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ATLANTIC RICHFIELD HANFORD COMPANY
SEMIANNUAL REPORT
02 PROCESS DEVELOPMENT
NOVEMBER 1, 1972 THROUGH APRIL 30, 1973

Edited by
H. H. Hopkins, Jr.

Research and Development Department
Chemical Processing Division

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TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	3
SUMMARY AND HIGHLIGHTS	5
PROCESS DEVELOPMENT PROGRESS	9
PLUTONIUM SCRAP PROCESSING	9
Dissolution Capability	9
Plutonium Oxide Dissolution	9
Leaching Plutonium from Soil	10
Characterization of Covered Trench Soil Samples	11
Solvent Extraction and Ion Exchange	13
Solvent Quality Improvement	13
Solvent Cleanup with Macroreticular Resin	15
Radiolysis Resistant Solvents	16
Amine Solvent Extraction of Plutonium	18
Separation of Plutonium and Thorium	19
Anion Exchange Recovery of Plutonium from Contaminated Soil	20
Separation of Americium	22
Incineration Capability	24
Wet Oxidation of Plutonium Scrap	24
Fused Salt Alternatives	25
Instrumentation Improvement	27
In-Canyon Inventory Monitor	27
WASTE MANAGEMENT	29
Solidification and Encapsulation	29

TABLE OF CONTENTS (Contd)

	<u>Page</u>
Concentration of Nonboiling Wastes	29
Conversion to Stabilized Salt Cake	30
Characterization of Waste Tank Sludge	31
Solidification by the Aqueous Silicate Process	32
Corrosion Studies	33
Cesium Purification	36
Strontium Purification	38
Barium-Strontium Separation	39
Public Protection Assurance	41
Sorting and Assay Instrumentation	41
Airborne Release of Radioactive Particles	42
Radionuclide Transport Model	46
Field Measurement Methods	48
Soil-Waste Reactions	50
Actinides on Sediments	51
Behavior of Waste Radionuclides in Soil-Plant Systems	52
Uptake of Radionuclides by Goldfish and Ducks from Aquatic Biota and Sediments	55
REFERENCES	57
DISTRIBUTION	59

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INTRODUCTION

This document presents summary statements of the objectives, prior work, current accomplishments, evaluations, and future plans for the various tasks performed with 02 Program process development funds. The Research and Development Department of the Atlantic Richfield Hanford Company has programmatic responsibility for 02 Program process development. A number of the tasks are performed by Battelle Pacific Northwest Laboratories (BNW) with sponsored funds. This work is done for the U. S. Atomic Energy Commission's Division of Production and Material Management.

A discussion of accomplishments partially supported by process technology funds is included. Some development activities have matured, thus they have been moved from process development to process technology funding. Those items which continue to contribute to process development objectives are included in this report. Studies supported by PT funds are indicated by an asterisk and footnote.

The "Project Managers" listed at the beginning of each summary statement are those persons with budgetary responsibility, while those listed as "Principal Investigators" are responsible for project technical direction, evaluation, and reporting.

This report continues the same organizational changes that were introduced last period. The first section (formerly titled Basic Production) has been consolidated as "Plutonium Scrap Processing." This grouping of work comes under AEC Budget Activity 02 50 09 02 0.

The second section, now called "Waste Management," includes two subdivisions. The first, "Solidification and Encapsulation," contains those studies supporting final solidification of wastes in the tanks and those activities supporting fission product fractionization and encapsulation. The second subdivision, "Public Protection Assurance," includes studies to assure that the offsite public is not exposed to harmful effects of radioactive and other hazardous materials resulting from 200 Area operations. (The former title, "Environmental and Regulatory Technology," has been dropped.) These two subdivisions are supported under AEC Budget Activity 02 50 09 11 0.

A financial summary follows:

PROCESS DEVELOPMENT BUDGET SUMMARY
(Thousands of Dollars)

	<u>FY 1973</u>	<u>FY 1974</u>	<u>FY 1975</u>
Plutonium Scrap Processing (02 50 09 02 0)	192	205	202
Waste Management (02 50 09 11 0)			
Solidification and Encapsulation	498	401	404
Public Protection Assurance	<u>374</u>	<u>159</u>	<u>159</u>
Total	1064	765	765

This report continues a series of semiannual progress reports. References to summary reports related to the past two years' activities and the corresponding budget documents are presented under REFERENCES.

The Battelle Pacific Northwest Laboratories issues monthly reports including discussions on many of the topics discussed in this semiannual report. The reports covering this time period are listed in references 5 through 10, page 57.

SUMMARY AND HIGHLIGHTS

PLUTONIUM SCRAP PROCESSING

Process development tasks under this title are designed to establish the technology required to fulfill Hanford's plutonium scrap processing responsibilities. The general objectives include improved processing capability, improved measurements, reduced product losses, and reduced operating costs.

Dissolution Capability

The kinetics of dissolution of powdered plutonium oxide (PuO_2) in nitric-hydrofluoric acid mixtures are being studied in order to improve oxide dissolution rates. The dissolution rate appeared to be controlled by diffusion of fluoride through an unreactive layer on the surface.

New samples taken from the Z-9 covered trench showed the presence of a thin concentrated plutonium surface layer. ✓

Techniques were developed for examining the properties of sediments and the plutonium distribution from soil cores in the upper two feet of Z-9 covered trench soil.

Solvent Extraction and Ion Exchange

Further testing of solvent cleanup shows that either diazomethane addition or iron (ferric) scavenging will counteract dibutyl phosphate. ✓

Macroreticular resin was successfully used to clean up the tributyl phosphate (TBP) solvent during a process test at Z Plant. ✓

Benzene halide diluents with TBP extractant yield a solvent that has superior resistance to radiation damage than existing TBP-CCl_4 solvent. Physical properties and distribution coefficients of TBP in benzene halide diluent are similar to those of TBP-CCl_4 so that substitution in existing solvent extraction facilities may be considered.

Mixer-settler runs and irradiation tests continue to indicate that a secondary amine solvent (Amberlite LA-2)^R is a promising replacement for TBP in plutonium recovery operations.

Di-sec-butyl phenylphosphonate (DSBPP) in CCl_4 preferentially extracts plutonium from plutonium(IV)-thorium solutions. Hydroxylamine effectively strips plutonium(III) from DSBPP solvents. Flowsheets were proposed.

^R Trade Name - Rohm and Haas Company

SUMMARY AND HIGHLIGHTS (Contd)

Recovery of plutonium from crib soil leach liquors may be possible with weak-base macroreticular resins. Plutonium absorption and elution rate studies indicate that the anion exchange process may be operated as efficiently at 25° C as it has previously been operated at 60° C.

A special purification procedure was developed for the high efficiency bidentate extractant under test for americium removal.

Incineration Capability

Tests of wet oxidation processes are promising. Corrosion problems must be solved.

In tests of a fusion process for incinerator ash, use of NaOH-Na₂O₂ salt mixture in mild steel cans requires stirring of the molten salt mixture to prevent excessive localized corrosion.

Instrumentation Improvement

Development of the in-canyon inventory monitor is pending background measurements with actual plutonium samples.

WASTE MANAGEMENT

This title covers those activities supporting the attainment of Hanford Waste Management Program objectives. Sections are included on "Solidification and Encapsulation," and "Public Protection Assurance." The new category "Public Protection Assurance" combines in one section those studies aimed at providing technology to assure that the offsite public is not exposed to harmful effects from radioactive and other hazardous materials resulting from Hanford 200 Area operations.

Solidification and Encapsulation

The concentration capability of in-tank solidification (ITS) heaters can be increased by partial neutralization of ITS liquors with nitric or sulfuric acid. Scaling of heat surfaces has not been a problem in laboratory tests.

The solid mass formed by phosphoric acid addition to fission product wastes contained up to 60 weight percent water. The hydrated phosphate solids have a low melting point.

Methods for characterizing waste tank sludge have been developed and await the receipt of actual plant salt cake samples.

Bentonite clay reacted with ITS recycle waste to fix the ¹³⁷Cs in a solid phase.

SUMMARY AND HIGHLIGHTS (Contd.)

Tests were made of the effect of partial neutralization on the corrosiveness of simulated high-level solidified waste to carbon steel. Lowering of the caustic content effectively reduced the corrosion rate of the resulting solids.

Tests of the corrosion of 304L stainless steel under simulated conditions of the vacuum crystallizer indicate a corrosion rate less than 10 mils per year.

A draft of a document, "Cesium Purification with Zeolon-900 Cation Exchanger," has been completed.

Refinement of the strontium purification flowsheet indicates that excellent strontium-calcium separation is possible with a reduction in sulfate usage and a reduction in overall waste volume. Preliminary laboratory tests indicate that a barium DF of five can be obtained with a strontium loss of two percent.

Strontium fluoride precipitation tests showed that the separation of barium from strontium during fluoride precipitation of strontium is not governed by the solubility product constants of SrF_2 and BaF_2 . The barium coprecipitates with strontium fluoride and the amount of barium left in solution is less than would be expected from the solubility product of pure barium fluoride.

Public Protection Assurance

The Automatic Radioactive Inventory System (ARIS) was adapted to provide rapid analysis of gamma emitters as well as the analysis of beta-emitting isotopes.

Towers were erected, samplers installed, and background experiments were conducted in studies of radioactive particle resuspension and transport from the U Pond and from the contaminated BC area.

A computer model, which traces the paths of particles using wind fields determined from several meteorological stations, was developed and is under verification.

Data from studies of airborne release of radioactive particles in accidents involving gasoline fires were compiled.

Reports describing the mathematical models developed to date in the Radionuclide Transport Model Tasks were written, reviewed and are in a final draft stage.

For the Field Measurement Methods Task, draft reports describing the methods and techniques developed and data collected to date were written, reviewed and are in a final draft stage.

SUMMARY AND HIGHLIGHTS (Contd)

For the Soil-Waste Reaction Task, draft reports describing the laboratory experiments and measurement techniques developed to date were written, reviewed, and are in a final draft stage.

The leachability of plutonium from Z-9 covered trench soil varies with depth. Part of the plutonium is present as an organic soluble complexed species.

Studies to date have revealed that goldfish do not accumulate body burdens of radioactivity high enough to be of consequence for possible transmittal through food-webs to higher consumers, including man. There is both an areal and depth nonuniformity in radionuclide concentrations in the sediments.

Plant uptake of plutonium into shoots is increased by chelating agents. Root-to-shoot uptake ratios were measured as a function of chelating agent. Increased plant uptake of actinides is partly due to increased solubility in soil solution.

PROCESS DEVELOPMENT PROGRESS

PLUTONIUM SCRAP PROCESSING

These process development tasks are designed to establish the technology required to fulfill Hanford's plutonium scrap processing responsibilities. The general objectives include improved processing capability, operating safety, lower product losses, and reduced operating costs.

Dissolution CapabilityPlutonium Oxide Dissolution

Project Manager: M. H. Campbell
Principal Investigator: G. S. Barney

Objective and Scope

The purpose is to improve the recovery of plutonium from scrap based on an understanding of the behavior of plutonium dioxide (PuO_2) in nitric-hydrofluoric acid mixtures.

Prior Work

Preliminary studies revealed that a faster dissolution rate could be obtained with rapid stirring, thus liquid-phase diffusion was important and in all remaining experiments the oxide-solvent mixture was rapidly stirred. The rate of dissolution also increased as the oxide-to-acid ratios were increased. The initial rate (at $t = 0$ sec) was found to be proportional to the surface area of the oxide; however, this relationship did not hold as dissolution proceeded.

Progress During Report Period

The kinetics of dissolution of powdered PuO_2 in nitric-hydrofluoric acid mixtures were determined. The dissolution rate of PuO_2 appeared to be controlled by diffusion of undissociated hydrofluoric acid (HF) through an unreactive layer on the surface of the solid PuO_2 . The thickness of this layer increases as the reaction progresses and rapidly slows dissolution.

Approximately the first 20 percent of the dissolution can be described by the parabolic rate law $[\text{Pu}] = Kt^{1/2}$. The effect of dissolution variables on K can be summarized

$$K = k_1 a_{\text{HF}}^{1/2} e^{-(E_a/RT)}$$

where k_1 is the rate constant, a_{HF} is the activity of undissociated HF, W is the PuO_2 /solvent ratio, and E_a is the apparent activation energy. The parabolic rate law was observed for PuO_2 with both uniform and nonuniform particle sizes.

PLUTONIUM SCRAP PROCESSING (Contd)

Fluoride was removed from solution during the dissolution by either adsorption on oxide surfaces or formation of insoluble plutonium fluoride compounds. The large decrease of $[\text{HF}]_{\text{total}}$ at higher initial fluoride concentration is due to precipitation of PuF_4 . The removal of fluoride from solution at low $[\text{HF}]_{\text{total}}$ considerably slows the dissolution. This observation lends proof to the premise that the rate-controlling step in the dissolution is diffusion of HF from solution to the PuO_2 surface.

Evaluation of Effort

Work to date has revealed the initial mechanism of plutonium dissolution. Further understanding of these mechanisms is expected to provide a basis for correctly designing dissolution processes.

Future Work

Equations will be developed which completely describe the dissolution of PuO_2 . The effect of elevated temperature and the effect of cerium on the dissolution rate will be determined.

Reports Issued

ARH-SA-148, January 1973, G. S. Barney, "Plutonium Dioxide Dissolution in Nitric/Hydrofluoric Acid Mixtures - Kinetics and Mechanisms."

Leaching Plutonium from Soil*

Project Managers:	L. M. Knights M. H. Campbell
Principal Investigators:	N. C. Foster V. L. Schuelein

Objective and Scope

Develop a process compatible with Plutonium Reclamation Facility equipment for leaching plutonium from Z-9 covered trench soil.

Prior Work

Soil leaching was effective with a mixture of nitric and hydrofluoric acids at 100°C . Two or more contacts yielded greater than 95 percent plutonium recovery. After dilution of three parts leach solution with three parts water and with four parts of

* Supported by PT.

PLUTONIUM SCRAP PROCESSING (Contd)

monobasic aluminum nitrate solution, solvent extraction tests indicated no process interference due to silicon.

Progress During Report Period

A series of new samples was taken to update the status of the Z-9 covered trench compared with the results from previous samples taken in 1963. Samples were carefully handled, photographed, and gamma-counted to establish plutonium levels. There was clear evidence of a thin sludge layer containing up to 15 grams plutonium per liter at the surface of the soil.

Laboratory-scale studies showed that a static column dissolver (with recirculated dissolver solution) would yield better plutonium recovery than a batch dissolver.

Evaluation of Effort

The new samples which were taken late in the report period provided a more accurate and complete description of Z-9 soil. These new data are helping to confirm projected processing flowsheets.

Future Work

Leaching studies will be performed on the new samples. Leaching solutions will be analyzed to identify impurities which could interfere with purification of plutonium. Recovery of plutonium from the sludge on top of the crib will be investigated. Column studies will be completed and a recommendation made for a leaching procedure.

Reports Issued

None.

Characterization of Covered Trench Soil Samples

Project Managers:	R. E. Isaacson D. B. Cearlock (BNW)
Principal Investigators:	T. R. McKenzie L. L. Ames (BNW)

Objective and Scope

The objective of this work is to characterize the mineralogy and rock types comprising the soils found in the 216-Z-9 covered trench and to determine the relationships, if any, between plutonium distribution and soil mineralogy.

PLUTONIUM SCRAP PROCESSING (Contd)Prior Work

None. Present work began on February 5, 1973.

Progress During Report Period

Uncontaminated soil cores taken alongside of the Z-9 covered trench were used to determine the mineralogy and rock types which would be encountered in the contaminated soil rock fragments. The one-inch diameter, uncontaminated soil cores were subjected to the same techniques to be used in the investigations of the contaminated, plastic-impregnated soil cores. Briefly, these techniques included cutting, grinding, and polishing of the plastic-impregnated, uncontaminated soil cores in preparation for optical examination with photomicrographs.

After the optical examination, the core mounts were coated with a thin layer of conducting gold and examined by an electron microprobe. From the microprobe data mineral phase distributions within soil rock fragments were obtained, as well as chemical analyses of specific minerals contained in the soil rock fragments. From these data, several randomly chosen soil rock fragments were classified as to rock types. The majority of the rock fragments comprising the uncontaminated soil were metamorphic in origin and contained such minerals as spene, albite, microcline, quartz, garnet, chlorite, and actinolite. About 30 percent of the rock fragments comprising the uncontaminated soil cores were of igneous origin and chiefly basaltic in rock type. The basaltic rock types contained augite and pigeonite, labrodorite, and andesine feldspars, ilmenite, and apatite.

The metamorphic mineral assemblages were typical of the greenschist facies (390° C to 530° C) represented by the rock of the Precambrian to Cambrian Belt Series found in Northern Idaho, Montana, part of Northeastern Washington and Canada. Similar metamorphic rocks occur in Okanogan County, Washington. The metamorphic rocks, then, were transported south by the ancestral Columbia River and deposited in their present locations. Basaltic-type rocks, on the other hand, are locally abundant.

Two contaminated soil cores, each two feet by four inches from Z-9 covered trench surface soils were available in March. Several one-inch diameter cores of these were taken in six-inch sections. These small cores were dried and vacuum-impregnated with plastic and sawed to produce mounts to show vertical plutonium distribution in relation to soil mineralogy. Grinding and polishing of these mounts is presently under way.

PLUTONIUM SCRAP PROCESSING (Contd)Evaluation of Effort

Progress has been made toward the objectives in that techniques have been developed for examination of soil cores. Determining the relationship between rock structure and plutonium distribution lies ahead.

Future Work

Mounts will be prepared from the contaminated soil, and optical and electron microprobe examination of these mounts will be carried out to identify the plutonium distribution within the core mounts relative to the soil mineralogy. Where possible, the plutonium compounds will be identified and the soil mineral-plutonium relationship quantified by microprobe chemical analyses.

Reports Issued

None.

Solvent Extraction and Ion ExchangeSolvent Quality Improvement

Project Managers:	R. E. Isaacson H. H. Van Tuyl (BNW)
Principal Investigator:	E. C. Martin (BNW)

Objective and Scope

The objective of this work is to determine techniques for the improvement of solvent quality for the Plutonium Reclamation Facility.

The presence of degraded solvent containing dibutyl phosphate (DBP) results in product losses, extensive solvent cleanup, poor decontamination factors, increased radioactivity in the waste (aqueous wash water), shortened life of solvent system, and reduced plant capacity because of column flooding. The objective of this work is to find a simple, economic and effective solution to these problems.

Prior Work

Investigations attempted the inhibition of DBP formation from TBP by the addition of potential suppressants such as iodine, urea and urea derivatives. The suppressants examined did not materially reduce TBP degradation in a radiation (gamma) environment.

PLUTONIUM SCRAP PROCESSING (Contd)

Diazomethane (CH_2N_2) had already been employed as a methylating agent for DBP as an analytical technique. The use of this material was extended as a solution for these problems.

Progress During Report Period

The problem of degraded solvent was attacked from two directions: the use of diazomethane as an esterifying agent for DBP and the addition of ferric ion as a DBP precipitant.

The addition of diazomethane to DBP-containing solutions results in the formation of a new extracting species, dibutylmethyl phosphate, which appears to have about the same plutonium extracting capacity as TBP.

The only byproduct in this reaction is nitrogen gas.

Further laboratory-scale demonstrations were made. Two samples of solvent (20 percent TBP in CCl_4 contaminated with 0.02M DBP) were contacted with a feed solution of 1M ANN, 2M HNO_3 , spiked with 1 g/l plutonium. One of the solutions was treated with CH_2N_2 ; the second untreated. Plutonium was stripped from the organic solution using 0.15M HNO_3 and 0.25M hydrazine nitrate. After three strips, the CH_2N_2 -treated solution showed a 1400-fold improvement in Pu stripping. This indicates virtually complete conversion of DBP to a triester.

In a second series of experiments similar to the above, ferric ion was added to one of the organic solutions. The addition of this ion caused a precipitate with the suggested formula of $\text{Fe}(\text{DBP})_3$. The precipitate was removed from the solution before contacting with the feed solution. The Pu stripping from the organic solution showed improvement in the same range (1400-fold) as with the CH_2N_2 -treated solution. This indicates that the DBP must have been virtually completely precipitated from the solution.

Evaluation of Effort

These results offer solutions to the problem of solvent degradation. Diazomethane can restore the degraded material to a usable extractant. Alternately, ferric ion will remove the TBP degradation products leaving the solution slightly extractant-deficient.

Diazomethane is a toxic, low-boiling material, unstable in high concentrations. However, in the dilute concentrations proposed in this research project, the material has proven stable. A plant test would substantiate these claims.

PLUTONIUM SCRAP PROCESSING (Contd)Future Work

Generation of diazomethane in an inert solvent (CH_2Cl_2) will be undertaken. Present synthesis requires an ethyl ether solvent. The change of solvent would result in a more acceptable reagent.

The stability of the dibutylmethyl phosphate will be examined over a range of operating conditions. Extension of the use of diazomethane to other solvent systems, such as used in Purex, will be examined.

Reports Issued

Two invention reports have been submitted to the Atomic Energy Commission:

ARH-IR-190, L. E. Bruns, E. C. Martin, "Ferric Ion as an Organic Impurity Scavenging Agent in a Scrap Recovery Solvent System"

BN-IR-277, E. C. Martin, L. E. Bruns, "Improvement in Uranium-Plutonium Extraction Process, An Invention Using Diazomethane as an In Situ Reagent for Restoring Uranium and Plutonium Degraded Extracting Solutions"

Solvent Cleanup with Macroreticular Resin

Project Managers:	L. M. Knights M. H. Campbell
Principal Investigator:	W. W. Schulz

Objective and Scope

Develop solvent treatment processes which will significantly reduce the volume of radioactive aqueous waste generated by present solvent wash processes.

Prior Work

The applicability of Amberlyst A-26 (trade name, Rohm and Haas Company) macroreticular anion exchange resin to treat solvents used in Purex and Z Plants was demonstrated. Amberlyst A-26 resin removed dibutyl phosphoric acid and fission product activity from Purex process solvent, thereby eliminating one carbonate wash step and reducing the volume of stored liquid waste. This resin also removed plutonium and dibutyl phosphoric acid from the Plutonium Reclamation solvent, 20 percent TBP in CCl_4 , thus extending organic life and reducing discards. Cleanup of the 30 percent DBBP in CCl_4 used in the Z Plant continuous waste treatment process was demonstrated.

PLUTONIUM SCRAP PROCESSING (Contd)

Incineration of the resin was readily accomplished, yielding only a small volume of ash.

Progress During Report Period

An alternate means of resin disposal was demonstrated using the procedure reported by Lerch and Cooley⁽¹⁾. Resin was carbonized by sulfuric acid (H_2SO_4) and oxidized to carbon dioxide and carbon monoxide by nitric acid. The plutonium from the resin was in the final H_2SO_4 solution. The effectiveness of Amberlyst A-26 resin in improving organic quality was successfully demonstrated in a process test at the Z Plant Plutonium Reclamation facilities. The treated TBP was essentially identical to fresh organic. The flowsheet found successful in the laboratory was completely verified on a plant scale.

Evaluation of Effort

The ion exchange process for cleaning organic was successfully demonstrated on a plant scale and shows promise for other applications.

Future Work

Application to the purification of other process solvents as well as experimental solvents will be tested.

Reports Issued

None.

Radiolysis-Resistant Solvents

Project Managers:	L. M. Knights M. H. Campbell
Principal Investigators:	G. S. Barney R. A. Hamilton

Objective and Scope

The objective is to develop an optimum solvent composition for plutonium solvent extraction. The approach is to compare radiolysis of TBP- CCl_4 with that of other plutonium extractants and other diluents.

- (1) HEDL-TME 73-22, April 1973, R. E. Lerch and C. R. Cooley, "Treatment of Low-Level Alpha-Contaminated Solid Waste by Acid Digestion"

PLUTONIUM SCRAP PROCESSING (Contd)Prior Work

Benzene halide diluents for TBP offered greater resistance to radiation degradation than CCl_4 . These diluents possessed the attractive features of high density and high flash points; thus, they could be substituted for CCl_4 . Trichlorobenzene appeared to be the most likely benzene halide to replace CCl_4 because of its low cost.

Progress During Report Period

Physical and chemical property studies were performed with radiolysis-resistant TBP solvent systems. Physical properties were determined for 20 percent TBP in bromobenzene or 1,2,4-trichlorobenzene. Bromobenzene has a flash point of 52°C , whereas the more attractive 1,2,4-trichlorobenzene has a 110°C flash point.

Distribution coefficients for plutonium between 20 percent TBP in the alternate diluents and aqueous phases of differing acidities were determined. Distribution coefficients were slightly higher for TBP-bromobenzene than for TBP-1,2,4-trichlorobenzene. Both distribution coefficients were somewhat lower than the plutonium distribution coefficients in TBP- CCl_4 solvent.

Evaluation of Effort

Extractant-diluent combinations have been found which are less susceptible to radiation damage than TBP- CCl_4 . Other properties are essentially similar so that replacement of TBP- CCl_4 could occur without great difficulty. Further search for improved solvents appears warranted.

Future Work

Other potential diluents for TBP will be characterized for radiation stability and plutonium distribution coefficients. In particular, chloroethylene diluents are suspected to possess several advantages over both TBP- CCl_4 and TBP-benzene halide solvents.

Reports Issued

ARH-2785, April 1973, R. A. Hamilton, "Physical and Chemical Studies of Radiolysis-Resistant Tributyl Phosphate Solvent Systems for the 880 Process"

PLUTONIUM SCRAP PROCESSING (Contd)Amine Solvent Extraction of Plutonium

Project Managers:	L. M. Knights M. H. Campbell
Principal Investigators:	W. W. Schulz D. G. Bouse

Objective and Scope

The objective is to improve solvent extraction performance in the Plutonium Reclamation facilities while decreasing costs by development of an amine extraction flowsheet to replace the currently used TBP flowsheet.

Prior Work

Equilibrium data were obtained from the distribution of plutonium between aqueous HNO_3 - $\text{Al}(\text{NO}_3)_3$ solutions and CCl_4 solutions of Amberlite LA-2[®], a secondary amine commercially available from the Rohm and Haas Company. A conceptual reflux-type flowsheet using 30 percent LA-2 in CCl_4 as the extractant was devised and satisfactorily demonstrated in one miniature mixer-settler run. In this run, plutonium was quantitatively stripped by 0.25M HNO_3 solution even though the plutonium-loaded amine had aged two weeks prior to stripping.

Progress During Report Period

The secondary amine solvent, 30 volume percent Amberlite LA-2 in CCl_4 , showed preferential extraction of plutonium from uranium. It also possesses excellent radiolytic and chemical stability. Plutonium distribution ratios for LA-2 solvents irradiated to doses as high as 27 watt hours per liter were comparable to those of unirradiated solvent. A 30 percent LA-2/ CCl_4 solvent was contacted one week with a synthetic feed containing 0.025M NaNO_2 with no measurable effect on the solvent. Inasmuch as nitrous acid (HNO_2) is known to react with secondary amine to produce nitrosoamines, small amounts of urea may need to be added to the scrub stream in the extraction column to destroy any radiolytically generated HNO_2 .

Mixer-settler runs verified the importance of high aqueous feed nitrate concentration to the extraction of plutonium by LA-2. Optimum plutonium extraction occurred with feed nitrate molarities of 6.5.

PLUTONIUM SCRAP PROCESSING (Contd)

<u>Feed Nitrate Molarity</u>	<u>Plutonium Extracted</u>
5.5	93.0%
6.0	98.4%
6.25	99.4%
6.50	99.94%

Evaluation of Effort

The advantages of Amberlite LA-2 over TBP were confirmed. Initial findings have encouraged a more thorough evaluation of this new solvent.

Future Work

Alpha radiolysis of 30 percent LA-2/CCl₄ will be extended to doses as high as 100 to 200 watt hours per liter. Plutonium stripping from aged solvent will be investigated. Decontamination from various impurities will be determined. An evaluation will be made of the reaction between LA-2 and HNO₃, including the effect of urea, as well as further flowsheet tests under countercurrent conditions.

Reports Issued

None.

Separation of Plutonium and Thorium

Project Managers:	M. H. Campbell
	L. M. Knights
Principal Investigator:	W. W. Schulz

Objective and Scope

A portion of the plutonium scrap inventory includes plutonium contaminated with thorium. A solvent extraction process is needed to separate plutonium and thorium in the Plutonium Reclamation facilities.

Prior Work

Scouting studies showed that di-sec-butyl phenylphosphonate (DSBPP) preferentially extracted plutonium from plutonium(IV)-thorium solutions. Comprehensive data for equilibrium distribution of plutonium(IV) and nitric acid between 10 or 20 volume percent

PLUTONIUM SCRAP PROCESSING (Contd)

DSBPP-CCl₄ and aqueous HNO₃-Al(NO₃)₃-HF solutions were obtained. Favorable plutonium extraction coefficients were obtained with 20 volume percent DSBPP-CCl₄ and 5M HNO₃ containing aluminum nitrate added for salting strength.

Progress During the Report Period

Data for the distribution of Pu(III) between the DSBPP solvents and aqueous nitric acid-hydroxylamine nitrate solutions were obtained. Over the range of conditions studied, Pu(III) distribution ratios varied from about 1×10^{-5} to 5×10^{-3} ; these results demonstrate that hydroxylamine (NH₂OH) solutions can be used very effectively to strip plutonium from DSBPP solvents. Thus, Pu(IV) can be selectively extracted from thorium into DSBPP; subsequently the plutonium can be readily stripped by reducing it to Pu(III).

Evaluation of Effort

All equilibrium distribution data needed to prepare a study flowsheet for DSBPP separation of plutonium from thorium have now been obtained. Data accumulated to date indicate that a successful flowsheet can be prepared.

Future Work

Two conceptual flowsheets have been prepared. These will be tested under countercurrent conditions using mixer-settlers and actual thorium-contaminated scrap. Kinetics of extraction and stripping of plutonium and radiolysis of DSBPP will be studied.

Reports Issued

None.

Anion Exchange Recovery of Plutonium From Contaminated Soil

Project Managers:	M. H. Campbell L. M. Knights H. H. Van Tuyl (BNW)
Principal Investigators:	W. W. Schulz J. L. Ryan (BNW)

Objective and Scope

The objective of this study is to determine the feasibility of and develop the optimum conditions for the anion exchange purification and concentration of plutonium from nitric acid leachates of crib

PLUTONIUM SCRAP PROCESSING (Contd)

soils, particularly Z-9 covered trench soil. The feasibilities of 25° C operations and of adapting the process to continuous fluidized bed ion exchange are to be determined.

Prior Work

Work performed under "Leaching Plutonium from Soil" during the previous report period showed that the plutonium concentration of the leaching solution was too low (less than 1 g/l) to be considered for the existing solvent extraction flowsheet in the Plutonium Reclamation facilities. Recommendations were made to concentrate the leaching solution.

Progress During the Report Period

Studies were initiated to determine whether any of the anion exchange resins developed since the original work in 1958 might show improved plutonium absorption and elution kinetics. There are incentives for a process to be operated at 25° C and to be operated in fluidized bed equipment. Ion exchange resin manufacturers were contacted with requests for information on currently manufactured anion exchange resins. On the basis of the information obtained, samples of several resins were obtained. Samples of 13 resins (all nominally 20- to 50-mesh) were tested for plutonium absorption and desorption kinetics. Several of these resins show very much faster absorption rates than that of Permutit SK (which was the 20- to 50-mesh resin of choice in 1958 and was used for approximately 15 years in Purex). The two best of these, Amberlite IRA-458 and Amberlite XE-270 both show elution rates comparable to Permutit SK (which, in turn, had exhibited an exceptional elution rate compared to all other resins studied prior to 1959).

The resin showing the fastest absorption rate, IRA-458, absorbs plutonium about 2.5 times as fast at 25° C as Permutit SK does at 60° C. The absorption rate for XE-270 is about a factor of 1.4 below that for IRA-458 on a resin weight basis (about a factor of 2.5 slower on a resin volume basis).

Batch distribution tests revealed that 25- to 50-mesh XE-270 resin sorbs plutonium from 6 to 9M HNO_3 solutions almost as well as 20- to 50-mesh Dowex 21K resin, a strong-base exchanger. Column tests with the XE-270 resin are in progress to define suitable operating conditions for recovery of plutonium from simulated and actual leach liquors and to measure decontamination factors.

Very preliminary testing of the chemical stability of IRA-458 indicates that it will be satisfactorily stable to chemical attack. Measurements of physical characteristics indicate that it has a

PLUTONIUM SCRAP PROCESSING (Contd)

higher density in 7.5M HNO_3 than XE-270 (1.33 g/ml versus 1.24 g/ml); and the higher density is desirable for possible fluidized bed contactor use.

Evaluation of Effort

Initial test results are favorable in that good kinetics were found. Absorption and elution rate data indicate that with some of the anion exchange resins now available a plutonium nitrate anion exchange process can be operated efficiently at 25° C. Flowsheet details remain to be worked out.

Future Work

Future work includes column loading and elution of Amberlite IRA-458 and Amberlite XE-270 resins to verify the efficiencies predicted by kinetic data. Resin shrinkage during plutonium loading will also be determined. The optimum eluant acidity (which is known to vary with the resin) will be determined, and the maximum product concentration attainable will be determined.

Another series of column runs have been planned to study plutonium loading and elution as a function of temperature. Load-wash-elution cycles will then be conducted with simulated and actual leach liquor.

Resin stability to nitric acid attack will be evaluated. In the event that these resins show any undesirable characteristics in these studies, alternate resins will be examined.

Reports Issued

None.

Separation of Americium-241 by Bidentate Organophosphorous Solvent Extraction

Project Managers:	M. H. Campbell L. M. Knights
Principal Investigator:	W. W. Schulz

Objective and Scope

Investigate bidentate organophosphorus extractants for complete extraction of actinides from the Plutonium Reclamation facilities' waste stream. An attractive advantage appears to be the ability to recover actinides from acid streams, thus avoiding the reduction of acidity to the pH range as is now required in the current solvent extraction process.

PLUTONIUM SCRAP PROCESSING (Contd)Prior Work

An organic was sought which could extract plutonium and americium from acid waste streams and thereby negate the need to neutralize two molar acid waste to pH 1 for the current solvent extraction process. A great deal of waste volume would be eliminated because (1) cooling water which carries off the heat of neutralization to an open ditch would not be necessary, (2) the volume of feed for plutonium and americium recovery in continuous waste treatment would be reduced nearly two-fold, and (3) the final volume of waste sent to Tank Farm evaporators would be reduced more than two-fold. In addition, the chance of producing nonextractable insoluble plutonium or americium species below pH 1 will be eliminated.

Thirty percent dihexyl N,N-diethylcarbonylmethylene phosphonate (DHDECMP) in CCl_4 extracted both plutonium and americium from synthetic acid waste. Americium was selectively stripped by 0.1M HNO_3 , whereas 0.1M HNO_3 -HF completely stripped plutonium from the organic phase.

Progress During Report Period

A procedure was developed to remove a neutral, americium-bonding impurity from DHDECMP received from the manufacturer. The impurity is hydrolyzed by an eight-hour contact at 60° C with 6M nitric or hydrochloric acids. The acidic form of the impurity may then be removed by washing the solvent with 1M sodium hydroxide and passage through OH-form Amberlyst A-26 resin; however, consistent removal of all the impurities has not been attained.

Evaluation of Effort

The necessity of purifying the as-received reagent has slowed flowsheet development. However, recent emphasis on minimizing waste volumes has increased the importance of developing a DHDECMP solvent extraction process.

Future Work

Additional hydrolysis-purification experiments are planned. Distribution data to establish suitable stripping conditions for plutonium from solvent containing trace levels of impurity will be obtained. Distribution ratios for various impurity elements will also be determined.

Reports Issued

None.

PLUTONIUM SCRAP PROCESSING (Contd)Incineration CapabilityWet Oxidation of Plutonium Scrap

Project Manager: M. H. Campbell
Principal Investigators: V. L. Schuelein
J. V. Panesko

Objective and Scope

Investigate the application of wet oxidation processes to recovery of plutonium from incinerable scrap forms.

Prior Work

None.

Progress During the Report Period

Initial wet air oxidation tests were performed on contract with ZIMPRO, Inc., a subsidiary of Sterling Drug. ZIMPRO, Inc., had several years' experience with wet oxidation and possessed the elaborate pressure equipment and skilled personnel to perform scouting studies on nonradioactive scrap. Their personnel provided interpretation and quickly solved problems with an effectiveness that comes from years of experience. Thus, contract-research with an experienced firm yielded technology with a minimum of cost and time.

Wet air oxidation of a mixture of paper, rags, and polyvinyl chloride (PVC) decreased the mass from 29.2 grams solids per liter of solution to 0.1 grams solid per liter of solution (>99.6 percent solids weight reduction). The foremost problem was that hot, molten polyvinylchloride, before it oxidized or charred, was extremely corrosive to materials, attacking platinum, titanium, zirconium, and Hastelloy. The corrosion problem might be solved with the use of ceramic liners which would prevent PVC from attacking the pressure vessel.

Sulfuric acid oxidation decreased a mass of 33 grams of scrap contaminated with 3 grams of PuO_2 to 0.3 grams of solids. The plutonium was found in the H_2SO_4 solution and aqueous leaches of the solids.

Evaluation of Effort

In preliminary tests two wet oxidation processes were shown to oxidize carbonaceous material and thereby reduce the weight and

PLUTONIUM SCRAP PROCESSING (Contd)

volume of solids. For the wet air oxidation process, a satisfactory liner material and a solution disposal scheme need to be developed.

Future Work

A prototype autoclave is being ordered for cold testing, safety analysis, and installation in a glove box where wet oxidation studies can be conducted directly on plutonium-contaminated scrap. Development of liner applications will proceed. Additional studies are also planned for sulfuric acid oxidation to evaluate application to other scrap forms.

Reports Issued

None.

Fused Salt Alternatives

Project Managers:

R. E. Isaacson

H. H. Van Tuyl (BNW)

Principal Investigators:

R. E. Felt

L. E. Bruns

T. R. McKenzie

E. J. Wheelwright (BNW)

J. A. Partridge (BNW)

Objective and Scope

One objective of this project is to determine the feasibility of decomposing radioactively-contaminated combustible waste in a low-pressure molten salt system. Another objective is to develop an effective process to recover plutonium from both existing incinerator ash and any residues of the molten salt process. Investigations will include a laboratory-scale demonstration of the processes.

Prior Work

The decomposition of carbonaceous waste materials in molten salt systems was investigated utilizing two alternate processes: direct combustion in a supply of oxygen, and pyrolysis in the absence of oxygen. Eight salt systems were tested using equipment designed for recirculation of the molten salt during processing. The operating temperatures ranged from 500 to 800° C. A $\text{KNO}_3\text{-NaNO}_3$ salt proved satisfactory as an "oxidizing" salt and $\text{K}_2\text{CO}_3\text{-Li}_2\text{CO}_3\text{-NaNO}_3$ was found to be a satisfactory "inert" salt. In the pyrolysis mode of operation, using the inert carbonate salt, a residual carbon ash is produced which can be removed by filtration or air oxidation.

PLUTONIUM SCRAP PROCESSING (Contd)

The decomposition of an amount of simulated carbonaceous waste, equal in weight to the weight of the carbonate salt, was demonstrated using the pyrolysis/oxidation cycles.

The dissolution of incinerator ash by molten salts was tested as a preparatory step for the recovery of plutonium from ash. Fusion tests were performed in nickel crucibles at temperatures of 500 - 700° C and times of one to three hours. When cooled, the frozen salt buttons were dissolved in nitric acid. The best results were obtained using a peroxide system with the composition 35 g NaOH, 35 g Na₂O₂, 10 g ash.

Progress During Report Period

Fusion tests with the NaOH-Na₂O₂ salt mixture in mild steel cans have shown that stirring of the salt mixture while it is molten is necessary to prevent excessive corrosion. Tests in which the melt was kept at 600° C for one hour with no stirring resulted in corrosion of 23-26 mils of the mild steel can wall at a height corresponding to the middle of the melt. In tests in which the salt mixture was stirred the maximum corrosion was about 7-11 mils at the surface of the melt. Three methods of stirring or mixing the molten salt were investigated, and each worked equally well in preventing excessive localized corrosion of the mild steel. The methods were (1) a motor-driven stirring rod with propeller, (2) an air sparge, and (3) continuous rotation of the can at 140 rpm. The cans are 4 inches high by 2 inches in diameter, and a baffle approximately 1/2 x 3 5/8 inches was welded in the cans used for testing the third method.

Equipment has been designed and assembled for glove box demonstrations of plutonium recovery from the incinerator ash by the use of the mild steel cans as "single-use crucibles" for the fusion, followed by dissolution of the can and contents in a nitric acid dissolver system. A four-foot packed column has also been assembled for testing NO₂ removal from the dissolver off-gas by means of aqueous hydroxylamine nitrate.

Evaluation of Effort

The favorable effect of peroxide fusion upon the recovery of plutonium from incinerator ash provides a promising approach to the processing of this scrap form. The materials problem is now better understood and work on flowsheet details can follow.

Future Work

Establish flowsheet conditions for use of peroxide fusion. The feasibility of processing incinerator ash by peroxide fusion using

PLUTONIUM SCRAP PROCESSING (Contd)

regular waste cans as "single-use crucibles" will be investigated, followed by dissolution of the can and contents in a nitric acid dissolver system. Removal of NO_2 from the nitric acid dissolver off-gas stream by means of hydroxylamine nitrate will be tested. /

Reports Issued

None.

Instrumentation ImprovementIn-Canyon Inventory Monitor

Project Managers:	L. M. Knights
	J. W. Bartlett (BNW)
Principal Investigators:	M. H. Curtis
	O. H. Koski (BNW)

Objective and Scope

The objective of this study is to develop a remote monitor for assaying the plutonium inventory in the vessels and equipment within the Plutonium Reclamation canyon.

Prior Work

Prior work consisted of studies associated with telemetering devices that might be compatible with the latest technology on gamma sensing devices and electronics. Literature was surveyed, contacts made with space system personnel and vendors to determine possible setups applicable to the Plutonium Reclamation canyon.

Evaluations of vendors' products indicated that a remote system for assaying actinides should be possible.

Progress During Report Period

Work on the in-canyon counter reached a point where a re-evaluation of instrument criteria was required. A series of experiments is needed to define background conditions. Suitable plutonium samples were ordered and delivered for this purpose.

Evaluation of Effort

The initial groundwork for this activity has been completed. Measurement of actual background conditions will put this project on a firm basis.

PLUTONIUM SCRAP PROCESSING (Contd)Future Work

Test equipment will be used under conditions simulating the radiation levels from canyon vessels. Criteria for the instrument system will be rewritten and submitted to vendors.

Reports Issued

None.

WASTE MANAGEMENT

This section includes those activities supporting the attainment of Hanford Waste Management Program objectives. Sections are included on "Solidification and Encapsulation" and "Public Protection Assurance."

Solidification and Encapsulation

Concentration of Nonboiling Wastes

Project Managers:	G. L. Borsheim M. H. Campbell
Principal Investigators:	J. S. Buckingham D. J. Larkin D. A. Puryear

Objectives and Scope

Develop a process to lower the boiling point of bottom liquors from the in-tank solidification process, thus enabling existing in-tank heaters to yield additional concentration.

Prior Work

In-tank concentration of fission product nonboiling waste increases the caustic concentration of the liquid waste. Consequently the boiling point rises to ca. 120° C where the in-tank heaters cannot drive off additional water. Partial neutralization of the concentrated liquor lowers the boiling point, permitting additional concentration, and thus allowing greater volume reductions. Neutralization with nitric acid is effective. In other laboratory tests with 95 percent sulfuric acid, a neutralized solution was produced which was concentrated to almost half the volume of the original liquor.

Progress During Report Period

Scaling tests were run on ITS bottoms liquid as received and as partially neutralized with sulfuric or nitric acids. No significant scaling of heat transfer surfaces was observed.

Evaluation of Effort

Work progressed to the point that nitric acid was selected for full-scale test evaluation. However, considerable backup laboratory support remains.

Future Work

Partial neutralization will be tested and the composition of solids and supernatant liquids formed will be determined in the laboratory.

WASTE MANAGEMENT (Contd)

The effect of complete neutralization and concentration of caustic wastes using nitric and sulfuric acids will be studied. Additional scaling tests will be performed.

Reports Issued

ARH-2744 (unclassified), March 1973, J. S. Buckingham, "Composition of Saturated Supernatant Liquids and Associated Solids at Boiling Points Expected in a Vacuum Evaporator as a Function of Concentration"

Conversion to Stabilized Salt Cake

Project Managers:	G. L. Borsheim M. H. Campbell
Principal Investigators:	J. S. Buckingham D. A. Puryear J. O. Skolrud

Objective and Scope

Develop a process to complete the conversion of residual ITS liquors to a stabilized salt cake.

Prior Work

Immobilization of fission product wastes was investigated using phosphoric acid to form a solid mass. Near-optimum solids production was achieved by adding one mole of phosphoric acid to waste containing three moles of sodium hydroxide plus sodium aluminate. The use of less expensive dilute phosphoric acid (72%) required that waste solutions be more concentrated in order to achieve the same degree of solidification.

Progress During Report Period

Solids produced by the addition of phosphoric acid to caustic salt waste contain up to 60 weight percent water. The water is contained in the salt as water of hydration and as interstitial liquid held by adhesion and van der Waals forces. The measurement of pressable liquid (liquid which can be forced out by pressure) from the phosphoric acid solidified waste is an indicator of solid stability.

Since the melting point of the phosphate-solids is near 70° C, the heat generated by radioactivity could affect the stability of the solidified waste. The amount of flowable liquid which can be removed from phosphoric acid solidified waste at different temperatures is given below.

WASTE MANAGEMENT (Contd)

Temperature, ° C	25	50	60	70	80	90
Liquid removed by pressing - Wt.%	1.0	30	63	56	66	72

Evaluation of Effort

Laboratory work on phosphoric acid solidification is essentially complete. A method for measuring retained liquid is in hand.

Future Work

Investigation of processes to stabilize tank bottoms will continue.

Reports Issued

None.

Characterization of Waste Tank Sludge

Project Managers:	G. L. Borsheim
	M. H. Campbell
Principal Investigators:	J. S. Buckingham
	D. A. Dodd
	D. G. Bouse
	W. P. Metz
	D. A. Puryear

Objective and Scope

Tests need to be developed to characterize waste sludges and to assure that a stable solid form will remain after solidification completion.

Prior Work

Analytical techniques and procedures were established to measure chemical and physical properties of sludge. Techniques were developed to measure the liquid released from sludge upon pressing and also the amount of water held by the pressed sludge. Thermal conductivity measurements showed that the rate of heat transfer decreased as solids were dewatered. American Society for Testing and Materials Methods D-5 and D-217 for measuring penetration in solids were set up and tested. Equipment for receiving, sampling, and analyzing highly radioactive solids was constructed and tested.

WASTE MANAGEMENT (Contd)Progress During Report Period

A test was devised to measure the permeability of solids produced by waste solidification processes. The test consisted of removing interstitial liquid from a salt slurry in a millipore pressure filter at 25 psig. After the depth of the solid bed is measured, mother liquor similar to interstitial liquid is forced through the bed at 25 psig. The volume of liquid pressed through the solid is plotted against time and the slope of the line is taken as the rate which is expressed in terms of milliliters-minute⁻¹ cm⁻³ at 25 psig.

The ASTM Methods D-5 and D-217 for measuring penetration were found to be unsuitable when testing synthetic salt cakes. An inexpensive soil "Pocket Penetrometer" manufactured by Soil Test, Inc., has been tested on synthetic salt cakes and appears to produce valid and reproducible data.

A microcalorimeter has been set up and preliminary calibrations were established. Noise and baseline drifts interfered with the accuracy and precision of results. A new dual-point recorder and new standards have been ordered to assist in the investigation of the reasons for noise and drift.

Evaluation of Effort

Essentially all analytical procedures for salt cake are in place. The need for additional procedures may arise when actual sampling of plant salt cakes begins.

Future Work

Evaluate procedures using actual plant salt cake. Put a microcalorimeter into service to measure actual salt cake heat output.

Reports Issued

None.

Solidification by the Aqueous Silicate Process

Project Managers:	M. H. Campbell G. L. Borsheim
Principal Investigator:	G. S. Barney

Objective and Scope

Develop a process using aqueous silicate chemistry to complete solidification of radioactive waste solutions left after concentration.

WASTE MANAGEMENT (Contd)Prior Work

New project.

Progress During Report Period

Bentonite clay was mixed with ITS recycle waste and was reacted at 100° C for seven days. With clay-liquid ratios exceeding 1 gram per milliliter, 99.9 percent of the ^{137}Cs was fixed in the solid product. The ^{137}Cs leach rate was $0.03 \times 10^{-13} \text{ g/cm}^2/\text{day}$. A tentative flow-sheet is presented in Figure 1.

Evaluation of Effort

A process has been tested for immobilizing ITS recycle wastes. A high degree of cesium retention warrants further development.

Future Work

The volume increase for the aqueous silicate process will be measured for the case of predried bentonite. The quality gained by sintering the product will be determined. Leach rates will be determined as a function of pH and temperature.

Reports Issued

None.

Corrosion Studies

Project Manager:	G. L. Borsheim
Principal Investigators:	E. L. Moore
	R. F. Maness (BNW)

Objectives and Scope

The objectives of this project are to evaluate materials of construction, estimate life of existing equipment, recommend process changes affecting equipment life, and evaluate and recommend fabrication techniques and materials of construction for use in the waste processing systems.

Prior Work

A laboratory study was made to duplicate a preferential liquid-vapor interface attack of the mild steel liners which has been observed in some waste tanks. Mild steel coupons exposed to two boiling simulated alkaline high-level waste solutions (fluoride-free and fluoride-bearing) revealed no preferential attack at the

AQUEOUS SILICATE REACTION PROCESS

FIGURE 1

WASTE MANAGEMENT (Contd)

liquid-vapor interface after 736 days' exposure. A 0.1 volume percent of 30 percent TBP-NPH solvent was added at routine intervals during the test.

Pre-cracked mild steel C-ring coupons and weldment coupons were used to study stress corrosion cracking (SCC) in nitrate solutions. Time-to-failure was evaluated as a function of nitrate concentration between 10 and 0.05M. Cracking occurred at all concentration levels evaluated at boiling temperatures, while the time-to-failure increased from a few hours to about one week as the nitrate concentration decreased from 10 to 0.05M. In tests with 5 and 10M NaNO_3 solution at 60, 80, and 90° C, SCC occurred at 80 and 90° C in four days or less, whereas SCC did not occur after five months' exposure at 60° C. The effect of sulfate additions above 0.5M to boiling 5M NaNO_3 solution was to inhibit completely SCC of as-fabricated weldments. The effect of sulfate addition on SCC of pre-cracked C-rings was to increase time-to-failure.

Progress During Report Period

The study to evaluate the corrosiveness of simulated high-level solidified waste was continued. Variables included caustic content (25 and 34 percent), water content (5 and 15 percent), and temperature (60, 80, and 95° C). In addition, corrosion tests were made with waste prepared from solutions in which about 90 percent of the caustic content had been neutralized with either phosphoric, sulfuric, or nitric acid. A corrosion coupon and a pre-cracked C-ring (both 1020 mild steel) were exposed under each test condition. The tests were made in sealed mild steel containers or in mild steel or Teflon containers equipped with reflux condensers. Corrosion rates of specimens exposed to unneutralized waste for seven months ranged from 0.5 to 2.6 mils/year as determined by weight loss. Pitting occurred in all cases. The maximum pit depth on the various specimens varied from 1 to 9 mils. Corrosion rates at 60 and at 80° C were essentially the same and were about two-fold higher than those obtained at 95° C. Increasing the water content from 5 to 15 percent doubled the corrosion rate. Very low (<1 mil/year) corrosion rates with no pitting attack were found for specimens exposed to waste prepared from solutions in which the caustic content had been largely neutralized with phosphoric, sulfuric, or nitric acid. It is planned to continue these tests for an additional year.

Corrosion data pertinent to operation of the new vacuum crystallizer were obtained with a range of caustic concentration and temperature that would enable an estimate of corrosion regardless of the mode of operation. On the basis of these data, 304L corrosion, even on heat transfer surfaces, is expected to be less than 10 mils/year. Stress corrosion cracking of C-rings and U-bend specimens was evaluated in all test solutions. Early in this study a U-bend

WASTE MANAGEMENT (Contd)

specimen was found to be cracked after five weeks' exposure. All attempts to duplicate the cracking met with failure. Additional U-bend and C-ring specimens were exposed to all test solutions at 80° C and at the boiling point for exposure times in excess of one year. No stress corrosion cracking was noted.

Evaluation of Effort

In cold test evaluations of the corrosiveness of simulated high-level solidified waste to carbon steel, results to date show that use of phosphoric, nitric, or sulfuric acid to reduce the free caustic content effectively reduces the corrosion rate.

The cold-testing 304L stainless steel coupons under simulated operating conditions of the new vacuum crystallizer shows that corrosion rates can be expected to be less than 10 mils/year.

Future Work

Evaluation of the corrosivity of high caustic waste solutions (as they approach solidification) to carbon steel will continue. Methods of measuring corrosion rates of carbon steel in radioactive solidified waste will be evaluated and a program conducted to obtain such data.

Reports Issued

None.

Cesium Purification *

Project Managers:	G. L. Borsheim M. H. Campbell H. H. Van Tuyl (BNW)
Principal Investigators:	R. E. Van der Cook J. S. Buckingham G. Jansen (BNW) J. A. Partridge (BNW)

Objectives and Scope

The objective is to develop and optimize a process for purifying the fractionization plant (B Plant) cesium to the degree required for encapsulation. A secondary objective is to determine the effects of cesium loading and feed composition on the purification of cesium from potassium and sodium. Design parameters for scale-up will be estimated.

* Partially supported by PT

WASTE MANAGEMENT (Contd)Prior Work

Zeolon-900 cation exchanger (The Norton Co.) has been selected as the optimum exchanger for cesium purification based upon laboratory investigations. A process flowsheet has been developed and the effect of variation of process parameters has been investigated.

The flowsheet was tested in the 325-A High-Level Radiation facility with cesium nitrate feed from B Plant tank 37-1. Four runs were made resulting in 63,000 Ci of ^{137}Cs product which was 96.5 wt% Cs, 1.63 wt% Rb, 1.74 wt% K, and 0.13 wt% Na.

Progress During Report Period

A draft of the document BNWL-B-248 "Cesium Purification with Zeolon-900 Cation Exchanger" describing the results of the investigation has been completed.

Evaluation of Effort

The results of ion exchange tests with both simulated feed and plant feed have demonstrated that the flowsheet can be successfully used to prepare purified cesium from the stored cesium nitrate. Data are available on the effect of process variables on the yield of acceptable cesium product.

Future Work

The data from the laboratory and hot cell column experiments may be used to re-examine the QUATEX computer program model of an ion exchange column and investigate the model's ability to accurately describe the performance of a Zeolon-900 exchanger column during the cesium purification process.

Investigation of the nature of the solids in the stored cesium nitrate has been limited. Additional characterization of the solids is necessary to identify the optimum method of treating them for recovery of the cesium. The flowsheet development work will be documented.

Reports Issued

None.

WASTE MANAGEMENT (Contd)Strontium Purification

Project Managers:	G. L. Borsheim
	H. H. Van Tuyl (BNW)
Principal Investigators:	L. A. Bray (BNW)
	R. E. Van der Cook
	W. G. Wilson

Objectives and Scope

The objective of this program is to develop a process for purifying the B Plant strontium product to the degree necessary for encapsulation. Strontium will be purified using a multiple sulfate precipitation process which will be optimized for scale-up to plant application.

Prior Work

The purification of strontium by sulfate precipitation can provide the encapsulation plant with a feed that will meet purity requirements. Plant testing of these flowsheets verified the reliability of this process for a variety of flowsheet conditions.

Further studies were initiated on the sulfate precipitation and waste strike processes, aimed primarily at revising the flowsheet to allow efficient purification of "first cycle" Purex acid sludge (PAS) crude strontium (calcium/strontium mole ratios of >6).

To purify one megacurie of ^{90}Sr from PAS feed would require ~16,000 gallons of 1M Na_2SO_4 . Since the sulfate waste must be reworked to recover strontium losses, there is a strong incentive to reduce this waste volume.

Laboratory studies and previously-developed equations (to predict strontium and calcium solubility) show that a decrease in the $\text{SO}_4^{=}$ concentration (0.2 - 0.5M) should increase the calcium solubility and effectively reduce the volume of sulfate solution required.

Progress During Report Period

Laboratory studies were completed to test lower sulfate concentrations in the sulfate strike and waste streams. Greater calcium removal, lower waste volumes, and reduced sulfate utilization resulted. By using a 0.5M to 1M initial sulfate strike at a pH of 1 followed by a 0.2M HEDTA dissolution of the sulfate cake (as opposed to a Na_2CO_3 - NaOH metathesis and acid dissolution), it was possible to reduce reagent concentration in the second and third cycles to 0.1M Na_2SO_4 at a pH of 1. Further testing of this concept resulted in second and third cycles requiring lower concentrations ranging from only 0.05 to 0.1M Na_2SO_4 in the 0.5M HNO_3 .

WASTE MANAGEMENT (Contd)

Additional testing was completed to determine the effects of various strontium, sulfate, and rare earth concentrations on the strontium concentration in the strike waste supernate. The concept of recycling the "rare earths" used in the waste strike process for scavenging strontium by redissolving them in HEDTA was also investigated.

Attempts were initiated to selectively precipitate barium from a simulated purified strontium solution by adding a small, calculated amount of Na_2SO_4 at an optimum HNO_3 concentration. Barium DF's of 3 and 5 were obtained for 0.01 and 0.02M $\text{SO}_4^{=}$ at 0.5M HNO_3 , while the strontium losses were 1 and 2 percent. An attempt to combine this procedure with the hydroxide (pH 9) precipitation flowsheet is in progress.

Evaluation of Effort

The purification of strontium by sulfate precipitation will normally provide the encapsulation plant with a feed that will meet requirements (assuming a hydroxide precipitation final step). Modifications in the flowsheets to reduce the sulfate concentration and volume of waste now appear feasible for feeds (PAS) containing a high Ca/Sr mole ratio.

Future Work

In the laboratory, the barium removal study will be concluded. Other impurity problems will be studied. The purification tests will be integrated with purification studies using a hydroxide strike. A report covering the laboratory work will be issued.

Reports Issued

None.

Barium-Strontium Separation

Project Managers:	G. A. Nicholson
	J. W. Bartlett (BNW)
Principal Investigators:	G. E. Benedict
	H. T. Fullam (BNW)
	J. A. Partridge (BNW)

Objective and Scope

The objective of this project is to optimize the strontium fluoride precipitation flowsheet for maximum barium separation.

WASTE MANAGEMENT (Contd)

Barium removal will decrease the number of capsules required in the Waste Encapsulation and Storage facility.

The effect of the following variables on the barium-strontium separation in the SrF_2 precipitation flowsheet will be determined:

- ° pH of strontium solution prior to NaF addition and final pH.
- ° NaF addition rate.
- ° NaF/Sr ratio or Ba separation versus strontium loss.
- ° Digestion time.
- ° Digestion temperature.
- ° Calcium influence on Ba-carrying by precipitate.

Prior Work

The published solubility product constants for BaF_2 and SrF_2 differ by almost three orders of magnitude with BaF_2 being more soluble. One data point had been obtained which indicated separation should be possible.

Progress During Report Period

Strontium fluoride precipitation tests showed that the separation of barium from strontium during fluoride precipitation is not governed by the solubility product constants of SrF_2 and BaF_2 . The barium coprecipitates with strontium fluoride and the amount of barium left in the solution is much less than would be expected from the solubility product of pure barium fluoride.

The precipitation tests demonstrated that barium decontamination factors (DF's) of only 1.3 to 2.3 can be expected under conditions where strontium losses are kept to four percent or less. In solutions in which the initial strontium concentration was 0.28M, the barium DF varied from 3.5 to 11 when only 75% of the strontium was precipitated. With test solutions in which the initial strontium concentration was 0.08M, an increase in barium DF with a decrease in percentage strontium precipitated was not observed. With 0.08M strontium feed the barium DF varied from 1.1 to 3.5, with most of the values being in the range of 1.3 to 2.3.

The pH of the solution, NaF addition rate, digestion time and temperature, and presence of calcium in the solution were found to not have an effect on the barium DF in the strontium fluoride precipitation tests.

WASTE MANAGEMENT (Contd)Evaluation of Effort

The precipitation tests demonstrate that incomplete barium separation will be obtained during the strontium fluoride precipitation process. Variations in the flowsheet parameters do not appear to result in any significant improvement. Further work on this approach is not warranted.

Future Work

The laboratory work will be documented.

Reports Issued

None.

Public Protection AssuranceSorting and Assay Instrumentation

Project Manager:	M. H. Campbell
Principal Investigator:	W. H. Zimmer

Objective and Scope

Develop instrumentation which will nondestructively and automatically inventory radionuclides for sorting, for accounting, and for field measurement purposes.

Prior Work

The Automatic Radioactive Inventory System (ARIS) includes a sorting station consisting of one to three NaI (Tl) detectors and inventory station with three independently operated Ge(Li) diode detectors. A small computer automatically controls all data acquisition and reduction, and provides a printed report.

The ARIS simultaneously sorted and analyzed up to 32 gamma-emitting radionuclides, including actinides, fission products, and irradiation products. The system was sensitive enough to perform analyses of naturally occurring radioisotopes in core samples from deep wells and analyses of gamma emitters at fallout activity levels in surface soil, water, and vegetation.

Progress During the Report Period

The capability of the ARIS was developed to measure beta emitters. The system will sample channel contents at variable positions in

WASTE MANAGEMENT (Contd)

the observed gamma spectrum and test for the presence of bremsstrahlung emission. When the test is positive, a rough energy analysis is performed to determine the probable beta-emitting isotope causing the emission. A corrected quantitative analysis is then reported. This system has been calibrated for ^{90}Sr , ^{90}Y , ^{147}Pm , and ^{99}Tc ; and provides a rapid analysis no more than a factor of two less accurate than gamma energy analyses at a comparable activity level.

The ARIS data reduction capabilities were developed as a central data reduction station with remotely located Ge(Li) detector-analyzer satellite stations. The first of these is a mobile analyzer with an in situ Ge(Li) detector for the assay of B-C Crib environmental contamination. Spectral data will be recorded in a minimum cost and capability pulse height analyzer system, recorded on cassette magnetic tape, played back into ARIS, and automatically analyzed.

Evaluation of Effort

The new development for measuring beta-emitting isotopes with ARIS is a breakthrough in analytical instrumentation. This development provides a beta analysis within minutes, whereas previous methods required hours.

Future Work

Refinements will be made to improve counting capabilities and capacity. Analyses will be made of the B-C area environmental contamination.

Reports Issued

ARH-2632 (unclassified), April 1973, W. H. Zimmer, "Automatic Radioactive Inventory System Operating Procedures"

Airborne Release of Radioactive Particles

Project Managers:	R. E. Isaacson
	L. C. Schwendiman (BNW)
Principal Investigators:	L. E. Bruns
	R. K. Woodruff (BNW)
	J. Mishima (BNW)
	G. A. Sehmel (BNW)

WASTE MANAGEMENT (Contd)Objectives and Scope

One objective of this project is to assess the inhalation potential due to the release of radionuclides to the atmosphere when protective barriers are breached. Another objective is to determine the aerodynamic processes affecting radioactive particle behavior in the environment. In each of several potential accident situations, the chemical and physical properties and amounts of airborne particles are to be determined. Resuspension, transport, and trajectories of radioactive particles from contaminated areas, under the influence of wind and surface disruptions, are to be investigated.

Prior Work

In laboratory and engineering-scale studies, airborne plutonium compounds were characterized when heated or when involved in fires with combustible materials. Airborne release of uranium compounds, representing plutonium, was measured in larger scale experiments in which the source was involved in gasoline fires. No single parameter was identified as having an overriding influence on the quantity or nature of the material released. A typical release was 11 percent airborne from uranium nitrate hexahydrate (UNH) solution deposited on a stainless steel surface during a 10-minute gasoline fire. About 34 percent of the particles airborne were less than 10 μm aerodynamic equivalent diameter. Fractional airborne release from fires in stored combustible materials ranged from about 3×10^{-5} to 5×10^{-4} . In 8 of 11 experiments, greater than 80 percent of the active material airborne was associated with particles less than 10 μm aerodynamic equivalent diameter.

Large volume samples collected from about one foot above the ground in an area contaminated to a very low level showed that airborne plutonium was present at a measurable level, and thus the site might prove suitable for resuspension studies. Equipment was designed and tested to permit classification of particles in large volume samples.

Wind direction and speed data from the 400-foot meteorology tower were correlated with similar data from two towers approximately five and eight miles away. Correlation of wind data decreased with distance. The study indicated that a spatial analysis of tower wind data would be required for assessing the transport of resuspended particles.

Progress During Report Period

Formal reports describing the experiments simulating transportation and storage fires have been written. Data available in the literature relating to the release and nature of airborne plutonium

WASTE MANAGEMENT (Contd)

particles was compiled. This compendium will emphasize the fractional release and aerosol characteristics to assist those making accident analysis. It will also include information on atmospheric transport, resuspension, and sampling.

Wind-caused particle resuspension was measured with an array of high volume samplers and cascade impactors mounted on towers along the east side of the U Pond area. Radiochemical analyses are in process for the initial experiment. Resuspension flux will be determined from vertical and crosswind concentration profiles and related to meteorological variables.

A similar study was initiated at the B-C Crib area with the erection of towers. A preliminary part of this study included air sampling with low-volume samples at 0.3 meters and 1 1/2 meters from the ground. The airborne concentrations were too low to permit crosswind differences in airborne active material to be measured. Collectors at each elevation were composited in an effort to reach a detectable level. Samples are being processed.

The computer program for trajectory analysis was completed and made ready to use with operational wind data.

Twelve constant-volume balloons were launched and tracked by double theodolites. One was released as a trial flight, five were subsequently released from the U Pond area, and six from the B-C Crib area. Analysis of tower wind data and the constant-volume balloon trajectories is in progress.

Evaluation of Effort

All studies are on schedule. Two milestones in the plutonium aerosol release study were reached. These were the study of uranium (as a stand-in for plutonium) released during the burning of wastes, and the study of active particles released in gasoline fires. The reports completed to date and the report to be issued as a compendium on aerosol release in fires and other accidents will provide readily accessible information for use in hazards analysis. Information on radioactive airborne particles from the U Pond and the B-C Crib area will provide the reference background data for evaluating resuspension data taken during cleanup operations, or other soil disturbances.

The computer program for trajectory analysis holds promise for relating the position of an air parcel released from a given point to the wind field influencing the position with time. Actual verification awaits data analysis.

WASTE MANAGEMENT (Contd)Future Work

Studies of airborne radioactive particles will include the generation, characterization, and behavior in energetic releases from powders and liquids. The rate of removal either by natural settling or by ventilation will be investigated theoretically and experimentally. The interaction of radioactive particles with various materials such as soil particles will be studied.

Resuspension of radioactive particles from the U Pond and the B-C Crib area will be studied under various weather conditions and disturbances caused by work activities. Arrays of high-volume samplers will be used to measure the flux of radioactive particles as a function of wind speed, surface conditions, and particle size. Seasonal and diurnal effects will be examined. Models to predict airborne concentrations will be formulated.

The trajectory study will include verification, evaluation, and extension of the computer model. The following topics will be included:

- ° Feasibility of including the influence of vertical and directional wind shear on particle trajectories, and adapting the computer program to account for this influence.
- ° Computation of three-dimensional trajectory.
- ° Application of diffusion calculations to define spatial limits of resuspended materials.
- ° Incentives for expansion of the wind tower network.
- ° Particle trajectories from additional constant-volume balloon launches and verification of computer programs for trajectories.

Reports Issued

BNWL-1730 (unclassified), April, 1973, J. Mishima and L. C. Schwendiman, "Fractional Airborne Release of Uranium (Representing Plutonium) During the Burning of Contaminated Wastes"

G. A. Sehmel, "Particle Resuspension from an Asphalt Road Caused by Car and Truck Traffic," Atmospheric Environment, Vol. 7, pp. 291-309, 1973.

WASTE MANAGEMENT (Contd)Radionuclide Transport Model*

Project Managers:

R. E. Isaacson
D. E. Olesen (BNW)

Principal Investigators:

M. D. Veatch
D. B. Cearlock (BNW)

Objective and Scope

The objective of this project is to develop the technology required for predicting the transport of radionuclides in aqueous solution through sediments underlying the Hanford Reservation and to develop the capability for managing the rate and direction of radionuclide movement through Hanford sediments. A visual display of the computer solution to groundwater flow problems will be provided to graphically show the degree of safety with which radioactive wastes are managed.

Prior Work

Extensive research has been conducted at Hanford on the behavior of radionuclide migration through the partially saturated sediments underlying waste disposal sites and in the saturated groundwater flow system. Mathematical models have been written to describe subsurface water movement and radionuclide transport in both the saturated and unsaturated sediments. The Variable Thickness Transient (VTT) Flow Model for the Hanford groundwater flow system is operational and has been applied to several groundwater flow problems. The groundwater flow system was simulated from March 1968 through September 1971 with the VTT model of the Hanford Reservation. Good agreement between computed results and observed data was achieved over a large portion of the region. The large discrepancies appeared to be in modeling Gable Butte and in transmissivity distributions for the western part of the Hanford Reservation.

The Transport Model is operational and error and sensitivity analyses on the model have been completed. The accuracy of the model was verified by simulating the movement of tritium in the groundwater east of 200 East Area. Agreement between computed and observed tritium concentrations was excellent for the four-year simulation period. Application of the Transport Model in the vadose zone was tested on a hypothetical tank leak problem in which the movement of ^{137}Cs and ^{90}Sr was simulated.

* Partially supported by PT.

WASTE MANAGEMENT (Contd)

Progress During Report Period

Additional error and sensitivity tests were run on the VTT model of the Hanford Reservation. It was determined that the quality of the simulation is largely dependent on the transmissivity distribution. Steps have been initiated to improve the lithographic and boundary data used in the Transmissivity Iterative Sequence so that the transmissivity distribution can be recalculated in areas of poor model performance.

The major effort was directed toward thorough documentation of the work associated with this program. Six formal reports have been drafted and reviewed during the reporting period. These documents are in the final draft stage and will be issued by the end of the fiscal year.

Evaluation of Effort

Completion of the work described in the draft reports will allow a more precise definition of any land and/or water use restrictions that may be required on or adjacent to the Hanford Reservation.

Future Work

The program will be reviewed and research objectives of new work will be evaluated relative to the cost and value to the Hanford Waste Management Program.

It is anticipated that emphasis will be placed on completing the laboratory verification and error and sensitivity analysis of the partially saturated transient (PST) model. Field verification of the PST and Transport models will be accomplished by simulating the movement of waste from an existing crib where good historical data are available.

The work will also include historical verification of the VTT model for the period 1944 to 1972 and modification of the model to handle vertical variations in permeability.

Reports Issued

None.

WASTE MANAGEMENT (Contd)Field Measurement Methods*

Project Managers:	R. E. Isaacson D. B. Cearlock (BNW)
Principal Investigators:	M. D. Veatch L. E. Brownell** A. E. Reisenaur (BNW)

Objective and Scope

The objectives of this project are to develop methods for economically obtaining hydrologic data which would be useful in managing the Hanford groundwater system, to provide a better understanding of soil-moisture relationships in the Hanford area, and to evaluate the magnitude of the critical rainfall and capillary pressures required for meteoric water to percolate to the underground water.

Prior Work

A "water potential gradient" technique was used to help determine whether precipitation infiltrates to the Hanford water table or cycles in the vadose zone with eventual return to the atmosphere. The total water potential of numerous sediment samples from a well drilled through the vadose zone (300 feet) was approximated from matrix potential measurements. The lowest water potential occurred at a depth of 45 feet.

Preliminary studies were based on tritium analyses of water, vacuum distilled, from soil samples recovered by dry drillings in the vadose zone on the Hanford site. The analyses indicated that tritium (from the testing of nuclear weapons) in meteoric water had penetrated to a depth of only about 18 feet in the vadose zone of the Hanford 200 Area plateau. Virgin water with a low tritium concentration (characteristic of water before testing of nuclear weapons) was found at depths from 20 feet to the water table. This indicated that meteoric water had not percolated to the water table in these areas and that radioactive wastes stored in these areas would not be subject to leaching. An understanding of the amount of precipitation required for percolation and the mechanisms of percolation is considered essential. Thermocouple psychrometers and soil temperature sensors between the ground surface and the water table were installed in a backfilled bore hole and are being regularly monitored.

Two large lysimeters for studying the movement of moisture under the Hanford climatic regime were constructed south of the 200 East Area.

* Partially supported by PT.

** ARHCO Consultant

WASTE MANAGEMENT (Contd)

A simple reliable method for determining the unsaturated hydraulic conductivity and diffusivity was developed and successfully tested. This technique can be used economically to obtain input for the PST flow model. A method (Transmissivity Iterative Routine) was developed and successfully tested for calculating the transmissivity distribution for steady-state groundwater systems using a minimum number of field measurements. This method was extended to handle transient groundwater system.

Progress During Report Period

Collection of temperature and psychrometer data at the instrumented wells, 2D and 2C, continued through the report period. Neutron measurements for soil water content in the lysimeters were also continued during the report period. These data were recorded on IBM cards and put into computer files. Analysis of the data is continuing in order to insure that the data being collected are accurate and to complete the understanding of soil moisture relationships in the Hanford area.

Documentation on the entire program received major emphasis during the report period. Final drafts have been completed on 12 formal documents describing methods and techniques developed to date. These documents will be issued by the end of the fiscal year.

Evaluation of Effort

Collection and plotting of data collected from the lysimeter and the instrumented wells have continued. These data are building the necessary base on which to develop an understanding of soil moisture relationships in the Hanford area.

Future Work

Future work will include monitoring of in situ soil psychrometers and temperature sensors. More emphasis will be directed toward theoretical considerations involved in accurate field data interpretation.

Emphasis will be placed on modifying the Transmissivity Iterative Sequence to calculate transmissivity (hydraulic conductivity) and the storage coefficient simultaneously. A new transmissivity map of the Hanford Reservation will be constructed using the modified routine.

Reports Issued

None.

WASTE MANAGEMENT (Contd)Soil-Waste Reactions*

Project Managers:	R. E. Isaacson
	D. B. Cearlock (BNW)
Principal Investigators:	M. D. Veatch
	R. C. Routson (BNW)

Objectives and Scope

The objective of this project is to develop a fundamental understanding of the parameters which control reactions of radionuclides with Hanford sediments. This information will be used to predict the consequences of planned and unplanned releases of radionuclides to the environment.

Prior Work

Extensive research has defined the reaction characteristics of radionuclides with Hanford sediments as a function of pH, temperature, species of accompanying ions, etc. Six principal types of parameters were identified which control sediment-radionuclide reactions. These parameters are the initial solution ion concentration, solid phase calcium carbonate in sediments, cation exchange capacity of the sediments, ion exchange constants, the soluble components in the sediments, and sorption parameters. Laboratory studies directed at measuring the sorption of ^{85}Sr on sediments as a function of pH, $[\text{Na}^+]$, $[\text{K}^+]$, and $[\text{Ca}^{+2}]$ were completed. Tests over a wide range of particle sizes indicate that the radionuclide relationships which have been developed are valid for the range of sediments encountered beneath the Hanford Reservation. Cation exchange capacity and particle size data were found to be the best indicators of sorption properties of sediments. Studies have been completed in which the number of theoretical sediment types necessary to allow high precision mathematical simulation in column studies was determined. A linear regression analysis was used to determine a relationship between permeability and the sorption coefficient in the saturated zone of the Hanford Reservation. Laboratory column experiments under unsaturated conditions showed that the number of sorption sites are essentially independent of soil saturation for saturations greater than 45 percent.

An empirical equation for calculating the activity coefficients for high ionic strength waste was evaluated. Comparison of measured and calculated activity coefficients for some of the salt solutions showed that this method accurately predicted activity coefficients in mixtures of ionic strength up to 6M.

* Partially supported by PT.

WASTE MANAGEMENT (Contd)Progress During Report Period

The major effort during the report period was thorough documentation of the models and laboratory experiments and techniques. Four formal documents were drafted and reviewed during the report period. These documents are in the final draft stage and will be issued by the end of the fiscal year.

Evaluation of Effort

Draft reports describing work accomplished under this program were written and reviewed. The reports are now in final draft stage. This program can now be evaluated and the cost and value to the Hanford Waste Management Program of new research objectives determined.

Future Work

An extension of this work will be the evaluation of actinide behavior in soil/water environments. Future work would also include examination of techniques for reducing the costs of obtaining model input data.

Reports Issued

None.

Actinides on Sediments

Project Managers:	R. E. Isaacson J. W. Bartlett (BNW)
Principal Investigators:	T. R. McKenzie J. L. Swanson (BNW)

Objective and Scope

The objective of this program is to determine the nature of the actinide species present in contaminated soils from various locations on the Hanford Reservation.

Prior Work

None.

Progress During Report Period

Data have been obtained regarding the rate and extent of leaching of plutonium and americium contained in samples of the top 61 centimeters

WASTE MANAGEMENT (Contd)

of soil in the 216-Z-9 covered trench. These data will aid in the definition of the nature of the species which are present.

The leachability in nitric acid solutions was found to vary with sample depth. More complete leaching occurred at the lower depths. Below about 30 centimeters, the leach behavior was similar in the two locations tested. Pronounced differences in leachability were apparent in the near-surface samples, however.

Plutonium polymer has not been detected in the acid leach solutions. The test for polymer involved measurement of the extractability into TBP solution (polymer does not extract).

Samples from one of the locations contained organic extractants such as TBP and/or dibutyl butylphosphonate (DBBP). Ethyl alcohol leaches removed some of the plutonium from these samples, indicating the presence of organic-soluble complexed species. Less than 10 percent of the plutonium is present as such species in these samples. In most cases, americium leached more readily than did the plutonium.

Evaluation of Effort

The data obtained to date are insufficient for definition of the species which are present in the Z-9 trench soil.

Future Work

Complete the definition of the species present in the Z-9 trench and perform similar studies with soils from other locations.

Reports Issued

None.

The Behavior of Waste Radionuclides in Soil-Plant Systems*

Project Managers:	R. E. Isaacson
	W. H. Rickard (BNW)
Principal Investigators:	T. R. McKenzie
	K. R. Price (BNW)

Objective and Scope

The objective of this study is to provide the biological and ecological bases for the management of radioactive wastes in the

* Partially supported by PT.

WASTE MANAGEMENT (Contd)

Hanford environment. The goal is to identify the ecological fate and behavior of important radionuclides, especially actinides, in soil-plant systems.

Prior Work

Plant uptake of transuranic elements applied to soil as nitrates or organic acid complexes was determined for two locally important weeds. Tumbleweed uptake from nitrate sources resulted in a large amount of ^{237}Np occurring in shoot tissue. With cheatgrass, uptake was about 10-fold less than tumbleweed uptake.

When the neptunium or plutonium was complexed in the soil with process chemicals such as glycolate, oxalate, or citrate, tumbleweed shoot uptake was enhanced. With cheatgrass, plutonium uptake also was enhanced over that from nitrate forms. However, plant shoot uptake of americium or curium from organic acid complexes added to soil was suppressed.

Test plants were grown on contaminated weeds collected from a waste storage site. Uptake of ^{90}Sr was comparable to published data, but ^{137}Cs uptake was about 100 times greater. Test plants also were grown on contaminated organic mud from a cooling water pond, and ^{137}Cs uptake was far greater than expected.

Progress During Report Period

Tumbleweed and cheatgrass plants were grown on soil treated with chelated transuranic elements. Neptunium-237, ^{239}Pu , ^{241}Am , or ^{244}Cm were chelated with ethylenediamine tetraacetic acid (EDTA) or diethylenetriamine pentaacetic acid (DTPA), and Np or Pu were chelated with di-2-ethylhexyl phosphoric acid (HDEHPA) or TBP. The HDEHPA and TBP organic solvents were found to be toxic, but EDTA and DTPA had no detectable effect on plant growth. Transuranic uptake into plant shoots was greatly increased when chelated transuranics were added to soil. The EDTA induced a 10-fold increase in plutonium uptake, whereas plutonium uptake from DTPA chelate resulted in more than an 800-fold increase compared to uptake from nitrate application. Americium or curium uptake was affected only slightly by EDTA, but DTPA chelation resulted in about a 100-fold increase compared to nitrate sources. The relative order of uptake $\text{Np} > \text{Am} \approx \text{Cm} > \text{Pu}$ remains the same regardless of chemical form tested.

The increase in shoot uptake associated with complexation or chelation could result from improved transport from root to shoot, or it could result from increased movement from soil into the root. Root-to-shoot uptake ratios (R/S) were determined for transuranics

WASTE MANAGEMENT (Contd)

in nitrate form; R/S values for Np were > 1 , Pu $\gg 1$ and Am or Cm about 1. Neptunium and Pu R/S values were reduced when the Np or Pu was added to soil as organic acid complexes, whereas Am or Cm R/S values were only slightly affected. The addition of transuranic chelates further reduced the R/S value for Pu, but increased those for Am or Cm. Similar results were noted for cheatgrass. The changes in R/S values for Np and Pu may be the result of increased transport of Np or Pu from root to shoot, and for Am and Cm the change may be a result of a slight increase in Am or Cm uptake from soil. It is also likely that complexation and chelation resulted in increased root uptake of Np and Pu from soil.

The solubility of transuranic elements in the soil solution was determined to see if increased plant uptake was related to increased solubility. Soils were prepared by adding ^{237}Np , ^{239}Pu , ^{241}Am , or ^{244}Cm solutions as nitrates, organic acid complexes, or chelates. Results show that for fresh soil preparations the amount of soluble Np in the soil is relatively constant. Soluble plutonium in nitrate, acetate, glycolate, or oxalate preparations was virtually nonexistent, whereas citrate, EDTA and DTPA preparations induced significant increases in solubility. Nearly 70 percent of the Pu-DTPA added to soil remained soluble, for example. Americium and curium preparations showed similar results; about 90 percent of the DTPA chelates remained soluble.

Evaluation of Effort

This work has shown that the biological availability of the actinides Np, Pu, Am, and Cm is greatly influenced by natural chemical processes and by the chemical form of the actinide introduced to the environment. Plant uptake varies with the actinide species involved, the species of plant, the chemical nature of the soil environment, and the chemical form of the actinide. It is necessary to understand the influence of these various factors and their interrelationships if the hazards of actinides in the environment are to be correctly assessed.

Future Work

Studies are in progress to determine (1) plant uptake of ^{137}Cs , ^{90}Sr , and transuranic elements from other surface materials, (2) the effect on plant uptake of the depth of placement of the radionuclide in the soil, (3) the distribution of transuranic elements within the plant body following uptake from soil, and (4) the effect of plant age on uptake of transuranic elements.

Studies are planned to investigate the effect of fire on the availability of waste radionuclides from naturally contaminated materials.

WASTE MANAGEMENT (Contd)

A continuation of studies on the effects of chemical form may lead to the development of a soil or plant treatment which will suppress or inhibit plant uptake of transuranic elements.

Reports Issued

K. R. Price, "A Review of Transuranic Elements in Soils, Plants and Animals," Journal Environmental Quality, 2:62-66, 1973.

BNWL-1738 (unclassified), 1973, R. E. Fitzner and K. R. Price, "The Use of Hanford Waste Ponds by Waterfowl and Other Birds"

Uptake of Radioactivity by Goldfish and Ducks from Aquatic Biota and Sediments

Project Managers:	R. E. Isaacson
	B. E. Vaughan (BNW)
Principal Investigators:	T. R. McKenzie
	D. G. Watson (BNW)
	C. E. Cushing (BNW)

Objective and Scope

The purpose of this work is to determine whether radionuclides in the cooling water ponds can be transferred offsite and become a threat to man.

The near-term objective is to define the pathways of radioactive materials from cooling water ponds through the aquatic food-web, including waterfowl, and to investigate the areal and depth distribution of radionuclides in the sediments of cooling water ponds.

Prior Work

Initial studies of this project were designed to see if the goldfish in Gable Mountain Pond could accumulate significant body burdens of various radionuclides from their food organisms. It was concluded that free-ranging goldfish were not accumulating significant, or potentially hazardous, concentrations from Gable Mountain Pond. cursory sampling of sediments, however, revealed gross differences in concentration of radionuclides in different parts of the pond.

Progress During Report Period

During this report period, the pond has been gridded with a system of four stations along each of five transects. Samples of bottom

WASTE MANAGEMENT (Contd)

sediments were collected at each station on January 2 and 3 and March 7, 1973. Lithium fluoride dosimeters (TLD) were placed upon the surface sediments at each station in January and readings were collected on March 7, 1973, to measure the dose rate. (The TLD dosimeters showed daily dose rates from the sediments ranging from 2 to 229 millirads per day.)

The principal radionuclide, ^{137}Cs , was present in concentrations in the sediments ranging from 64 to 30,000 pCi/g wet weight. The ^{95}Zr and ^{60}Co levels were orders of magnitude less.

Evaluation of Effort

The work is currently behind schedule since cold weather caused a delay of about a month in the arrival of the duck broods.

The initial sampling of the sediments was not sufficiently precise and resampling with better techniques is under way.

The objectives of the summer's planned work should be met.

The two sets of data on sediment activity revealed substantial differences at some of the same stations between the two sampling dates; other stations were comparable. Sampling of these sediments may have involved a slight differential in depth of penetration of the sediments by the sampler. This means that radioactive concentrations may vary with depth.

Future Work

Research planned for aquatic studies includes:

- ° Further characterization of the areal and depth variations in radioactivity of the sediments. This will be done by using core samplers to investigate discrete layers of the sediments. The TLD's will continue to be used to measure dose rates from the sediments.
- ° Uncontaminated goldfish will be kept in 8' by 16' pens placed over areas of more intensely radioactive sediments and over sediments with relatively low levels of radioactivity. Sequential sampling of the fish and their food items will reveal what potential body burdens can be accumulated in fish restricted to these areas.
- ° Fifteen broods of mallard ducks (one hen and an average of eight young per brood) will be marked and restricted to the pond by rendering them unable to fly. Sequential sampling should reveal if these birds can build up body burdens of radioactivity high enough to be of concern in offsite dispersal.

WASTE MANAGEMENT (Contd)Reports Issued

None.

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