H_2O_2 addition has provided adequate destruction of citrate with as little as 4 moles of H_2O_2 added per mole of citrate⁽³⁸⁾.

Nitric acid is also used up during the radiolytic-peroxide reaction, and recent Strontium Semiworks experience demonstrates that very careful control of the HNO_3 concentration is necessary to avoid operational problems during citrate destruction. If HNO_3 is not added as fast as it is destroyed by radiolysis, the product concentrator solution can become acid deficient. Severe foaming occurred when this happened in one Semiworks run; the foaming was stopped by cooling the concentrator and acidifying the solution with HNO_3 . Also, when the HNO_3 concentration becomes too high ($< 7\text{M}$) a fast denitration reaction can occur. Such reactions can occur also at lower HNO_3 concentrations ($\leq 3\text{M}$) when peroxide addition is stopped. Laboratory investigations indicate that the fast denitration is a formic acid- HNO_3 reaction and that it is initiated by the presence of nitrite ion. Nitrite is known to be a product from the radiolysis of nitrate, and formic acid is thought to be one of the intermediate degradation products of citric acid. Hydrogen peroxide is a nitrite suppressant, and the reaction has not occurred while peroxide was being added under conditions where the HNO_3 concentration was less than 3M and the organic acid concentration (calculated as "equivalent" citric acid) was less than 2M except during periods when the peroxide flow was stopped.

The denitration reaction that occurs under high acid conditions is quite violent compared to the foaming that occurs when the product solution becomes acid deficient. Process control of the citrate destruction re-

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action is thus pointed toward low acid operations. At the time this manual was written, tests were in progress in the Semiworks to define optimum reaction conditions. It is anticipated that results of these tests will be applicable to destruction of citric acid in the B-Plant.

4.3.6 Disposition of Strontium Product

The concentrated strontium product solution obtained after destruction of citrate and peroxide will be stored pending transfer to a Fission Product Program. Alternatively, the strontium can be adsorbed on zeolite for long-term storage (see Section F of this chapter).

Strontium-90 decays by the scheme:

Consequently, significant quantities of zirconium grow into the purified strontium as it is allowed to stand. A precipitation process for separating the zirconium from strontium has been developed⁽¹⁴⁾; present B-Plant plans, however, do not call for purification of the stored strontium from zirconium.

4.4 Chemical Flowsheet

A detailed chemical flowsheet for purification of the strontium fraction from current acid waste is given in Figure IV-54. A similar flowsheet would be used for purification of the strontium fraction from stored sludge with the feed flow adjusted to provide about the same strontium and calcium loading in the solvent.

4.5 Alternate Precipitation Purification Process

Precipitation of insoluble hydroxides has been studied by Bray⁽¹⁶⁾ as a means of purifying the strontium fraction obtained from current acid waste. Bray's work was performed with a synthetic crude strontium feed containing 0.058M Sr, 0.017M Mg, 0.012M Ca, 0.01M Fe, 0.001M Cr, 0.002M RE, 0.2M Na, and 0.12M HNO₃. Neutralization of this feed to pH 10 (by addition of NaOH to a warm (80-90 C solution) precipitated essentially all the cerium and iron and over 95% of the magnesium. Approximately 98, 51, and 8% of the calcium remained in solution at the respective pH values of 11, 12.4, and 13. Less than 2% of the initial strontium was lost below a pH of 11, but the loss increased to 15% at a

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pH of 13. According to Bray, the final precipitate occupied a volume less than 8% that of the original solution and was somewhat gelatinous but centrifuged well.

This precipitation process is particularly suited for purification of strontium from magnesium if such purification might be required. Currently, there is very little magnesium in the uranium metal or other essential materials used in the Hanford Purex Plant, but suggested alterations in the metallurgical processes used by uranium suppliers may result in the introduction of significant quantities of magnesium. Bray reports the D2EHPA solvent extraction of magnesium is identical to that of strontium even in the presence of DTPA; thus magnesium will quantitatively follow strontium through the D2EHPA extraction process.

5. Semi-Purification of Rare Earth - Americium Fraction

5.1 Introduction

When operated with feeds prepared from current waste (PAW and ZAW solutions) the 1C Column in the mainline D2EHPA extraction process will be used to separate cerium from the other rare earths and americium (see Section C 3.5.3). The aqueous rare earth - americium fraction from the 1C Column will be contaminated with sulfate, silver, and sodium ions, all resulting from the silver-catalyzed persulfate oxidation of Ce(III) to Ce(IV). Sulfate is also derived from the decomposition of persulfate by radiation and reaction with water. Its removal is necessary to prevent precipitation of double rare earth sulfates and to allow concentration of the rare earth - americium fraction to volumes small enough for storage and/or eventual transfer to a Fission Product Program. Purification is achieved by the batch D2EHPA extraction process described in this section.

5.2 Feed Material and Impurities

The estimated composition of the rare earth - americium fraction from the 1C Column when processing current acid waste is listed in Table IV-20.

TABLE IV-20

ESTIMATED COMPOSITION OF RARE EARTH - AMERICIUM FRACTION

(Source of Data: Figure IV-48)

Component	% of Total in PAW	Concentration, <u>M</u>
H	--	2.7
Na	--	0.8
Ag	--	0.005
Ca	92	0.0055
Sr	1	--
RE ^(a)	70	0.025
Pm	96	--
Ce	<2	--
Y	<5	--
NO ₃ ⁻	--	2.0
SO ₄ ⁼	--	0.8

(a) Total rare earths, including cerium and promethium.

5.3 Purification Process5.3.1 Process Concept - Chemical Flowsheet

A batch D2EHPA extraction process for purifying the rare earth - americium fraction from sulfate ion and other impurities⁽⁶²⁾ is illustrated by the flowsheet shown in Figure IV-55.

Extraction feed for the process is prepared by adding NaOH and HEDTA or citric acid to the aqueous promethium-americium solution from the LC Column. The HEDTA (or citrate) prevents precipitation of rare earth sulfates when NaOH is added to adjust the solution to the extraction pH of 3.5. Trivalent rare earths and americium are coextracted into the D2EHPA phase leaving the sulfate and most other impurities in the aqueous raffinate. After decanting the aqueous waste, the solvent is washed with 1M HNO₃ to recover americium, promethium, and other rare earths. Finally, the promethium-americium product solution is continuously concentrated, and denitrated (by addition of sucrose), and then stored for aging of the promethium. The solvent will normally be recycled without further washing to eliminate any promethium stripping losses.

5.3.2 Batch Extraction Step

Bray and Roberts have investigated the D2EHPA solvent extraction behavior of rare earths complexed with HEDTA in the presence of sulfate⁽²²⁾. Their results are shown in Figure IV-56 and indicate that a pH of 2.5 to 3.5 is optimum for nearly quantitative extraction of the

FIGURE IV-55

Chemical Flowsheet for Semi-Purification of
Rare Earth - Americium Fraction

(Based on the flowsheet presented in ISO-42)

FIGURE IV-56

Extraction of Rare Earths and Silver from Sulfate Solutions
Containing HEDTA as a Function of pH
(Source of Data: BNWL-187)

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rare earths. The extraction behavior of americium was not studied in these particular experiments, but americium is expected to follow promethium and the other rare earths into the organic phase. Some silver is also extracted but not enough to interfere with subsequent ion exchange separation of the individual rare earths.

The purpose of the HEDTA in the extraction feed is, as mentioned earlier, to prevent precipitation of rare earth sulfates. Bray and Roberts report that either 0.05M citrate or 0.05M HEDTA prevents precipitation of rare earths at pH's above 3 if the sulfate concentration is 0.4M or less⁽²²⁾. Conditions were not found which would prevent rare earth precipitation when the feed solution contained more than 0.4M sulfate. A summary of the results of their solubility studies is presented in Figure IV-57.

5.3.3 Batch Strip Step

Contact of the pregnant D2EHPA phase with 1.0M HNO_3 readily strips rare earths and americium as discussed earlier in Section C 3.5.2. Stripping is not quantitative at 1M HNO_3 , and the solvent is normally recycled without washing to prevent promethium loss.

5.3.4 Concentration - Denitration of Product

The HNO_3 solution from the strip contact constitutes the feed for further separation and purification of Pm-147 by chromatographic ion exchange techniques. Concentration and HNO_3 destruction are required to meet the storage volume and ion exchange requirements. A final product containing about 0.5M rare earths and 0.1 to 1M HNO_3 is desired⁽⁸⁰⁾. To meet this requirement denitration by sucrose addition during thermal concentration will be employed.

Sucrose denitration is a well-demonstrated process and is used routinely in the Hanford Purex Plant to prepare PAW solution from LWV solution^(11,19). Laboratory scale concentration and sucrose denitration of the HNO_3 strip solution have been tested successfully with both synthetic and Strontium-Semiworks solutions⁽²²⁾.

5.3.5 Disposition of Rare Earth - Americium Product

The concentrated, denitrated rare earth - americium product solution will be stored pending transfer to a Fission Product Program for recovery and purification of the Pm-147 content.

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FIGURE IV-57

Rare Earth Solubility in the Presence of Varying Concentrations
 of Sulfate and Complexant as a Function of pH
 (Source of Data: BNWL-187)

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5.4 Strontium Semiworks Process Demonstration

A chemical flowsheet similar to that shown in Figure IV-55 was used in the Strontium Semiworks to purify four batches of Pm-147 (plus associated Am-241 and other trivalent rare earths) from sulfate. Each batch comprised 50 to 100 kilocuries of Pm-147 in about 1000 liters; the composition of these feed solutions was essentially that listed in Section C 5.2 except that the sulfate concentration was 0.4M and the silver concentration was 0.02M. Extraction-strip performance was excellent; typically, 2-3% of the Pm-147 was not extracted from the feed, and about 2% of the Pm-147 was left in the solvent after stripping with 2M HNO_3 (63).

Continuous concentration and sucrose destruction of nitrate in the HNO_3 strip solution was also accomplished very satisfactorily in the Strontium Semiworks runs. The final concentrates approximated the composition indicated in the chemical flowsheet shown in Figure IV-55.

In the concentration - denitration runs, temperature and specific gravity measurements were used to control rates of addition of sucrose solution and of the dilute rare earth feed. These runs demonstrated the desirability of maintaining a steady state HNO_3 concentration greater than 3 or 4M in the concentrator to maintain rapid kinetics of nitrate destruction and to prevent precipitation of rare earth oxalates. (Oxalic acid is an intermediate in the conversion of sucrose to CO_2 .) Typically, one mole of sucrose destroyed 30 to 40 moles of HNO_3 . The steady state concentration of carbon compounds (calculated as sucrose) was about 0.05M. Normally, continuous concentration and denitration of a batch of Pm-147 strip solution was halted when the HNO_3 concentration fell to 1M. The residual carbon compounds were then sufficient to reduce the HNO_3 concentration to about 0.5M in a 72-hour digestion period.

6. Solvent Treatment

6.1 Introduction

The D2EHPA extractant used to recover strontium, rare earths, and americium from current acid waste and stored sludge waste will become contaminated with various inert and radioactive inorganic contaminants. Periodic removal of these contaminants and adjustment of the sodium to hydrogen ratio in the extractant is required. The chemical wash treatments designed to accomplish these objectives are discussed in this section.

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The same extractant used in the mainline recovery process (Section C 3) will also be used, as required, to purify the strontium and rare earth fractions (Sections C 4 and C 5). The chemical wash procedures discussed in this section will also apply for removing inorganic contaminants introduced into the solvent during these operations.

6.2 Solvent Contaminants

Solvent from the mainline D2EHPA processes for treating current acid waste and stored sludge waste will contain nearly all of the yttrium entering the process together with small amounts of "irreversibly" extracted iron, chromium, and zirconium. Yttrium follows the rare earths through the 1A, 1S, and 1B Columns but is not stripped into 2M HNO_3 in the 1C Column. The solvent leaving the 1C Column (when processing current acid waste) will contain about 0.00028 mole/liter of yttrium⁽⁶²⁾. Inert impurities will range, typically, within a factor of ten of this value.

On the basis of Strontium Semiworks experience, small amounts of uranium and fission products (principally Ce-144, ZrNb-95, Ru-103, and Ru-106) are also expected to be present in used mainline process solvent. The oxo cation UO_2^{++} , as noted earlier, is extracted more strongly than other divalent cations such as Ca^{++} and Sr^{++} and is not stripped in either the 1B or 1C Column.

In the mainline process, cerium is removed from the D2EHPA solvent leaving the 1C Column by batch stripping with a HNO_3 - NaNO_2 solution. The unused nitrite ion extracts nearly quantitatively into the solvent as nitrous acid and must be removed by an appropriate chemical wash treatment before reuse of the solvent.

The D2EHPA extractant used in auxiliary purification processes will contain about the same cation impurities as the used mainline solvent except, of course, to a lesser extent.

6.3 Washing Procedures

6.3.1 Sodium Hydroxide-Complexant

Treatment of used D2EHPA extractants with NaOH solutions containing either citrate or tartrate is a highly efficient way to remove metal contaminants from such solutions. This has been demonstrated in both laboratory experiments⁽⁷⁴⁾ and in Strontium Semiworks operation (Section C 6.5.1). Most effective removal of contaminants is realized when sufficient NaOH is used to convert all the extractant to the sodium salt form and to make the equilibrium wash solution 0.5 to 1.0M NaOH. Complexants such as citrate or tartrate in the alkaline wash aid in removal of contaminants and prevent precipitation of metals such as iron and yttrium

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by forming soluble complexes; uranium, if present, precipitates as the diuranate even in the presence of citrate or tartrate. Laboratory results presented in Table IV-21 show that slightly better decontamination performance is obtained with citrate than with tartrate⁽⁷⁴⁾. In laboratory studies, gravity phase separation was faster at 50 C than at 25 C.

TABLE IV-21
NaOH - COMPLEXANT SOLVENT WASHES
(Source of Data: HW-84592)

Conditions: Unwashed Strontium Semiworks solvent^(a) contacted 15 min. with one-fifth volume of indicated aqueous wash.

Wash Composition	Temp. C	Decontamination Factor ^(b)				
		Y-91	Ce-144	ZrNb-95	Ru-103	Gross Gamma
2.5M NaOH	50	37	43	32	3	31
2.5M NaOH	25	15	24	26	4	22
2.5M NaOH - 0.1M Na ₂ Tar.	50	15	57	33	4	27
2.5M NaOH - 0.1M Na ₃ Cit.	50	240	220	87	4	75

(a) 0.35 M D2EHPA, 0.22M TBP, Soltrol-170 containing 0.164 Ci/l Y-91, 0.0745 Ci/l Ce-144, 0.08 Ci/l ZrNb-95, and 0.0045 Ci/l Ru-106.

(b) Ratio of concentration in unwashed and washed solvents.

6.3.2 Nitric-Oxalic Acid Washes

Nitric acid washes alone are not effective in removing tightly bound impurities, and laboratory washing studies⁽⁷⁴⁾ have demonstrated that very little additional fission product activity is removed by a HNO₃ wash following sodium hydroxide washes. Addition of oxalic acid to the HNO₃ wash gives slightly increased decontamination from ZrNb-95 and Ce-144 activity as illustrated by the results in Table IV-22.

TABLE IV-22
MULTIPLE BATCH WASHING OF STRONTIUM SEMIWORKS SOLVENT
(Source of Data: HW-84592)

Conditions: Portions of unwashed Strontium Semiworks solvent^(a) washed (15 min. at 50C) consecutively with equal volume portions of following washes:

Wash 1 - 2.0M sodium tartrate or 0.1M sodium citrate

Wash 2 - Same as Wash 1

Wash 3 - 2.0M HNO₃, 0.1M oxalic acid

Contaminant	Sodium Tartrate			Sodium Citrate		
	Wash 1	Wash 2	Wash 3	Wash 1	Wash 2	Wash 3
Y-91	73	(b)	(b)	150	(b)	(b)
Ce-144	19	34	5	240	6	2.5
ZrNb-95	55	13	1.6	78	6.6	2
Ru-106	2	1	1	7	1	1

(a) 0.35M D2EHPA, 0.22M TBP, Soltrol-170 containing 0.0164 Ci/l Y-91, 0.0745 Ci/l Ce-144, 0.08 Ci/l ZrNb-95, and 0.0045 Ci/l Ru-106.

(b) Y-91 not detected in organic phase after second wash.

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6.3.3 Nitric Acid-Permanganate Washes

Both laboratory⁽⁷⁴⁾ and Strontium Semiworks experience⁽⁶³⁾ indicate that the Ce(IV) extraction capacity of a D2EHPA-TBP-diluent solvent deteriorates on repeated solvent use. A large fraction of this decreased capacity appears to be caused by the generation, either chemically or radiolytically or both, of reducing impurities in the extractant. These impurities appear to arise from attack of the hydrocarbon diluent, and, in this connection, NPH is more stable to generation of such impurities than is Soltrol-170^(21,22).

Results obtained by Schulz and Beard⁽⁷³⁾ demonstrate that HNO_3 - KMnO_4 washes are very effective in restoring Ce(IV) extraction capacity of degraded D2EHPA solvents. In contrast, Ce(IV) extraction capacity is little, if any, affected by normal NaOH-complexant or HNO_3 -oxalic acid washing. The effectiveness of KMnO_4 washing appears to be connected in some way with the production of MnO_4 when the solvent contacts the aqueous KMnO_4 solution. The MnO_4 which collects at the organic-aqueous interface at the conclusion of the wash can be destroyed by reaction with either H_2O_2 or oxalic acid without impairing the improved Ce(IV) extraction capacity. Some typical data illustrating the effectiveness of HNO_3 - KMnO_4 washing are listed in Table IV-23.

TABLE IV-23
 HNO_3 - KMnO_4 WASHING OF D2EHPA SOLVENTS
(Source of Data: HWIR-1836)

Conditions: 0.37M D2EHPA, 0.2M TBP solvents of various histories washed one hour at 25C with an equal volume of 2M HNO_3 , 0.05 to 0.25M KMnO_4 . Ce(IV) extraction capacity measured by contacting washed solvent with an equal volume of 2M HNO_3 , 0.2M $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 0.02M AgNO_3 , 0.007M $\text{Ce}(\text{NO}_3)_3$ for one hour at 25C.

Diluent	M KMnO_4 in Wash	Cerium E_a^0	
		Unwashed	Washed
Soltrol-170 ^(a)	0.25	27.8	360
Soltrol-170 ^(b)	0.05	0.17	21.4
Soltrol-170 ^(b)	0.10	--	360
Soltrol-170 ^(b)	0.25	--	1320
Soltrol-170 ^(c)	0.10	5.7	620
NPH ^(c)	0.10	19.3	980

(a) Strontium Semiworks solvent washed previously with NaOH and HNO_3 -oxalic acid.

(b) Laboratory solvent prepared with chemically degraded (HNO_3 - NaNO_3) Soltrol-170.

(c) Laboratory solvent irradiated to about 400 watt-hrs/liter.

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As this manual was written there were no plans for routine washing of B-Plant D2EHPA solvents with HNO_3 - KMnO_4 solutions. The present choice of a hydrocarbon diluent for B-Plant use is NPH. On the basis of Strontium Semiworks experience, this diluent should not degrade sufficiently to impair Ce(IV) oxidation and extraction under countercurrent flow conditions in the mainline process LC Column.

6.3.4 Nitrous Acid Removal

Sulfamate ion reacts rapidly and completely with nitrous acid in acid systems according to the reaction⁽⁸²⁾

Sulfamic acid and sulfamic-nitric acid washes have been successfully used in pilot plant studies⁽⁶¹⁾ and Strontium Semiworks campaigns⁽⁶³⁾ to remove nitrous acid from solvent after Ce(IV) stripping. The reaction rate is too slow in alkaline systems (above pH 5) to be of value.

Caustic washing should also effectively remove nitrous acid by converting it to the inextractable nitrite. A small sulfamic acid addition during solvent acidification should provide additional assurance of nitrite removal.

6.4 Chemical Flowsheet

A tentative chemical flowsheet for batch washing of the used D2EHPA extractant from the processing of current acid waste is presented in Figure IV-58. It is anticipated that this flowsheet will also be followed in washing solvent from the processing of stored sludge waste and from the auxiliary strontium and rare earth purification processes. In these latter processes, nitrite will not be introduced into the extractant and addition of sulfamic acid to the 100 stream will not be necessary. Also, during D2EHPA purification of the strontium fraction from both current and stored waste (Section C 4) only three of the four available pulse columns will be used; thus if desirable, the fourth column can be used to perform the solvent washing step on a continuous rather than a batch basis.

The chemical flowsheet specified in Figure IV-58 involves only a NaOH-complexant wash and a HNO_3 butt to the desired Na/H mole ratio. If necessary or desirable, additional washes (HNO_3 -oxalic or HNO_3 - KMnO_4) can be made.

6.5 Strontium Semiworks Process Demonstration

Chemical washing of the D2EHPA extractant used in Strontium Semiworks operation for Sr-90 recovery has been performed routinely for more

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than two years with satisfactory results⁽⁶³⁾. Equally successful performance was obtained in either batch or continuous countercurrent column washing, both at about 50 C. In batch washing, the solvent was first washed with a double volume of 2M NaOH-0.2M citrate (or tartrate). This was followed by washing with an equal volume of 2M HNO₃-0.2M oxalic acid. Typical over-all decontamination factors were about 70 for Ce-144 and ZrNb-95, about 10 for Ru-106, and about 70 to 200 for Y-91. Hydraulic and chemical performance of the washed solvent in Sr-90 recovery operations were excellent throughout.

The procedure used for column washing was similar to the batch wash procedure except that the A/O ratios were 1 and 5 for the caustic and acid washes, respectively. The pulse columns were operated at volume velocities of 360 (caustic washing) and 1100 gph/ft² (acid washing). The cartridge geometries were comparable with those used in the B-Plant 1A and 1B Columns, respectively.

FIGURE IV-58

Chemical Flowsheet for Washing D2EHPA Extractant

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D. STRONTIUM AND RARE EARTH SOLVENT EXTRACTION PROCESSES:
PROCESS ENGINEERING

1. Types of Contactors

Solvent extraction processes can be performed in a variety of equipment, depending on the objectives, available space, economics, etc. The simplest type of contactor consists of a batch mixing tank in which the two phases are stirred together, allowed to settle, and decanted. Continuous operation can be achieved by providing a separate settling vessel or by incorporating a settling zone in the mixing tank. The Turbo mixers provided in the Purex Plant are examples of this type⁽¹⁷⁾. For any given ratio of solvent to feed, the maximum amount of solute which may be extracted is fixed solely by equilibrium considerations. Because of this, simple batch extraction is economically justified only when the distribution ratio of the transferring component is high enough to permit quantitative extraction with only one stage of contact.

Several types of continuous mixer-settlers are available. These are usually composed of a series of mixing chambers or stages separated by settling chambers, all enclosed in the same shell. The most familiar type in radioactive service is the "Pump-Mix" mixer-settler used in the Savannah River Plant and, in miniature form, in many laboratories⁽⁷⁾. In this contactor, the stages are arranged horizontally, and flow from stage to stage is promoted by pump-type impellers used as agitators. Mixer-settlers and other multistage contactors are operated most efficiently with countercurrent flow of feed and solvent phases. Fresh extractant first contacts low-solute-concentration raffinate and then contacts more concentrated raffinate as its own solute concentration increases. If a sufficient number of contacts are made and a sufficiently large volume of solvent is used, the concentration of the extracted component in the final raffinate may be reduced to almost any desired low value. Mixer-settler equipment can frequently be operated at high stage efficiencies (80% of theoretical or better), thus indicating with a fairly high degree of certainty the number of stages to provide for the desired separation.

Columns are used to accomplish solvent extraction by a countercurrent differential contact method wherein a very large number of infinitesimally small contacts are achieved by subdividing (dispersing) one phase and passing it countercurrently through the other (continuous) phase. Either of the phases may be continuous or dispersed. For example, if the lighter phase is to be continuous, the dispersed heavy phase is introduced at the top and allowed to fall by gravity through the continuous phase, and conversely. The simplest type of column is the spray column, which is simply a vertical pipe with an appropriate nozzle for introducing the dispersed phase. The packed column contains a packing material, such as Raschig rings or Berl saddles, to break up the dispersed phase and force it to follow a tortuous path. Although packing improves the extraction efficiency of the column, still more effective contacting can be obtained by adding mechanical energy to

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the contents. Prominent examples of this type of column are the rotating-disk contactor, the Scheibel column, and the pulse column. The latter has been the most widely used column in radioactive service⁽⁹⁾ and will be used in the B-Plant.

Pulse columns impose a reciprocating pulsing movement to the column contents by means of a piston or bellows connected hydraulically to the bottom of the column. The contacting section of the column usually contains closely-spaced horizontal, perforated plates. The up-and-down motion of the liquid phases through the perforations provides agitation resulting in more or less intimate mixing of the two countercurrently flowing phases. The resulting dispersion permits an important, often more than two-fold, reduction in column height from the heights needed with conventional packed columns. Additional advantages of pulse columns are a less pronounced dependence of extraction effectiveness (HTU values) on throughput rate and the greater ease of a temporary shutdown and start-up with the property of very little flow through the plates in the absence of pulsing. The need of a pulse generator, with its first cost and maintenance requirements, is a disadvantage. The performance characteristics of pulse columns as a function of design and operating conditions are discussed in Section D. 4.

2. Special Terms

The terms defined in this subsection are those used frequently in discussing the operation or evaluating the performance of solvent extraction columns. Convenient colloquial terms which have come into use at Hanford are included in the following discussion:

Extraction is used at Hanford to describe mass transfer from the aqueous to the organic phase as, for example, extracting strontium in the 1A Column.

Stripping is used to describe mass transfer of product ions from the organic to the aqueous phase; thus, strontium is stripped from the organic feed to the aqueous effluent stream in the 1B Column.

The removal of weakly-held impurities in the organic product stream by contacting it with an aqueous stream is referred to as scrubbing. For example, sodium is scrubbed from the 1A Column product stream by contacting it with a buffered scrub stream in the 1S Column. Analogously, an organic scrub can be used to re-extract solvent-favoring impurities from an aqueous product stream, as in the persulfate-oxidized 1C Column.

A simple column is one designed to perform only one solvent extraction function (extraction, scrubbing, stripping). A dual-purpose column combines two separate functions, such as extraction and scrubbing. The 1C Column can be operated as a dual-purpose column with the upper half used to strip rare earths from the solvent feed and the lower half used to re-extract tetravalent cerium.

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Flooding in a pulse column occurs when flow rates are so high that the two phases cannot pass countercurrently through the column, with the result that one of the phases leaves the column at the same end at which it enters. Local flooding in the column consists in an unusually large accumulation of dispersed phase at some location in the two-phase zone. It may occur as an accumulation of closely packed dispersed-phase droplets or, more frequently, as a series of large, coalesced globules channeling through a tightly packed dispersion. When this occurs on a cyclic basis, as it often does, it is termed cyclic local flooding. As long as local flooding does not propagate into complete flooding, the column may be operated indefinitely and give satisfactory extraction performance.

In some of the columns, a portion of one or more of the solutes may be extracted in one part of the column and stripped in the other. This phenomenon is referred to as internal reflux. For example, if the 1A and 1S Columns are considered as one column, strontium is quantitatively extracted in the 1A portion, partially stripped back into the aqueous phase in the 1S portion, and returned to the 1A Column where it is again extracted.

The pulse amplitude is the magnitude of the up-and-down motion of the pulse-column liquid contents, as measured between the extreme positions. The pulse frequency is the time rate of pulsing, expressed in cycles per minute. The amplitude-frequency product is frequently used as a simple means of correlating the pulsing conditions with column performance. It is equal to the pulse amplitude times the frequency and is conveniently expressed in inches per minute.

The superficial volume velocity is defined as the sum of the net volumetric flow rates of the two phases in the column divided by the total cross-sectional area of the column, neglecting the cross-section of the column occupied by packing or plates. The volume velocity for comparable performance in columns with like plates or packing but with different diameters is essentially constant. The pulsed volume velocity is simply the amplitude-frequency product expressed in volume-velocity units and, in gal/hr-ft², is equal to 74.81(amplitude)(frequency), where the amplitude is given in inches and the frequency in cycles per minute. The pulsed volume velocity represents the pumping capacity of the pulse and is the upper capacity limit for sieve plate columns.

The decontamination factor (DF) for a feed contaminant is defined as the weight ratio of contaminant to the desired component in the feed divided by the same ratio found in the product. For convenience, it is frequently calculated as the reciprocal of the fraction of feed component found in the product, ignoring the efficiency of product recovery.

An equilibrium line is a graphical representation of the equilibrium solute distribution between the phases for the chemical conditions existing in the countercurrent solvent-extraction contactors.

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An operating line is a locus of points depicting the actual solute concentrations of the aqueous and organic phases at various heights within the column. The operating-line equation is developed from a solute material balance made around either end of a column section. The schematic diagram below represents the bottom of the 1A Column.

Values of X and Y indicate the solute concentrations in the aqueous and organic phases, respectively; values of A and O indicate the volume flow rates of the aqueous and organic phases, respectively. At steady-state operating conditions, the weight of diffusing solute entering the above section of column over a given time period via the aqueous and organic streams must equal the weight of solute leaving via the effluent streams. The weight of solute carried by each of the four flowing streams in unit time is the product of the flow rate times the solute concentration: $Y_X O$, $X_W A$, $Y O$ and $X A$, respectively. Equating the influent flow of solute to the effluent flow gives

$$X A + Y_X O = Y O + X_W A, \quad (1)$$

which on rearrangement gives the operating line equation:

$$Y = (A/O)X + Y_X - (A/O)X_W. \quad (2)$$

(Recent investigations have shown that this equation is valid only in the absence of longitudinal or back mixing, and that the true operating line in column contactors may have considerable curvature⁽¹⁶⁾. The effect of back mixing is usually ignored in column performance calculations because of the difficulty of determining its magnitude.)

Together, the operating and equilibrium lines make up the operating diagram from which the number of stages required to make a desired separation or the efficiency of a column can be calculated. An operating diagram for the removal of sodium from the solvent in the 1S Column is illustrated in Fig. IV-59 in Section D.3.2. Calculation techniques are summarized below.

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3. HTU and HETA Calculations

The mass transfer effectiveness of solvent-extraction columns may be evaluated in terms of the height of contactor which is required to perform the same extraction as a single theoretical stage. A theoretical stage is achieved in a column when two influent streams (not at equilibrium) entering a section of the column mix and produce effluent streams which are in equilibrium with one another. For solvent-extraction columns containing several theoretical stages, the HETS (height equivalent to a theoretical stage) may be obtained by dividing the height of the contacting section by the number of theoretical stages required to accomplish the same extraction being carried out by the column. The number of stages can be stepped off graphically on a McCabe-Thiele-type operating diagram, such as that shown in Fig. IV-59. When the operating and equilibrium lines are straight, or nearly so, it is more convenient to calculate the number of stages by Colburn's equation⁽⁶⁾:

$$N_S = \frac{\ln [M(1-P) + P]}{\ln (1/P)} \quad (3)$$

where P = the extraction factor, the ratio of the slopes of the operating and equilibrium lines ($P = A/mO$ for extraction and mO/A for stripping).

$$M = \frac{X_1 - Y_2/m}{X_2 - Y_2/m} \quad \text{for extraction and} \quad \frac{Y_1 - X_2m}{Y_2 - X_2m} \quad \text{for stripping.}$$

A/O = slope of the operating line, (volume of aqueous phase per unit time)/(volume of organic phase per unit time).

m = slope of the equilibrium line, (concentration in the organic phase)/(concentration in the aqueous phase in equilibrium with the organic phase). For straight equilibrium lines, m is equivalent to the E_Q .

X = the solute concentration in the aqueous phase.

Y = the solute concentration in the organic phase.

Subscripts 1 and 2 refer to concentrated-end and dilute-end concentrations, respectively.

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The HTU (height of a transfer unit) is also a measure of mass-transfer effectiveness. It is less sensitive than the HETS to variations in the value of the extraction factor and has been widely used at Hanford for design and development of solvent extraction columns. For most purposes, the number of transfer units can be expressed by the following integrals:

$$N_t = \int_{X_2}^{X_1} \frac{dX}{X - X^*} \text{ for extraction and } \int_{Y_2}^{Y_1} \frac{dY}{Y - Y^*} \text{ for stripping,} \quad (4)$$

where N_t = the number of transfer units, over-all raffinate-film basis, for transfer from the raffinate to the extract phase.

X = the concentration of the diffusing component in the aqueous phase.

X^* = the concentration of the diffusing component in the aqueous phase in equilibrium with an organic phase of composition Y .

Y = the concentration of the diffusing component in the organic phase.

Y^* = the concentration of the diffusing component in the organic phase in equilibrium with an aqueous phase of composition X .

Thus, the number of transfer units is an integrated ratio of the change in diffusing component concentration to the concentration driving force which causes transfer between phases. When the equilibrium and operating lines are straight, as they frequently are at the dilute end of the column, the number of transfer units may be calculated from Colburn's equation⁽⁶⁾:

$$N_t = \frac{\ln [M(1-P) + P]}{1 - P} \quad (5)$$

where M and P were previously defined. The over-all HTU is then calculated by dividing the height of the contacting section by the number of transfer units.

Colburn's equation has been used extensively for calculating HTU's for strontium and rare earth extraction processes. Conservative HTU values were obtained by selecting those equilibrium data which yielded a minimum value of the extraction factor. Internal reflux (between the 1A and 1S Columns) was generally ignored in HTU calculations; it normally amounted to less than 10% of the material in the feed, and its effect was within the experimental error of the calculation method.

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3.1 Example HTU Calculations

3.1.1 1A Column, Strontium Extraction

Assume that the following data were taken during the steady-state period of a typical 1A Column run using a 12-ft-tall perforated plate cartridge:

<u>Stream(a)</u>	<u>Flow Rate, L/Min.</u>	<u>Sr-90, Ci/l</u>	<u>% of Sr-90 in Feed</u>
1AF	1.0	5.0	100
1SW	0.2	2.0	8.0
1AX	1.0	0.005	0.1
1AP	1.0	5.4	108
1AW	1.2	0.020	0.48

(a) See Fig. IV-48 for identification of streams.

Assume further that the strontium E_a^O decreased from 20 at the waste end of the column to 10 at the feed point under the operating conditions of the column.

Using Colburn's equation, let $m = 10$ (the minimum E_a^O) and the feed point Sr-90 concentration = 4.5 Ci/l (by material balance adding together the 1AF and 1SW streams). Then

$$M = \frac{X_1 - Y_2/m}{X_2 - Y_2/m} = \frac{4.5 - 0.005/10}{0.020 - 0.005/10} = 231,$$

$$P = \frac{A}{mO} = \frac{1.2}{(10)(1.0)} = 0.12, \text{ and}$$

$$N_t = \frac{\ln [M(1-P) + P]}{1-P} = \frac{\ln 203}{0.88} = \frac{5.32}{0.88} = 6.05$$

$$\text{The strontium HTU} = \frac{12}{6.05} = 2.0 \text{ ft.}$$

The strontium reflux in the example above amounted to 8% of the feed strontium. If reflux were ignored in the calculation, the feed point concentration, X_1 , would have been 4.17 and the resulting HTU would have been $\frac{12}{5.95} = 2.0 \text{ ft.}$

The use of an average or weighted E_a^O also has little effect on the calculation. For example, if the raffinate E_a^O of 20 were used as m , the HTU would have been $\frac{12}{5.70} = 2.1 \text{ ft.}$

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3.1.2 1B Column, Strontium Stripping

Again, assume that the following typical data were obtained from a 1B Column run using a 12-ft-tall cartridge:

<u>Stream</u>	<u>Flow Rate, L/Min.</u>	<u>Sr-90, Ci/l</u>	<u>% of Sr-90 in Feed</u>
LSP-LBF	1.0	5.0	100
LFX	0.2	0.0	0
LBP	0.2	24.8	99.2
LBW	1.0	0.04	0.8

Feed point Sr-90 $E_a^0 = 0.04$

Waste (raffinate) Sr-90 $E_a^0 = 0.013$

The feed point E_a^0 in this example reflects the increased pH at the feed end of the column due to sodium and strontium stripping (see Section C 3.4). The lower E_a^0 more nearly reflects the distribution ratio in the major portion of the column and will be used in Colburn's equation:

$$M = \frac{Y_1 - X_2^m}{Y_2 - X_2^m} = \frac{5.0 - 0.0}{0.04 - 0.0} = 125$$

$$P = \frac{mO}{A} = \frac{(0.013)(1.0)}{0.2} = 0.065$$

$$N_t = \frac{\ln [M(1-p) + P]}{1-P} = \frac{\ln(117)}{0.935} = \frac{4.76}{0.935} = 5.09$$

$$\text{Strontium HTU} = \frac{12}{5.09} = 2.4 \text{ ft.}$$

Had the feed point E_a^0 of 0.04 been used, the strontium HTU would have been $\frac{12}{5.76} = 2.1 \text{ ft.}$, a relatively minor difference.

3.2 Example Calculation of a 1S Column Sodium Operating Diagram

The conceptual PAW flowsheet (Fig. IV-48) will be used to illustrate the calculation of a sodium operating diagram for the 1S Column. This calculation also illustrates the steps involved in designing the chemical flowsheet for this column.

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First, estimate the concentration of free D2EHPA in the LAP. Assume that all of the strontium, calcium, and rare earths extract, along with about 0.7% of the iron and aluminum. By material balance the concentrations of these elements in the LAP and the amount of solvent complexed are:

	<u>M in LAP</u>	<u>Moles D2EHPA Complexed Per Mole of Cation^(a)</u>	<u>M D2EHPA Complexed</u>
Sr	0.0006	4	0.0024
Ca	0.006	4	0.0024
RE	0.0036	6	0.0216
Fe + Al	0.0013	2.5	<u>0.0033</u>
Total			0.0297

(a) See Section C 2.5.1

Thus the "free" D2EHPA will be $0.3 - 0.03 = 0.27M$.

The aqueous phase sodium concentration and pH remain relatively constant throughout the 1A Column and can be assumed equal to the 1AW values. Hence the sodium concentration in the LAP can be calculated from Fig. IV-36 as that in equilibrium with $1.15M Na^+$, pH 4.0:

$$\frac{M_{Na, org}}{M_{free D2EHPA}} = 0.278,$$

or

$$Na = (0.278)(0.27) = 0.075M \text{ in the LAP.}$$

The required hydroxyacetate concentration was set by inspection at $0.6M$ for the trial calculation. This was assumed to be sufficient to assure that the operating line would fall above the equilibrium line over its entire length. The equilibrium data for this calculation were interpolated from Fig. IV-35, using $0.27M$ "free" D2EHPA, and plotted in Fig. IV-59 on logarithmic coordinates.

A sodium concentration in the LSS of $0.038M$ was defined by the minimum pH allowed by strontium reflux considerations (pH 2.4) and the hydroxyacetate concentration. The sodium concentration in the LSP was set at $0.001M$ by 1B Column requirements. The operating line can then be calculated by the equation:

$$Y = \frac{A}{0} (X - X_B) + Y_P = 0.2 (X - 0.038) + 0.001.$$

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FIGURE IV-59

Sodium Operating Diagram - 1S Column
PAW Flowsheet Conditions
(From Figure IV-48)

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FIGURE IV-60

Calculation of the Number of Transfer Units (N_t)
by Graphical Integration

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Starting at the "feed" end of the operating diagram, stages are stepped off. As shown in Fig. IV-59, 3.7 stages are required to obtain the desired separation. This is within the range of stages available in conventional extraction equipment, including the B-Plant columns, and the assumed scrub composition is satisfactory.

Extraction efficiency is more often correlated by HTU's. The number of transfer units required in the above example was 5.6, calculated by graphical integration of the area under the curve shown in Fig. IV-60. Here, values of Y and the corresponding equilibrium Y^* were taken from Fig. IV-59 and plotted as $1/(Y-Y^*)$ versus Y in accordance with Equation (4).

4. Pulse Column Variables

4.1 General Performance Characteristics

Five distinct types of behavior have been observed in conventional perforated plate pulse columns as a function of the throughput rate and the pulsing conditions. These are shown in the sketch below, a typical plot of the total volumetric flow rate versus the product of the pulse amplitude and frequency.

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The first zone is flooding due to insufficient pulsing (without down-comers, there is essentially no countercurrent flow in sieve plate columns without the pumping action of the pulser). A mixer-settler type of operation occurs as the frequency is increased beyond this pulsed volume velocity threshold. This is characterized by coarse drops of the dispersed phase and pronounced settling of the two phases into discrete layers in the quiescent portions of the pulse cycle. Although very stable, this type of operation is relatively inefficient. Emulsion-type operation occurs at still higher energy input. This highly efficient type of operation is characterized by small drop size and fairly uniform dispersion throughout the pulse cycle. As the throughput rate or frequency is increased still further, complete flooding eventually results. This is defined as the exit of one of the entering streams through the effluent line intended for the other phase.

Frequently, but not always, an unstable region of operation occurs as the flow rate or frequency is increased to values just less than flooding. This is usually characterized by periodic coalescence of the dispersed phase in a zone of high dispersed-phase holdup and subsequent channeling of these large drops through the column. This type of instability is typical of coalescing systems. In such systems, the ease of dispersion and coalescence appears to be related to the rate of mass transfer favoring coalescence and a low rate favoring dispersion. Generally the extraction efficiency is impaired in the unstable region and often fluctuates widely.

The factors affecting pulse column performance can be divided into two broad groups: those which are fixed by design of the column or of the associated pulse generator and those which may be varied in the course of operating a column of fixed design. Only the general direction and order of magnitude of the effects will be presented.

4.2 Design Variables

The major design variables influencing pulsing column efficiency and capacity are:

- (a) pulse amplitude and wave shape,
- (b) wetting characteristics and choice of continuous phase,
- (c) sieve plate geometry,
- (d) plate section height, and
- (e) column diameter.

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4.2.1 Pulse Amplitude and Wave Shape

The pulse amplitude affects column performance primarily as a contributory component to energy input, that is, as a function of the arithmetic product of amplitude and frequency. This product represents a useful, simple means of correlating the pulsing conditions with column performance. In many systems, the flooding capacity in the high pulse energy region can be correlated by an equation of the form

$$\log (\text{volume velocity}) = C_1 - C_2 (\text{amplitude} \times \text{frequency}), \quad (6)$$

where C_1 and C_2 are constants for a given system.

With appropriate adjustment of the frequency, the pulse amplitude may usually be varied within a 1.5 to 2-fold range without capacity and HTU effects significantly in excess of normal experimental error. This fact enables selection of a minimum number of pulse generator sizes for a plant using columns of different diameters. Generally the pulse amplitudes are about 50% of the plate spacing, a factor believed important for optimum performance and minimization of excessive backmixing (or recycle) of the dispersed phase by the pulse.

A near-sinusoidal pulse wave shape is used in Hanford columns. Limited experience has shown that pulse wave shapes substantially deviating from sinusoidal often give optimum HTU's comparable with a sine wave.

4.2.2 Wetting Characteristics and Choice of Continuous Phase

It is generally considered advantageous from the standpoint of extraction effectiveness to establish the continuous phase with the liquid having the smaller flow rate and to disperse the phase with the larger flow. In nuclear separations processing, however, this advantage is outweighed by the benefits to be gained by maintaining the interface at the "waste" end of the column. Interface-seeking impurities are continually carried to the interface by the films surrounding the dispersed phase droplets and, after building up to a stable depth at the interface, tend to leave the column by the nearby effluent line. These inter-facial films and solids, consisting of substances such as silica or solvent degradation products, usually become extremely contaminated with adsorbed fission products, and their entrainment in the product stream may severely limit fission product decontamination.

For satisfactory operation it is essential that the dispersed phase not wet the sieve plates. When the sieve plates are wet by the dispersed phase, the droplets coalesce on the plates as a film which tends to

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leave reluctantly in streamers or as "balloons" enclosing droplets of the continuous phase. This type of performance usually is less efficient and provides lower capacity than the normal emulsion-type operation.

Stainless steel nozzle plates, a recent Hanford development for pulse columns, are a special class of sieve plates. They are characterized by the indentation of the holes to form many tiny jetting nozzles usually oriented toward the dispersed-phase exit of the column, although satisfactory operation can be obtained with the nozzles pointing the other way. Stainless steel nozzle plates can be used with either phase continuous. Their action differs from that of the sieve plates in that the dispersed phase, when it wets the plate, cannot cling to the nozzle tip and is readily redispersed with the pulse. The nozzle depth must be at least 0.035 inch from the base of the nozzle to the tip for optimum performance. Well designed nozzle plates have given capacities about 50% higher and HTU's up to 30% lower than equivalent-geometry flat sieve plates.

The excellent performance obtained with nozzle plates may be related to improved separation of dispersed and continuous phase (the jet produced by the pulse propels droplets up to three or four times the length of the pulse, a distance adequate to reduce the number of drops pulled back with the reverse cycle of the pulse) and to the smoother flow characteristics of nozzles as contrasted to sharp-edged orifices.

4.2.3 Sieve Plate Geometry

Both the capacity and HTU attainable in a pulse column increase with increasing hole size, plate spacing, and percentage of free area of the sieve plates. A cartridge consisting of two-inch-spaced stainless steel plate with 1/8-inch-diameter holes and 23 percent free area has generally proved to be a desirable compromise between high capacity and efficiency and has been designated as the "standard cartridge". In the neighborhood of standard cartridge geometry, up to two-fold variations in capacity and HTU are encountered as hole size, plate spacing, or free area are varied three- to four-fold. Diametric clearances up to 1/8 inch between the plates and the wall of a three-inch diameter column have been noted to have little or no effect on HTU values. Three-eighths inch diametric clearances are used in large columns to permit remote installation of the plate cartridges.

4.2.4 Height of Plate Cartridge

HTU values generally increase with increasing column height. This is believed due to a general trend toward higher HTU values with decreasing diffusing-component concentration. Usually the heights of the plant

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cartridges are chosen to equal the product of the number of transfer units required times the maximum HTU obtained in pilot plant studies under near optimum conditions - plus a 25 to 100 percent safety margin (the value added depending on whether the pilot plant cartridge height was near or appreciably less than the calculated height). Column height usually has a negligible effect on the flooding capacity; however cases have been noted where the stable capacity was decreased 15 to 30 percent with 50 to 100 percent increases. Possibly some minimum height is required to establish the ultimate dispersion profile.

4.2.5 Column Diameter

As the column diameter increases, the counter flowing liquid phases display an increasing tendency to channel in portions of the cross section rather than to distribute evenly across. Such channeling markedly decreases efficiency. Columns in which channeling is most likely to occur are those in which the continuous phase density is appreciably greater at the top than at the bottom. Louver plate redistributors are often added to counteract potential channeling.

4.3 Operating Variables

The important operating variables are:

- (a) pulse frequency,
- (b) volume velocity,
- (c) flow ratio,
- (d) solute concentration,
- (e) physical properties of liquids, and
- (f) temperature.

4.3.1 Pulse Frequency

The effect of pulse frequency and the correlation of amplitude-frequency product have already been discussed. As shown in the sketch on the opposite page, HTU values generally decrease sharply with increasing frequency within the region of stable operation. On the threshold of instability there may be a slight reversal of the trend. Experience indicates that minimum HTU values generally lie in a zone between 75 and 95 percent of the flooding frequency.

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4.3.2 Volume Velocity

Pulse column HTU values are relatively insensitive to variations in throughput rate. At constant pulsing conditions, plots of HTU values against volume velocity are usually convex downward and shallow, as shown above. Nearly constant HTU's over a wide range of throughput rates may be obtained by appropriately adjusting the frequency.

4.3.3 Flow Ratio

Although not of practical importance, both HTU values and capacity generally increase slightly with increasing continuous-to-dispersed phase flow ratio. Because of channeling or backmixing tendencies, the extract-to-raffinate flow ratio is usually maintained at least 15 to 20 percent above the minimum value theoretically required to provide the desired extraction service.

4.3.4 Solute Concentration

HTU values are generally higher at the dilute end of a column than at the concentrated end. This results from the trend for HTU values to increase with decreasing solute concentration.

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4.3.5 Physical Properties of Liquids

The flooding capacity of a pulse column using non-coalescing systems has been shown to be approximately proportional to the 0.7 power of the density difference between the phases, the 0.4 power of the interfacial tension, and the 0.3 power of the continuous phase viscosity. Recent studies using three- and four-inch diameter columns have shown that the flooding capacity can be increased in many instances by adding about 50 ppm Mistron* (a finely-divided talc) or bentonite to the dispersed phase. Addition of either material greatly increases the coalescing tendency of the dispersed phase, typically reducing the disengaging time of an equal-volume emulsion of 30% TBP and water from 60 to 15 seconds. Other additives or impurities, such as colloidal silica or ferric hydroxide, have been observed to decrease the capacity by increasing the emulsification tendency. The inter-action of such trace impurities greatly increases the difficulty of predicting flooding capacities from fundamental relationships.

Since individual film HTU values are believed to vary with the dimensionless Schmidt number (viscosity divided by density and diffusivity of diffusing component) raised to about 0.6 the power, low viscosity and high diffusivity should favor low HTU values.

4.3.6 Temperature

An increase in temperature increases the flooding capacity and decreases the HTU, presumably because the higher temperature reduces the viscosities and increases the diffusivities involved. An increase in temperature also decreases strontium distribution coefficients. Pulse columns are usually operated at temperatures up to 50 C; much higher temperatures run the risk of accelerated solvent degradation and the possibility of approaching or exceeding the solvent flash point.

5. B-Plant Pulse Column Specifications

Specifications for the B-Plant pulse columns are presented in Table IV-24 on page 4158.(14)

The 1A and 1C Columns were designed to operate at nominal volume velocities of 300 to 400 gal/hr-ft². The over-all design recoveries were 95% for strontium and 90% for cerium and the promethium-rare earth - americium fractions.

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TABLE IV-24

B-PLANT PULSE COLUMN SPECIFICATIONS

Column	Overall Height, ft.	ID in.	Cartridge Specifications ^(a)				Pulse		Interface Position
			Height feet	Plate Spacing, inches	Hole Diam. inches	% Free Area	Ampl. inches	Freq. Range Cycles/min.	
1A	18.5	20	14	2	3/16	23	1.3	35-90	Bottom
1S	14.5	20	11	2	1/8	10	1.3	35-90	Bottom
1B	18.5	20	14	2	1/8	10	1.3	35-90	Bottom
1C	18.5	15	10(strip) 4(scrub) 2	4	1/8	10	(b)	(b)	Top

- a. Cartridges are made of stainless steel nozzle plates with the nozzle indented about 0.04 in. beyond the adjacent plate face. The 1A, 1S, and 1B columns each contain a lower plate redistributor in the middle of the cartridge with 6 inches of free space on each side.
- b. Not determined at time of writing.

The specifications were derived from pulse column studies made in 3-inch-diameter glass pulse columns containing 6 to 12-ft tall nozzle-plate cartridges. Highlights of these studies and corroborative data obtained from full-level runs in the Strontium Semiworks with similar cartridges are discussed in the following sections.

6. Cold Semiworks Pulse Column Studies

"Cold" pulse column development runs were made in 3-in.-diameter columns containing 6 to 12-ft tall cartridges of 2 to 4-in. spaced stainless steel nozzle plates. Cartridges used in work applicable to B-Plant are described in Table IV-25.

TABLE IV-25

NOZZLE PLATE CARTRIDGE USED IN CSW RUNS

(Source of Data: HW-72666, Section 4; HW-79762PT2; BNWL-173)

	Column			
	1A	1S	1B	1C ^(a)
Height, feet	6 to 13	6 to 10	9 to 10	9 to 10
Plate spacing, inches	2 to 4	2 to 4	2 to 4	2 to 4
Hole diameter, inches	3/16	1/8	1/8	1/8
Percent free area	23	10	10	10

(a) A dual-purpose 1C column with a 4 foot tall scrub section added to the bottom is also investigated.

Feed streams simulated the compositions of PAW, ZAW, and several potential Strontium Semiworks crude strontium feeds. Typical feed compositions are presented in Table IV-26. In many runs, feeds were traced with Sr-85, Ce-144, and/or Eu-152-154 to improve analytical precision.

The solvents normally contained 0.2 to 0.4M D2EHPA, 0.12 to 0.2M TBP in various hydrocarbon diluents. Flowsheet conditions were similar to those presented in Figures IV-48, IV-49 and IV-62.

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TABLE IV-26
TYPICAL "COLD" SEMIWORKS 1AF COMPOSITIONS
(Nitrate System)

Constituents	M Adjusted 1AF				
	PAW ^(10,11)	ZAW ⁽¹³⁾	Sr Crude #1 ^(5a)	Sr Crude #2 ^(5a)	Sr Crude #3 ⁽¹²⁾
Na	1.8	2.0	1.0	1.6	1.5
Fe	0.075	0.165	0.06	0.02-0.10	0.0088
Al	0.038	0.323	0	0	0
Cr	0.015	0.0068	0	0	0
Ni	0.0075	0.0034	0	0	0
Pb	0	0	0.001	0.003-0.04	0.0336
Zr	0	0	0-0.005	0-0.002	0
Ca	0.00068	0.00062	0.09	0.002-0.026	0
Sr	0.00068	0.00055	0.02	0.002	0.0012
Rare Earths	0.0041	0.0027	0.003	0.002	0.0064
SO ₄ ⁻	0.11	0.051	0	0-0.012	0.080
F ⁻	0	0.13	0	0	0
Buffer ^(a)	0-0.3	0	0.8	0.5	0.26
Complexant ^(b)	0.185-0.27	0.56-0.6	0-0.16	0.15	0.11
"Free" Complexant ^(c)	0.05-0.1	0.06-0.1	0-0.09	0.05-0.1	0.07
pH	3.6-5.5	4.0-4.7	1.9-5.4	3.8-4.9	1.8-3.8

(a) Acetate or hydroxyacetate.

(b) Complexants included EDTA, HEDTA, tartaric acid, citric acid and mixtures of HEDTA or citric acid with tartaric acid.

(c) Defined as the total complexant molarity minus the molarities of iron, aluminum, chromium, nickel, lead, and zirconium.

6.1 1A Column Performance

6.1.1 Capacity Studies - PAW Feeds⁽¹⁰⁾

The maximum demonstrated capacity of the 1A Column was 1070 gph/ft², using a 9-ft-tall cartridge with 2-in. plate spacing. A rather wide range of flooding frequencies was observed at any given flow rate. This variation was attributed to feed impurities, possibly colloidal ferric hydroxide. The choice of interface position had little effect on the flooding capacity, but increasing the temperature from 25 to ca. 50 C usually increased the flooding threshold frequency by 10 to 20 cycles/minute.

A summary of the capacity studies is presented in Table IV-27. The maximum demonstrated frequency shown in this table is presented as an indication of the frequencies obtainable at operating conditions where no flooding determinations were made.

Several solid impurities in the PAW are known to be emulsion stabilizers. These include such compounds as silica and zirconium phosphate (from TBP decomposition). The effects of these two additives on capacity were relatively minor, lowering the flooding frequency about 10 to 15 cycles per minute. The adverse effect could be countered by adding about 60 ppm Mistrion to the feed.

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TABLE IV-27
1A COLUMN CAPACITY SUMMARY
(Source of Data: HW-79762PT2)

Pulse amp. = 1 in.; cartridge ht. = 9 ft.

Volume Velocity, gph/ft ²	Temperature, Centigrade	Frequency, Cycles/min.	
		Max. Demonstrated	Flooding
<u>Bottom Interface</u>			
180	25	--	120
360	25	--	68 to 70
360	45	70	--
550	25	--	66 to 83
550	50	--	85
710	25	--	39 to 70
710	50	--	48 to >84
1070	25	--	42
1070	50	44	--
<u>Top Interface</u>			
270	25	--	69
360	25	60	--
550	25	--	53 to 58
710	25	--	53 to 69
710	50	70	--

The stability of the 1A Column when processing citrate-complexed PAW was greatly improved when the pH adjustment was made at 50 C and the adjusted feed was digested for about an hour at 70 to 90 C. This procedure evidently prevented the formation of emulsion-stabilizing hydroxides by increasing the rate of complexing.

6.1.2 Extraction Efficiency - PAW Feeds⁽¹⁰⁾

Optimum strontium HTU's were about 1.5 ft for citrate and tartrate complexed feeds and were fairly insensitive to operating conditions. Cerium HTU's were much more dependent on feed compositions and operating conditions and ranged from 3.2 to greater than 9 ft. The effects of some of the major variables on the HTU's are discussed below.

Effect of Solvent Composition

Variations in the D2EHPA composition from 0.16 to 0.48M appeared to have no effect on extraction performance other than that caused by the effect on the strontium distribution ratio. Addition of 0.04 to 0.1M NaOH to the solvent minimized pH changes at the bottom of the column (caused by sodium extraction) and may have contributed to a slight

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improvement in performance. The addition of BAMBP to the solvent in Csrex process demonstration runs (see Section C 2.6.3) had little or no effect on cerium and strontium HTU's(11).

Effect of Feed Composition

Strontium HTU's were virtually unaffected by feed composition over the range tested. Cerium HTU's, however, were extremely sensitive to the nature of the feed. Cerium HTU's as low as 1.4 ft were measured at 25 C in an organic-continuous column using a simple, citrate-complexed NaNO_3 feed. Under comparable operating conditions, the cerium HTU's ranged from 8 to 10 ft with citrate-complexed PAW and, in a limited number of runs, with tartrate-complexed PAW⁽¹⁰⁾. In more extensive tests with Csrex process solvent, however, cerium HTU's of 5 to 10 ft with citrate and HEDTA-complexed PAW's were lowered to 3 to 6 ft with tartrate-complexed PAW⁽¹¹⁾.

The poor performance with PAW feed has been traced to the presence of chromium and the formation of cerium-chromium complexes which greatly reduce the rate of cerium extraction, as discussed in Section C 3.2.3.

Of the complexants studied, only citrate, tartrate, and HEDTA permit simultaneous recovery of strontium and the rare earths while suppressing the extraction of bulk inert and radioactive impurities. Laboratory tests described in Section 3.2.2 indicate that the effectiveness of complexing increases in the order tartrate-citrate-HEDTA. Thus, the use of tartrate to improve rare earth recovery will be dependent on whether the increased extraction of impurities can be tolerated.

Effect of pH

No effect of pH on extraction was observed with citrate and tartrate complexed feeds over the range studied (4.0-5.5)⁽¹⁰⁾. Laboratory work described in Section C 3.2, however, indicates that high pH's decrease the rare earth extraction kinetics. It is also essential that the feed pH may be properly adjusted so that the pH of the combined feed and scrub streams is high enough to permit strontium extraction.

Effect of Temperature

Increasing the temperature greatly improved the rate of cerium extraction. Cerium losses in an organic-continuous column with citrate-complexed PAW decreased from 50% to 7% (3.5 ft HTU) when the temperature was increased from 25 to 50 C⁽¹⁰⁾. Temperature had no significant effect on strontium losses provided that the flow ratio was adequate to counter the adverse effect of increased temperature on the strontium distribution ratio.

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Effect of Interface Position

The preferred interface location in an extraction column is at the bottom to aid in flushing interface-seeking solids from the system; however, putting the interface at the top in the 1A Column increases the aqueous holdup time three-to four-fold and should thereby decrease the cerium loss. This effect was observed in several runs, as shown in Table IV-28⁽¹⁰⁾. A two-fold reduction in cerium HTU's was also observed in Csrex process runs with aqueous-continuous operation⁽¹¹⁾.

TABLE IV-28
EFFECT OF TEMPERATURE AND INTERFACE POSITION
ON CERIUM EXTRACTION

(Source of Data: HW-79762PT2)

1AF = Citrate complexed PAW. Cartridge ht. = 9 ft.

<u>Temp. C</u>	<u>Interface Position</u>	<u>% Ce Loss</u>	<u>Ce HTU, ft.</u>
25	Top	18-35	5 - 9
	Bottom	32-50	8 - 10
45-50	Top	1.4-6.2	2 - 3.2
	Bottom	5-8	3 - 3.5

Effect of Flow Rate

Decreasing the total flow rate also tended to decrease the cerium losses. The effect was relatively minor and was not always observed. Strontium losses were unaffected by flow rates up to a volume velocity of 1060 gal/hr-ft², the maximum rate tested⁽¹⁰⁾.

Effect of Pulse Frequency

Generally, frequencies had to be within 20% of the flooding frequency for optimum performance; the frequency goal was usually within 10% of flooding for most of the runs. Frequency sensitivity was not as pronounced in the 1A Column as it was in the stripping studies reported in following sections. Typical results of frequency variation studies are shown in Table IV-29⁽¹⁰⁾.

Cyclic flooding was rare in these runs; usually local flooding or phase inversion, if it occurred, would build up until a meta-stable condition was reached. This might progress to the extent of having an interface at both ends of the column. Local flooding or instability, such as that occurring in the last run above, did not appear to increase the losses.

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TABLE IV-29
EFFECT OF FREQUENCY ON 1A COLUMN PERFORMANCE

(Source of Data: HW-79762PT2)

Citrate complexed PAW, Cartridge ht. = 9 ft.

Temp. °C	Frequency		% Loss		Estimated HTU, Ft.	
	Cycles/Min.	% of Flood	Sr	Ce	Sr	Ce
50	60	ca. 85	--	15	--	4.7
50	69	ca. 95	--	7.5	--	3.5
35	50	ca. 78	0.62	12	1.7	4.1
35	64	ca. 100 ^(a)	0.09	7.5	1.2	3.5

(a) Local flooding observed during the run.

6.1.3 ZAW Flowsheet Demonstration⁽¹³⁾

Purex wastes derived from zirconium-clad fuels will contain considerable amounts of aluminum added to complex residual fluoride from the Zirflex decladding process. Laboratory studies⁽⁴⁾ have shown that aluminum extraction by D2EHPA from complexed feeds is time dependent and can be appreciable after several minutes of contact. A special series of pilot plant runs was made to determine the path of aluminum in the D2EHPA process as a function of complexing agent, pH, and temperature. The feed, shown in Table IV-26, also contained about two-fold more iron than the earlier PAW feeds, and the effect of both iron and aluminum loading in the solvent on strontium and rare earth extraction was of interest. The flowsheet was similar to that shown in Fig. IV-49 except that two complexants were tested. The first was 0.55M HEDTA with 0.0125M tartrate added, as discussed in Section C 3.2.3, to improve rare earth extraction kinetics; the other was 0.6M tartaric acid.

The amount of iron and aluminum extracted from the HEDTA-complexed ZAW was 5 to 10-fold less than that extracted from the tartrate feed. The lower solvent loading with HEDTA feeds also contributed to about 10-fold lower strontium losses. Optimum cerium losses with both complexants ranged from 1 to 4% with the lower loss obtained at elevated temperatures. Cerium losses were highly dependent on the HEDTA feed pH, increasing to 40% as the pH was increased from 4.0 to 4.7. A summary of the extraction performance is presented in Table IV-30. The pilot plant runs were made in a 13-ft-tall column, simulating the B-Plant 1A Column geometry. It was operated at a volume velocity of 360 gal/hr-ft² with a 1-in. pulse amplitude and frequencies of 70 to 90 cycles/min. The organic phase was continuous.

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TABLE IV-30
1A COLUMN PERFORMANCE WITH ZAW FEED

(Source of Data: Ref. 13)

A/O = 1.2, Bottom interface, Cartridge ht. 15 ft.

Complexant	Feed pH	Temp. °C	% in 1AP ^(c)		% in 1AW ^(c)		Approx. HTU, ft.	
			Fe	Al	Sr	Ce	Sr	Ce
HEDTA ^(b)	4.0	40	0.4	0.7	0.3	<3.9	1.9	<4.0
HEDTA ^(a)	4.0	50	0.6	1.1	0.1	0.2	1.6	2.0
HEDTA ^(a)	4.7	25	--	--	<0.1	44	<1.6	>10
HEDTA ^(a)	4.7	50	--	--	<0.1	79	<1.6	>10
Tartrate ^(a)	4.0	25	2.5-7.5	~5.0	1.4	2.0	2.4	3.3
Tartrate ^(b)	4.0	25	2.0	2.3	1.0	3.7	2.0	4.0
Tartrate ^(a)	4.0	45	5.6	5.5	1.8	1.4	2.3	3.1
Tartrate ^(b)	4.5	25	--	--	1.7	7.9	2.2	5.2
Tartrate ^(b)	4.5	35	2.0	5.7	0.4	6.7	1.8	4.9
Tartrate ^(b)	4.5	40	5.2	4.6	2.6	3.1	2.4	3.8

(a) Feed used with no elevated temperature digestion.

(b) Feed digested at 90°C for one hour.

(c) Percent of the indicated component entering in the 1AP.

A comparison of the data in this table with data obtained with PAW feeds shows that optimum strontium HTU's were 10 to 50% higher with ZAW feeds, probably because of less favorable strontium distribution ratios and taller column height. Cerium HTU's were essentially unchanged.

Unstable column operation, accompanied by a flocculent precipitate, was observed in one run with freshly prepared tartrate feed. The phenomena was not observed after the feed was aged for one day or after it was digested 1 hour at 90°C. Feed digestion may have increased the cerium losses about 2-fold or more.

6.1.4 Strontium Crude Purification Flowsheet Demonstration⁽⁵⁾

The original strontium extraction process was developed to recover and purify strontium-90 from crude fractions prepared in the Purex Plant by lead sulfate precipitation (see Section B 2). The process developed in these early studies has since been refined and used to recover over 10 megacuries of purified Sr-90 in the Strontium Semiworks (SSW).

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Compositions of feeds used in pilot plant runs are included in Table IV-26. The composition of Strontium Crude #2 most nearly resembled the typical SSW feed; Strontium Crude #1 represents an earlier processing concept with a more concentrated feed. The solvent in all of the purification runs contained 0.4M D2EHPA, 0.2M TBP in various saturated hydrocarbon diluents. After the initial scouting efforts, flowsheet development was concentrated on minimizing the extraction of impurities, including cerium and rare earths.

Capacities as high as 1000 and 1300 gal/hr-ft² were demonstrated in the pilot plant column with bottom and top interface positions, respectively (5a). Stable operating capacities as high as 1170 gal/hr-ft² have been obtained in the SSW 1A Column with its 10-ft cartridge of 4-in.-spaced nozzle plates (5b). A wide range of flooding frequencies was observed in these studies, as well as in the PAW studies described in Section D 6.1.1; and, within experimental precision, the results of the PAW capacity studies should apply also for the strontium purification flowsheets.

Strontium HTU's were estimated at 1 to 2 ft at volume velocities of 700 to 900 gal/hr-ft² in both the presence and absence of complexing agents and with strontium feed concentrations from 0.004 to 0.04M (5a). The effects of major flowsheet variables on strontium and impurity extraction are discussed below.

Effect of Complexant - Three complexants were extensively tested: HEDTA, EDTA, and DTPA. All three were quite effective in suppressing the extraction of iron, lead, and zirconium. In "cold" studies (5a), less than 1% of the iron, 3% of the lead, and 6% of the zirconium were extracted with excess HEDTA present. The amount of lead and zirconium extracted was apparently lowered several fold by using EDTA. In the absence of any complexant, essentially all of the zirconium and lead extracted at pH 4 to 5, along with about 70% of the iron.

The effectiveness of the complexants in preventing cerium extraction decreased in the order DTPA EDTA HEDTA. Strontium Semiworks runs at pH 4.3 to 4.7 (5b) demonstrated that 20 to 30% of the cerium extracted from EDTA-complexed feeds but only 4% or less extracted from DTPA feeds. In runs described in Section D 6.1.3, about 26 to 56% of the cerium extracted from an HEDTA-complexed feed at pH 4.7.

Complexant concentrations as high as 0.12M in excess of that required to complex the impurities had, at most, only a minor effect on strontium waste losses.

Effect of Buffer Composition - Acetic acid has been used exclusively to buffer the feed pH in strontium purification runs. Its pK value (the pH at which 50% of the acid is neutralized) is 4.76, the optimum pH for obtaining high cerium decontamination without excessively decreasing the strontium distribution ratio. Concentrations of 0.4 to

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1.0 have proved satisfactory for maintaining the aqueous phase pH, with the higher value being desirable for feeds containing over 0.05M calcium plus strontium. Some improvement in pH control can be achieved by partially neutralizing the solvent with NaOH, but no attempt was made in either pilot plant or SSW runs to use solvent buffering with strontium crude feeds.

Effect of Strontium and Calcium Concentration - Calcium quantitatively extracted under all conditions favoring strontium extraction. Adequate strontium extraction was achieved with strontium plus calcium feed molarities ranging from 0.002 to 0.14 by using sufficient solvent to maintain at least 0.2M free D2EHPA in the solvent. Higher solvent loadings can be used with high feed concentrations because the increased solvent requirement lowers the A/O flow ratio and tends to counter the adverse effect on the extraction factor of lower strontium distribution ratios.

6.1.5 Kinetics of Europium Extraction from HEDTA-Complexed Feed

Laboratory studies, summarized in Section C 3.2, have shown that HEDTA complexing decreases the rate of rare earth extraction as well as the magnitude of the distribution ratios. The rate of extraction decreased with increasing pH and increasing atomic number (i.e., Ce Pm Eu). A series of pilot plant runs, using Strontium Crude #3 (Table IV-26) was made to study in detail the effect of operating variables on rare earth extraction from an HEDTA-complexed SSW feed⁽¹²⁾. The feed was traced with Eu-152-154 to ensure the applicability of the results to promethium extraction. All runs were made at a volume velocity of 680 gal/hr-ft² and an A/O of 1 in a 10-ft-tall pulse column containing 10% (rather than 23%) free area nozzle plates.

Effect of Feed pH - The europium loss was highly dependent on the feed pH, increasing by a factor of 17 as the pH was increased from 1.8 to 3.8. A summary of the results of room temperature, bottom interface runs is shown in Table IV-31.

TABLE IV-31

EFFECT OF FEED pH ON EUROPIUM EXTRACTION

(Source of Data: BNWL-173)

Bottom interface; 25C; A/O = 1; Cartridge ht. = 10 ft.

pH	Aqueous Residence Time, Min.	Europium in 1AW, percent
1.8	2.7	≤2.1
2.4	2.6	3.7
3.8	2.5	36

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Laboratory kinetic studies made with the same feeds gave comparable extraction results⁽³⁾. For example, within 2 min 99% of the europium was extracted at pH 2.3 while only 63% was extracted at pH 3.8. In the latter case, the europium extraction was increased to 96% with a 5 min contact.

The stability of the column was also affected by the pH, with lower pH's favoring increased stability; however a white precipitate, presumably lead sulfate, formed slowly in the column with the pH 1.8 feed.

Effect of Temperature and Interface Position - The increased aqueous-phase residence time obtained by moving the interface from the bottom of the column to the top lowered the europium loss by three-fold at pH 3.8 and 25 C. A still greater factor of improvement was obtained by heating the column to 50 C, as shown in Table IV-32. The europium loss of 0.39% at optimum operating conditions indicated an HTU of 1.8 ft, about as low as that reported for the D2EHPA extraction of strontium and cerium under less severe complexing conditions⁽¹⁰⁾ and approaching the 1.2 to 1.4 ft cerium HTU's observed with uncomplexed feeds.

TABLE IV-32

EFFECT OF TEMPERATURE AND INTERFACE POSITION ON EUROPIUM EXTRACTION

(Source of Data: BNWL-173)

Feed pH = 3.8; A/O = 1; Cartridge ht. = 10 ft.

Column Temperature, C	Interface Position	Aqueous Residence Time, Min.	Europium in 1AW, %	Europium HTU, feet
25	Bottom	2.5	36	10
25	Top	10	12	4.7
50	Bottom	2.5	13	4.9
45-50	Top	12	0.39-0.94	1.8-2.2

The 4.9 ft europium HTU obtained at 50 C with the organic phase continuous was about 2-fold higher than the cerium HTU obtained under similar conditions with HEDTA-complexed ZAW feed (Section D 6.1.3). The slower kinetics of europium extraction may account for the difference, but the ZAW feed also contained a small amount of tartrate which has been shown to improve the rate of rare earth extraction (Section C 3.2.3).

6.2 1S Column Performance

6.2.1 Capacity Studies⁽⁵⁾

Most of the 1S runs were made in a dual-purpose 1A Column with the scrub section (1S Column) mounted above the 1AF feed point. Since the scrub section was generally more stable than the extraction section, very few flooding runs as a function of flow rates were made. Table IV-33, however, is representative of operating conditions that can be achieved in the 1S Column.

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TABLE IV-33
1S COLUMN CAPACITY SUMMARY

(Source of Data: HW-79762PT2)

Amplitude = 1 in; Cartridge Ht. = 6 to 10 ft.

Plate Spacing inches	Volume Velocity gph/ft ³	Temperature, Centigrade	Frequency, Cycle/min.	
			Max. Demon.	Flooding
Bottom Interface				
2	200	25	--	70 to 86
2	390	25	--	62 to 72
2	590	25	42	--
4	200	25	61	--
4	200	ca. 40	70	--
4	390	25	--	62 to 74
4	590	ca. 40	70	--
4	550	25	40	--
4	550	ca. 40	44	--
Top Interface				
4	200	25	60	--
4	200	ca. 40	58	--
4	390	25	69	--
4	590	ca. 40	70	--

6.2.2 Sodium (and Cesium) Scrubbing Results

Citric, hydroxyacetic, and formic acids have been extensively studied as sodium reagents^(5a,10,13). All three buffer well in the desired pH range of 2.4 to 4 and were about equally effective in removing sodium from the LAP. Mole-for-mole, citric acid supplies about 60% more buffer capacity than either of the other two reagents over the desired pH range, but relative costs per mole of buffer capacity favor the use of formic acid and hydroxyacetic acid, in that order. Other factors affecting the choice of reagent composition are discussed in Sections C 3.3 and D 3.2.

Residual sodium concentrations in solvent scrubbed in pilot plant 1S Columns containing cartridges similar to that in the B-Plant 1S Column are shown in Table IV-34. Many of the runs were made in dual purpose columns under relatively inefficient pulsing conditions, and these results are not necessarily indicative of the optimum performance that can be achieved.

The results illustrate the importance of using a low pH in the 1SS; however, in one series of runs at pH 1.7, excessive strontium reflux resulted in gross strontium loss in the 1A Column. Strontium reflux

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TABLE IV-34
1S COLUMN SODIUM SCRUBBING PERFORMANCE

(Source of Data: HW-72666 Section 4; HW-79762PT2; Ref. 13)

Bottom Interface; 25-40C; A/O = 0.2-0.25

M D2EHPA	1AF pH	1SS pH	1SS Composition ^(d)	1S Column Ht., ft.	MNa in 1SP	
					Average	Minimum
0.2	4.0-4.4	2.2-2.6	0.25 M H ₃ Cit.	6 ^(a)	0.004	<0.0001
0.2	4.0-4.4	2.9-3.0	0.25 M H ₃ Cit.	6-9 ^(a)	0.004	0.0005
0.2	4.6-4.7	1.7 ^(c)	0.25 M H ₃ Cit.	6 ^(a)	0.002	0.0002
0.2	4.6-4.7	2.6	0.25 M H ₃ Cit.	6 ^(a)	0.004	0.0003
0.4	3.7-3.8	2.3	0.6 M H ₃ Cit.	9 ^(a, b)	--	<0.006
0.4	4.6	2.3	0.6 M H ₃ Cit.	9 ^(a, b)	0.04	0.036
0.2	4.3-4.7	3.0	0.5 M HAcOH	6 ^(a)	0.007	0.0023
0.2	4.6	2.4	0.5 M HAcOH	10	0.0008	<0.0001
0.3	4.5	2.4	0.5 M HAcOH	10	--	0.0002
0.2	4.3	3.1	0.5 M HCOOH	6 ^(a)	--	0.0019
0.2	4.2-4.5	3.2	1.0 M HCOOH	6 ^(a)	0.005	0.0024
0.3	4.5-4.9	2.4	1.0 M HCOOH	10	0.002	0.0012

(a) Part of dual-purpose 1A columns.

(b) Frequency well below the flooding threshold.

(c) Excessive strontium reflux occurred at this pH.

(d) H₃Cit. = citric acid
HAcOH = hydroxyacetic acid
HCOOH = formic acid

at low solvent loading amounted to only 4 to 11% with the 1SS pH adjusted to 2.4⁽¹⁰⁾. Generally, higher scrub pH's can be used in conjunction with a low pH in the 1A Column since sodium extraction and, hence, the sodium scrubbing duty will be lower.

The runs described above were made in an organic continuous 1S Column. Comparable sodium scrubbing was obtained in a limited number of runs with the aqueous phase continuous⁽¹⁰⁾.

The path of cesium was followed with Cs-134 tracer in the runs using a 1M formic acid scrub. Only 1 to 3% of the cesium extracted in the 1A Column, and less than 0.1% was found in the scrubbed product⁽¹⁰⁾.

6.2.3 Nickel Scrubbing Results

Nickel behavior in separate 1A and 1S Columns was determined in one series of runs with tartrate-complexed PAW and with 1M formic acid, pH 2.4 scrub. The final run also contained 0.005M EDTA in the 1SS. The results, as shown in Table IV-35, indicated that appreciable nickel extracted from the tartrate feed and that its removal in the 1S Column was improved by EDTA addition. Nickel extraction from an HEDTA or EDTA system should be negligible.

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TABLE IV-35

NICKEL EXTRACTION AND SCRUBBING BEHAVIOR

(Source of Data: HW-79762PT2)

Cartridge ht. = 10 ft.; A/O = 0.2; Temp. = 25C

1AF pH	MEDTA in 1SS	% of 1AF Ni in		
		1AP	1SP	1BP(a)
5.5	0	--	--	5.0 ^(b)
4.9	0	92	12	4.4
4.5	0	23	2.8	2.4
4.6	0.005	32	1.4	0.8

(a) Nickel in the 1SP should be quantitatively stripped in the 1B column and appear in the 1BP.

(b) Average of 3 runs.

6.3 1B Column Performance6.3.1 Capacity Studies

A summary of 1B Column capacity studies is presented in Table IV-36(5a,10). The amplitude-frequency product was chosen as the measure of pulse energy input to correct for amplitude variation.

TABLE IV-36

1B COLUMN CAPACITY SUMMARY

(Source of Data: HW-79762PT2; HW-72666 Section4)

Ampl. = 0.6 to 1 in.; Cartridge ht. = 9 to 10 ft.; 1BP pH ≤ 3; Temp. = 25C

Plate Spacing inches	Volume Velocity, gph/ft ²	Ampl. x Frequency, in./min.	
		Max. Demonstrated	Flooding
Bottom Interface			
2	200	--	63 to 92
2	390	64	--
2	590	53	--
4	390	--	54 to 60
Top Interface			
2	390	53	--
2	590	--	>45
4	190	70	--
4	390	--	71 to 74
4	500	70	--
4	640	--	80
4	790	60	--

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The flooding threshold values were relatively insensitive to plate spacing, flow rate and LBX composition; and results from runs using both dilute nitric acid and 1M citric acid are included in the above table. With nitric acid, however, the stability of the LB Column was greatly decreased whenever the LBP pH exceeded 4(10). This condition existed only when there was insufficient acid in the LBX to strip the strontium. The cause of this pH effect was not determined, but the milky appearance and poor settling characteristics suggested the presence of a third phase.

6.3.2 Strontium Stripping Performance(5a,10)

Optimum strontium HTU's ranged from 1.6 to 2.1 ft with either 0.03M HNO_3 or 1M citric acid used as LBX. The HTU's were estimated by using the strontium E_a^0 at the pH of the LBX. This procedure leads to conservatively high HTU's since the pH, and hence the strontium E_a^0 , increase toward the product end of the column. The effects of major variables on strontium HTU's and waste losses are presented in the following paragraphs.

Effect of LBX Composition and Flow Ratio - At optimum pulsing conditions, the main factor affecting strontium loss was the pH of the LBP. This, in turn, was determined by the amount of acid supplied in the LBX and on the amount used up in stripping strontium and sodium from the LBF. The sodium content in the LBF is a function of the scrubbing efficiency of the LS Column and can vary independently of the strontium concentration. Whenever the LBF contains an unusually large quantity of sodium, additional acid must be supplied to keep the LBP pH from increasing above a value which will inhibit or block strontium stripping. This pH limit was about 2.4 to 2.8, depending on the solvent concentration and the flow ratio. Three methods of supplying the additional acid were tested in PAW flowsheet development: increasing the HNO_3 concentration in the LBX, using a buffer acid, and increasing the LBX flow. All of these were successful, but increasing the LBX flow proved to be the simplest method(10).

Buffer acids are currently favored for stripping high concentrations of strontium from the LBF because of their reservoir of exchangeable hydrogen ions. For example, 1M citric acid will give up 0.14M H^+ as the pH increases from 1.7 to 2.2. The same pH change with HNO_3 corresponds to an exchange of only 0.014M H^+ . Both citric and tartaric acid at 1 to 1.5M have been successfully used in pilot plant runs to obtain LBP product compositions of 0.04 to 0.06M Sr and 0.1 to 0.2M Na(5a).

Effect of Interface Position - The interface position had little or no effect on strontium HTU's. Steady state operation, however, was gained much faster with the interface at the bottom because of the higher relative flow of the solvent phase. In addition, the LBP pH was more

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responsive to adverse operating conditions because of the lower aqueous holdup. For high product purity, however, top interface operation may be preferred to divert interfacial solids to the LBW.

Effect of Flow Rate - Strontium HTU's were not appreciably affected by volume velocity. They ranged, typically, between 1.6 and 2.1 ft at flow rates from 200 to 580 gph/ft².

Effect of Solvent Composition - There was no evidence that variation in solvent concentrations from 0.08M to 0.4M D2EHPA affected the results in any way other than caused by variation in the distribution ratios.

6.3.3 Decontamination from Calcium and Cerium

The decontamination factors for calcium and cerium in the LB Column are approximately equal to their respective extraction factors; i.e., $DF \approx E_a^O/(A/O)$. Thus, the optimum decontamination performance will be obtained by operating at the highest pH and lowest LBX flow rate compatible with strontium recovery. Because of strontium and sodium transfer, the aqueous phase pH varies throughout the LB Column with the highest pH occurring at the product end. Although the LBP pH should be controlling as far as decontamination performance is concerned, in practice the pH (or acidity) of the LBX also has an important effect on the DF's, as illustrated in Table IV-37.

TABLE IV-37

CALCIUM AND CERIUM DECONTAMINATION PERFORMANCE

(Source of Data: HW-79762PT2)

PAW Flowsheet, A/O = 0.2 to 0.3

<u>M HNO₃ in</u> <u>1 BX</u>	<u>1BP pH</u>	<u>Ca DF</u>		<u>Ce DF</u>	
		<u>Ave. (a)</u>	<u>Max.</u>	<u>Ave. (a)</u>	<u>Max.</u>
0.03	1.5-1.7	3.0	4.5	1000	3300
	1.8-2.0	5.8	8.5	ca. 1400	7000
	2.1-2.3	24	48	ca. 1000	2000
	2.4-2.6	54	82	ca. 2000	>4900
0.10	1.5	--	1.6	--	≥60
	2.0	--	2.2	--	660

(a) Average results for four or more runs.

High solvent loadings had an adverse effect on calcium decontamination in strontium crude purification runs with LBX solutions containing 1M citric acid^(5a). The calcium DF's increased from 3 to an average of 40 when the calcium concentration in the LBP was decreased from 0.056M

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to 0.015M(5a). Calcium DF's of 10 to 40 have been obtained in the SSW under similar operating conditions with about 0.015M Ca in the LBF(5b).

Cerium decontamination factors ranged from 55 to 100 in the SSW LB Columns(5b). These values are considerably lower than those obtained in "cold" runs with dilute nitric acid, perhaps because of citrate complexing.

6.3.4 Decontamination from Fe, Al, and Cr

Over-all iron decontamination factors (LAF to LBP) were $> 10,000$ in ZAW flowsheet demonstration runs (< 0.005 g/l Fe in the LBP)(13). Corresponding aluminum DF's were about 20,000 with HEDTA-complexed LAF and 2500 with tartrate-complexed feed. The aluminum DF in the LB Column alone averaged 160 for both ZAW feeds. DF's of these magnitudes probably cannot be maintained under plant conditions because of entrainment. For example, over-all iron DF's as low as 400 and 1300 have been measured in SSW runs(1) and 200 to 7000 in Csrex process demonstration runs(11).

Chromium behaves much like iron under process flowsheet conditions. When properly complexed, very little chromium will extract and that that does should remain in the solvent. Under Csrex process conditions, over-all chromium DF's ranged from 200 to 2000(11).

6.4 1C Column Performance

6.4.1 Capacity Studies

The flooding behavior of the 1C Column was very similar to that of the 1B Column. A summary of the capacity studies is presented in Table IV-38.

The stability of the 1C Column (bottom interface) was improved by increasing the pulse amplitude to 1.8 ± 0.2 in.; the maximum stable amplitude-frequency product was 68 in./min at 0.8 in. amplitude, 92 in./min at 2 in. amplitude, and 66 in./min at 4.7 in. amplitude. The plate spacing was 2 in., and the volume velocity was 390 gal/hr-ft² for this test.

6.4.2 Total Rare Earth Stripping

The majority of the efficiency studies were made to demonstrate total stripping concepts, using Ce-144 tracer and 0.3 to 2M HNO₃ as LCX. The results of these studies should apply also to promethium-rare earth

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stripping in the Ce(IV) partitioning flowsheet studies described in Section C 3.5.2. The effects of major variables on stripping efficiency are discussed in the following paragraphs.

TABLE IV-38
1C COLUMN CAPACITY STUDIES

(Source of Data: HW-79762PT2)

Amplitude = 0.6 to 1 in.; Cartridge ht. = 10 ft.; 1CY = 0.3 to 2M HNO₃

Plate Spacing, inches	Volume Velocity, gph/ft ²	Temperature, Centigrade	Ampl. x Frequency, in./min. Max. Demonstrated Flooding
Bottom Interface			
2	110	25	94 --
2	190	25	-- 75 to 84
2	190	40	83 --
2	290	40	74 --
2	390	25	74 --
4	280	25	-- 60 to ≥68
4	390	44	45 --
4	600	25	-- ≥45 to 53
4	600	50	53 --
4	660	41	45 --
Top Interface			
2	390	25	-- 64 to 66
2	570	25	57 --
2	770	25	-- ≥30
4	390	25	60 --
4	390	40-50	-- 55 to 80
4	600	25	-- ≥45 to 53
4	600	25	45 --
4	710	25	-- ≥40
4	800	25	-- 44

Effect of Interface Position, Flow Rate, and Pulsing Conditions -

The cerium stripping efficiency was apparently diffusion controlled; those variables which increased the organic holdup time and intimacy of contact were the most effective in reducing cerium losses and HTU's. Optimum cerium HTU's of 1.5 to 2.2 feet (0.2 to 1.2% loss in the 10-ft-tall column) were obtained by operating with a bottom interface at volume velocities less than 400 gph/ft² and amplitude-frequency products within about 85% of the flooding threshold value. Cerium waste losses were increased two- to eight-fold typically by operation at flow rates of 600 gph/ft² or with top interface. A summary showing the effect of these variables is presented in Table IV-39(10).

Effect of Pulse Amplitude - The effect of pulse amplitude was studied using an air-driven pulse generator to supply the variable amplitude(10). The frequency was varied to maintain a constant dispersed phase holdup, as measured by static pressure. The results showed that increasing the pulse amplitude from 0.8 to 2 inches had a negligible effect on waste losses, but a further increase to ca. 3 inches increased the loss three-fold. The "threshold" amplitude of 2 inches, perhaps coincidentally, was the same as the plate spacing.

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TABLE IV-39
CERIUM STRIPPING EFFICIENCY STUDIES

(Source of Data: HW-79762PT2)

Amplitude = 0.6 to 1 in.; Cartridge ht. = 10 ft.; LCX = 1 to 2M HNO₃; Temp. = 25°C

Interface Position	Volume Velocity, gph/ft ²	Ampl. x Frequency, in./min.			Approximate Ce HTU, feet
		In./Min	% of Flooding	% Ce Loss	
Top	390	45	68	23	7.1
Top	390	56	85	2.8	2.8
Top	390	60	91	1.7	2.4
Top	390	64	97	1.7	2.4
Top	580	45	ca. 75	24	7.1
Top	580	48	ca. 80	13	4.8
Top	580	52	ca. 87	6.2	3.6
Top	580	57	ca. 95	5.8	3.4
Bottom	280	50	74	24	7.1
Bottom	280	56	83	ca. 6	ca. 3.5
Bottom	280	62	91	ca. 1	ca. 2.1
Bottom	280	68	ca. 100	2.1	2.5
Bottom	390	33	ca. 43	32	9.1
Bottom	390	64	ca. 84	0.7	1.9
Bottom	390	74	ca. 97	0.2	1.5
Bottom	580	39	74	31	8.2
Bottom	580	45	85	4.9	3.3
Bottom	580	50	94	≤1.8	≤2.5

Effect of Temperature - Cerium HTU's were reduced 20 to 30% by increasing the temperature from 25 to 40°C. Optimum HTU's of 1.6 to 2.1 ft were obtained at 40 to 50°C (volume velocity = 390 gal/hr-ft²) in an aqueous continuous column with a 10-ft-tall cartridge of 4-in-spaced, 10% free area nozzle plates^(12,13).

Effect of LCX Composition and Flow Ratio - The concentration of HNO₃ in the LCX had little or no effect on waste losses or HTU provided that the flow ratio was adjusted to keep the extraction factor constant. The minimum flow ratio demonstrated to give good stripping performance was 0.09 with 2M HNO₃ plus 0.094M H₂SO₄ in the LCX. Lowering the flow ratio to 0.06 increased the losses in the 10-ft-tall, top interface column from 0.6 to 2.0% at 50°C⁽¹²⁾. The sulfuric acid was added to stimulate the effect of persulfate decomposition products during normal partitioning runs.

6.4.3 Cerium-Rare Earth Partitioning by Persulfate Oxidation⁽¹²⁾

Continuous separation of cerium from the other rare earths can be accomplished in the LC Column by adding persulfate and silver catalyst to the LCX to oxidize cerium to highly extractable Ce(IV) according to the reactions discussed in Section C 3.5.3. A short scrub section must be added below the feed point to assure complete extraction of Ce(IV).

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The assumed mechanism for the separation of cerium from the other rare earths in a countercurrent solvent extraction column involves the following steps:

- (1) The rare earths, including cerium, are stripped from the solvent by the $2M$ HNO_3 in the LCX (fast).
- (2) The cerium is oxidized in the aqueous phase to Ce(IV) by silver-catalyzed persulfate (relatively slow).
- (3) The Ce(IV) is re-extracted into the solvent phase (relatively fast).
- (4) The extracted Ce(IV) is reduced by the solvent to Ce(III) in an undesired side reaction (slow).

Factors that should improve the separation include:

- . Using a long aqueous phase residence time (low LCX flow rate and aqueous-continuous operation) to provide adequate time for cerium oxidation.
- . Using a short solvent phase resident time to minimize Ce(IV) reduction by the solvent.
- . Adding a scrub section below the LCF feed point to recover that small fraction of cerium that will be pulled below the feed point before it can be oxidized and re-extracted.
- . Operating the system at an elevated temperature to improve the kinetics of mass transfer and cerium oxidation.

Scouting runs confirmed the validity of these assumptions and demonstrated that scrub section heights of 2 to 4 ft were generally adequate to assure removal of over 95% of the cerium from the rare earth product. (In the absence of any scrub section, 20 to 30% of the cerium was found in the LCP.)

The remaining pilot plant demonstration runs used a 14-ft-tall column divided to give a 10 ft stripping section and a 4 ft scrub section. The plate spacing was graded, with 2-in. spacing in the scrub section and 4-in. in the stripping section, to improve dispersion characteristics. The rare earth feed (LCF) contained $0.004M$ rare earths, including $0.001M$ cerium, in $0.3M$ D2EHPA- $0.15M$ TBP-hydrocarbon diluent. The LCX contained $2M$ HNO_3 and varying amounts of persulfate and silver. The flow rates of the LCF and LCS (solvent scrub) streams were 320 and 64 gal/hr-ft², respectively; the LCX flow was normally 10 to 20% of the LCF flow. Pulsing conditions were set at 80 to 90% of the estimated flooding frequency. The following results were obtained:

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Effect of Interface Position - Moving the interface from the top of the column to the bottom increased the cerium loss to the LCP from $\leq 3.7\%$ to 79% of the entering cerium. This result demonstrated that long aqueous phase residence times are required for quantitative cerium oxidation and re-extraction, since the immediate effect of the move was to decrease the aqueous phase residence time from 120 to 17 min. (The long solvent residence time obtained with the bottom interface also favors the reduction of extracted Ce(IV) by the solvent.)

Effect of LCX Flow Rate - The LCX flow rate also affects the aqueous phase residence time, but 3-fold rate variations (aqueous residence times of 80 to 200 min) did not appear to affect the cerium separation performance. The results may reflect the lack of sufficient runs to define the effect properly. Certainly, under some conditions, a high aqueous rate would not provide enough residence time for complete cerium oxidation; and an unusually low aqueous rate might not only permit destruction of the persulfate before it reached the feed point but also be inadequate to strip all of the trivalent rare earths from the LCF, as discussed in D 6.4.2.

Effect of Silver and Persulfate Concentrations - As discussed in C 3.5.3, most of the persulfate used up in the column will be lost by side reactions with water, solvent, and solution impurities; hence it is important to use low silver concentrations to increase the persulfate life and to maintain the desired reaction rate by starting with high persulfate concentrations. In the present application, the maximum persulfate concentration will be restricted by the stability of the resulting rare earth sulfates.

The validity of the above analysis was confirmed by the pilot plant results shown in Figure IV-61, where the amount of cerium left in the rare earth product is plotted as a function of silver and persulfate concentrations in the LCX. (The data for the full test range of LCX flow rates were included in the absence of any definite effect of such rates on cerium behavior.) The data show that optimum performance was obtained at $0.3M$ persulfate concentration with as little as $0.0012M$ Ag^+ present. Acceptable cerium losses were also obtained at $50^\circ C$ with $0.18M$ persulfate and 0.02 to $0.03M$ silver; however, the losses appeared to be quite sensitive to the silver concentration: high losses at $0.04M$ silver were attributed to premature persulfate destruction, while high losses at $0.01M$ silver were tentatively attributed to an inadequate oxidation rate. Runs with $0.1M$ persulfate or less were completely unsuccessful.

The persulfate concentrations shown in Figure IV-61 were corrected for persulfate decomposition in the LCX storage tank. The persulfate loss during storage was minimized by adding silver to the column in a separate stream.

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FIGURE IV-61

Effect of Silver and Persulfate Concentration
on Cerium Loss to the 1CP
(Source of Data: BNWL-173)

Effect of Temperature - The reaction rate of persulfate ion is highly dependent on temperature, as discussed in Section C 3.5.3. The poor performance observed at 40 C using 0.18M persulfate (illustrated in Figure IV-61) can thus be explained as an adverse effect of low temperature on the cerium oxidation rate. This effect could be overcome either by increasing the temperature to 50 C or by increasing the silver concentration to about 0.04M. The temperature effect at 0.3M persulfate was much less pronounced, and low cerium losses were obtained at temperatures ranging from 30 to 53 C.

Elevated temperature operation also favors rare earth stripping, as discussed in D 6.4.2.

Effect of Diluent and Solvent Pretreatment

Comparable performance was obtained with solvents containing either Soltrol-170 or NPH as diluents. Experiments described in

Sections C 3.1.3 and H 1.4, however, indicate that Ce(IV) is more stable in NPH solvent than in Soltrol solvents under radiation, and NPH has been recommended as the diluent to be used when partitioning Ce-144 from the other rare earths.

Several solvent washing procedures were tested during the pilot plant program, including washes with 2M HNO_3 containing either persulfate or permanganate to oxidize reducing impurities in the solvent; but the only treatment that appeared to be essential was sulfamic acid addition to destroy nitrous acid remaining from the standard HNO_3 - NaNO_2 cerium-removal step. About 0.02 to 0.04 g-mole of sulfamic acid per liter of solvent (added as a concentrated solution in dilute HNO_3) was sufficient. No attempt was made to decant the small amount of associated aqueous phase before reusing the treated solvent.

1CP Solution Stability

Precipitates found in several 1CP samples after prolonged standing were tentatively identified as the double sulfate salts of sodium or potassium and rare earths. Approximate threshold conditions for precipitate formation in 2M HNO_3 are shown in Table IV-40.

TABLE IV-40
THRESHOLD CONDITIONS FOR PRECIPITATION OF
RARE EARTH SULFATES IN THE 1CP

(Source of Data: BNWL-173)

1CP = 2M HNO_3 ; 0 to 0.3M Ag^+ ; 25 C

<u>Persulfate Cation</u>	<u>M of Persulfate Cation</u>	<u>M $\text{SO}_4 =$</u>	<u>Approximate RE Solubility, M</u>
Na ⁺	0.58	0.58	≤ 0.03
	0.78	0.78	0.02 ± 0.01
K ⁺	0.4	0.4	0.45 ± 0.013
	0.68 ± 0.1	0.68 ± 0.1	0.03
NH ₄ ⁺	0.72	0.72	> 0.1

The data indicate that rare earths are much more stable in sulfate solutions derived from ammonium persulfate than in the corresponding sodium or potassium solutions and that the potassium system is slightly more stable than the sodium. Unfortunately, the potassium persulfate concentration at 25 C is limited to 0.46M by its solubility in 2M HNO_3 (Section H 3.1), and the use of ammonium salts in separations plants is avoided whenever possible because of the potential for plugging off-gas filters by the deposition of ammonium nitrate solids.

6.4.4 Iron and Aluminum Contamination in the LCP

The LCP derived from ZAW process demonstration runs (Section D 6.1.3) contained 0.006 to 0.02% of the iron and 0.6 to 4% of the aluminum entering in the IAF⁽¹³⁾. The average aluminum contamination in the LCP was about 2- to 3-fold higher in runs using tartrate-complexed feed than with HEDTA-complexed feed. The material balances across the LC Column were poor, but evidently 40 to 100% of the aluminum in the LCP was stripped from the solvent by the LCX (2M HNO₃, A/O = 0.2, 40 C).

7. Strontium Semiworks Process Demonstrations

Since 1961, the Strontium Semiworks (formerly the Hot Semiworks) has been used to recover and purify over 10 megacuries of Sr-90 from crude concentrates prepared in the Purex Plant by PbSO₄ precipitation techniques^(1,2,5,8,15). More recently, the same facility has been used to demonstrate the proposed B-Plant solvent extraction flowsheets presented in Section C 3.6 at approximately full-level fission product activity⁽¹⁴⁾. Highlights of the production and demonstration runs are presented in the following sections.

Two 4-in-diameter pulse columns, variously known as the 1A and 1B Columns^(5b) or the HA and HC Columns⁽⁸⁾, were used as the principal solvent extraction contactors. The 1A Column is a dual-purpose column with a 15-ft-tall scrub section surmounting a 10-ft-tall extraction section. The 1B Column contains a 16-ft-tall cartridge and has recently been modified so that it also can be operated as a dual-purpose cerium-rare earth partitioning column with a 10-ft-tall stripping section above a 6-ft-tall scrub section⁽¹⁴⁾. The 1A extraction cartridge is made up of 23% free area stainless steel nozzle plates (3/16-in.-diameter holes); the 1A scrub and 1B cartridges contain 10% free area stainless steel nozzle plates (1/8-in. holes). All plates are spaced 4 in. apart. With the exception of plate spacing and height, the cartridge geometries were similar to the corresponding B-Plant cartridges.

7.1 Strontium Crude Purification

A typical flowsheet used in the strontium crude purification runs is presented in Figure IV-62. Excellent performance as measured by strontium losses and the purity of the recovered product has been achieved in this process, particularly with NPH as the diluent. A summary of this experience is presented in Table IV-41. The columns were operated at ambient temperatures with the organic phase continuous in the 1A Column and the aqueous phase continuous in the 1B Column. Typical volume velocities were about 700 and 350 gph/ft² in the 1A and 1B Columns, respectively.

TABLE IV-41
SUMMARY OF TYPICAL STRONTIUM SEMIWORKS EXPERIENCE
IN PURIFYING STRONTIUM CRUDES

(Source of Data: G. L. Ritter, Isochem Inc., unpublished data)

Feed Material

Run No.	Ion/Sr-90 Mole Ratio					Isotope/Sr-90 Curie Ratio		
	Ca	Ba	Fe	Pb	Na	Ce- 144	ZrNb- 95	Ru- 106
SSW-2	0.86	0.034	6.8	0.86	--	2.0	0.20	0.03
SSW-6	1.63	0.22	5.7	0.21	150	0.35	0.28	0.014
SSW-7	1.1	0.051	7.5	1.3	110	0.48	0.098	0.017
SSW-8	1.2	0.17	11	2.1	750	0.45	0.013	0.010
SSW-9	0.80	<0.06	8.1	1.3	400	0.45	0.22	0.018
SSW-10	3.5	0.32	31	1.0	1300	1.2	0.04	0.035

A. Decontamination Factors

Run No.	Ca	Ba	Fe	Pb	Na	Ce- 144	ZrNb 95	Ru- 106
SSW-2	20	20	>1000	--	--	1650	8000	>750
SSW-6	4	50	320	16	--	3500	1950	35
SSW-7	11	3	7500	1300	--	480	120	34
SSW-8	16	30	450	160	120	2800	>150	>80
SSW-9	26	--	400	750	600	6900	1200	460
SSW-10	35	--	560	600	20	920	>50	>15

B. Recovery Performance

Run No.	Kilocuries Sr-90 Processed		% Sr-90 Lost	
	Feed	Product	To 1AW	To 1BW
SSW-2 ^(a)	975	95	2	7.5 ^(c)
SSW-6 ^(a)	1200	1100 ^(d)	4-2 ^(c)	10-3 ^(c)
SSW-7 ^(a)	940 ^(d)	890 ^(d)	4	5
SSW-8 ^(b)	940	885	<1	<1
SSW-9 ^(b)	550	510	<1 ^(e)	<1
SSW-10 ^(b)	890	910	7 ^(e)	0.4

(a) Soltrol-170 diluent.

(b) NPH diluent.

(c) Solvent changeout during run. Losses decreased as shown when new solvent was used.

(d) Includes 140 kilocurie rework from Run No. SSW-6.

(e) High loss because of unfavorable aqueous/organic ratio and Na and Ca feed content.

FIGURE IV-62

Typical Strontium Semiworks Chemical Flowsheet
for Purification of Strontium
(Source of Data: RL-SEP-20)

7.2 PAW Flowsheet Demonstration

7.2.1 IA - IB Columns

A process test of an HEDTA-complexed PAW flowsheet similar to that shown in Fig. IV-48 was completed in October, 1965 (Pm Process Test No. 4) (14). Rare earth extraction and separation from strontium was excellent; however the low IAF and IAW pH's (3.6 and 3.2, respectively) prevented quantitative extraction of strontium. Extraction losses were about 25% for strontium, 1% for cerium, and 2% for promethium. The strontium loss was 1% in the IB Column (using 0.04M HNO₃ as IBX), and the decontamination factor from cerium was 1300. The rare earths were quantitatively stripped from the solvent by a batch contact with 3M HNO₃. A detailed material balance summary is presented in Table IV-42.

The IA and IB Columns were operated at 40 to 50 C with the aqueous phase continuous; volume velocities were 620 and 440 gph/ft², respectively. Relative flows of the IAF, IAS(1SS), IAX, and IBX streams were 100, 25, 100, and 20. The solvent used in this and the remaining tests was 0.4M D2EHPA-0.2M TBP-NPH diluent.

TABLE IV-42

PAW FLOWSHEET DEMONSTRATION RUN SUMMARY

Pm Process Test No. 4

(Source of Data: G. L. Ritter⁽¹⁴⁾)MATERIAL BALANCE

<u>Stream</u>	<u>Promethium</u>		<u>Cerium</u>		<u>Strontium</u>	
	<u>KCi</u>	<u>%</u>	<u>KCi</u>	<u>%</u>	<u>KCi</u>	<u>%</u>
1AF	112	100	580	100	107	100
1AW	2	2	2	<1	22	20
1BP	< 0.1	0.1	0.3	< 0.1	75	70
1CP ^(a)	105	94	530	92	1	1
Total	107	96	532	92	98	91

DECONTAMINATION FACTORS

	<u>Strontium Product (1BP)</u>	<u>Rare Earth Product (1CP)^(a)</u>
Fe	> 3200	> 2000
Pb	50	25
ZrNb	200	100
Ru	>350	>250
U	> 60	> 40
Pu	> 17	> 11
Y	100	20
Np	>350	>250
Sr	--	150
Pm	750	--
Ce	1300	--
Ca	4.1	1.2
Na	> 14	> 9
Al	--	30

(a) Resulting from batch strip with 3M HNO₃.

7.2.2 1C Column

Promethium Process Test No. 2 was the first full-level demonstration, and the most successful to date (June 1966), of the persulfate oxidized 1C Column flowsheet. The results fully verified the Cold Semi-works tests described in Section D 5.4.3. The steady-state loss of promethium in the cerium product (1CW) was 1% and that for cerium in the promethium-rare earth product (1CP) was 1%^(12,14).

1AF for this run contained 0.0048M rare earths, including 0.0015M cerium, 0.06M HEDTA, and 0.2M hydroxyacetic acid. It was prepared from Purex waste that had been treated with a lead sulfate precipitation and a D2EHPA solvent extraction cycle to eliminate most of the impurities. The rare earths were extracted with 0.4M D2EHPA-0.2M TBP-NPH that had been used in previous SSW runs and was reused during the run after stripping the cerium out with a nitric acid-sodium nitrite solution and destroying the residual nitrite with sulfamic acid. A 1AS stream containing 0.025M HNO₃ was used as the 1A Column scrub to simulate the 1B Column treatment. The 1CX, after blending separate silver and persulfate streams, contained 2M HNO₃, 0.2M K₂S₂O₈ and 0.02M AgNO₃. Relative flow ratios 1AF:1AS:1AX:1CX:1CS were 1.05:0.25:1.0:0.2:0.2; 1A and 1C Column velocities were 840 and 510 gph/ft², respectively. The columns were operated at ca. 40 C with the organic phase continuous in the 1A Column and the aqueous phase continuous in the 1C Column. An over-all material balance summary is presented in Table IV-43.

TABLE IV-43

OVER-ALL PROMETHIUM, CERIUM, AND STRONTIUM
MATERIAL BALANCES FOR Pm PROCESS TEST NO. 2

(Source of Data: G. L. Ritter⁽¹⁴⁾)

Stream	Promethium		Cerium		Strontium	
	KCi	%	KCi	%	KCi	%
1AF(a)	171	100	908	100	58	100
1AW	14	8	16	1.8	47	81
1CP	151	88	16	1.8	1	2
1CW	7	4	858	95	0.8	1.4

(a) Ca. 1.2 watts/liter.

The steady-state 1A Column rare earth losses were 2 to 4-fold less than the over-all losses, which for both the 1A and 1C Columns reflect the effects of deliberate process upsets and the usual start-up and shut-down losses. Typical steady-state losses in the 1AW were 1 and 4% for cerium and promethium, respectively.

7.3 ZAW Flowsheet Demonstration

7.3.1 1A-1B Columns

The 1A and 1B Column portion of the ZAW flowsheet presented in Fig. IV-49 was tested in June, 1965⁽¹⁴⁾. The only significant changes in the flowsheet were the use of slightly less tartrate in the feed (0.013 vice 0.025M) and more HNO_3 in the 1BX (0.03 vice 0.02M). The rare earths were batch stripped from the 1BW with 3M HNO_3 .

The feed was derived from a Purex head-end product to which large amounts of ferric and aluminum nitrate and other lesser amounts of other cold chemicals were added to simulate ZAW. The feed was adjusted to pH 4.0. The columns were operated at 40 to 45 C with volume velocities of 400 and 220 gph/ft² in the 1A and 1B Columns, respectively. The 1A Column was operated with the organic phase continuous, and the 1B Column was operated with the aqueous phase continuous. Material balances and decontamination factors are tabulated in Table IV-44.

The performance was excellent except for the high rare earth loss in the 1A Column. The promethium and cerium losses in the 1AW correspond to HTU's of 7.2 and 4.3 ft., respectively. For comparison, the cerium HTU in a Cold Semiworks demonstration runs under the same conditions was 4.0 ft (Table IV-30).

The behavior of americium-curium was also followed in this run. The over-all material balance was poor, but the results of this and earlier tests indicate that americium and curium will follow the trivalent rare earths. Americium comprised 36% of the Am-Cm in the feed and 41% in the product.

TABLE IV-44
ZAW FLOWSHEET DEMONSTRATION RUN SUMMARY
(Source of Data: G. L. Ritter⁽¹⁴⁾)

Stream	MATERIAL BALANCE							
	Promethium		Cerium		Strontium		Americium	
	KCi	%	KCi	%	KCi	%	Ci	%
1AF	100	100	580	100	93	100	3.5	100
1AW	22	22	60	10	3	3	0.17	6
1BP	0.14	0.14	0.05	<0.01	88	95	<0.03	1
1CP(a)	75	75	540	93	0.6	0.6	1.9	55
1CW(a)	--	--	--	--	--	--	--	--
Total	97	97	614	106	92	98	2.1	60

Impurity	DECONTAMINATION FACTORS	
	Strontium Product	Rare Earth Product ^(a)
Fe	> 100,000	4,000
Pb	50	20
Al	> 13,000	120
U	> 120	> 36
Pu	> 320	> 100
Na	450	150
Ca	5.4	1.2
Cr	> 4,000	1,200
Ce	11,000	--
Pm	800	--
Sr	--	100
ZrNb	125	> 7.5

(a) Resulting from the batch strip with 3M HNO₃.

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E. BATCH D2EHPA EXTRACTION OF NEPTUNIUM AND PLUTONIUM
FROM PUREX ACID SLUDGE SOLUTION

1. Introduction

A large fraction of the sludge now contained in the Purex self-boiling tanks was derived from Hanford Purex plant high-level waste produced before the start-up of Np-237 recovery operations in the Purex plant proper. Considerable Np-237 and also plutonium, the latter from normal small Purex process losses, have thus accumulated in the sludge.

This part of the manual is devoted to discussing the chemistry of the batch solvent (D2EHPA) extraction process which has been developed for recovering neptunium and plutonium from PAS solution⁽¹⁾. Current interest in recovering Np-237 stems from its use in producing Pu-238, an isotopic power source useful in space vehicles.

Also to be noted is that much of the stored Redox process sludge contains amounts of Np-237 and plutonium judged worth recovering⁽²⁾. It is anticipated that this neptunium and plutonium will report largely to the HNO₃ leach solution used to recover Sr-90 from the Redox sludge. It is also anticipated, although not demonstrated experimentally, that the D2EHPA extraction process described in this section can be used satisfactorily to recover neptunium and plutonium from RAS solutions.

2. Process Concept

The concept of the batch extraction process for recovery of neptunium and plutonium from PAS solution is illustrated in Figure IV-63.

Core of the process is a sequence of extraction-strip batch contacts. The first series of contacts serves to recover neptunium and plutonium from the PAS solution by D2EHPA extraction followed by oxalic acid stripping. These first contacts also serve to free the plutonium and neptunium from the bulk of the radioactive and inert contaminants present in the PAS solution; uranium and iron are the principal contaminants after the first contacts.

To provide further decontamination from uranium, iron, and other contaminants, neptunium and plutonium are again extracted into the D2EHPA extractant. Feed for this final extraction contact is prepared by destroying oxalate in the first oxalic acid strip solution by reaction with HNO₃ and H₂O₂. A nine-fold reduction in volume at this stage also serves to concentrate the plutonium and neptunium. Plutonium and neptunium are again removed from the organic phase by stripping with oxalic acid. This final strip solution is treated with HNO₃ and H₂O₂ and concentrated to yield a solution suitable for transmittal to the Hanford Purex plant for final separation and purification of the neptunium and plutonium. Present plans call for accumulation of the plutonium and neptunium from 9000 gallons of PAS solution in 5 gallons of final product solution.

FIGURE IV-63

D2EHPA Extraction of Np-Pu from PAS Solution

3. Extraction Step

The D2EHPA extraction of plutonium and neptunium from HNO₃ and HNO₃-nitrate solutions has been investigated in great detail by Weaver and Horner⁽³⁾. Highlights of their findings are:

- a. The order of extraction of plutonium in different oxidation states is Pu(IV)>Pu(VI)>>Pu(III). Similarly, the order of extraction of neptunium is Np(IV)>Np(VI)>>Np(V).
- b. Extraction of Np(IV) from HNO₃ is inversely proportional to the square of the acidity above about 1M HNO₃; below 1M HNO₃ it is directly proportional to acidity.
- c. Extraction of Pu(IV) from nitrate solutions is somewhat similar to that of Np(IV) but several times as high.
- d. Dilute oxalic acid is an effective reagent for stripping plutonium and neptunium from D2EHPA solutions.

In the range from 10^{-4} to 10^{-2} M D2EHPA in Amsco 125-82 diluent Weaver and Horner found that extraction of Pu(IV) from 1M HNO_3 was proportional to the square of the uncomplexed D2EHPA concentration. On the other hand, Peppard and coworkers⁽⁴⁾ find that in the D2EHPA (toluene) vs (perchlorate + nitrate) system the Np(IV) extracted species contains one nitrate group. They suggest the extraction reaction is:

where $(\text{HR})_2$ is dimerized D2EHPA.

In PAS solution plutonium is present as Pu(IV) but neptunium is present, at least to some extent, in the inextractable Np(V) state. A key point in the extraction process, therefore, is the need to establish both elements in the quadrivalent state to permit extraction of both neptunium and plutonium into the same organic phase. Attempts to find a combination of oxidizing and/or reducing agents which would establish both neptunium and plutonium simultaneously in the quadrivalent state in PAS solution failed. A successful procedure consists of extracting Pu(IV) into the D2EHPA phase, and, after allowing the two phases to separate but without removing the organic phase, treating the aqueous phase with ferrous sulfamate and hydrazine to obtain Np(IV). Recontact of aqueous and organic phases then extracts the Np(IV). Satisfactory recovery of both actinides depends on the great affinity of D2EHPA for Pu(IV) so that serious back-extraction of plutonium does not occur during valence adjustment and extraction of neptunium.

This approach to recovery of neptunium and plutonium has been extensively tested in laboratory experiments with both synthetic and actual PAS solutions. Some typical results with actual PAS solutions are given in Table IV-45. These data demonstrate the extractant should be at least 0.1M D2EHPA to realize satisfactory recovery of both neptunium and plutonium.

TABLE IV-45
D2EHPA EXTRACTION OF NEPTUNIUM AND PLUTONIUM FROM PAS SOLUTION

(Source of Data: W. W. Schulz, BNW, Unpublished Data)

PAS solutions obtained from stored waste contacted 30 min. at 25 C with an equal volume of indicated D2EHPA-TBP-diluent solution. Without phase separation, aqueous phase made indicated N_2H_4 and ferrous sulfamate concentration and allowed to stand 30 min. at 25 C. Finally, aqueous and organic phases recontacted 30 min. at 25 C.

PAS Description		D2EHPA, M	TBP, M	FS ^(a) , M	N_2H_4 , M	% Not Extracted	
Sludge from Tank Number	PAS H ⁺ , M					Np	Pu
101	4.48 ^(b)	0.10	0.10	0.01	0.01	0.32	0.39
101	2.24	0.06	0.06	0.01	0.01	6.56	33.5
101	0.72	0.04	0.02	0.01	0.01	14.9	57.1
101	0.72	0.04	0.02	0.00	0.00	52.9	81.8
104	0.50	0.10	0.05	0.01	0.01	0.1	1.11
104	0.50	0.10	0.05	0.00	0.00	74.7	0.84

(a) Ferrous sulfamate

(b) Adjusted to 1.0M by addition of NaOH before extraction

Experiments with both synthetic and actual PAS solutions demonstrate ferrous sulfamate, either by itself or in combination with hydrazine, efficiently and rapidly reduces Np(V) to Np(IV). Hydrazine by itself is inadequate for this purpose. The combination of ferrous sulfamate with hydrazine appears preferable over ferrous sulfamate by itself to provide additional capacity for destroying nitrite ion and thereby preventing nitrite-catalyzed HNO_3 oxidation of Fe(II). Concentrations of both reductants in the range of 0.01 to 0.05M have been found adequate for reduction of Np(V). Satisfactory reduction is achieved at 25 C in as little as 10 minutes.

4. Strip Contact

Aqueous-soluble oxalate complexes of both Pu(IV) and Np(IV) are well-known⁽⁵⁾. Depending on conditions (acidity, oxalate concentration) one or more of the complexes $[\text{M}(\text{C}_2\text{O}_4)_4]^{2+}$, $[\text{M}(\text{C}_2\text{O}_4)_3]^{2-}$, and $[\text{M}(\text{C}_2\text{O}_4)_4]^{4-}$ may be formed where M = Pu(IV) or Np(IV). Formation constants for these complexes are so high that, under proper conditions, dilute oxalic acid solutions quantitatively strip Pu(IV) and Np(IV) from the D2EHPA extractant. Data illustrating this point are presented in Table IV-46.

TABLE IV-46
OXALIC ACID STRIPPING OF PLUTONIUM AND NEPTUNIUM

(Source of Data: W. W. Schulz, BNW, Unpublished Data)

Initial organic contained either 5×10^{-5} M Pu(IV) or 2×10^{-5} M Np(IV) from extraction of PAS solution.

Organic Composition		Strip Conditions				E_a^0	
D2EHPA, M	TBP M	$\text{H}_2\text{C}_2\text{O}_4$ M	Time Min.	Temp. C	Vol. Ratio, Aq/Org	Pu	Np
0.1	0.05	0.1	30	25	1:1	0.0021	0.0011
0.1	0.05	0.25	30	25	1:1	0.0007	0.0004
0.1	0.05	0.1	30	50	1:1	0.17	--
0.1	0.05	0.1	30	50	1:2	1.0	--

Based on these data a single equal volume contact at 25 C with 0.1M $\text{H}_2\text{C}_2\text{O}_4$ is specified in the chemical flowsheet (Figure IV-47) for stripping plutonium and neptunium. Pu(IV) is stripped less efficiently at 50 C than at 25 C according to these data. Higher temperatures favor oxalic acid stripping of iron (Section E-5) and should be avoided for this reason also.

If desirable for some reason, other complexants such as carbonate, citrate, EDTA, etc., could probably be used successfully to strip plutonium and neptunium from the D2EHPA phase. Oxalic acid, however, is smoothly and readily destroyed by reaction with HNO_3 and/or H_2O_2 (Section E8) and can be used without any danger of precipitating plutonium such as might occur during neutralization of alkaline solutions.

TABLE IV-47

EXTRACTION CONTACT - DECONTAMINATION PERFORMANCE

(Source of Data: W. W. Schulz, BNW, Unpublished Data)

Synthetic (a) PAS solution, traced with various radioisotopes, contacted 60 minutes at 25 C with an equal volume of the indicated extractant.

Contaminant	0.1M D2EHPA, 0.1M TBP, NPH			0.04M D2EHPA, 0.02M TBP, Soltrol-170	
	E _g	% Ext'd.	DF	E _g	DF
Uranium	38.7	97.7	-	-	-
Iron	0.108	9.7	-	0.0220	46
Yttrium	5.46×10^{-3}	-	180	0.0169	60
Europium	1.03×10^{-3}	-	970	0.0053	185
Ruthenium	-	-	-	0.0027	360
Cerium	2.86×10^{-4}	-	-	1.79×10^{-3}	620
Chromium	-	-	-	$<1.45 \times 10^{-3}$	>680
Americium	-	-	-	1.03×10^{-4}	9700
Strontium	-	-	-	$<2.0 \times 10^{-5}$	>4900
Manganese	-	-	-	$<1.0 \times 10^{-5}$	>10,000
Cesium	-	-	-	5.0×10^{-6}	21,000

(a) 0.5M H⁺, 0.42M Na⁺, 0.36M Fe³⁺, 0.55M Al³⁺, 0.021M Cr³⁺, 0.012M Ni²⁺, 0.01M Mn²⁺, 0.032M UO₂²⁺, 0.004M Zr⁴⁺, 0.0017M Sr²⁺, 0.002M Ce³⁺, 0.026M SO₄²⁻, 0.057M PO₄³⁻, 3.6M NO₃⁻.

5. Decontamination Performance

Of the constituents of PAS solution only uranium and iron, besides plutonium and neptunium, extract into the D2EHPA solvent to any extent. Data illustrating this point are presented in Table IV-47.

Considerable decontamination from extracted iron and, especially, uranium is obtained across the oxalic acid strip step provided high oxalic acid concentrations and high temperatures are avoided. Some typical results for the strip step are shown in Table IV-48. The excellent decontamination performance observed in extraction-strip contacts (performed according to the flowsheet conditions shown in Figure IV-47 with actual PAS solutions substantiates the work with synthetic solutions⁽¹⁾. For example, an oxalic acid strip solution derived from Tank 104 sludge was 0.0007M U and 0.0092M Fe; predicted values from experiments with synthetic PAS were 0.001M and 0.0094M, respectively. The oxalic acid solution from the Tank 104 sludge also contained less than 0.02 g/l of Zr, less than 5 ppm Mo, and only a trace (spectroscopic analysis) of Al, Si, and Mg.

TABLE IV-48

STRIP CONTACT - DECONTAMINATION PERFORMANCE

(Source of Data: W. W. Schulz, BNW, Unpublished Data)

Indicated D2EHPA extractants contacted with synthetic PAS solution and then contacted 30 minutes with oxalic acid strip according to listed conditions.

Extractant		Strip			E _g		% Stripped	
D2EHPA M	TBP M	H ₂ C ₂ O ₄ M	Aqueous Organic	Temp. C	U	Fe	U	Fe
0.1	0.1	0.1	1:1	25	26.4	2.95	4.8	25.6
0.1	0.1	0.25	1:1	25	8.9	0.49	12.5	67.4
0.04	0.02	0.1	1:1	25	1.8	0.64	36.6	60.8
0.04	0.02	0.25	1:1	25	0.98	0.23	49.5	84.0
0.04	0.02	0.1	1:2	50	1.45	<0.014	25.4	~100

6. Purification Extraction - Strip Contacts

The primary extraction-strip contacts discussed in Sections E 3 and E 4 serve to recover the neptunium and plutonium and to free them from the bulk of the contaminants with which they are associated in PAS solution. Further purification and concentration are necessary and desirable, however, to provide a small volume of purified material to route to the Hanford Purex plant for final separation and purification.

The desired purification is accomplished by a further extraction-strip cycle using essentially the same flowsheet conditions employed in the primary contacts. Feed for the purification extraction contact is prepared by accumulating (after oxalate destruction) the neptunium and plutonium from several batches of PAS solution in 1M HNO_3 solution. It is estimated that this feed solution will also be about 0.09M $\text{Fe}(\text{NO}_3)_3$, and 0.01M $\text{UO}_2(\text{NO}_3)_2$; smaller (<0.01M) amounts of other contaminants (Al, Zr, Y, etc.) may also be present.

Batch contact of the 1.0M HNO_3 feed with an equal volume of 0.1M D2EHPA-0.1M TBP-NPH solution serves to extract the Pu(IV). To recover the neptunium, the aqueous phase (without phase separation) is made 0.01 to 0.05M in both ferrous sulfamate and hydrazine to reduce Np(V) to Np(IV). Subsequent recontact of the aqueous and organic phases then extracts the Np(IV) without significant loss of Pu(IV) to the aqueous phase as illustrated by the data in Table IV-49⁽¹⁾. Essentially all of the uranium and about 15% of the iron are co-extracted with the neptunium and plutonium.

TABLE IV-49
PURIFICATION CYCLE EXTRACTION CONTACT

Synthetic feed^(a) contacted 30 minutes at 25C with an equal vol. of 0.1M D2EHPA, 0.1M TBP, NPH. Without phase separation, aqueous phase made 0.01M ferrous sulfamate and 0.01M hydrazine and allowed to stand 30 minutes at 25C. Aqueous and organic phases then recontacted 30 minutes at 25C.

Element	First Contact		Second Contact	
	$E\%_a$	% Extracted	$E\%_a$	% Extracted
Plutonium	1500	99.9	980	99.9
Neptunium	0.234	20.0	2620	99.9
Uranium	137	99.3	113	99.1
Iron	0.111	9.8	0.176	15.0

(a) 1.0M HNO_3 , 0.089M $\text{Fe}(\text{NO}_3)_3$, 0.01M $\text{UO}_2(\text{NO}_3)_2$, 0.002M $\text{Zr}(\text{SO}_4)_2$, 0.08M $\text{Al}(\text{NO}_3)_3$, 4.1×10^{-4} M $\text{Pu}(\text{NO}_3)_4$, 1.4×10^{-4} M NpO_2NO_3 .

To complete the purification cycle, the extracted plutonium and neptunium are stripped into an equal volume of 0.1M oxalic acid. Accompanying the plutonium and neptunium into the oxalic acid strip are about 84% of the extracted iron and 4% of the uranium. The oxalic acid solution is treated with HNO_3 or $\text{HNO}_3\text{-H}_2\text{O}_2$ to destroy the oxalate and then concentrated to about 5 gallons to yield a solution for shipment to the Purex plant for further purification. This concentrated product is expected to contain about 5 g/l Np and about 15 g/l Pu and to be also about 5.0M HNO_3 , 0.1M $\text{UO}_2(\text{NO}_3)_2$, and 1 to 2M $\text{Fe}(\text{NO}_3)_3$. Small (<0.1M) amounts of aluminum and zirconium may also be present in some cases.

7. Solvent Treatment

The 0.1M D2EHPA extractant after each recovery extraction and strip contact is expected to contain about 2 to 5 g/l U and 1 to 3 g/l Fe. Smaller amounts of the other inert contaminants (i.e., Al, Zr, etc.) present in PAS solution will also likely be present in this used solvent. Radioactive contaminants will include Y-90 (from beta decay of Sr-90) and, from the younger sludges, small amounts of ZrNb-95 and RuRh-106.

Routine removal of the uranium and iron from the solvent is necessary to prevent over-loading the extractant and thereby impairing extraction recovery of neptunium and plutonium. Efficient removal of uranium and iron, as well as yttrium and zirconium, if present, can be readily accomplished by washing the D2EHPA solvent with a Na_2CO_3 -sodium citrate (or sodium tartrate) solution as illustrated by the data in Table IV-50.

TABLE IV-50
SOLVENT WASHING STUDIES

(Source of Data: W. W. Schulz, BNW, Unpublished Data)

0.1M D2EHPA, 0.1M TBP, NPH extractant from extraction and strip contacts with synthetic or actual PAS solution, washed for 15 minutes at 25C with indicated solution.

Wash Composition, M			Aqueous Organic	EG		% Not Recovered		
Na_2CO_3	$\text{Na}_2\text{ Tart. (a)}$	$\text{Na}_3\text{ Cit. (b)}$		U	ZrNb-95	U	Y-90(c)	ZrNb-95
1.0	0.1	0.0	1/5	0.0062	-	3.7	-	-
1.0	0.1	0.0	1/3	0.0084	-	2.8	-	-
1.0	0.1	0.0	1/1	0.013	0.0008	0.9	-	0.09
1.5	0.0	0.1	1/5	0.0067	-	3.4	5.7	-
1.5	0.0	0.1	1/3	0.0063	-	2.1	7.0	-
1.5	0.0	0.1	1/1	0.011	0.0011	0.7	5.4	0.11

(a) Sodium Tartrate.

(b) Sodium Citrate.

(c) Solvent from contact with PAS from actual TK-101 sludge.

Sodium hydroxide solutions such as used in washing the mainline process D2EHPA extractant (Section C 6.3.1) could also be used to wash uranium from the 0.1M D2EHPA extractant. With NaOH solutions, however, uranium precipitates as the diuranate even in the presence of citrate or tartrate. Precipitation of uranium is avoided with Na_2CO_3 washes because of the formation of soluble uranium carbonate complexes. Addition of citrate or tartrate to the Na_2CO_3 solution prevents precipitation of hydrated iron oxide.

A second organic phase (Section C 2.6.1) formed when 0.1M D2EHPA-0.05M TBP-NPH solutions were contacted with 0.5 to 1.0M Na_2CO_3 solutions⁽¹⁾. When the TBP concentration was increased to 0.1M a third phase did not form if the initial Na_2CO_3 concentration was 1.0M or greater. Because of this restriction on Na_2CO_3 concentration, it is economically desirable to use only a small volume of wash solution in each batch wash. Removal of contaminants is adequate with 1.0 to 1.5M Na_2CO_3 solution at an aqueous-to-organic flow ratio as low as 1 to 5 and this amount of carbonate is still sufficient to prevent precipitation of uranium.

Washing of the 0.1M D2EHPA extractant with Na_2CO_3 solution converts it to the sodium form. Reconversion to the hydrogen form can be accomplished by washing the extractant with a small volume of HNO_3 .

8. Destruction of Oxalic Acid

In the neptunium - plutonium recovery process, dilute oxalic acid solution is used to co-strip neptunium and plutonium from the D2EHPA phase in both the primary and purification extraction-strip cycles. Destruction of oxalic acid in these strip solutions is mandatory before satisfactory concentration and purification of the neptunium - plutonium fraction can be accomplished either in the D2EHPA purification cycle or, finally, in the Purex plant.

Many familiar oxidizing agents (e.g., KMnO_4 , $\text{Ce}(\text{SO}_4)_2$, etc.) can be used to destroy oxalic acid. The use of most of these reagents would introduce metallic impurities into the neptunium - plutonium product. Nitric acid also reacts with oxalic acid according to the reaction

The reaction is first order with respect to oxalic acid. Typical data are presented in Figure IV-64. These data illustrate a major disadvantage of using HNO_3 alone to destroy oxalic acid; namely, that the rate of reaction is intolerably slow at HNO_3 concentrations below about 9M.

Hydrogen peroxide in acid solution is a powerful oxidizing agent; the potential for the couple

is -1.77 volts⁽⁶⁾. (The use of H_2O_2 to oxidize citric acid in solutions containing Sr-90 is a well-established practice at Hanford as discussed in detail in Section C 4.3.5.) Oxidation of oxalic acid in accordance with the reaction

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was studied as early as 1923 by Hatcher⁽⁷⁾ who found ready oxidation occurred in various dilute acid (HNO_3 , HCl) solutions at 20 C. Further applications (both uncatalyzed and catalyzed) of H_2O_2 to oxidize oxalic acid have been alluded to in recent AEC project literature. As this manual was written, H_2O_2 was under active laboratory consideration as the preferred reagent for destruction of oxalic acid in the strip solutions of the neptunium - plutonium recovery process.

9. Chemical Flowsheet

A chemical flowsheet for batch D2EHPA extraction of neptunium and plutonium from PAS solution is given in Figures IV-65 and IV-66.

FIGURE IV-64

Kinetics of Destruction of Oxalic Acid with Nitric Acid
(Source of Data: W. W. Schulz, BNW, Unpublished Data)

FIGURE IV-65

Chemical Flowsheet for Recovery of Neptunium and Plutonium from Purex Acid Sludge - Recovery Cycle

Notes

(1) Organic from strip contact in recovery cycle (Fig. IV-65) washed in same way.

(2) Product from treating six 1500 gallon batches of PXS

(3) Estimated conditions

FIGURE IV-66

Chemical Flowsheet for Recovery of Neptunium and Plutonium from Purex Acid Sludge - Purification Cycle

10. References

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F. ION EXCHANGE PROCESSES1. General Principles of Ion Exchange

Ion exchangers are insoluble solid materials which carry exchangeable cations or anions. These ions can be exchanged for a stoichiometrically equivalent amount of other ions of the same sign when the ion exchanger is in contact with an electrolyte solution. Carriers of exchangeable cations are called cation exchangers, and carriers of exchangeable anions, anion exchangers. Typical reactions are

and

where X represents a structural unit of the ion exchanger, and solid phases are underlined.

Ion exchange is, with few exceptions, a reversible process. Thus, the calcium loaded on the cation exchanger in the example above can be eluted by passing a concentrated sodium salt solution through the exchanger.

Ion exchangers owe their characteristic properties to a peculiar feature of their structure. They consist of a framework which is held together by chemical bonds or lattice energy. This framework carries a positive or negative electric surplus charge which is compensated by ions of opposite sign, the so-called counter ions. The counter ions are free to move within the framework and can be replaced by other ions of the same sign. The framework of a cation exchanger may be regarded as a macromolecular or crystalline polyanion, that of an anion exchanger as a polycation. According to this simple model, the counter-ion content of the ion exchanger -- the ion-exchange capacity -- is a constant which is given solely by the magnitude of the framework charge and is independent of the nature of the counter ion⁽⁹⁾.

When an ion exchanger containing one species of counter ions is placed in a solution containing a second species, an exchange of counter ions takes place. After a certain time, determined by the mobilities of the counter ions, ion exchange equilibrium is attained. As a rule, the ion exchanger selects one species in preference to the other depending on ionic charge (valence), charge distribution, complex formation, and ion size. The selectivity is usually expressed as a mass action quotient, such as the following for the sodium-calcium exchange reaction presented above:

$$K_{Na}^{Ca} = \frac{(CaX_2)(Na^+)^2}{(NaX)^2(Ca^{++})} \quad (3)$$

where the terms in parentheses are concentrations in consistent units (molarities or equivalent fractions, for example). The "K" defined by the above equation is not the thermodynamic equilibrium constant and can vary over a wide range depending on the temperature and the relative concentrations of the different counter ions in the system. The concept is quite useful, however, in predicting exchange equilibria when the value of K as a function of solution composition is known.

The use of binary exchange data to predict the equilibrium distribution is often complicated by the presence of more than two exchanging counter ions; however, Mercer and Ames⁽¹⁴⁾ have shown that binary equilibrium data can be used to predict equilibrium concentrations of cesium and strontium on zeolites loaded from dilute solutions containing three or more cations. If the concentrations of the various cations on the zeolite are expressed in equivalent fractions, then the sum of all the cation equivalent fractions on the zeolite is unity:

$$A_z + B_z + C_z + \dots = 1 \quad (4)$$

To solve for A_z , the mass action expressions are substituted in place of B_z and C_z for the exchange of A with B and A with C, respectively. For example, where A and B are univalent and C is divalent, the following equation is obtained:

$$A_z + \frac{(B^+)}{K_B^A A^+} A_z + \frac{(C^{++})}{K_C^A A^{+2}} A_z^2 = 1, \quad (5)$$

where the concentrations of cations A^+ , B^+ , and C^{++} in solution are expressed in equivalents/liter and the concentration of A on the zeolite, A_z , is expressed as the equivalent fraction. In column applications where the zeolite-containing column is loaded to ≥ 50 percent breakthrough and the breakthrough curve is steep, the zeolite is essentially in equilibrium with the feed; and A_z can be determined by solving the simple quadratic equation if K_B^A and K_C^A are known. (B_z and C_z can be solved by similar substitutions.) The calculation method is not restricted to zeolites but is applicable to any ion exchange media where suitable values of the mass action quotients are known or can be determined experimentally.

2. Ion Exchange Materials

2.1 Inorganic Cation Exchangers

Several naturally occurring and synthetic minerals exhibit a high cation exchange capacity and specificity for strontium and cesium. Among the most important members of this class are the zeolites. These are hydrated, crystalline aluminosilicates with the molecular structure $(M, N_2)O \cdot Al_2O_3 \cdot nSiO_2 \cdot mH_2O$, where M is an alkaline earth and N an alkali metal. The zeolites have a relatively open three-dimensional framework structure with channels and interconnecting cavities in the aluminosilicate lattice. The zeolite lattice consists of SiO_4 and AlO_4 tetrahedra which have their oxygen atoms in common. Since aluminum is trivalent, the lattice carries a negative electric charge (one elementary charge per aluminum atom). This charge is balanced by alkali or alkaline earth cations, which do not occupy fixed positions but are free to move in the channels of the lattice framework. These ions act as counter ions and can be replaced by other cations. Specificity and exchange capacity are determined by the SiO_2/Al_2O_3 ratio and by the crystalline structure. Increase in exchange capacity is gained from the lower silica/alumina ratios, greater acid stability from the higher ratios⁽²³⁾.

Synthetic zeolites are prepared by gelling sodium silicate, sodium aluminate, and sodium hydroxide in fixed ratios followed by digestion to permit crystallization to 0.1 to 10 micron particle size. The zeolite crystals are then mixed with a clay binder extruded, dried, and rotary-kiln fired at about 1200 F⁽²³⁾. The synthetic zeolites have been most widely used as "molecular sieves" which, because of their very small and uniform pore structure, can sorb small molecules but completely exclude molecules larger than the pore openings. Typical pore openings range from 3 to 13 Å, depending on the zeolite type.

Selected properties of some of the more important zeolites studied at Hanford are presented in Table IV-51. One non-zeolite (Decalso) is included in this table because of its similarity to the zeolites in properties and applications. Decalso is an amorphous aluminosilicate gel, produced by Ionac Chemical Co., with the empirical formula $Na_2O \cdot Al(OH)_3 \cdot 6Si(OH)_4 \cdot xH_2O$. Unlike the zeolites, water forms an integral part of the Decalso structure; and dehydration of the loaded gel at temperatures above 100 C will prevent complete elution of the sorbed cation.

2.2 Organic Ion Exchangers

Ion exchange resins are typical gels. Their framework consists of an irregular, polymeric, three-dimensional network of hydrocarbon chains which carry active ionic groups such as $-SO_3^-$ and $-COO^-$ in cation exchangers and $-N(CH_3)_3^+$ and $-NH_3^+$ in anion exchangers. The framework of the resins, in contrast to that of the zeolites, is a flexible, random

TABLE IV-51
ZEOLITE PROPERTIES
(Ca. 20-50 mesh particles)

Source of Data: References (1) (12) (13) (23)

Structural Type	Clinoptilolite		Linde		Norton "Zeolon"	Ionac "Decalso" (a)
	4A	4A XW	13 X	AW-400		
SiO ₂ /Al ₂ O ₃ Ratio	8 - 10	2	2.5	6 - 7	10	gel 3(a)
Total Exchange Capacity meq./gm.	1.7	3.5	3.6	2.0	1.9	2.0(Cs)
Particle density, gm/cc (dry beads)	--	1.1	1.0	1.2	1.2	1.66
Packed density, gm/cc	0.7 - 0.8	0.7 - 0.8	0.6 - 0.7	0.8	0.8	0.7 - 0.8
Volumetric Exchange capacity, Eq./l (b)	1.3	2.6	2.3	1.5	1.4	1.5(Cs)
Effective Pore Diameter, Å	<4	4	7-9	4	9-10	---
Internal Void Volume, %	--	45	51	--	41	---
Binder, Wt %	5-15	20	20	25	--	---
Water, lbs/100 lbs. absorbent at 25C	12	25	25	12	12	---
pH Tolerance Range	1 - 12	5 - 12	4 - 12	4 - 12	1 - 14	(5 - 13)
Maximum Temperature, degrees C (c)	(700)	550	--	550	(700)	100

(a) Not a zeolite. Empirical formula is Na₂O·Al(OH)₃·xH₂O

(b) Based on average packed density.

(c) Adsorbed ions are difficult to remove if mineral is heated above indicated temperature.

network. The chemical, thermal, and mechanical stability and the ion-exchange behavior of the resins depend chiefly on the structure and the degree of crosslinking of the matrix and on the nature and number of the fixed ionic groups⁽⁹⁾.

The degree of crosslinking determines the mesh width of the matrix and thus the swelling ability of the resin and the mobilities of the counter ions in the resin. The latter, in turn, determine the rates of ion exchange. Highly cross-linked resins are resistant to swelling and chemical and radiation damage, but exchange kinetics are favored by lower crosslinkages.

Most of the commercial resins are based on a polystyrene matrix with a small proportion of divinylbenzene added to cross-link and stabilize the resin form. The degree of crosslinkage in cation resins is usually indicated by giving the proportion of divinylbenzene added; thus, an "X8" resin is one containing 8 weight percent divinylbenzene. Anion resins may also have a considerable amount of crosslinking through the amine structure. The polystyrene resins are produced in the shape of small spheres. The standard size is about 20-50 mesh, but smaller sizes are available. Since the rate controlling step in most ion exchange reactions is diffusion, decreasing the size of the resin particles materially decreases the time required for the resin to reach equilibrium with a contacting solution. Conversely, however, the pressure drop for solutions flowing through a bed of resin increases rapidly with a decreasing particle size (by a factor of about 11 on going from 20-50 mesh resin to 50-100 mesh)⁽⁶⁾.

Phenolic resins, produced by phenol-formaldehyde condensation, are another, less common class of resins. They are always in the form of granular particles and possess the combination of excellent physical durability and high porosity. They are not stable in nitric acid solutions, however,

Resins are available in both strong and weak acid and base forms. The strong acid and base resins are analogous to strong acids and bases such as HCl and NaOH and remain ionized over a wide pH range. Weak acid groups, such as -COO^- , are ionized only at high pH. Likewise, weak base groups such as -NH_3^+ lose a proton to form uncharged -NH_2 when the pH is high. Only strong acid and base resins will be used in B-Plant although the cesium selectivity of Duolite C-3 at high pH's is related to the weak-acid phenolic group.

Selected properties of current and candidate ion exchange resins used in chemical separations at Hanford are shown in Table IV-52.

TABLE IV-52
ION EXCHANGE RESIN PROPERTIES
(20 - 50 mesh particles)
Source of Data: References (6)(7)(9)(11)

	Dowex 50, 50W	Duolite C-3	Permutit SK	Amberlite IRA-401
Type	Cation	Cation	Anion	Anion
Active Group	$-\text{SO}_3^-$	$-\text{CH}_2\text{SO}_3^- (-\text{OH})$	pyridinium	$-\text{CH}_2\text{N}(\text{CH}_3)_3^+$
Matrix	Polystyrene	Phenolic	Polystyrene	Polystyrene
Cross Linkage, %	8 ^(a)	--	~4	~4
Particle Density, g/cc (moist)	1.3	1.26 (Na^+)	~1.14 (NO_3^-)	1.1 (NO_3^-)
Bulk Density, g/cc (moist beads)	0.8	0.4	0.7	0.64
Total Capacity, meq/ml (wet)	1.7 (H^+)	1.2 (Na^+)	1.4 (NO_3^-)	1.2 (NO_3^-)
meq/g (dry)	5.0 (H^+)	2.9 (H^+)	4.3 (NO_3^-)	3.6 (NO_3^-)
Swelling Due to Exchange, % ^(b)	8	7	10	-9
% Water	53 (H^+)	60-80	45-55	49 (NO_3^-)
Maximum Temperature, °C ^(c)	150	60	60	60

(a) Available at 1 to 16% crosslinkage. Standard crosslinkage is 8% (X8).

(b) For exchange from Na^+ to H^+ form, cation exchange resins, and from OH^- to Cl^- for anion exchange resins.

(c) For thermal stability.

3. Engineering Concepts

3.1 Loading

Most ion exchange operations, including the B-Plant ion exchange processes, are carried out by passing a feed solution downflow through a bed of ion-exchange material where the desired ion is removed by selective adsorption on the ion exchanger. The performance of an ion-exchange column is usually defined by a breakthrough curve where the ratio of the effluent concentration to the feed concentration of the ion being removed is plotted versus the feed throughput. When the equilibrium is favorable the ion initially on the bed will be displaced and move faster through the bed than the incoming ions, producing a self-sharpening boundary between the loaded and unloaded portions of the bed. The shape of this boundary reaches a steady-state within a short distance and remains unchanged as it moves down the column. The breakthrough curve is, therefore, determined by the steady-state shape of this boundary.

Logarithmic-probability coordinates are frequently used for plotting breakthrough curves. The use of the probability scale for plotting the concentration ratio, C/C_0 , and the logarithmic scale for the feed throughput largely eliminates the S-shaped curvature obtained with linear scales and makes it possible to plot accurately those values which are either very small or very near to unity.

The equation for a straight line breakthrough curve on log-probability paper⁽²⁰⁾ is given by

$$C/C_0 = 1/2 [1 + P_i(A \ln n/n_0)] \quad (6)$$

where C/C_0 = ratio of the effluent concentration to the feed concentration.

$$P_i(x) = \text{normal probability integral} = \frac{1}{\sqrt{2\pi}} \int_{-x}^x e^{-\frac{t^2}{2}} dt.$$

A = slope of the line on log-probability paper, dimensionless.

n = column volumes of feed solution.

n_0 = column volumes of feed at 50% breakthrough ($C/C_0 = 0.5$).

This type of breakthrough curve is obtained in most, if not all, of the loading processes described in this section.

The slope, A , of the breakthrough curve is a measure of the process kinetics and is a complex function of the ion exchanger properties and operating conditions. It approximately corresponds to $\sqrt{N}$ and $\sqrt{\frac{N_R}{2}}$, where N is the number of theoretical plates in the correlation method of Gluekauf⁽⁸⁾ and N_R is the number of reaction units as defined by Heister and Vermeulen⁽¹⁸⁾:

$$N_R = \frac{k_F v}{F} \quad (7)$$

where k_F = reaction rate constant

v = packed bed volume (column volume)

F = volumetric flow rate

The ratio F/v represents the feed flow rate in column volumes per unit time; thus A should be inversely proportional to the square root of the flow rate in column volumes/hour.

A series of breakthrough curves are plotted in Figure IV-67 to illustrate the effect of variations in A . The use of the ratio n/n_0 rather than n in this plot eliminates the capacity of the exchange material as a variable and is a convenient way to compare kinetic behavior at different operating conditions or with different ion exchange materials. Note that increasing values of A correspond to improved utilization of the column capacity.

FIGURE IV-67

Logarithmic-Probability Plot of Breakthrough Curves
Showing the Effect of the Parameter "A"

The area under the breakthrough curve from 0 to n column volumes is a measure of cumulative loss to the effluent stream; that is,

$$\text{Waste Loss Fraction} = \text{WLF} = \frac{1}{n} \int_0^n \frac{C}{C_0} dn \quad (8)$$

After substitution of the value of C/C_0 from equation (6), this can be integrated to give

$$\text{WLF} = \frac{C}{C_0} - \frac{n_0}{2n} e^{1/2A^2} \left[1 + P_i \left(A \ln \frac{n}{n_0} - \frac{1}{A} \right) \right] \quad (9)$$

The effect of A on the waste loss fraction is shown as a function of n/n_0 and C/C_0 in Figures IV-68 and IV-69.

The capacity of the ion exchange bed in equilibrium with the feed solution can be expressed in terms of column volumes by the relationship

$$n_L = \frac{Qq\rho}{C_0} \quad (10)$$

where Q = maximum exchange capacity of the ion exchange material, meq/g.

q = equivalent fraction of the adsorbing ion on the ion exchanger in equilibrium with the feed,

C_0 = concentration of adsorbing ion in the feed, meq/ml

ρ = bulk density of the ion exchange bed, g/ml

Hence, n_L is equal to the equilibrium distribution ratio in volumetric concentration units and represents the minimum number of column volumes of feed solution required to fully load the bed (at $A = \infty$).

The term n_L is often used interchangeably with n_0 , the number of column volumes required to reach 50 percent breakthrough; however at low values of A , the two numbers differ considerably, as shown in the following derivation:

1. As n approaches infinity, the area above the breakthrough curve from $C/C_0 = 0$ to $C/C_0 = 1$ will approach n_L as a limit:

$$n_L = \lim_{n \rightarrow \infty} [n(1 - \text{WLF})]. \quad (11)$$

2. If the straight line breakthrough curve relationship on log-probability still applies as n approaches infinity, Equation (9) simplifies to

$$\text{WLF} = 1 - \frac{n_0}{n} e^{1/2A^2} \quad (12)$$

3. Thus,

$$n_L = n \left(1 - 1 + \frac{n_o}{n} e^{1/2A^2} \right) = n_o e^{1/2A^2} \quad (13)$$

A plot of $(n_L/n_o) - 1$ is presented in Figure IV-70. Note that the difference between n_L and n_o becomes less than 2 percent when A exceeds 5 and that n_L/n_o can be closely approximated by $1 + 1/(2A^2)$ when A is larger than 3.

The breakthrough curve is fully defined when n_L and A are known or can be estimated by empirical relationships. A is usually determined from experimental breakthrough data; n_L is readily determined from equilibrium distribution ratio data. Plots of n/n_o vs A at several levels of C/C_o are presented in Figure IV-71 to aid in the construction of breakthrough curves.

3.1.1 Sample Calculation: Estimation of Cesium Breakthrough Curve

Equilibrium data for loading cesium on Linde AW-500 zeolite are presented in Figure IV-78. For Purex alkaline supernate (PSN), the cesium concentration in the feed (C_o) is about 0.0008, the mole ratio of Cs^+/Na^+ is about $0.0008/4 = 0.0002$ and the corresponding cesium loading (neglecting the effect of trace amounts of competing potassium and rubidium) is about 0.061 mole of Cs/liter of AW-500. Then from Equation (10),

$$n_L = \frac{Q_{90}}{C_o} = \frac{0.061}{0.0008} = 76.3$$

A correlation for estimating the slope of the breakthrough curve for Purex supernate solution and 20-50 mesh zeolite is presented in Section F 4.2.3 (Equation 23). Assume that the column is operated at a superficial velocity of 1.8 gal/min-ft² and a total flow rate of 1.5 column volumes/hr. Then

$$A = \frac{7.1 V^{0.125}}{R^{0.55}} = \frac{7.1 (1.8)^{0.125}}{(1.5)^{0.55}} = 6.1$$

The volume of feed required to reach the 50 percent breakthrough point is given by Figure IV-70 or Equation (13):

$$n_o = n_L e^{-1/2A^2} = 76.3 e^{-0.0134} = 75.3 \text{ column volumes.}$$

The volume of feed required to reach any other cesium breakthrough point can be estimated from Figure IV-71. Thus, at $C/C_o = 0.01$ and $A = 6.1$, the value of $n/n_o = 0.69$ and $n = (0.69)(75.3) = 52$ column volumes. Similarly, $n = 61$ column volumes at $C/C_o = 0.1$. These data, plotted on log-probability coordinates, will lie on a straight line.

The cumulative loss for a given breakthrough level can be determined from Figure IV-69. For example at 10 percent breakthrough and $A = 6.1$, the cumulative cesium loss is 0.7 percent. Alternatively, the column can be operated to 23 percent breakthrough without exceeding a cumulative loss of 2 percent.

FIGURE IV-68

Cumulative Percent Breakthrough Loss
As a Function of A and the Throughput Ratio, n/n_0

FIGURE IV-69

Cumulative Percent Breakthrough Loss
As a Function of A and C/C_0

FIGURE IV-70

n_L/n_0 As a Function of A

FIGURE IV-71

Cross Plot of Figure IV-67

3.2 Elution

Many elution techniques operate with unfavorable equilibria; that is, the ion being eluted favors the ion exchanger more than the eluting agent. When this occurs, the boundary between loaded and eluted portions is nonsharpening and becomes more diffuse on its way through the column. Eventually the spread of the boundary increases in proportion to the distance traveled. As a result, the elution curve (a plot of the effluent concentration of the ion being eluted vs the volume of eluting solution) is bell-shaped and usually has a long trailing edge. The trailing portion of this curve can often be represented by the equation

$$\log \frac{C_2}{C_1} = -k (n_2 - n_1) \quad (14)$$

where C_2 = the effluent concentration after n_2 column volumes

C_1 = the effluent concentration after n_1 column volumes

k = a constant dependent on the equilibrium constant and exchange kinetics of the system (column volume⁻¹).

The initial point (C_1, n_1) may be any point on the elution curve for which Equation (14) holds true (i.e., when a plot of $\log C$ vs n is a straight line).

Two points on the elution curve are sufficient to determine k :

$$k = \frac{-\log(C_2/C_1)}{n_2 - n_1} \quad (15)$$

The amount of the eluted ion left on the ion exchange bed after n_1 column volumes of eluting solution have been passed through the bed can be determined by integrating Equation (14) from $n = n_1$ to $n = \infty$

$$\frac{Y}{v} = \int_{n_1}^{\infty} C \, dn = \int_{n_1}^{\infty} C_1 (10)^{-k(n-n_1)} \, dn = \frac{C_1}{2.3k} \quad (16)$$

where Y = the total equivalents of the eluting ion left on the bed

v = column volume, liters

C_1 = concentration of the eluting ion in the effluent solution, eq./liter, after n_1 column volumes of eluting solution have been collected.

k = constant determined by Equation (15), column volumes⁻¹.

Another useful method of treating elution data is to plot the fraction of the initially loaded ion retained by the bed against the volume of eluant. If the amount of the eluting ion on the bed at the start of the elution is known or can be estimated and if Equation (14) holds true, then the fraction remaining at any value of n can be determined by dividing values of Y obtained by Equation (16) by the initial loading on the bed. As n increases, the curve will approach a straight line on semilog paper where the fraction remaining is plotted on the logarithmic scale. The equation of the straight line portion of the curve is

$$\log (Y/Y_L) = -k(n - n'_0) \quad (17)$$

where Y_L = initial loading of eluted ion on the bed.

n'_0 = n at the intercept of the straight line extrapolated to $Y/Y_L = 1.0$.

k = the rate constant defined by Equation (15).

Elution curves plotted in this way are shown in Section F 4.3 and F 4.4.

3.2.1 Sample Calculation: Estimation of Cesium Fraction Not Eluted

Typical data obtained during elution of cesium from clinoptilolite are shown in the sketch below.

The elution curve approaches a straight line in this semilog plot at elution volumes greater than 4 column volumes. The slope of this line, k , is given by Equation (15):

$$k = \frac{-\log(C_2/C_1)}{n_2 - n_1} = \frac{-\log(0.0017/0.0056)}{7-5} = 0.26$$

The average concentration of cesium left on the bed after 7 column volumes of eluate are collected is given by Equation (16):

$$\frac{Y}{V} = \frac{C_2}{2.3k} = \frac{0.0017}{(2.3)(0.26)} = 0.0028 \frac{\text{mole Cs}}{\text{of bed}}$$

The initial cesium loading was about 0.07 mole/ ; thus the cesium left on the bed after 7 column volumes represents 4 percent of the cesium loaded.

The column volumes required to lower the cesium content to 1 percent of that loaded can be estimated by letting $Y/v = (0.01)(0.07) = 0.0007$. From Equation (16), $C = 2.3k(Y/v) = 0.000419$. From Equation (15),

$$n - n_2 = \frac{1}{k} \log(C/C_2)$$

$$n = \frac{1}{0.26} \log \frac{0.000419}{0.0017} = 9.3 \text{ column volumes.}$$

3.3 Pressure Drop

Pressure-drop data on the flow of fluids through beds of granular solids are not readily correlated because of the variety of granular materials and of their packing arrangement. For laminar flow of a single incompressible fluid through a given bed of granular solids, the pressure drop can be expressed empirically in terms of solution viscosity and superficial flow rate by the equation

$$\frac{\Delta P}{L} = K_F \mu V \quad (18)$$

where ΔP = pressure drop, psi

L = bed depth, ft

μ = solution viscosity, centipoise

V = superficial flow rate, gal/min-ft² (equivalent to the linear solution velocity calculated as if the column were empty; the velocity in inches/min times 0.623 or cm/min times 0.245 equals V in gal/min-ft²)

K_F = an empirical constant, consistent units.

The constant, K_F , is a function of particle shape, size, and packed density and can best be determined in a laboratory column using a bed similar to the one to be used in the production plant. Some representative values of K_F have been determined, as follows:

TABLE IV-53
EMPIRICAL CONSTANTS FOR DETERMINING PRESSURE DROPS IN
BEDS OF ION EXCHANGE MATERIAL

<u>Material</u>	<u>Mesh Size</u>	<u>K_F, $\frac{\text{lb-ft-min}}{\text{cp-gal-in}^2}$</u>	<u>Reference</u>
Dowex 50	20-50	0.10	(6)
Dowex 50	50-100	1.06	(6)
Permutit SK	20-50	0.10	(17)
Linde AW-500	20-50	0.095	(24)
Decalso	20-50	0.09	(5)
Clinoptilolite	20-40	0.11	(4)
Duolite C-3	20-40	0.013	(10)
Duolite C-3	20-60	0.15	(10)

Equation (18) holds only in the laminar flow region (up to modified Reynold's numbers of 10). Anticipated B-Plant flow rates fall well within this range.

3.4 Fluidization

Upflow through the packed bed will tend to fluidize the particles. Onset of fluidization occurs when the forces tending to raise the par-

ticles (buoyancy plus frictional drag) are equal to the total weight of the particles. The pressure drop where this occurs is

$$\frac{\Delta P}{L} = 0.43 (\rho_s - \rho) (1 - \epsilon) \quad (19)$$

where ρ_s = particle density*, g/cm³

ρ = solution density, g/cm³

ϵ = fraction void volume in the bed

The flowrate at the onset of fluidization can be determined by equating Equations (18) and (19) to give

$$V_{mf} = \frac{0.43 (\rho_s - \rho) (1 - \epsilon)}{K_f \mu} \quad (20)$$

where V_{mf} = minimum fluidizing velocity, gal/min-ft².

Increasing the flow rate will expand the bed proportionately to the velocity until the superficial velocity of the fluid exceeds the free-settling velocity of the solid particles. At this point the particles in the bed no longer maintain an "interface" with the fluid but will move in the direction of the fluid.

Terminal settling rates for spherical particles are presented in Perry's Chemical Engineers' Handbook⁽¹⁹⁾ as a function of particle size. For 50 mesh particles of density 1.25 g/cm³ settling in water, the terminal velocity is 0.03 ft/sec. The corresponding minimum superficial fluid velocity which would just prevent settling in an infinitely expanded bed would be 13 gal/min-ft². The settling rate is directly proportional to the density difference between the particle and fluid, so increasing the particle density in the above example to 1.5 would approximately double the settling rate.

Fluidization with water was briefly studied in a 4-in. diameter Lucite column using 20 to 50 mesh clinoptilolite⁽⁴⁾. The bed was 20 percent expanded at a flow rate of 7 gpm/ft². The expansion was linear with flow rates up to 15.5 gpm/ft², where the bed was completely fluidized.

* The weight contributed by the internal liquid must be considered. The particle densities given in Tables IV-51 and IV-52 were, respectively, for dry zeolites and water-soaked resins.

4. Recovery of Cesium from Stored Supernates

4.1 Introduction

The high cesium selectivity of certain mineral and organic cation exchangers will be utilized to remove cesium from stored alkaline supernates. Currently, two zeolites - Linde AW-400 and AW-500 - are favored for Purex supernate (PSN) and an organic exchanger - Duolite C-3 - is favored for treating Redox supernate (RSN). Typical flowsheets for the two supernatant wastes are shown in Figures IV-72 and IV-73⁽²¹⁾. The processes are similar and involve the following steps:

1. The supernatant solution, clarified and diluted as necessary for solution stability, is passed through the conditioned ion exchange bed until a pre-determined cesium breakthrough level is reached.
2. The column is flushed with water or dilute NaOH to remove supernatant solution. (This step may be essential only for Redox supernatant to avoid aluminum precipitation on the succeeding elution step.)
3. Sodium is selectively eluted with $0.2M (NH_4)_2CO_3$ - $0.1M NH_4OH$.
4. The cesium is eluted at 55 C with 4 to 8M NH_4^+ with about 75 percent of the NH_4^+ added as $(NH_4)_2CO_3$ and 25 percent added as NH_4OH .
5. The column is reconditioned by flushing excess ammonia ion from the column with water or, in the use of Redox waste, by eluting the ammonium ion with $1M NaOH$ to prevent aluminum precipitation in the succeeding loading cycle.
6. The cesium product is concentrated, and the distilled ammonium carbonate eluant is recovered by condensation and absorption of the distillate. Ammonia and CO_2 are added as necessary to maintain the desired eluant concentration.

The ion exchange portions of the flowsheets are carried out at flow rates of 50 gal/min (about 2 column volumes/hr and 2 gal/min-ft²) at ambient temperatures, except for elution which is more efficient at higher temperatures.

The laboratory and engineering development work that led to the selected flowsheets are described in the following sections.

FIGURE IV-72

Cesium Recovery from Purex Alkaline Supernatant by Linde AW-500 Zeolite Ion Exchange
(Source of Data: HW-78061)

FIGURE IV-73

Cesium Recovery from Redox Alkaline Supernatant by Duolite C-3 Ion Exchange
(Source of Data: HW-78061)

4.2 Loading Studies

4.2.1 Equilibrium Data

The equilibrium loading characteristics and exchange capacities of several natural and synthetic zeolites have been determined for binary systems of cesium, strontium, and other cations found in separations plant wastes^(2,14). The equilibrium data for three candidate zeolites, shown in Figures IV-74, IV-75 and IV-76, have been correlated by use of the mass action law quotient, as discussed in Section F 1. The equilibrium cesium loading on a zeolite column can be determined from these figures when the feed composition is known. For a simple two-component feed, the equilibrium fraction of cesium on the zeolite is given by

$$Cs_z = \frac{K_B^{Cs} \left(\frac{Cs^+}{B^+} \right)}{1 + K_B^{Cs} \left(\frac{Cs^+}{B^+} \right)} \quad (21)$$

A multicomponent mixture of mono-valent ions can be treated as several binary systems, using the technique described in Section F 1. Thus,

$$Cs_z = \frac{1}{\frac{(B^+)}{K_B^{Cs} (Cs^+)} + \frac{(C^+)}{K_C^{Cs} (Cs^+)} + \dots} \quad (22)$$

The equilibrium data shown in the above figures was obtained at 25 to 27 C with 20 to 50 mesh crushed and sieved zeolites and at total solution normalities of 0.1 to 1. Over this range of normalities, the total solution normality had little effect on the equilibrium distribution, but extrapolation of the data to higher solution normalities may introduce some error. Column loading studies, however, show the error to be slight for synthetic supernatant solutions up to 5M Na⁺.

Increased temperature had a significant adverse effect on the equilibrium cesium loading from sodium solutions. This effect is caused by partial dehydration of the sodium ions at elevated temperatures which in turn increases their ability to compete for zeolite exchange sites with the essentially unhydrated cesium ions⁽¹⁵⁾.

Most of the cesium-bearing solutions to be processed in B-Plant contain only trace quantities of monovalent ions other than sodium and cesium. Where this is true, only the binary cesium-sodium equilibrium need be considered (see Section F 4.2.2). The Cs-Na data in Figures IV-74, IV-75, and IV-76 have been replotted in Figures IV-77 and IV-78

in a more usable form. Figure IV-77 represents the cesium/sodium mole ratio on the three zeolites as a function of the Cs^+/Na^+ mole ratio in the feed. In Figure IV-78, the equilibrium fraction of cesium on the zeolite has been converted to the equilibrium loading in moles of cesium per liter of packed bed, using a packed bed density of 0.8 g/ml and the zeolite capacity presented in Table IV-51. The equilibrium capacity of Decalso is also indicated in Figure IV-78 for reference since Decalso has also been extensively used to adsorb cesium from stored supernates(12,27).

4.2.2 Sample Calculation: Estimation of Cesium Equilibria in the Presence of Competing Cations

A typical supernate feed is that used by Popovich in cold pilot plant studies (Table IV-54). Mass action quotients for loading the competing cations Cs^+ , Rb^+ , and K^+ from this sodium-based feed onto Linde AW-500 can be estimated from the data in Figure IV-76.

$$\frac{(\text{Cs}^+)}{(\text{Rb}^+)} = \frac{0.00076}{0.00019} = 4.0, \text{ and } K_{\text{Rb}}^{\text{Cs}} = 1.2.$$

$$\frac{(\text{Cs}^+)}{(\text{K}^+)} = \frac{0.00076}{0.00060} = 1.3, \text{ and } K_{\text{K}}^{\text{Cs}} = 2.3.$$

$$\frac{(\text{Cs}^+)}{(\text{Na}^+)} = \frac{0.00076}{4.37} = 0.00017, \text{ and } K_{\text{Na}}^{\text{Cs}} = 190.$$

From Equation (22), the equivalent fraction of Cs on the zeolite in equilibrium with this feed is given by

$$\text{Cs}_z = \frac{1}{1 + \frac{0.00019}{(0.00076)(1.2)} + \frac{0.00060}{(0.00076)(2.3)} + \frac{4.37}{(0.00076)(190)}} = 0.031$$

The equivalent fractions of Rb and K can be estimated from the respective mass action quotients and Cs_z :

$$\text{Rb}_z = \frac{(\text{Cs}_z)(\text{Rb}^+)}{(\text{Cs}^+)(K_{\text{Rb}}^{\text{Cs}})} = \frac{(0.031)(0.00019)}{(0.00076)(1.2)} = 0.0065$$

$$\text{and K} = \frac{(0.031)(0.00060)}{(0.00076)(2.3)} = 0.011.$$

If the effect of trace competing cations on cesium loading is neglected, Equation (21) or Figure IV-27 may be used to estimate equilibrium cesium loading.

Thus,

$$Cs_z = \frac{K_{Na}^{Cs} \frac{Cs^+}{Na^+}}{1 + K_{Na}^{Cs} \frac{Cs^+}{Na^+}} = \frac{(190)(0.00017)}{1 + (190)(0.00017)} = 0.031.$$

This answer is the same as that determined previously, thus confirming that interference from trace element loading can safely be ignored.

FIGURE IV-74

Mass Action Quotients for the Exchange of Cesium With Sodium, Potassium, Rubidium, Ammonium and Hydrogen Form Clinoptilolite (Source of Data: HW-74609 and HW-78461)

FIGURE IV-75

Mass Action Quotients for the Exchange of Cesium With Sodium, Potassium, Rubidium, and Ammonium Form Linde AW-400
(Source of Data: HW-74609 and HW-78461)

FIGURE IV-76

Mass Action Quotients for the Exchange of Cesium With Sodium, Potassium, Rubidium, and Ammonium Form Linde AW-500
(Source of Data: HW-74609 and HW-78461)

FIGURE IV-77

Equilibrium Ca/Na Ratios in Zeolite and Solution Phases at 25C
(Source of Data: HW-74609 and HW-78461)

FIGURE IV-78

Equilibrium Cesium Loading on Zeolites
From Cesium-Sodium Solutions at 25C
(Source of Data: HW-74609, HW-78461, and HW-70874)

4.2.3 Column Loading Studies

The effects of several operating variables on the shape of the breakthrough curve have been correlated in terms of the slope "A" of the breakthrough curves plotted on log-probability paper, as discussed in Section F 3.1. The data were obtained in laboratory and pilot plant column runs using the feed compositions shown in Table IV-54.

TABLE IV-54
SYNTHETIC ALKALINE SUPERNATE WASTE COMPOSITIONS
USED IN COLUMN LOADING STUDIES

Constituent	Molarity		
	PSN		RSN: Knoll HW-84105 ⁽¹⁰⁾
	Nelson & Mercer HW-76449 ⁽¹⁶⁾	Popovich HW-83461 ⁽²⁰⁾	
Na ⁺	4.5	4.37	4.89
K ⁺	0	0.00060	0.00028
Rb ⁺	0	0.00019	0.000027
Cs ⁺	0.005	0.00076	0.000108
AlO ₂ ⁻	0	0	0.85
NO ₃ ⁻	1.3	0.58	2.65
NO ₂ ⁻	2.1	2.00	0.35
Cl ⁻	0	0.051	0.08
OH ⁻	0	0	0.9
CO ₃ ⁼	0.5	0.77	0
SO ₄ ⁼	0.045	0.09	0.03
PO ₄ ⁼	0.014	0.051	0
Na ⁺ /Cs ⁺	9000	5750	45,000

The following summary illustrates the effects of some of the more important variables on the slope of the breakthrough curve, A.

Particle Diameter. The log-probability slope varied inversely with the particle diameter (i.e., $A \sim \frac{1}{D_p}$)⁽¹⁶⁾. Since the

effective particle diameter is inversely proportional to the sieve mesh size, A is directly proportional to the average mesh size. This effect is illustrated in Figure IV-79 for Linde AW-400 zeolite. For the data shown here, $A \cong (0.12)(\text{average mesh size})$. An average 20 to 50 mesh particle size has been chosen for the B-Plant columns as a compromise dictated by exchange kinetics and flowrate (pressure drop) considerations.

Type of Zeolite. The slope varies slightly with different zeolites, increasing with increased cesium selectivity. This effect is illustrated in Figure IV-80⁽¹⁶⁾. Although Linde AW-400 is slightly better than Linde AW-500, the latter may be used in B-Plant because of the limited availability of Linde AW-400.

Purex vs. Redox Supernate. Breakthrough curves for Purex⁽¹⁶⁾ and Redox⁽¹⁰⁾ wastes are shown in Figure IV-81. The zeolite breakthrough curves were steeper for Purex supernatant, apparently because of the lower salt strength and viscosity of the Purex waste relative to the Redox waste. The Duolite C-3 breakthrough curve, however, was steeper with the Redox waste than with Purex waste. This may be due to the higher pH and corresponding greater cesium selectivity of the Redox waste.

Temperature. The slope of the breakthrough curve was nearly unaffected by temperature for Linde AW-400 zeolite (see Figure IV-82)⁽¹⁶⁾. Since elevated temperatures lower the breakthrough capacity, low operating temperatures are recommended for the Plant columns during loading.

Superficial Velocity. The superficial velocity, V (the flow rate divided by the cross-sectional area of the column), had a relatively minor effect on the breakthrough slope, as shown in Figure IV-83⁽²⁰⁾. The slope was approximately proportional to $V^{0.125}$ up to 2 gal/min-ft². An apparent maximum slope was obtained at 2 gal/min-ft², the design velocity of the B-Plant column.

Flow Rate. The effect of flow rate, expressed in column volumes/hour R , on cesium breakthrough for Linde AW-500 is shown in Figure IV-84⁽²⁰⁾. The log-probability slopes obtained from this and comparable data are shown in Figure IV-85 as a function of flow rate. From this plot, A is shown to be proportional to $R^{-0.55}$, in good agreement with the relationship presented in Section F 3.1.

The superficial velocity and flow rate correlations may be combined for a given zeolite bed and feed system. For example, with 20-50 mesh Linde AW-500 and Purex supernatant feed at 25 C,

$$A = \frac{7.1 V^{0.125}}{R^{0.55}} \quad (23)$$

A similar expression can be derived from laboratory column data for Linde AW-400⁽¹⁶⁾:

$$A = \frac{7.6 V^{0.125}}{R^{0.55}} \quad (24)$$

In both equations, V is expressed gal/min-ft² and R in column volumes/hr.

FIGURE IV-79

Effect of Particle Size on Cesium Breakthrough Curves
(Source of Data: HW-76449)

FIGURE IV-80

Cesium Breakthrough Curves for Several Zeolites
(Source of Data: HW-76449)

FIGURE IV-81

Comparison of Cesium Breakthrough from
 Purex and Redox Supernatants
 (Source of Data: HW-76449 and HW-84105)

FIGURE IV-82

Effect of Loading Temperature on Cesium Breakthrough
 (Source of Data: HW-76449)

FIGURE IV-83

Effect of Superficial Flow Rate on Cesium Breakthrough
(Source of Data: HW-83461)

FIGURE IV-84

Effect of Column Volumes per Hour on Cesium Breakthrough
(Source of Data: HW-83461)

FIGURE IV-85

Effect of Column Volumes per Hour on the Constant A
(Source of Data: HW-83461)

Cesium Concentration. Varying the cesium concentration in the feed from 10^{-5} to $2 \times 10^{-3}M$ had little effect on the breakthrough curve slopes (shown in Figure IV-96) when processing Purex acid waste solution through clinoptilolite⁽¹⁵⁾. This appeared to be true also of Purex supernatant over the limited range of concentrations studied.

4.3 Wash and Scrub Studies

Following loading, the ion exchange beds are washed with several column volumes of water or dilute NaOH to remove the supernatant solution. This wash is essential for the Redox exchanger bed to prevent aluminum hydroxide precipitation in subsequent ammonia-ammonium carbonate elution steps; however, Purex supernatant does not contain aluminum, and the water wash prior to the ensuing sodium scrubbing step is optional.

Virtually all of the ion exchange sites are occupied by sodium ions after the loading step. The sodium can selectively be removed without displacing cesium by passing dilute solutions of ammonium salts or weak acids through the bed.

For alkaline supernatant waste flowsheets, nonacidic solutions are advantageous for sodium removal. Two of these have been tried; dilute solutions of ammonium carbonate and ammonium oxalate⁽¹⁶⁾. Data on sodium removal from clinoptilolite by these chemicals and oxalic acid are shown in Figure IV-86, and data on sodium removal from AW-400 exchanger, including a higher concentration of ammonium carbonate, are shown in Figure IV-87.

FIGURE IV-86

Removal of Sodium from Clinoptilolite with Various "Scrub" Solutions
 (Source of Data: HW-76449)

FIGURE IV-87

Removal of Sodium from Linde AW-400
 with Various "Scrub" Solutions
 (Source of Data: HW-76449)

Over 95 percent of the sodium was readily removed by the dilute ammonium solutions, but the final 2 to 5 percent eluted much more slowly. Thus, little practical benefit is gained by eluting with more than 5 column volumes of 0.2M $(\text{NH}_4)_2\text{CO}_3$ or 8 column volumes of 0.1M $(\text{NH}_4)_2\text{CO}_3$ unless very high purity cesium is desired. Sodium removal from Duolite C-3 was similar; over 98 percent of the sodium was eluted with 6 column volumes of 0.2M $(\text{NH}_4)_2\text{CO}_3$.⁽¹³⁾

Dilute ammonium carbonate would be the least costly solution for a flow sheet employing aged alkaline waste. However, zirconium-niobium removal is improved by using ammonium oxalate. Oxalic acid solutions can be effectively used in acid waste flowsheets (see Section F 5) where a high degree of zirconium-niobium removal is necessary; however, a subsequent ammonium hydroxide wash is required in this case to prevent gassing when ammonium carbonate is added to the acid mineral.

Cesium losses during sodium removal are dependent on the degree of cesium loading as shown in Figure IV-88⁽¹⁶⁾. Losses are not greatly different using the dilute alkaline scrub solutions than with nitric or oxalic acids⁽¹⁵⁾. In a practical operation, loading would be stopped at less than one percent breakthrough so that cesium loss would be low in the scrubbing step.

FIGURE IV-88

Cesium Loss from Clinoptilolite During Scrubbing
 for Two Cesium Breakthrough Levels
 (Source of Data: HW-76449)

4.4 Cesium Elution

Cesium can best be removed from zeolites by cations that are similar in size and charge to cesium. Potassium and rubidium ions are good eluting agents, but the subsequent separation from cesium is difficult. Ammonium ion is not as efficient an eluting agent as potassium and rubidium but is much easier to separate from cesium. Elution curves for several ammonium compounds are shown in Figure IV-89(15). The differences can be explained on the basis of dissociation and thus availability of ammonium ions in solution. (The elution curves in this and subsequent figures were obtained with eluant upflow, i.e., counter to the loading flow, unless otherwise noted.)

FIGURE IV-89

Elution of Cesium-137 from Clinoptilolite
by Various 2N Ammonium Salts
(Source of Data: Reference 15)

Ammonium acetate and ammonium carbonate have the advantage of being volatile. If a solution of ammonium acetate and cesium acetate is evaporated to dryness, all of the ammonium acetate is volatilized, leaving only solid cesium salts. The boiling point gradually increases from a little more than 100 to about 160 C. However, ammonium carbonate begins to volatilize rapidly at about 70 C, and the volatilization is complete before 100 C. Thus, with ammonium carbonate, it is possible to stop the evaporation at a point where a relatively pure aqueous solution of cesium carbonate is obtained.

Experimental work with ammonium carbonate elutions indicated that elution efficiency could be greatly improved by increased temperatures for several reasons: relative bonding strength of cesium is lower at higher temperatures, ammonium carbonate dissociation increases with increased temperatures, ionic mobilities and diffusion rates are improved, and solution viscosity is lowered. With solutions of other ammonium compounds, elution has been accomplished at 80 C. but the temperature of ammonium carbonate solutions is limited by gassing. Gassing is also influenced by the ammonia content.

Ammonium carbonate solutions are actually equilibrium solutions of ammonium bicarbonate-ammonium carbonate-ammonium carbamate and are displaced toward the carbamate at high pH and high ammonia content. Table IV-5 shows the relationship of temperature and ammonia content with gas evolution during elution⁽¹⁵⁾.

TABLE IV-5

EFFECT OF TEMPERATURE AND AMMONIA CONCENTRATIONS
ON GASSING OF $(\text{NH}_4)_2\text{CO}_3$ SOLUTIONS

(Source of Data: Reference 15)

Column: 75 ml of 20 x 50 mesh clineptilolite

Flow Rate: 75 ml/min

<u>Solution Composition</u>		<u>% NH_3 Added as NH_4OH</u>	<u>Temp., °C</u>	<u>Gas evolution, ml/min</u>
<u>M CO_2</u>	<u>M NH_3</u>			
1.9	3.8	0	40	0.0094
			50	0.036
			60	2.0
1.9	4.3	12	40	Trace
			50	0.0023
			60	0.006
1.9	4.8	30	40	Trace
			50	Trace
			60	0.0023

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Elution efficiency per mole of total ammonia is slightly improved by moderate additions of ammonium hydroxide to the ammonium carbonate. From the available information, 55 C has been chosen as a practical elution temperature, with about 25 percent of the ammonium being added as the hydroxide⁽¹⁵⁾.

Cesium elution curves for cesium removal from clinoptilolite by three concentrations of elution solution are shown in Figure IV-90. As would be expected, the dilute solutions elute cesium more effectively per mole of ammonium; however, the advantage of lower volumes outweighs the loss in efficiency, and thus the 8N solution is the choice eluting solution⁽¹⁶⁾.

FIGURE IV-90

Elution of Cesium from Clinoptilolite by Three Concentrations of Ammonium Carbonate - Ammonium Hydroxide Solutions
(Source of Data: HW-76449)

Comparison of cesium elution from several exchangers is shown in Figure IV-91^(10,16). There appears to be a significant difference in the elution performance depending on the solution used to load the exchangers. For example, cesium was eluted much more readily from a clinoptilolite column loaded from PSN than from a similar column loaded from RSN. On the other hand, cesium loaded on Duolite C-3 was more readily eluted from a RSN-loaded column than from a PSN-loaded column. A slight fraction of the cesium does not elute from Linde AW-400 and AW-500 and is probably retained by the binder. This amounted to 4 to 8 percent of the cesium loaded from PSN⁽¹⁶⁾ and 3 to 17 percent of the cesium loaded from RSN⁽¹⁰⁾. This fraction does not appear to lower the capacity on subsequent loading cycles nor does it build up any further; therefore, for practical purposes it can be ignored. This fraction was not included in the calculations for the AW-400 and AW-500 curves.

Column - 0.8 cm ID x 20 cm long
 Particle size - 20-50 mesh
 Temperature - 55°C
 Flow rate - 2 col. vol./hr.
 Superficial velocity - 0.16 gpm/ft²

FIGURE IV-91

Elution of Cesium from Several Ion Exchangers with
 Ammonium Carbonate - Ammonium Hydroxide Solutions
 (Source of Data: HW-76449 and HW-84105)

The effect of particle size and flow rate on cesium elution from Duolite C-3 is shown in Figure IV-92. It can be seen that the elution is limited by kinetics and is considerably improved by decreased particle sizes and flow rates. The effect of flow rate on cesium elution from clinoptilolite was less pronounced, as shown in Figure IV-93. All of the elution studies were made in 0.8 cm columns, 20 cm long; and the effect of the superficial velocity on elution efficiency was not investigated independently.

4.5 Ion Exchanger Reconditioning

The ion exchange beds used for Purex supernatants require only a simple water flush following elution to remove the ammonium carbonate eluant prior to the next loading cycle. For Redox wastes, however, the ammonium ion must be eluted from the bed with sodium hydroxide to keep aluminum in the RSN from precipitation with ammonium hydroxide generated during loading. The flowsheet for Redox supernatant (Figure IV-73) indicates the use of 3 column volumes of 1M NaOH. The standard laboratory procedure⁽¹⁰⁾ also included recycling 4 column volumes of 8M NaOH to assure elimination of ammonia.

4.6 Ammonia-Ammonium Carbonate Recovery

Carbon dioxide evolution from ammonium carbonate eluant solutions begins when the solution is heated to about 55 C. Further heating will result in the rapid evolution of both CO₂ and ammonia at 70-80 C. The concentrations of NH₃ and CO₂ in the product solution eventually reach an equilibrium value, depending on the vapor pressure of the ammonium and carbonate salts in solution. In one pilot plant experiment⁽²⁵⁾, residual concentrations of 0.076M NH₃ and 0.40M CO₂(CO₃⁼), were found after boiling a simulated ion exchange column eluant containing 0.41M Na⁺ for 1 hour. The final pH was 9.8. In continuous operation, the solution composition in the evaporator will always be at an equilibrium value similar to this.

A semi-continuous process based on the volatility of ammonium carbonate will be used for recovering and reconstituting the cesium eluant. The flowsheet is included in Figures IV-72 and IV-73 and discussed below:

1. The concentrator must be brought to boiling with water or concentrated product from a preceding run. (Startup with ammonium carbonate solution can pressurize the system and overload the absorber.)
2. The concentrator will operate at the boiling point of the cesium product solution; and water, CO₂, and NH₃ will be continuously evolved at essentially the mole ratio in the eluant solution. The boil-up rate is set equal to the feed rate to maintain a constant level in the evaporator.

3. For most efficient ammonium carbonate recovery, the off-gases from the concentrator are passed through a down-draft condenser. Up to 95 percent of the NH_3 and CO_2 were absorbed in this step in a pilot plant unit⁽²⁵⁾. The heat transfer surface must be continuously wetted with unsaturated solution to prevent deposition of crystallized $(\text{NH}_4)_2\text{CO}_3$; however, surfaces warmer than 60 C will not allow deposits to form. The heat generated by absorption of NH_3 and CO_2 must be removed by the condenser. The combined heat of formation and solution for $(\text{NH}_4)_2\text{CO}_3$ is 118.4 kcal/g-mol, and the heat of solution for NH_3 is 8.8 kcal/g-mol.
4. The volume of vapor leaving the condenser is essentially that of the non-condensable off-gases (purge air, etc.); consequently, the absorber unit can be quite small. Even when a pre-condenser is not provided, low gas flows through the absorber are observed because condensation and absorption of most of the condensable gases occurs in the bottom few inches of the absorber tower.
5. Make-up NH_3 and CO_2 are added to the bottom of the tower and make-up water is added to the top.
6. Absorption is accomplished by recycling a portion of the recovered eluant to the top of the absorber tower. Mass transfer coefficients in the pilot plant absorber packed with 1/2 in. Intalox saddles were unaffected by flow rate over the range of 10 to 300 gph/ft².
7. Ammonia and CO_2 losses are dependent on the partial pressure of the $(\text{NH}_4)_2\text{CO}_3$ recycle solution in the absorber off-gas. Typical partial pressures in the off-gases from the pilot plant absorber ranged from 14 to 24 mm Hg for NH_3 and 12 to 35 mm Hg for CO_2 with 10 to 20 F recycle solutions containing about 8 to 10M NH_3 and 4M CO_2 .
8. About 90 percent of the residual NH_3 and CO_2 can be recovered by passing the off-gas through a small scrubber, using eluant makeup water as the scrub stream. A suggested flow diagram using this modification is shown in Reference (25).

4.7 Cesium Product Purification and Packaging

The purity of the cesium product after one cycle of ion exchange is determined primarily by the sodium remaining on the bed after the sodium scrubbing step, as discussed in Section F 4.3. Typical Na/Cs mole ratios should be about 1 to 10 with Purex supernatants and 10 to 50 with Redox supernatants.

FIGURE IV-92

Elution of Cesium from Duolite C-3 with 2M Ammonium Carbonate
(Source of Data: HW-76449)

FIGURE IV-93

Effect of Flow Rate on Elution of Cesium from Clinoptilolite
with 4N Ammonium Carbonate Solution
(Source of Data: HW-76449)

Most of the remaining sodium can be removed by a second cycle of ion exchange using the same zeolite (Linde AW-500). Steep breakthrough curves are obtained, as shown in Figure IV-94 along with equilibrium loadings in excess of 0.8 mole of Cs/liter of zeolite⁽¹⁴⁾. Scrubbing with dilute ammonium carbonate should remove over 95 percent of the sodium as before, and ultimate product Na/Cs mole ratios as low as 0.05 should be obtained on elution with concentrated ammonium carbonate. Contamination from other alkali metals (Rb and K) would be about the same as for sodium.

Cesium in excess of market demand for Cs-137 will be loaded on Linde AW-500 and stored⁽²¹⁾. The proposed flowsheet is shown in Figure IV-95. It differs from the above purification flowsheet in that the cesium in the effluent approaches 100 percent breakthrough and in having no scrub or elution steps.

Most of the cesium stored on zeolite can be recovered by eluting with ammonium or nitric acid solutions. In two experiments, 86 and 90 percent of the cesium were eluted from Linde AW-500 with 2M NH_4NO_3 and 1M HNO_3 , respectively, after the loaded zeolite was held at $30 \pm 3^\circ\text{C}$ for 24 hours⁽²⁾. The 1M nitric acid solution also leached aluminum from the zeolite lattice.

FIGURE IV-94

Cesium Breakthrough Curves for Cesium Product Concentrate
 (Source of Data: HW-78461)

FIGURE IV-95

Flowsheet for Cesium Waste Packaging
(Source of Data: HW-78061)

5. Recovery of Cesium from Purex Acid Wastes

A flowsheet for removing cesium from Purex Acid Waste (PAW) with clinoptilolite ion exchange is presented in Figure IV-96⁽¹⁵⁾. The basic procedure is similar to that used for alkaline supernatant wastes, with the exception of the scrubbing and acid elution steps.

An oxalic acid scrub is required to elute sorbed zirconium and niobium, in addition to sodium. The hydrogen ion on the bed is then removed with ammonia to prevent gassing during the following ammonium carbonate elution step. Because ammonium hydroxide is only slightly ionized, it effectively replaces hydrogen ions without displacing the cesium.

Typical loading curves showing the effect of flow rate and cesium concentration on the cesium breakthrough are shown in Figure IV-97 and IV-98⁽¹⁵⁾; equilibrium data for clinoptilolite was previously presented in Figure IV-76, IV-77, and IV-78. Generally, the effects of temperature, particle size, and flow rate were similar to those found with supernatant feeds.

The effectiveness of various scrub solutions in removing ZrNb-95, is shown in Figure IV-99⁽¹⁶⁾. Oxalic acid, the preferred scrub, removes the small amount of sorbed zirconium in the first one or two column volumes, while the niobium is removed at a slightly slower rate than sodium.

A small continuous decrease in cesium capacity, averaging 2 percent per cycle was found on re-using the clinoptilolite for several complete cycles of the preceding flowsheet⁽¹⁵⁾. This loss in capacity appears to be due to a very slow dissolution of the mineral in the acid influent. Other zeolites, such as Linde AW-400 and AW-500, are considerably less acid stable and cannot be used for PAW processing.

FIGURE IV-96

Extraction of Cesium from Purex Acid Waste
(Source of Data: Reference 15)

FIGURE IV-97

Effect of Flow Rate on Cesium Breakthrough with Purex Acid Waste
 (Source of Data: Reference 15)

FIGURE IV-98

Effect of Cesium Concentration on Cesium Breakthrough With Purex Acid Waste
 (Source of Data: Reference 15)

FIGURE IV-99

Removal of ZrNb-95 from Clinoptilolite by Four Solutions
 (Source of Data: HW-76449)

6. Strontium Packaging6.1 Introduction

The recovered strontium product in excess of Sr-90 market demand will also be loaded on a suitable zeolite for storage. The major contaminant will be sodium ion, with lesser amounts of calcium and magnesium. Three of the zeolites in Table IV-51 are strontium selective under these conditions: Linde 4A, 4A XW, and 13 X. The 4A and 4A XW zeolites have the same crystalline structure, differing only in the amount of binder, and can be used interchangeably.

A flowsheet using Linde 4A zeolite is shown in Figure IV-100. The zeolite is loaded to ca. 100 percent capacity with the strontium collected for recycling after breakthrough is observed.

FIGURE IV-100

Strontium Waste Packaging Flowsheet
(Source of Data: Reference 13)

6.2 Equilibrium Data

Equilibrium data for Linde 4A XW and 13 X are presented in Figures IV-101, IV-102, and IV-103⁽¹⁴⁾. The mass action quotients presented in these figures were obtained at 25 C; however, the Sr-Cs and Sr-Na equilibrium are only slightly affected by temperature, and the data may be used to predict loadings (by the method described in Section F 1) at temperatures as high as 70 C. The mass action quotients are defined by the equations:

$$K_{Na}^{Sr} = \frac{(Sr_z) (Na^+)^2}{(Na_z)^2 (Sr^{++})} \quad (25)$$

$$K_{Ca}^{Sr} = \frac{(Sr_z) (Ca^{++})}{(Ca_z) (Sr^{++})} \quad (26)$$

$$K_{Ca}^{Na} = \frac{(Na_z)^2 (Ca^{++})}{(Ca_z) (Na^+)^2} \quad (27)$$

where concentrations in the zeolite phase - Sr_z , Ca_z , Na_z - are expressed as equivalent fractions and concentrations in solution are normalities (equivalents/liter).

FIGURE IV-101

Variation of Mass Action Quotients with Solution Normality Ratios for the Exchange Reaction $2Na_{zeolite} + Sr_{solution} = Sr_{zeolite} + 2Na_{solution}$
(Source of Data: HW-78461)

FIGURE IV-102

Variation of Mass Action Quotients with Solution Normality Ratios for the Exchange Reaction $\text{Ca}_{\text{zeolite}} + \text{Sr}_{\text{solution}} = \text{Sr}_{\text{zeolite}} + \text{Ca}_{\text{solution}}$
(Source of Data: HW-78461)

FIGURE IV-103

Variation of Mass Action Quotients with Solution Normality Ratios for the Exchange Reaction $\text{Ca}_{\text{zeolite}} + 2\text{Na}_{\text{solution}} = 2\text{Na}_{\text{zeolite}} + \text{Ca}_{\text{solution}}$
(Source of Data: HW-78461)

6.3 Loading Studies

The effects of operating variables on strontium breakthrough for loading a synthetic, concentrated LBP (solvent extraction product) on Linde 4A zeolite are shown in Figures IV-104 through IV-106⁽¹⁴⁾. In general, increasing the temperature and decreasing the particle size will reduce the loading cycle time and the amount of recycle effluent. Decreasing the flow rate will reduce the amount of recycle effluent but will increase the loading time. Column length had no significant effect on the slope of the breakthrough curve with the column volumes/hour (or holdup time) held constant.

The addition of citrate ion to feed solutions containing Sr-90 and rare earths is recommended to complex Y-90 and Ce-144. If not complexed, these isotopes may absorb in a narrow band at the influent end of the column and cause heating problems at this point. A concentration of 0.005M citrate was sufficient to prevent significant absorption of yttrium and cerium⁽¹⁴⁾.

FIGURE IV-104

Effect of Particle Size on the Strontium Breakthrough Curves at 25C
 (Source of Data: HW-78461)

FIGURE IV-105

Effect of Flow Rate on Strontium Breakthrough Curve
 (Source of Data: HW-78461)

FIGURE IV-106

Effect of Temperature on Strontium Breakthrough Curves
 (Source of Data: HW-78461)

6.4 Recovery of Strontium from Zeolites

Strontium can be recovered from the stored zeolite by nitric acid elution. In one test, 99 percent of the strontium was eluted from Linde 4A with 1M HNO₃ after the loaded zeolite had been heated at 600 C for 24 hours⁽²⁾.

7. Recovery of Technetium from Stored Supernates

7.1 Introduction

Technetium-99 exists as the soluble pertechnetate ion in Purex and Redox alkaline supernate wastes. The pertechnetate ion readily loads on strong-base anion exchange resins from the waste supernatant solutions and can be conveniently recovered by passing the effluent from the cesium ion exchange columns through an anion resin bed. A flowsheet for this purpose is presented in Figure IV-107⁽³⁾.

FIGURE IV-107

Technetium Recovery from Purex Alkaline Supernatant Waste
(Source of Data: HW-83348)

The process consists of passing about 40 column volumes of alkaline supernate through the column. After the column is loaded, the bed is washed first with dilute sodium hydroxide to remove contaminating fission product, nitrite, and carbonate ions. The resin is then converted to the nitrate form with dilute nitric acid. (The nitric acid-hydroxide reaction is exothermic and is more easily controlled with dilute acid.)⁽²⁶⁾ The technetium is eluted with 6M HNO₃, and the bed is prepared for re-loading by displacing the acid with water.

The technetium product is concentrated, and the distilled nitric acid is condensed and reused in the next elution. A small amount of technetium is volatilized during concentration but is recovered and returned to the process in the recycled acid.

7.2 Equilibrium Data

The equilibrium distribution of technetium between synthetic Purex waste supernate solutions and various organic anion resins is shown in Table IV-56 as a function of waste dilution⁽²²⁾. The distribution ratio, K_d , is defined as

$$K_d = \frac{\text{Amount of Tc in Resin}}{\text{Amount of Tc in Solution}} \times \frac{\text{ml solution}}{\text{Grams dry resin}}$$

The strong-base resins had the highest distribution coefficients, and two of these, Dowex 1 and Amberlite IRA-401, were examined more extensively.

TABLE IV-56
TECHNETIUM DISTRIBUTION FROM SIMULATED
PUREX WASTE SUPERNATES AT VARIOUS DILUTIONS

(Source of Data: HW-73121)

	Technetium K_d in Supernates ^(a) of Strength:				
	100%	75%	67%	50%	25%
<u>Strong-Base Resins</u>					
Amberlite IRA-400	414	318	--	271	440
Amberlite IRA-401	--	--	325	--	--
Dowex 1	340	299	290	271	448
Dowex 2	220	226	--	218	320
Dowex 21K	186	202	--	156	202
Duolite A-101	373	335	--	389	529
Duolite A-102	194	213	--	209	294
Permutit S-2	226	193	--	201	297
Permutit SK	118	92	88	85	116
<u>Intermediate-Base Resin</u>					
Duolite A-30B	23	25	--	22	27
<u>Weak-Base Resins</u>					
Amberlite IR-45	139	138	--	147	178
Dowex 3	50	61	--	78	112

(a) Synthetic Purex Waste Supernatant Composition:

	M
NaNO ₂	4.2
NaNO ₃	2.6
Na ₂ CO ₃	1.0
Na ₂ PO ₄	9.02
Na ₂ SO ₄	0.07
Tc-99	$\sim 2 \times 10^{-4}$

Effect of Anion Composition. Neutralized Purex waste supernate is composed chiefly of sodium nitrate, nitrite, and carbonate salts. The effect of each of these separately and in combination is shown in Table IV-57, using Dowex 1 resin.

TABLE IV-57

EFFECT OF ANION COMPOSITION ON TECHNETIUM K_d AT pH 10

(Source of Data: HW-73121)

Concentration of Anions, Moles/l

<u>NO_3^-</u>	<u>NO_2^-</u>	<u>$\text{CO}_3^{=}$</u>	<u>K_d</u>
0	0	1	126
0	3	1	410
0	3	0	240
3	3	1	220
3	0	1	165
3	3	0	144
3	0	0	96

These data show that carbonate enhances the absorption and nitrate reduces it.

Effect of Hydrogen Ion Concentration. The effect of hydrogen ion concentration on the technetium distribution ratio is shown in Figure IV-108⁽²²⁾. The total nitrate composition was held constant at 7.5M by varying the ratio of HNO_3 and NaNO_3 . The data show a sharp increase in K_d as the hydrogen ion concentration falls below 0.5M.

The distribution ratios were unaffected by pH over the range pH 1 to pH 11. Average K_d values for IRA-401 resin were 305 ± 50 at 1M NaNO_3 , 138 ± 12 at 4M NaNO_3 , and 133 ± 12 at 7.5M NaNO_3 ⁽²²⁾.

The effect of nitric acid concentration on the technetium K_d in the absence of NaNO_3 is shown in Figure IV-109⁽²²⁾. The data show that technetium-loaded resin can be washed with dilute nitric acid without excessive loss and that technetium elution will be rapid at concentrations above 4M HNO_3 .

7.3 Column Studies

Breakthrough curves obtained in pilot plant runs with actual Purex waste supernate (Tank 103A) are shown in Figure IV-110⁽²²⁾. The feed composition corresponded approximately to a 50 percent dilution of the synthetic feed composition shown in Table IV-56 (with the exception of Run 3 which had 2M added NaOH). The technetium concentration was 0.0112 g/l.

The data show that the slower flow rate used in Runs 2 and 3 greatly sharpened the breakthrough curve and that the added caustic was not beneficial. Approximately 90 column volumes of supernate were passed through the column to reach 50 percent breakthrough, corresponding to an equilibrium resin loading of about 1 g Tc/l of resin and a volumetric distribution ratio of 90.

The loaded pilot plant columns were washed with about 6 column volumes of either water or 0.25M HNO_3 , and the technetium was eluted with 8M HNO_3 . The elution curves are presented in Figure IV-111⁽²²⁾. Essentially all of the technetium was eluted by 4 column volumes of eluant. The products from Runs 2 and 3 were decontaminated by factors of about 20,000 from Cs-137; 200 from Ru-106; ca. 200 from Ce-144; and 300 to 500 from ZrNb-95.

FIGURE IV-108

Technetium Distribution on IRA 401 Resin as a
Function of Hydrogen Ion at Constant 7.5M Nitrate
(Source of Data: HW-73121)

FIGURE IV-109

Technetium Distribution on Dowex 1x8 from Nitric Acid Solutions
(Source of Data: HW-73121)

FIGURE IV-110

Technetium Breakthrough Curves
(Source of Data: HW-73121)

FIGURE IV-111

Elution of Technetium from IRA 401 with 8M Nitric Acid
(Source of Data: HW-73121)

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G. CESIUM PRECIPITATION PROCESSES

Two precipitation processes have been investigated at Hanford for possible use in removing cesium from fission product wastes. One used phosphotungstic acid to precipitate the dicesium salt from acidic waste solutions; the other used nickel ferrocyanide to precipitate cesium nickel ferrocyanide from alkaline wastes. Although both processes provided excellent cesium recovery in full-level Purex Plant tests, they have been relegated to back-up processes because of unfavorable economics.

1. Cesium Phosphotungstate Process

1.1 Introduction

The cesium salts of many of the heteropoly acids are highly insoluble; and in recent years cesium has been separated as the silicomolybdate, the silicotungstate, the phosphomolybdate, and the phosphotungstate. The latter two compounds are the most insoluble and have been the most extensively studied^(5,6,7).

Two cesium salts of phosphotungstic acid have been isolated^(5,6). The tricesium salt ($\text{Cs}_3\text{PW}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$) is preferentially precipitated whenever the mole ratio of cesium to phosphotungstic acid (PTA) exceeds 3. The less soluble dicesium salt ($\text{Cs}_2\text{HPW}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$) is formed exclusively when the cesium to PTA ratio is 2 or less. Similarly, the neutral and acid salts of rubidium, ammonium, and, to a lesser extent, potassium are precipitated because of their low solubility, although cesium is preferentially precipitated in a mixture of those ions. The cesium precipitate is very heavy but settles slowly. Colloidal suspensions have been prepared in the absence of electrolytes, but the presence of 0.3 to 0.5M concentrations of most electrolytes prevents peptization.

1.2 Effect of Variables on Cesium Precipitation

The solubilities of the alkali phosphotungstates are essentially unaffected by nitric acid concentrations over the range of 2 to 10M HNO_3 . The solubilities are decreased two- to three-fold by lowering the acid concentration from 2M to zero. Solubilities of the acid phosphotungstate salts of cesium, rubidium, and ammonium in 2M HNO_3 are 0.20, 0.25, and 0.78 g/liter, respectively, at 20 C. An excess of 5 g PTA/liter (0.0016M) lowered the cesium solubility by a factor of 13 under the conditions shown above; the cesium solubilities in 1, 4, 8 and 12M HNO_3 were 0.00084, 0.00125, and 0.0017 g/ Cs/liter, respectively, at 20 C⁽⁵⁾. Temperature had no effect on cesium solubility over the range 20 to 80 C⁽⁹⁾.

The soluble phosphotungstates do not interfere in the precipitation of the cesium salt, and traces can be removed by washing with dilute nitric

acid. The insoluble phosphotungstates are those of Rb, K, NH_4 , Th, Ag, and Hg(II), and these do interfere unless sufficient PTA is present to precipitate them quantitatively⁽⁵⁾. The chief interfering ion in Purex acid waste would be Rb at about 20 mole percent of the cesium concentration.

1.3 Dissolution of Precipitate

The phosphotungstate salts are not stable in basic solution, breaking down into the constituent phosphates and tungstates⁽⁵⁾. Thus, the precipitate can be dissolved in either ammonia or sodium hydroxide solutions and further purified by ion exchange, as in Section F. The phosphotungstate ion cannot be regenerated, and its loss represents over 95 percent of the chemical cost of the process.

1.4 Chemical Flowsheet and Process Demonstration

The phosphotungstate process was demonstrated in the Purex Plant with full-level acid waste (LW), using the flowsheet shown in Figure IV-112⁽³⁾. The process involved 5 steps:

- 1) Precentrifugation to remove solid impurities.
- 2) Precipitation of the cesium by adding dilute PTA to a final concentration of 0.0024M (approximately 0.0016M in excess of that required for the cesium salt) and digesting at 25 C for one hour.
- 3) Centrifugation to separate the cesium precipitate from the supernatant liquor (using a bowl holdup time of 9 minutes at 1500 C).
- 4) Cake washing with four separate portions of 1M HNO_3 (introduced to the centrifuge bowl via high pressure sprays).
- 5) Cake dissolution with 1M NaOH, using six separate portions introduced via the high pressure spray. (The dilution water shown in the figure would ordinarily not be added.)

The material balance showed 1.5 percent of the cesium in the combined wastes and 92 percent in the product. The cesium loss was slightly (2 to 3-fold) higher than predicted from the above solubility data. Decontamination factors could not be obtained because of cross-contamination of the product with the feed.

*Neglects the phosphotungstate ion associated with the cesium in the product tank.

FIGURE IV-112

Cesium Phosphotungstate Flowsheet (Source of Data: HW-81092)

2. Cesium Nickel Ferrocyanide Process

2.1 Introduction

Nickel ferrocyanide scavenging has been extensively used at Hanford to remove cesium from Uranium Recovery Plant waste⁽⁴⁾. The process has since been extended to the removal of cesium from Purex alkaline waste supernates⁽⁸⁾ and demonstrated in the Purex Plant with full-level waste⁽²⁾. The process is based on the formation of the insoluble double salt of cesium nickel ferrocyanide [$\text{Cs}_2\text{NiFe}(\text{CN})_6$] in slightly alkaline solutions (pH 7 to 10). Several other metal ferrocyanides also form insoluble cesium salts [notably those of zinc and iron(III)] but nickel ferrocyanide was selected because it is effective over a wider pH range and to a higher pH (10.6) than the other candidates. Since the pH of Purex tank farm supernates is generally less than 10.5, no pretreatment of the waste appears necessary. Silver ion will displace cesium and nickel from the compound and the cesium can be recovered relatively pure by metathesizing the precipitate with an insoluble silver compound such as Ag_2CO_3 .

2.2 Effect of Variables on Cesium Precipitation

The following discussion was abstracted from Reference 8, and is based on laboratory studies with synthetic Purex tank farm supernate (ca. $8 \times 10^{-4}\text{M}$ Cs).

2.2.1 Effect of pH

Cesium losses were insensitive to the pH of the alkaline waste solution up to and including pH 10.6. Losses increased sharply to greater than 50 percent at pH 11. The normal tank farm supernate pH, however, is less than 10.5 and no pH adjustment should be required.

2.2.2 Effect of Excess Reagents

Cesium losses of 2 percent or less were obtained whenever the mole ratio of nickel to cesium was ≥ 1.25 and the mole ratio of ferrocyanide to cesium was ≥ 6.25 . (For comparison, the stoichiometric mole ratios of nickel and ferrocyanide to cesium would be 0.5.) The cesium loss was more sensitive to the ferrocyanide concentration than to the nickel as the stoichiometric limit was approached; reversing the above mole ratio limits increased the cesium loss from 1.4 percent to 4.9 percent. Thus it appears that sufficient ferrocyanide must be present to provide an excess in solution after stoichiometric precipitation of both the cesium-nickel and nickel ferrocyanides. The precipitate volume in all cases was less than 2 ml/l of feed (with up to 2.5 millimoles of nickel added).

2.2.3 Effect of Temperature

The waste solution was normally digested at room temperature for 30 min after addition of nickel nitrate and for an additional hour after adding potassium ferrocyanide. The losses increased 2 to 3-fold when the digestion temperature was increased to 50 C.

2.3 Metathesis and Dissolution

Silver carbonate, oxide, and nitrate were satisfactorily used to metathesize the cesium nickel ferrocyanide precipitate⁽⁸⁾. Cesium recoveries ranged from 87 to 97 percent when a water slurry of ferrocyanide precipitate was digested for one hour at 80 C with at least a two-fold excess of silver over the theoretical requirement to metathesize a mixture of $\text{Cs}_2\text{NiFe}(\text{CN})_6$ and $\text{Ni}_2\text{Fe}(\text{CN})_6$ to $\text{Ag}_4\text{Fe}(\text{CN})_6$. The digestion temperature must be high; cesium recovery from a zinc ferrocyanide precipitate was only 34 percent when digested at 40 C, compared with 99 percent recovery at 80 C.

The use of an insoluble silver salt, such as the carbonate, in the metathesis provides the cleanest cesium product. With silver nitrate, the excess reagent and the metathesized nickel will remain in solution with the cesium. The silver and nickel can, of course be precipitated later as the carbonates.

2.4 Chemical Flowsheet and Process Demonstration

The nickel ferrocyanide process was demonstrated in a full-scale plant test using aged high-level waste supernatant solution as feed and the Purex Plant head-end precipitation equipment⁽²⁾. The cesium recovery was 99 percent with a sodium decontamination factor of 900 using the flowsheet shown in Figure IV-113. The following procedure was employed:

- 1) The supernatant solution was adjusted with nickel nitrate and sodium ferrocyanide to 0.001 and 0.005M, respectively. The resulting solutions contained 4 and 20 times the respective theoretical nickel and ferrocyanide requirement.
- 2) The treated solution was digested for one hour at 25 C and centrifuged at 1500 G's at a bowl holdup of 10 to 20 min.
- 3) The precipitate was washed in the centrifuge with 0.1M NaNO_3 and slurried from the centrifuge with 0.05M AgNO_3 metathesis solution (3.8 times the theoretical amount required).
- 4) The slurry was digested at 90 C for one hour and settled at 25 C for one hour before decanting the cesium product through the centrifuge.
- 5) The remaining solids were metathesized a second time under similar conditions.
- 6) The waste silver cake was slurried from the centrifuge with 2M NaOH .

The following material balance and decontamination factors were obtained:

<u>Process Solution</u>	<u>Cs, % of Input</u>
Waste Supernate	0.4
Silver Waste Cake	0.4
Cesium Product (1st Metathesis) ⁽²⁾	90.5
Cesium Product (2nd Metathesis)	<u>12.0</u>
Total	103.3

- (a) The first product solution was decontaminated by a factor of 910 from sodium and by factors of 20 to 220 from ZrNb, Ru, and Ce. Less than 4 percent of the added silver and less than 12 percent of the nickel were found in the product.

I. Cesium Precipitation

II. Silver Metathesis

Note: Under production conditions
Second Product Fraction would
be combined with the First.

FIGURE IV-113

Nickel Ferrocyanide Process - Purex Plant Test
(Source of Data: HW-75051)

No attempt was made in this test to minimize silver consumption or to obtain high cesium concentrations in the product solution. An optimized flowsheet based on the minimum chemical requirements determined in laboratory studies is shown in Figure IV-114. Improved cesium recovery should be obtained by metathesizing the silver waste cake a second time, reserving the supernate solution for addition to the first metathesis solution of a succeeding run.

* Silver can be Added as Ag_2O and later Precipitated as the Carbonate or Hydroxide.

FIGURE IV-114

Optimized Cesium Nickel Ferrocyanide Process
(Derived from data in HW-70874)

3. References

1. M. D. Alford. Cesium Recovery Process, Wet Chemistry Plant Scale Development - Interim Report, HW-58535. January 20, 1959.
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4. R. E. Burns and M. J. Stedwell. "Volume Reduction of Radioactive Waste by Carrier Precipitation", Chem. Eng. Prog., vol 53, p 94, 1957.
5. T. V. Healy and Mrs. B. L. Davies. Alkali Phosphotungstates. Part I: Nature and Solubilities of the Cesium Salts, AERE-C-R-2528. April, 1958; Part V. Extraction of Cesium from Fission Product Solutions, AERE-R-2968, June, 1959.
6. T. V. Healy. "Heteropoly Salts. Part I. Preparation of Some Normal and Acid Phosphotungstates". Radiochimica Acta, 2(3), p. 146-156. 1964.
7. J. Van R. Smit. The AMP Process for Cesium Separation. 1. Adsorption of Cesium on Ammonium 12-molybdophosphate, AERE-R-3884.
8. H. H. Van Tuyt and L. A. Bray. Recovery of Cesium from Purex Tank Farm Supernatant Solution by Ferrocyanide Precipitation and Absorption on Decalco, HW-70874. October 18, 1961.
9. H. H. Van Tuyt, BNW, personal communication, November, 1965.

H. PROPERTIES OF PROCESS MATERIALS

Physical and chemical properties of many of the chemicals used in B-Plant processes are discussed in this section; however, properties of simple and well-known chemicals such as HNO_3 , NaOH , etc. are not discussed; and, for convenience, properties of ion exchange materials are discussed in Section F.

1. D2EHPA Extractant Components1.1 D2EHPA1.1.1 Introduction

Di-(2-ethylhexyl)phosphoric acid, $(\text{C}_8\text{H}_{17}\text{O})_2\text{POOH}$, (D2EHPA) is a viscous, yellow to amber liquid available from several commercial sources. Presumably, D2EHPA is made by the reaction of 2-ethylhexanol with POCl_3 with subsequent treatment with NaOH , but the exact details of manufacture are proprietary. It is a versatile cation exchanger, which, by proper adjustment of conditions, can be used to extract practically all of the actinide and fission product elements of interest in the Waste Management Program.

Commercially-available D2EHPA, as used at Hanford, generally contains only 95 percent to 98 percent D2EHPA. Impurities present include mono-(2-ethylhexyl)phosphoric acid, 2-ethylhexanol, pyro esters, and iron. The latter, if present in sufficient quantity, imparts a red color to the D2EHPA.

1.1.2 Specifications

Purchase specifications⁽¹⁾ for D2EHPA are given in the following table:

D2EHPA Content	95 - 100 Weight percent
Specific Gravity	0.970 - 0.984 20/20 C
Refractive Index	$n_D^{20} = 1.443$
Solubility	
1) In water	0.01 weight percent at 20 C
2) Water in	2.4 weight percent at 20 C
Flash Point	
Cleveland Open Cup	385 F

1.1.3 Physical Properties

Selected physical properties of D2EHPA are presented in Table IV-58. The properties listed are those considered to be of fundamental interest to the Waste Management Program.

TABLE IV-58

SELECTED PHYSICAL PROPERTIES OF D2EHPA

(Source of Data: Technical Bulletins Union Carbide Co.
and Mobil Chemical Co.)

<u>Property</u>	<u>Value</u>
Formula	$(C_8H_{17}O)_2POOH$
Molecular Weight	322.4
Color	Colorless ^(a)
Density, g/ml.	0.977 (20 C)
Melting Point, °C	<60
Flash Point, °F	385 ^(b) (196 C)
Viscosity, millipoises at 20 C	350
Solubility in water	0.01 Wt.% at 20 C
Solubility of water in	2.4 Wt.% at 20 C
Refractive Index	1.443 (n_D^{20})

(a) When pure. Impure material is frequently yellow to amber.

(b) Cleveland Open Cup.

1.1.4 Radiation Stability

Effects of radiolysis on D2EHPA were first studied by Wagner and Towle in 1958⁽²⁾. In a single experiment they irradiated (1 MEV electrons) 100 grams of as-received D2EHPA to a total dose of 2055 watt

hrs/liter and determined the amounts and composition of the resulting gaseous and liquid phases. Their results are summarized in Table IV-59 along with results, for comparison, of a similar experiment with TBP. These results demonstrate that D2EHPA is more susceptible to radiation damage than TBP. Thus, the $-G_m$ (target) value for D2EHPA was 50 percent higher than the value for TBP.

TABLE IV-59
G VALUES AND IRRADIATION PARAMETERS FOR D2EHPA STUDY

(Source of Data: AECU-4053)

<u>Parameters</u>	<u>D2EHPA</u>	<u>TBP</u>
Dose (watt hour/liter)	2055	1900
Dose (100 eV)	4.60×10^{22}	4.26×10^{22}
Dose Rate (100 eV/hr)	3.38×10^{22}	2.84×10^{22}
G (Gas)(a, b)	2.66	2.07
G (Total Acid)(c)	3.62	1.41
G (Monobasic Acid)	--	1.37
G (Dibasic Acid)	1.16	0.03
G (Phosphoric Acid)	2.46	<0.01
$-G_m$ (Target) (c, d)	3.42	2.15
G (Nonacidic Liquid Components)(f)	4.32	(e)
G H_2	2.35	(e)
G H_2O	0.84	(e)
G CO	0.06	(e)
G Ethane	0.07	(e)
G Butane	0.03	(e)
G Heptane	0.01	(e)
G Branched Octane	0.54	(e)
G Octanes + Octenes	2.82	(e)

(a) G represents number of molecules produced per 100 electron volts absorbed.

(b) Determined by mass spectrometry.

(c) Determined by electrotitrimetry.

(d) $-G_m$ represents number of molecules of target material destroyed per 100 electron volts absorbed.

(e) Not determined.

(f) Determined by gas chromatography.

Studies of the effects of radiation on D2EHPA-TBP-hydrocarbon diluent solvents have been made by Schulz⁽³⁾ under batch conditions simulating the B-Plant mainline (Section C 3) D2EHPA extraction process for PAW. In these studies solvents of the approximate composition 0.21M D2EHPA-0.09M NaD2EHP-0.2M TBP-diluted with either Soltrol-170 or NPH⁻ (Section H 1.3) were irradiated to a total exposure of 393 watt hrs/liter. This irradiation was accumulated in 20 increments (cycles) in each of which

the dose obtained was 19.6 watt hrs/liter. [This dose per cycle corresponds approximately with that expected for one pass of the D2EHPA extractant through the mainline 1A, 1S, 1B, 1C and cerium strip operations (Figure IV-48) and solvent wash operations (Figure IV-58)]. In each cycle the solvent was irradiated (Co-60) at about 40 C while in emulsion contact (at flowsheet volume ratios) successively with aqueous solutions of the approximate composition of the 1AF, 1SS, 1BX, cerium strip, 1OS and 1OO Butt streams. Contact times were adjusted so that the radiation dose in the various contacts were 1.6, 2.6, 2.1, 11.9, and 1.4 watt-hrs/liter in the extraction, scrub, partition, cerium strip, and solvent wash steps. Various physical and chemical properties of both solvents were determined at the end of selected cycles. Data obtained in this study are presented in Table IV-60. The strontium 1A Column and Ce(IV) distribution ratio data listed in Table IV-60 are also plotted in Figure IV-115.

FIGURE IV-115

Effect of Solvent Irradiation on Strontium and Cerium (IV) Extraction
(Source of Data: W. W. Schulz, BNW, unpublished data)

TABLE IV-60
PROPERTIES OF IRRADIATED D2EHPA-TBP-DILUENT SOLVENTS

(Source of Data: W. W. Schulz, BNL, unpublished data)

Cycle No.	Cumulative Exposure watt-hrs/liter	MD2EHPA (a)		M Organic Acidity (b)		Density		Viscosity, cP (c)		Disengaging Time, Seconds (d)	
		NPH	Soltrol-170	NPH	Soltrol-170	NPH	Soltrol-170	NPH	Soltrol-170	NPH	Soltrol-170
0	0	0.317	0.320	0.321	0.8078	0.7868	3.462	1.820	--	--	69
1	19.7	0.306	0.308	0.312	0.8090	0.7861	3.453	1.803	100	100	85
3	59.0	0.298	0.307	0.307	0.8094	0.7872	3.648	1.832	113	113	91
5	98.3	0.386	0.303	0.362	0.8101	0.7881	3.667	1.863	125	125	100
10	197	0.298	--	0.315	0.8121	0.7916	3.807	1.969	138	138	97
15	295	0.298	--	0.302	0.8140	0.7921	4.001	2.013	153	153	124
20	393	0.238	0.236	0.235	0.8158	0.7916	4.135	2.001	167	167	--

Cycle No.	Cumulative Exposure watt-hr/liter	Strontium E _g (e)		Cerium (III) E _g (f)		Cerium (IV) E _g (h)	
		1A Column Soltrol-170	1B Column NPH	1A Column Soltrol-170	NPH	Soltrol-170	NPH
0	0	--	11.6	--	0.0038	29.1	28.5
1	19.7	11.7	12.5	0.0075	0.0043	31.2	31.5
3	59.0	10.5	10.9	0.0033	0.0021	31.6	33.5
5	98.3	8.52	9.37	0.0022	0.0020	28.5	28.7
10	197	6.07	7.17	0.0088	0.0011	29.9	30.9
15	295	4.50	5.43	0.0041	0.0006	--	20.5
20	393	3.10	4.74	0.0034	0.0012	19.7	21.9

(a) Preliminary data obtained by gas chromatographic procedure outlined in RL-SA-32.

(b) Titrated with sodium hydroxide after washing with 6M nitric acid and water.

(c) Capillary tube viscometer.

(d) Ten ml solvent contacted with 10 ml of synthetic 1AF of composition listed in Table IV-10 (PAW-B). Disengaging time measured with standard apparatus described in HW-27807.

(e) Ten ml contacted at 25°C with an equal volume of synthetic 1AF as in (d) above except 1AF was 0.18M citrate and 0.20M acetate. The pH of the final aqueous was 4.7.

(f) The organic phase from (e) was scrubbed twice with 1/5 portions of 0.5M formic acid and then contacted for 10 minutes at 25°C with 1/5 volume of 0.028M nitric acid.

(g) Ten minute contact at 50°C with equal volume of 1AF of composition indicated in (d).

(h) Sixty minute contact at 25°C with equal volume of 2.0M HNO₃, 0.2M (NH₄)₂S₂O₈, 0.02M AgNO₃, 0.0071M Ce(NO₃)₃, 0.0144M La(NO₃)₃ solution.

The outstanding effects observed in these experiments was the decreased strontium extraction capacity of the irradiated solvents. Fall-off in strontium extraction capacity in these experiments was uniform (Figure IV-115) with irradiation dose and was greatest for the solvent containing Soltrol-170 as diluent. The decreased strontium extraction capacity is most easily accounted for in terms of radiolytic destruction of D2EHPA as expected from the results of Wagner and Towle cited earlier. D2EHPA concentrations of the final (20-cycle) solvents as determined by both titrimetry and gas chromatography indicate irradiation to 393 watt hrs/liter destroyed about 25 percent of the D2EHPA.

Irradiated solvents obtained in these experiments also extracted Ce(III) (Table IV-60) and Ce(IV) (Figure IV-115) less efficiently than unirradiated extractants. The decrease in Ce(III) extraction capacity probably also reflects destruction of D2EHPA. Most of the decrease in Ce(IV) extraction capacity, however, is due to generation of reducing impurities in the organic phase since treatment of the 20-cycle solvents with $\text{HNO}_3\text{-KMnO}_4$ according to the procedure described in Section C 6.3.3 restored Ce(IV) E_a 's to values typical of unirradiated solvent. Data in Figure IV-115 also offer additional proof (Section C 3.5.3) of the advantages of NPH over Soltrol-170 as the hydrocarbon diluent for B-Plant extractant.

Specific gravity and viscosity of both the NPH and Soltrol-170 solvents (Table IV-60) increased upon irradiation. Associated with these changes were increased disengaging times under LA Column conditions.

Consequences of solvent radiolysis with respect to economic and operating characteristics of B-Plant solvent extraction processes had not been evaluated fully at the time this part of the manual was written. Further laboratory studies to aid in defining these consequences were also in progress as this manual was written.

1.2 Tributyl Phosphate

1.2.1 Introduction

Tri-n-butyl phosphate (TBP), $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$, is a viscous, colorless liquid which is produced by the reaction of n-butyl alcohol with either phosphorous oxychloride (POCl_3) or phosphorous pentoxide (P_2O_5) with subsequent caustic treatment and distillation. It is used as the extractant in the Purex solvent-extraction process because of the specificity of the strong complexes it forms with uranium and plutonium. In the B-Plant it is added to D2EHPA-kerosene solutions to increase the solubility of salt forms of D2EHPA in hydrocarbon diluents.

1.2.2 Specifications

The purchase specifications⁽¹⁾ for TBP are given in the following table:

Butanol Content	Max. 0.05 weight percent
Acidity	Less than 0.02N
Water Content	No turbidity when one volume TBP is mixed with 19 volumes of 60° Be' gasoline at 20 C.
Suspended Solids	Max. 0.01 weight percent
Specific Gravity	0.973 to 0.983 at 20/20 C

1.2.3 Physical Properties

Selected physical properties of TBP are presented in Table IV-61. The properties listed are those considered to be of fundamental interest to the Waste Management Program. A more complete listing and discussion of the physical properties of TBP, particularly in connection with its use in the Purex plant, is given in Reference 4.

1.2.4 Chemical Properties

The chemical properties of TBP were investigated in detail in connection with the development of the Purex process and are discussed in detail in Reference 4. Only highlights of this chemistry are discussed here since in the B-Plant the functions of TBP are primarily those of a diluent and not an extractant.

In general, the chemical properties of TBP are those typical of esters derived from inorganic acids. The formation by TBP of coordination complexes with uranium and plutonium nitrates is, of course, the basis of the Purex process. Also of great importance to the Purex process is hydrolysis of dealkylation of TBP which can occur in both acid and alkaline systems. The acid hydrolysis occurs through cleavage of carbon-oxygen bonds to form butanol, dibutyl phosphate (DBP), mono-butyl phosphate (MBP); and eventually orthophosphoric acid. Alkaline hydrolysis involves cleavage of phosphorous-oxygen bonds and stops with the formation of the alkaline salt of DBP^(5,6,7). The acid hydrolysis rate increases with HNO₃ concentration and temperature and decreases with dilution of the TBP. Hydrolysis rates for DBP and MBP are not accurately known except that TBP hydrolyzes faster than DBP and DBP hydrolyzes faster than MBP⁽⁸⁾. Recent studies have shown that factors such as chemical composition of the diluent⁽⁹⁾, and the presence of

air(10), as well as the acidity(11) and radiation influence the rate of hydrolysis of TBP. In the Purex plant the presence of MBP and/or DBP in the solvent gives rise to several process problems including higher waste losses and poorer fission product decontamination.

Because the B-Plant extraction processes operate at acidities below $1M$ HNO_3 it is expected that acid hydrolysis of TBP will not occur to the same extent as it does in the Purex process. Also, since D2EHPA is itself an alkyl phosphoric acid, the consequences of formation of other alkyl phosphoric acids (i.e., DBP and MBP) are far less in the B-Plant than in the Purex plant. In all of the Strontium Semiworks experience there has been no indication whatsoever of any operational difficulties directly attributable to acid or base hydrolysis of TBP.

TABLE IV-61

SELECTED PHYSICAL PROPERTIES OF TBP

(Source of Data: HW-31000)

<u>Property</u>	<u>Value</u>
Formula	$(n-C_4H_9O)_3PO$
Molecular Weight	266.3
Color	Colorless
Density, g/ml	0.9730 (25 C)
Melting Point, °C	-80
Flash Point, °F	295 ^(a) (146 C)
Viscosity, millipoises at 20 C	37.4
Solubility in water	0.6 vol. %
Solubility of water in	7.0 vol. %
Refractive Index	1.4226 (n_D^{25})
Boiling Point, °C at 760 mm Hg pressure	289
Surface Tension, dynes/cm at 25 C	25

(a) Tag Closed Cup.

1.2.5 Radiation Stability

Studies of the radiolysis of TBP and TBP-diluent systems have been made by several investigators⁽¹²⁻¹⁶⁾. The most recent and most comprehensive studies have been made by Wagner and coworkers^(15,16). All workers agree the principal products of radiolysis are hydrogen, DBP MBP, and, at high doses, a polymeric solid of unknown composition. The data presented in Table IV-62 are typical of those obtained in irradiation of TBP.

Evidence presently available (Section H 1.1.4) indicates D2EHPA is more susceptible to radiation damage than is TBP. Hence the most important effects of radiolysis of B-Plant solvent (i.e., lower E_a^0 values) are associated primarily with destruction of D2EHPA molecules and only slightly with destruction of TBP.

There is no evidence to indicate any of the radiolytic products of TBP will seriously interfere with B-Plant D2EHPA extraction processes. Rather, it is estimated the principal consequences of TBP radiolysis will be associated with the disappearance of TBP itself.

TABLE IV-62
MATERIAL BALANCE DATA AND G VALUES FOR TBP IRRADIATION

	1900 watt hours/liter				
	(Source of Data: AECU-4052)				
	Wt. (gms)	(MW)	Moles	$G^{(a)}$	$-G_m^{(b)}$
TBP (Initial)	103.8	266	--	--	--
TBP (Recovered)	63.37	266	--	--	--
TBP (Destroyed)	40.43	266	0.152	--	2.15
Gas	2.64	18	0.147	2.07	--
DBP	20.35	210	0.097	1.37	--
MBP	0.33	154	0.0021	0.03	--
H ₃ PO ₄	0.03	98	0.0003	0.01	--
Polymer	17.08	266	0.0642	--	--

(a) G represents number of molecules produced per 100 electron volts absorbed.

(b) $-G_m$ represents number of molecules of target material destroyed per 100 electron volts absorbed.

1.3 Diluents

1.3.1 Introduction

The diluent for D2EHPA and TBP in B-Plant solvent extraction processes is a highly refined hydrocarbon mixture, boiling in the kerosene range (190 to 270 C). Two commercially available solvents meeting specifications for the diluent are Soltrol-170 (Phillips Chemical Co.) and NPH*. NPH is the Hanford designation for a mixture of normal paraffin

* Tentatively selected for the B-Plant at the time of writing.

hydrocarbons, principally C₁₀ through C₁₃, sold by the South Hampton Co., Houston, Texas. Other diluents which have been used at Hanford in laboratory studies of B-Plant processes are Shell E-23⁴² and Shell Deodorized Spray Base. Amsco 125-82 has been used at ORNL.

1.3.2 Physical Properties

The physical properties of some of the commercially available diluents that have been used or considered during the development of DEHPA solvent extraction processes for use in the B-Plant are shown in Table IV-63.

TABLE IV-63

PROPERTIES OF DILUENTS^(a)

<u>Property</u>	<u>NPH</u> ^(d,c)	<u>Soltrol-170</u> ^(d,e)	<u>Soltrol-170</u> ^(b,f)
Density at 25 C, g/ml		0.7728	0.7764
Index of Refraction, n _D ²⁵		1.4315	1.4289
Viscosity at 25 C millipoises	14	-	22.9
Flash Point, °F Tag Closed Cup	161	192	183
Aromatic Content, Vol. %	Nil	Nil	-
Boiling Range and Midpoint, °C		208-239 (225)	214-235 (225)

(a) The properties of commercial diluents are subject to slight variations from batch to batch.

(b) Properties as determined on one sample at Hanford.

(c) Data from memo by H. C. Rathvon, Isochem Inc., Feb., 1966.

(d) Properties as cited by manufacturer.

(e) Data supplied by Phillips Petroleum Co.

(f) Properties determined by L. Burger, Battelle-Northwest Laboratory.

The solubility of diluent in water is very slight. For example, the solubility of Shell E-23⁴² diluent in water is less than 0.004 gram per liter at 25 and 50 C⁽¹⁷⁾.

1.3.3 Chemical Properties

Chemical inertness toward process chemicals of of major concern in the selection of a diluent for use in the B-Plant. Under normal operating conditions the diluents preferred (NPH or Soltrol-170) for use in the B-Plant are chemically unreactive in contact with process solutions at ambient temperatures.

With the aim of finding an optimum diluent for use in the Purex process a considerable volume of laboratory work at various USAEC sites has been devoted to determination of the properties and reactions of various hydrocarbon diluents. One of the most significant reactions which such dilutes can undergo is nitration. Nitrogen oxides are known to nitrate aromatics and olefins and also to oxidize carbon side chains of aromatic nuclei to carboxylic acids at room temperature although the reactions are exceedingly slow. The reactions of nitrogen oxides with naphthenes or paraffins occur in the vapor phase and very slowly in the liquid phase at room temperatures⁽¹⁸⁾.

Investigations of the stability of diluents to HNO_3 and HNO_2 have shown that naphthenic-type diluents (such as Shell E-2342) are less stable to nitration reaction than paraffinic diluent (e.g. NPH and Soltrol-170)^(19,20). Nitration of diluents produces alkyl nitrites and nitrates, aliphatic nitro and nitroso compounds, and carboxylic acids⁽²⁰⁾. In the Purex process the presence of some of these nitration products in the process solvent increases fission product extraction and thus affects decontamination adversely.

The extent to which diluent nitration will occur, if at all, in B-Plant operation and the consequences thereof, if any, are unknown at the time this manual is written.

1.3.4 Radiation Stability

The effects of irradiation of D2EHFA-TBP-diluent solutions on B-Plant extraction processes are discussed in Section H 1.1.4. As pointed out there, the adverse effects of solvent radiolysis, except for decreased Ce(IV) extraction capacity, appear to be largely attributable to destruction of D2EHFA and/or TBP and not to radiation induced decomposition of diluents or of products produced thereby. Decreased Ce(IV) extraction capacity of irradiated B-Plant solvent appears, however, to be definitely related to the radiolytic production of reducing impurities from the hydrocarbon diluent as shown by the data in Figures IV-115 and IV-46. As stated before, NPH is more stable than Soltrol-170 to production of such impurities.

2. Complexants and Buffering Agents

2.1 Introduction

Various organic acids are used in B-Plant solvent extraction processes to suppress extraction of unwanted metal ions and to provide necessary pH control in extraction, scrub, and partition column operation. These reagents include carboxylic, polycarboxylic, and polyaminocarboxylic acids. Selected physical and chemical properties of these reagents are tabulated in this section of the manual.

2.2 Physical Properties

For convenience in B-Plant operations the complexants (Section C 2.4) EDTA, DTPA, and HEDTA are purchased and used as aqueous solutions of the sodium salts Na_4EDTA , Na_5DTPA , and Na_3HEDTA , respectively. Selected physical properties⁽²¹⁾ of these aqueous solutions are listed in Table IV-64. Certain other complexants and/or buffering agents - acetic, hydroxyacetic, citric, tartaric, and oxalic acids - are most conveniently purchased and used in the acid form. Selected physical properties^(22,23) of this latter group of reagents are listed in Table IV-65.

2.3 Chemical Properties

2.3.1 Tabulated Acid Dissociation Constants

Tabulated in Table IV-66 are acid dissociation constants for complexing agents of interest to B-Plant separation processes. These constants were used to calculate the amount of hydrogen ion complexed by the various ligands as a function of pH (Figure IV-116).

2.3.2 Tabulated Metal Complex Formation Constants

Formation constants for the formation of complexes between certain of the complexants and metal ions of interest to B-Plant processes are listed in Table IV-67. The significance of these formation constants is discussed in Section C 2.4.

Except for complexes with DTPA data listed in Table IV-67 were taken from the critical compilation of Bjerrum, Schwarzenbach, and Sillen from publication earlier than Jan. 1, 1956⁽²⁴⁾. Gaps in Table IV-67 ordinarily signify that the particular formation constant has not been measured. In some cases, however, the missing formation constant has been measured but not, in the opinion of Bjerrum et.al. with sufficient accuracy to warrant inclusion in their compilation. Formation constants for DTPA complexes have been measured since 1956 principally by Chaberek and coworkers^(25,26).

TABLE IV-64
PHYSICAL PROPERTIES OF COMPLEXANTS
(Source of Data: Technical Data Sheet 104, Fisher Scientific Co.)

Properties shown refer to as-purchased aqueous solutions of indicated complexants.

Structural Formula	Na ₄ EDTA		Na ₃ HEDTA		Na ₂ DTPA	
	$\text{NaOOCCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2)_3$	$\text{HOCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2)_3$	$\text{NaOOCCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2)_3$	$\text{NaOOCCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2)_3$	$\text{NaOOCCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2)_3$	$\text{NaOOCCH}_2\text{N}(\text{CH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COONa})_2)_3$
Molecular Weight	336.2	344.2	344.2	344.2	344.2	344.2
pH (1% solution)	11.3-11.5	11.3-11.5	11.3-11.5	11.3-11.5	11.3-11.5	11.3-11.5
Bulk Density (lbs/lead)	10.8	10.8	10.8	10.8	10.8	10.8
Specific Gravity (25/25°C)	1.25-1.32	1.25-1.30	1.25-1.30	1.25-1.30	1.25-1.30	1.25-1.30
Percent by Weight in Aqueous Solution	48	48	48	48	48	48
Freezing Point of Aqueous Solution (°F)	-27	-26	-26	-26	-26	-26
Calorim. Content Value (cal)	100	120	120	120	120	120
Complexant Concentration, M	1.40	1.57	1.57	1.57	1.57	1.57

(c) Methacrylates (MMA) per atom of chelating agent at pH 11.

TABLE IV-65
PHYSICAL PROPERTIES OF COMPLEXANTS
(Source of Data: Encyclopedia of Chemical Technology)

Apparatus	Carboxylic Acid		Carboxylic Acid Diethyl Ester		Hydroxyacetic Acid (c)	
	$\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2$
Physical Properties	CH_3COOH	CH_3COOH	CH_3COOH	CH_3COOH	CH_3COOH	CH_3COOH
Structure of Complex	CH_3COOH	CH_3COOH	CH_3COOH	CH_3COOH	CH_3COOH	CH_3COOH
Appearance	Colorless, crystalline	Colorless, crystalline	Colorless, crystalline	Colorless, crystalline	Colorless, liquid	Colorless, liquid
Melting Point (°C)	15	15	15	15	16.6	16.6
Specific Gravity (25/25°C)	1.25-1.32	1.25-1.32	1.25-1.32	1.25-1.32	1.0492 (25°C)	1.070 (25°C)
Refractive Index (20°C)	1.45	1.45	1.45	1.45	1.3718	1.3718
Boiling Point (°C)	118	118	118	118	118.1	118.1
Solubility in Water	Very soluble	Very soluble	Very soluble	Very soluble	Miscible in all proportions	Miscible in all proportions

(c) Also known as Glycolic Acid.

TABLE IV-66
SELECTED ACID DISSOCIATION CONSTANTS

(Source of Data: J. Bjerrum et.al. Stability Constants Part 1)

(Log Dissociation Constants ($pK = -\log_{10} K$), 20 - 30C)^(a)

Ligand	pK_1	pK_2	pK_3	pK_4	pK_5
Acetate	4.61	--	--	--	--
Hydroxyacetate	3.88	--	--	--	--
Tartrate	2.88	3.94	--	--	--
Citrate	3.06	4.76	6.40	--	--
HEDTA	2.64	5.33	9.73	--	--
EDTA	1.99	2.67	6.16	10.26	--
DTPA	1.79	2.56	4.42	8.76	10.42

(a) For reactions:

$$H_n L = H_{n-1} L + H^+; K_1 = \frac{[H_{n-1} L] [H^+]}{[H_n L]}$$

$$H_{n-1} L = H_{n-2} L + H^+; K_2 = \frac{[H_{n-2} L] [H^+]}{[H_{n-1} L]}$$

etc.

FIGURE IV-116

Hydrogen Ion Complexing by Ligands
(Source of Data: HW-72666)

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TABLE IV-67
SELECTED FORMATION CONSTANTS
(Source of Data: DTPA - Chabarek and co-workers,
Others - J. Bjerrum et.al. Stability Constants, Part I)
Log Formation Constants, 20-30C. See Discussion Section C 2.4

Metal Ion	Acetic Acid Log K ₁	Hydroxyacetic Acid Log K ₁	Citric Acid (H ₄ L)		DTPA		EDTA (H ₄ L)		HEDTA Log K ₁	NTA Log K ₁	Oxalic Acid Log K ₁		Tartaric Acid (H ₂ L)	
			Log K _{MHL}	Log K _M	Log K ₁	Log K ₁	Log K ₁	Log K _{MHL}			Log K ₁	Log K _M	Log K ₁	Log K _{MHL}
Ba ⁺²	0.39	1.02		2.84	8.63	7.76	2.07		--	6.41	ca. 2.3		1.62	0.88
Ca ⁺²	0.53	1.59		4.84	10.74	10.7	3.51		8.0	8.17	ca. 3		1.80	1.11
Pb ⁺²	2.52	--		6.50	--	18.04	10.61		--	11.8	--		--	--
Mg ⁺²	0.51	1.33		--	9.34	8.69	2.28		--	7.0	2.55		1.36	0.92
Mn ⁺²	--	--		--	15.1	14.04	6.9		10.7	7.44	3.89		--	--
Ni ⁺²	0.74	--		--	20.2	18.62	11.56		17.0	11.26	5.3		9.9	--
Sr ⁺²	0.43	1.31		2.85	9.68	8.63	2.30		--	6.73	2.54		1.65	0.91
UO ₂ ⁺²	2.38	--		--	--	--	--		--	--	--		--	--
Al ⁺³	--	--		--	--	16.13	8.4		--	--	--		--	--
Ce ⁺³	1.68	--		--	21.0	16.0	--		14.08	10.71	6.52		--	--
Eu ⁺³	--	--		--	22.91	17.35	--		15.21	--	--		--	--
Fe ⁺³	--	4.7		11.85	28.6	25.1	16.2		--	15.87	9.4		18.1	--
La ⁺³	--	--		--	19.96	15.5	--		13.22	10.37	--		--	--
Y ⁺³	--	--		--	22.4	18.09	--		14.49	11.41	--		--	--
Cr ⁺³	--	--		--	--	24.0	--		--	--	--		--	--

3. Other Process Materials

3.1 Sodium Persulfate (peroxy disulfate)3.1.1 Physical Properties⁽²⁷⁾

Formula	$\text{Na}_2\text{S}_2\text{O}_8$
Formula Weight	238.11
Appearance	White crystals
Solubility in water:	

Temperature, °C	Grams $\text{Na}_2\text{S}_2\text{O}_8$ per 100 ml H_2O
15	53.3
20	54.7
25	56.2
30	57.6
35	59.0
40	60.5
45	61.9
50	63.3

In contrast, the solubility of $\text{K}_2\text{S}_2\text{O}_8$ in water at 20 C is only 5.3 grams per 100 ml of water⁽²⁸⁾; primarily on this basis $\text{Na}_2\text{S}_2\text{O}_8$ is preferred over $\text{K}_2\text{S}_2\text{O}_8$ for oxidizing Ce(III) to Ce(IV) (Section C 3.5.3).

The solubility of $\text{Na}_2\text{S}_2\text{O}_8$ in 2M HNO_3 at 25 C is about 1.7M whereas the solubility of $\text{K}_2\text{S}_2\text{O}_8$ in 0, 1, 2, and 4M HNO_3 at 25 C is 0.22, 0.26, 0.28, and 0.37M, respectively⁽²⁹⁾.

3.1.2 Stability

Temperatures up to about 100 C applied to the solid $\text{Na}_2\text{S}_2\text{O}_8$ for short periods of time cause only negligible decomposition⁽²⁷⁾. Noticeable decomposition occurs upon further increase in temperature, and it becomes quite rapid in the 150 to 200 C range. The presence of moisture tends to increase the rate of decomposition by heat, but no tendency towards explosive decomposition has been observed.

Catalytic decomposition of solid $\text{Na}_2\text{S}_2\text{O}_8$ may take place in contact with various agents, notably platinum black and certain metals. Many metals such as lead, silver, copper, magnesium, zinc, cadmium, manganese, iron, nickel, and cobalt react easily with $\text{Na}_2\text{S}_2\text{O}_8$, as will organic oxidizable matter.

Aqueous solutions of $\text{Na}_2\text{S}_2\text{O}_8$ are reported to be quite stable at ordinary temperatures and may be kept for a few hours even at elevated temperatures⁽²⁷⁾. It is estimated a 5 percent solution of $\text{Na}_2\text{S}_2\text{O}_8$ in distilled water at 25 C would lose only 2 percent of its original active oxygen after one week. The same system, however after one week at 50 C would be expected to lose about 80 percent of the original active oxygen. Of course, contamination of the solution with catalytically active impurities such as traces of heavy metals, easily oxidizable organic matter, etc., will tend to decrease stability.

In pilot plant studies the decomposition of persulfate ion in 2M HNO_3 (silver free) followed a first-order rate law with a half-life of 11 to 12 days when stored at room temperature in either glass bottles or stainless steel tanks. The results, plotted in Figure IV-117, indicate that the decomposition rate is independent of the cation associated with the persulfate ion. The rate constant calculated from these data is $4 \times 10^{-5} \text{ min}^{-1}$, a value in agreement with published results for similar conditions⁽³⁰⁾.

Finally, an aqueous solution of $\text{Na}_2\text{S}_2\text{O}_8$, saturated at room temperature, has an initial pH of about 3.5. Hydrolysis according to the reaction

occurs with formation of acid and a drop in pH.

FIGURE IV-117

Persulfate Stability in Silver-Free 1CX
(Source of Data: BNWL-173)

3.2 Silver Nitrate

3.2.1 Physical Properties⁽³¹⁾

Formula	AgNO_3
Formula Weight	169.89
Appearance	Colorless rhombic crystals
Specific Gravity	4.352 (19 C)
Melting Point	212 C
Solubility in water:	

<u>Temperature,</u> <u>°C</u>	<u>Grams AgNO_3 per</u> <u>100 grams H_2O</u>
0	122
20	222
40	376
60	525
80	669
100	952
120	1900

3.2.2 Chemical Properties

Silver nitrate prepared by crystallization from aqueous solution has a neutral reaction. The salt and its solutions appear not to be sensitive to light in the absence of organic matter. When heated above its melting point, it decomposes, giving first AgNO_2 and oxygen, and finally silver and oxides of nitrogen.

The role of silver ion as a catalyst in oxidation of Ce(III) to Ce(IV) with $\text{Na}_2\text{S}_2\text{O}_8$ has been referred to in Section C 3.5.3.

3.3 Hydrogen Peroxide

3.3.1 Physical Properties⁽³²⁾

Since 100 percent H_2O_2 is not usually available or readily prepared, physical constants of aqueous solutions are of greater practical value than those of pure H_2O_2 . Selected properties for 0 to 50 percent H_2O_2 solutions are tabulated in Table IV-68; a more extensive listing is given by Schumb et. al.⁽³³⁾.

TABLE IV-68
SELECTED PHYSICAL PROPERTIES OF AQUEOUS HYDROGEN PEROXIDE SOLUTIONS
(Source of Data: Schumb, et.al. Hydrogen Peroxide)

Density at 20°C			Refractive Index		Viscosity at 20°C		Boiling Point 760 mm		Surface Tension at 25°C		Heat of Decomposition at 25°C and 1 atm.	
M	wt%	Density	wt%	n _D ²⁰	wt%	cP	wt%	C	wt%	dynes/cm	wt%	Kcal
H ₂ O ₂	H ₂ O ₂		H ₂ O ₂		H ₂ O ₂		H ₂ O ₂		H ₂ O ₂		H ₂ O ₂	gm-mole H ₂ O ₂
0.0	0.0	0.998	0.0	1.333	0.0	1.005	0.0	100.0	0.0	72.75	0.0	-22.62
3.04	10.	1.033	10.1	1.339	8.68	1.011	--	--	--	--	10.	-22.63
6.31	20.	1.071	20.	1.346	19.06	1.045	17.3	103.0	17.05	73.41	20.	-22.65
9.75	30.	1.111	30.1	1.353	37.33	1.120	32.0	106.9	26.31	74.12	30.	-22.68
12.3	40.	1.153	40.0	1.360	42.72	1.140	44.7	111.5	37.33	74.67	40.	-22.73
17.6	50.	1.196	50.1	1.367	49.05	1.170	55.7	116.7	49.76	75.68	50.	-22.80

3.3.2 Chemical Properties

Hydrogen peroxide acts both as an oxidizing and as a reducing agent. In general, substances with lower oxidation potential than H₂O₂ are readily oxidized, and substances with higher oxidation potential are readily reduced.

Hydrogen peroxide is used as an oxidizing agent with a large number of organic compounds⁽³⁴⁾. For example, amines are oxidized to amine oxides, certain alcohols to aldehydes, and, under proper conditions, carboxylic acids to carbon dioxide and water. It is this last reaction with oxalic and citric acids that is of most importance to B-Plant operations (Sections E 8 and C 4.3.5).

3.3.3 Stability

The stability of H₂O₂ depends upon the degree to which it has been purified. Schumb reports the decomposition of highly purified, unstabilized, concentrated H₂O₂ to be as low as 0.0008 to 0.00002% per hour at 50 C⁽³³⁾. Several factors seem to influence the decomposition of H₂O₂, the most important of which are: 1) temperature, 2) trace catalysis of certain cations, 3) certain active surfaces, 4) suspended matter, such as dust particles, 5) pH, and 6) radiation.

The heterogenous decomposition of H₂O₂ by a large number of surfaces is well known. Finely divided metals, such as silver, all the platinum group metals and their oxides, mercury, manganese, and its oxides, as well as activated charcoal decompose H₂O₂ very rapidly and completely. The most effective catalyst in this group is colloidal osmium, which catalyzes the decomposition in concentrations as low as 9 x 10⁻¹¹ grams per cu. cm.

Hydroxide ions cause rapid decomposition of H₂O₂. The effect of pH on the decomposition of H₂O₂ has been studied by Schumb⁽³³⁾.

3.4 Ferrous Sulfamate

3.4.1 Physical Properties⁽⁴⁾

Formula	$\text{Fe}(\text{SO}_3\text{NH}_2)_2$
Formula Weight	248.03
Appearance	2.5M solution is blue-green ⁽³⁵⁾
Melting Point	135 C ⁽³⁶⁾
Solubility	The saturation concentration in water is approximately 3.6 to 3.8M at 25 C.

The anhydrous salt is highly deliquescent and is believed to absorb 5 molecules of water of hydration⁽³⁷⁾.

3.4.2 Reactions and Stability

Ferrous sulfamate is employed in the D2EHPA extraction recovery of neptunium from PAS solution and is used to reduce Np(V) to the extractable Np(IV) state (see Section E 3).

High pH contributes to the stability of sulfamate ion towards hydrolysis, while low pH is necessary for the stability of Fe(II) towards air oxidation and consequently precipitation. The stability of a ferrous sulfamate solution toward precipitation of Fe(III) is satisfactory upon maintaining the pH of the solution at 2 or slightly less with a 2 to 3% excess of sulfamic acid⁽³⁵⁾. The over-all stability of a ferrous sulfamate solution maintained at a pH of 2 in a vessel containing an inert-gas blanket is limited by the rate of hydrolysis of sulfamate ion. This rate is approximately 0.1% per day at 25 C and increases to over 4% per hour at 80 C.

Fe(II) is autocatalytically oxidized to Fe(III) by HNO_3 . The oxidation mechanism involves HNO_2 , the destruction of which prevents the autocatalytic reaction. Sulfamate ion reacts rapidly and completely with nitrite ion according to the reaction⁽³⁸⁾:

Hydrazine (Section H 3.5) is also used in the D2EHPA neptunium extraction process to destroy nitrite.

3.5 Hydrazine

3.5.1 Physical Properties

For use in Hanford separation plants hydrazine is purchased as a 35 percent aqueous solution. Selected physical properties of this solution are listed below⁽³⁹⁾:

Formula	$\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$
Hydrazine Molarity in Solution	11.1
Appearance	Colorless liquid
Boiling Point	109.7 C (755.5 mm)
Melting Point	-63 C
Specific Gravity	1.02 (30 C)
Viscosity at 30 C	1.0149 centipoises
Solubility in water	Infinite
Freezing Point	-63.5 C
Flash Point	None
Fire Point	None

High concentrations of hydrazine can be ignited but aqueous solutions containing 40 percent N_2H_4 or less have no flash point.

3.5.2 Chemical Properties

Hydrazine is derived from ammonia by the substitution of an NH_2 group for a hydrogen. It forms two series of salts that may be represented by the formulas: $\text{N}_2\text{H}_4 \cdot \text{HA}$ and $\text{N}_2\text{H}_4 \cdot 2\text{HA}$. Its monoacid salts, characterized by the ion (N_2H_5^+), are correctly designated as hydrazonium (hydrazinium) salts.

Hydrazine is a basic substance which exhibits marked ability to act as an electron-pair donor to form coordination compounds. In aqueous solution N_2H_4 acts primarily as a monoacid base; $K_b = 10^{-6}$ at 25 C⁽⁴⁰⁾.

Hydrazine is also a strong reducing reagent as indicated by a potential of 0.23 volt for the couple⁽⁴¹⁾:

Hydrazine is thus capable of reducing metallic ions such as copper, silver, gold, and platinum to the elemental state. The standard oxidation potential for the Np(IV) - Np(V) couple,

is $E^{\circ} = -0.739$ volt⁽⁴¹⁾. Thus, thermodynamically N_2H_4 is capable of reducing Np(V) to Np(IV). The rate of N_2H_4 reduction of Np(V) to Np(IV) appears to be considerably slower than the rate with ferrous sulfamate, however (Section H 3.3 and Reference 42). In the D2EHPA neptunium recovery process (Section E) a mixture of ferrous sulfamate and N_2H_4 is used to adjust Np(V) to Np(IV) in Purex Acid Sludge solution. The primary role of N_2H_4 is to react with nitrite ion in the PAS solution according to the reaction:

and thereby prevent nitrite-catalyzed HNO_3 oxidation of Fe(II).

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