ERDA-76-43

VOL. 2 OF 5

Alternatives For Managing Wastes From Reactors And Post-Fission Operations In The LWR Fuel Cycle

**Volume 2:
Alternatives For Waste Treatment**

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Alternatives For Managing Wastes From Reactors And Post-Fission Operations In The LWR Fuel Cycle

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United States
Energy Research & Development
Administration

Volume 2
(2 of 5 Volumes)

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Report Coordinated By
Battelle, Pacific Northwest Laboratories
At The Request Of The
Division Of Nuclear Fuel Cycle and Production

FOREWORD

This report describes technical alternatives for managing wastes from the back end of the commercial LWR fuel cycle. It describes waste types, the alternative technologies that can be used to manage the wastes, and the state of availability of those technologies.

The report does not select preferred waste management technologies or make comparative assessments. Its purpose is to provide a comprehensive digest of technical information expected to serve as a basis for future decisions, assessments, and environmental impact statements. The technology is still evolving, and this report will be subjected to public review and comment. Its contents therefore serve as a baseline subject to future supplementation and updating.

There are four major waste management functions: treatment, interim storage, transportation, and final storage or disposal. This report is structured in five volumes that reflect these functions. Volume 1 summarizes the report, describes alternatives for the back end of the LWR cycle, and provides background information on waste types and quantities. Volume 2 describes alternatives for waste treatment. Volume 3 discusses interim storage and transportation. Alternatives for final storage and disposal are described in Volume 4. The Appendices, Volume 5, provide supplementary information, with emphasis on characteristics of geologic formations that might be used for final storage or disposal.

Preparation of this report was started in August of 1975, in response to a directive from ERDA's Nuclear Fuel Cycle and Production Division. The report was authored by personnel of ERDA's contractors, of industry, and of universities; coordination was provided by Battelle's Pacific Northwest Laboratories. The report was completed in March of 1976. The cutoff date for characterizing the status of the technologies was September 1, 1975.

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ALTERNATIVES FOR WASTE TREATMENT

INTRODUCTION

Contained in this volume are discussions of alternatives for modifying, treating and immobilizing the transuranic and nontransuranic radioactive wastes identified in Volume 1, Section 2.0 of this document. Treatment as used herein refers to any action performed upon the primary waste to alter its form for transport, storage or disposal. Immobilization infers an altered form of the primary waste which is less subject to actions of the environment into which it is placed than is the original form. For certain cases treatment and immobilization may not be required. Treatment and immobilization are considered to be of advantage when they either protect the public health and safety or reduce costs without compromising public health and safety.

The alternatives presented in Sections 5 through 16 describe treatments for application to specific types of waste generated in the "back-end" of the fuel cycle. In addition to descriptions, treatments are discussed on the basis of their status, whether or not the treatment is available. For those processes not presently available the stage of development is identified, and the work remaining to be completed before the process can be applied by industry is delineated. The information contained presents only the technology associated with the individual treatment and provides the bases for the reader to evaluate the technical aspects and status of each treatment. The treatments have not been optimized, and the authors have not attempted to draw conclusions or make recommendations regarding the efficacy of the various treatments.

Each treatment considered results in the generation of new, contaminated waste streams. For example, the densification by compaction of chopped and leached zirconium fuel bundle hulls creates contaminated compacting equipment and other miscellaneous wastes. The quantities of new waste generated vary with the different processes. Thus a key item to consider when assessing the various treatments is whether the waste quantities resulting from the treatment are greater than the waste stream being considered for treatment.

The process improvements presented in the first section in the volume, Section 5.0, are not strictly treatments by the above definition. Rather they present alterations to the basic fuel reprocessing flowsheet which modify the forms and/or the quantity of waste generated.

Treatments for two of the major radiogenic waste streams generated by current processes considered for spent fuel reprocessing are discussed in Sections 6.0 and 7.0: High-Level Liquid Waste Solidification in Section 6.0, Chop-Leach Fuel Bundle Residues in Section 7.0.

Alternatives for Treatment of Solid and Liquid Non-High-Level Wastes are presented in Sections 8.0, 9.0, 10.0 and 12.0. Combustible Organic Waste Treatments are incorporated under Section 9.0, Treatment of Combustible Wastes, rather than under Section 10.0, Non-High-Level Liquid Wastes.

Recovery of Transuranics for Economic Values from Non-High-Level Wastes is discussed in Section 11.0. Somewhat akin is partitioning, discussed in Section 16.0, which is the removal of actinides from high-level liquid waste. Section 16.0 also addresses use of selected fuel reprocessing wastes.

Treatment and Immobilization Processes for Gas and Volatile Radioisotopes are delineated in Sections 13.0 and 14.0, respectively.

Section 15.0 identifies treatments and presents strategies for decontaminating and decommissioning retired nuclear fuel cycle facilities. These facilities include light water reactors, spent fuel storage basins, fuel reprocessing plants, mixed oxide fuel fabrication plants, solid waste interim storage sites, and burial sites.

5.0 FUEL REPROCESSING MODIFICATIONS

5.0 FUEL REPROCESSING MODIFICATIONS

Some of the current practices in nuclear fuel reprocessing produce wastes that are difficult to manage because of unduly large volumes or the presence of materials in the wastes that interfere with treatment procedures and with processes for fixing the radioisotopes in stable, solid forms. Waste reprocessing methods can be improved by making modifications which emphasize "low-chemical-additive" flowsheets, recycling or combining essentially all low- and intermediate-level wastes, eliminating chemical reagents that complicate waste treatment, and implementing better control over waste-generating operations.

The long-range goal of this concept is to make waste management as simple as possible by integrating it with fuel reprocessing so that all emanating wastes are packaged and ready for final isolation. An overall schematic flow diagram for such a process is shown in Figure 5.1. The principal simplifying feature is the use of only a few versatile conditioning and packaging methods in contrast to the development of special methods for each waste stream. This presupposes that versatile methods can be developed, and that reprocessing methods will be modified where necessary to produce wastes compatible with the waste management methods. In other words, a continuing development program on process modifications will be required as the waste conditioning and packaging methods are developed and perfected.

Although this is the ultimate long-range goal, all of the improvements cannot be incorporated into existing or near-term reprocessing facilities. However, a number of process improvements can be developed in time for demonstration in existing reprocessing facilities. Most of the items discussed below are in this category.

A flowsheet indicating the origin and types of wastes generated in an advanced nuclear fuel reprocessing facility is shown in Figure 5.1. This, of course, does not show in detail how the waste streams are actually formed, their volumes, nor their compositions; neither does it show the many low- and intermediate-level wastes that are assumed to be recycled. A major part of needed future development is the preparation of detailed material-balance flowsheets that must be based on specific process conditions and actual plant practice. The following paragraphs describe some of the problem areas that have been identified from plant operating experiences.

FIGURE 5.1. Basic Flowsheet for Treatment of Fuel Fabrication and Reprocessing of Wastes

FIGURE 5.2. Generic Flowsheet Depicting Origins and Types of Wastes Generated in Fuel Reprocessing

5.1 INSOLUBLE RESIDUES GENERATED IN FUEL REPROCESSING

These solids pose problems to both waste management and the fuel reprocessing plant operation, and are of a magnitude that is not understood fully. Sufficient data are yet to be developed which will identify all of the solids generated and the amounts of these solids. The most troublesome solids appear to be the metal-cladding fines generated in the head-end treatment of fuels and the insoluble residues (primarily noble metals, zirconium, molybdenum, and niobium fission products) generated by the subsequent aqueous processing of the oxide fuel.⁽¹⁻⁵⁾ Some of these metal-cladding fines are transferred to the fuel dissolver vessel since complete separation from the sheared fuel is not effected in the head-end treatment. The pyrophoricity of zirconium fines may present problems in dealing with these mixed solids as wastes.

In previous commercial reprocessing, these mixed solids have been discharged to the high-level liquid waste stream by keeping them fluidized in the aqueous feed stream during uranium and plutonium recovery by the Purex process. It would be advisable to remove these solids from the liquid process streams in future plants for two reasons. First, potential

operability problems in reprocessing that are posed by the solids are eliminated. Second, problems posed by segregation of the solids in interim liquid waste storage or holdup tanks are not necessarily trivial. These segregated radioactive solids may be very difficult to remove from storage tanks. In addition, they may pose operability problems in liquid waste solidification processes in regard to plugging process fuel lines.

To prevent the above difficulties, any solids present in process streams could be removed and treated separately for waste isolation. Development studies would be needed to determine the best method of solids removal since adequate data do not exist concerning the chemical identity, amounts, and particle size distributions of solids in the various process streams.

5.2 SOLVENT TREATMENT FOR RECYCLE, AND WASTE SOLVENT DISPOSAL

Current and near-future reprocessing plants use tributyl phosphate (TBP) extraction processes which routinely perform treatment operations on the organic solvent to maintain extraction efficiency. Such treatments usually use a combination of alkaline and acid washes which are sometimes combined with alkaline permanganate solutions to remove hydrolysis products of TBP (viz., HDBP, H_2MBP , and phosphoric acid); residual fission products; uranium and plutonium; and limited amounts of degradation products of the hydrocarbon solvent. Chemical and radiolytic degradation of TBP extractants and solvent treatment processes have been reviewed by several investigators.⁽⁶⁻⁸⁾ A major disadvantage of these methods is the generation of large volumes of aqueous, alkaline wastes that are sufficiently contaminated with fission products and actinides to require treatment and long-term isolation. Solvent treatment practices that will minimize waste management problems of this type are an alternative.

Among potential candidates for solvent regeneration are alternative alkaline reagents such as organic bases, macroreticular resins,^(9,10) and distillation methods. Each alternative appears to offer solvent that has essentially virgin characteristics (i.e., low plutonium retention and good extraction behavior). Development of these processes could materially reduce waste volumes and eliminate many objectionable materials which affect subsequent waste processing.

Disposal of waste solvent is usually carried out by burning. Most solvent burning operations incur problems arising from the melting of phosphates, the potential risk of combustible organic nitrates, and solids plugging. Additionally, the burner off-gas systems are loaded with carbon dioxide, water, and volatile organics that must be trapped and disposed of.

Alternative routes to be considered for development are chemical decomposition (both acidic and alkaline), saponification,^(11,12) formic acid or formaldehyde reaction processes, and catalytic combustion processes. Byproducts of these reactions are usually trisodium phosphate and butanol, and it is conceivable that the butanol could be converted to tributyl phosphate and recycled.

5.3 RECYCLE OF AQUEOUS WASTE STREAMS

More efficient management of liquid wastes, such as those associated with the uranium and plutonium purification cycles, could be realized by more extensive recycle of liquid streams and better recovery of nitric acid. Greater recycling depends on developing a modified Purex process flowsheet that has a low additive requirement for chemical reagents and which does not build up impurities that cause process failure. Until now, significant amounts of chemical reagents (sodium nitrite, ferrous sulfamate, and sodium carbonate) have been employed in the routine operation of all reprocessing plants in the USA. Modern plants, such as the Allied-General Nuclear Services (AGNS) plant, propose to eliminate ferrous sulfamate and sodium nitrite from the process. This should permit the recycle of a number of aqueous waste streams and should also alleviate the problems associated with sodium and sulfate in waste solidification. AGNS proposes to use electrolytic reduction instead of ferrous sulfamate, and nitric oxide gas in place of sodium nitrite.^(13,14) In European reprocessing plants, U(IV) nitrate is substituted for ferrous sulfamate, which apparently results in an acceptable stream for recycle requirements.⁽¹⁵⁾ Electrolytic oxidation may be a viable alternative to nitric oxide gas.⁽¹⁶⁾ If satisfactory methods could be developed for recycling the acid waste streams, the number and types of waste streams could be reduced, better nitric acid utilization could be achieved, and the uranium and plutonium recoveries might be increased.

Successful development of techniques for recycling the waste streams depends upon the capability to carry out the recycle in a manner that would prevent the buildup of impurities deleterious to the recovery of fuel values and plant operation. Potentially serious buildup of impurities arise from solvent degradation products such as organics and phosphates, silica, chloride, and other contaminants present in process reagents, corrosion products, and fission-product ruthenium. Extensive development studies are required to determine the kinds and amounts of impurities, and whether deleterious effects would result from their accumulation. Even if such amounts do exist, it may be possible to develop methods for reducing them to levels which permit satisfactory operation.

5.4 OFF-GAS TREATMENT WASTES

The burden placed on waste management as a result of off-gas scrubbers would be substantially reduced if the liquids and dissolved chemical reagents in these wastes could be recycled. The preferred primary treatment used in reprocessing plants to remove kilogram quantities of iodine and nitrogen oxides from gaseous effluents is scrubbing with aqueous solutions of inorganic salts. Secondary removal of iodine is necessary to achieve the desired overall decontamination factors, but these operations (e.g., adsorption on solid silver zeolite) do not create large volumes of wastes.

Effort could be made to develop processes which have a potential for recycle of process streams, and which produce a concentrated iodine product. The Iodex process (see Section 13) is an example. In the Iodex process, the scrubbing agent (concentrated nitric acid) is recycled and the iodine is removed in its solid oxide form. Major questions need to be resolved in regard to the performance and operability of the process at full activity levels. At present, the chemical and equipment flowsheets are based on tracer-level studies. Effects of impurity buildup (soluble and particulate) in nitric acid recycle streams on iodine removal and plant corrosion have not been investigated.

In addition to concentrated nitric acid which is used in the Iodex process, aqueous scrubbing solutions of caustic or mercuric nitrate in nitric acid appear to have a potentially high efficiency for iodine removal. The economic and technical basis for choosing between these reagents has not been adequately defined at this time. Disadvantages to processes based on any of these reagents, however, must be overcome. At present, there is no clear indication that the reagents can be recycled or that spent scrubber solutions containing these reagents can be converted to acceptable storage forms for iodine. Although it may be possible to develop methods for recycle of mercury salts (e.g., via electrolytic reduction to metallic mercury), regeneration of caustic for recycle from the nitrate salts in the caustic wastes appears infeasible. Elemental mercury, which is toxic and volatile, presents special problems in regard to incorporating the waste into a satisfactory solid for storage. However, the conversion of caustic waste to solid sodium salts for incorporation in other solid storage forms is feasible.

5.4.1 Decontamination Waste Liquid

The volume of low- to intermediate-level liquid waste originating in the decontamination of cell areas, equipment, and process lines usually is variable and dependent upon the method of maintenance employed, as well as the prior process operation. The collection and disposal of decontamination

solutions is often complex due to the wide variety of reagents that are used, many of which are not compatible with existing solidification methods. Among the chemicals often used are film-stripping reagents, buffering reagents, corrosion inhibitors, complexing reagents, reducing and oxidizing agents, and surfactants.

Decontamination operations are usually carried out with a series of reagents whose concentration and volume is determined by the degree of decontamination desired. In addition to chemical methods, physical methods such as sand-blasting, brushing, swabbing, and ultrasonic cleaning are frequently used. A critical assessment would be needed to simplify these procedures and to limit the reagents used to those which can be processed into stable, solid forms suitable for final storage.

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6.0 HIGH-LEVEL LIQUID WASTE SOLIDIFICATION

6.0 HIGH-LEVEL LIQUID WASTE SOLIDIFICATION

United States policy is to convert high-level liquid radioactive waste (HLLW), generated in the reprocessing of spent power reactor fuel, to a "dry solid" which is "chemically, thermally, and radiolytically stable to the extent that the equilibrium pressure in the sealed container (canister) will not exceed the safe operating pressure for that container during the period from canning through a minimum of 90 days after receipt (transfer of physical custody) at the Federal repository."⁽¹⁾ At present no spent power reactor fuel reprocessing plants are in operation in the U.S. Consequently, solidification of HLLW is not being practiced.

Although solidification of HLLW is not being practiced commercially, 20 years' research and development in the U.S. and abroad⁽²⁻¹²⁾ has provided several solidification processing options ready for demonstration in a commercial plant plus others which can be implemented after varying degrees of development.

6.1 CHARACTERISTICS OF AS-GENERATED WASTE

Source

Spent power reactor fuel elements are dissolved in nitric acid at the reprocessing plant so that uranium and plutonium can be recovered for reuse in the nuclear fuel cycle. The solution remaining after recovery of uranium and plutonium, which contains the fission products and actinides produced by nuclear fission in the power reactor, is called high-level liquid waste. More technically, HLLW is the aqueous raffinate from the primary co-decontamination cycle of a nuclear fuel reprocessing facility. Aqueous raffinates from subsequent solvent extraction batteries in the reprocessing plant are generally "back-cycled" to the co-decontamination cycle. Solids removed by centrifugation during the feed clarification step are usually also combined with the HLLW.

Volume

The HLLW is generated at about 5000 liters per metric ton of uranium reprocessed (ℓ/MTU). The volume of HLLW is reduced to between 600 and 1100 ℓ/MTU by a process concentrator before transfer to an interim waste storage tank. Interim storage of HLLW is described in Section 19.0. Before solidification the HLLW may be further concentrated to about 380 ℓ/MTU.

Heat Generation

The heat generated in HLLW due to radioactive decay is shown in Table 6.1 as a function of time out of reactor. Heat generation is roughly proportional to fuel power level and time in reactor. The values shown are for fuel irradiated at a power level of 35 MW/MTU to a total burnup of 25,000 MWd/MTU, considered typical for the LWR fuel which is to be reprocessed in the next two to three decades (see Section 3).

TABLE 6.1. Radioactivity Decay Heat Generation Rates

<u>Time Out of Reactor</u>	<u>kW/MTU</u>
160 days	18.5
1 year	9.2
10 years	0.86

Composition

High-level liquid waste is a solution of nitrate salts in nitric acid. The constituents may be considered in three categories: inerts, fission products, and actinides (see Table 6.2). As shown in Table 6.2, the composition of HLLW can vary considerably.

The inerts are nonradioactive constituents arising from equipment corrosion (Fe, Cr, Ni), solvent degradation (PO_4^{3-}) and chemical additives required for reprocessing (Na, Fe, Gd, Cd, B, F, etc.). Variations in the chemical additions used during reprocessing cause the largest changes in HLLW composition, and hence have the greatest impact upon subsequent HLLW treatment. Since the chemical additives are controllable, an opportunity for a systems approach exists. The effects upon HLLW management can be factored into design of the reprocessing plant flowsheet (see Section 5.0).

The fission product content in HLLW represents over 99.99% of all the nonvolatile fission products originally in the spent nuclear fuel. Although volatile, enough iodine (0.1% to perhaps 5% of the total) remains in the HLLW that iodine traps must be included in all HLLW treatment off-gas facilities.

The concentration of the actinides uranium and plutonium in HLLW is dependent on the efficiency of the reprocessing plant. Uranium and plutonium losses to the HLLW generally range from 0.1 to 2% of the total originally in the spent fuel. At least 99.99% of the other actinides in the spent fuel end up in the HLLW.

Other Wastes Which May Be Combined with HLLW

Any remaining liquid waste streams generated by the reprocessing facility are candidates for inclusion in HLLW, if the plant operator considers such compositing beneficial. These wastes, usually combined and called intermediate-level liquid waste (ILLW), include:

- laboratory liquid wastes including samples and reagents
- solvent wash wastes including entrained and degraded solvent
- off-gas scrubber residues
- iodine scrubber residues

TABLE 6.2. Composition of HLLW

	Concentration, moles/l @ 378l/MTU			Kilograms Nonvolatile Oxide/MTU	
	Constituent	Possible Range	Reference for this Document ^(a)	Constituent	Reference for this Document
<u>Inerts</u> (Reprocessing Chemicals)	H ⁺	1-7	2.0	---	---
	Na	0-3.0	0.01	Na ₂ O	0.12
	Fe	0.05-1.4	0.054	Fe ₂ O ₃	1.6
	Cr	0.01-0.04	0.0096	Cr ₂ O ₃	0.28
	Ni	0.005-0.02	0.0034	NiO	0.19
	PO ₄ ⁼	0.025-0.30	0.042	P ₂ O ₅	1.1
	SO ₄ ⁼	0-0.90	0	SO ₄ ⁼	0
	NO ₃ ⁻	2.7-20	3.6	---	---
	F ⁻	0-0.25	0	F ⁻	0
	Gd ^(b)	0-0.2	0.150	Gd ₂ O ₃	10.0
	B ^(b)	0-5.0	0	B ₂ O ₃	0
	Cd ^(b)	0-1.5	0	CdO	0
				Subtotal	13.0
<u>Fission Products</u>	Rb	(c)	0.0095	Rb ₂ O	0.34
	Sr	(c)	0.017	SrO	0.68
	Y	(c)	0.0095	Y ₂ O ₃	0.41
	Zr	(c)	0.074	ZrO ₂	3.5
	Mo	(c)	0.071	MoO ₃	3.9
	Tc	(c)	0.017	Tc ₂ O ₇	1.0
	Ru	(c)	0.044	RuO ₂	2.2
	Rh	(c)	0.011	Rh ₂ O ₃	0.53
	Pd	(c)	0.030	PdO	1.4
	Ag	(c)	0.0015	Ag ₂ O	0.067
	Cd	(c)	0.0016	CdO	0.078
	Sn	(c)	0.0009	SnO ₂	0.052
	Sb	(c)	0.0002	Sb ₂ O ₃	0.013
	Te	(c)	0.0078	TeO ₂	0.47
	Cs	(c)	0.039	Cs ₂ O	2.2
	Ba	(c)	0.023	BaO	1.3
	La	(c)	0.018	La ₂ O ₃	1.1
	Ce	(c)	0.034	CeO ₂	2.2
	Pr	(c)	0.016	Pr ₆ O ₁₁	1.1
	Nd	(c)	0.055	Nd ₂ O ₃	3.5
	Pm	(c)	0.0005	Pm ₂ O ₃	0.035
	Sm	(c)	0.012	Sm ₂ O ₃	0.80
	Eu	(c)	0.002	Eu ₂ O ₃	0.13
	Gd	(c)	0.001	Gd ₂ O ₃	0.076
				Subtotal	27.0
<u>Actinides</u>	U	0.011-0.22	0.053	U ₃ O ₈	5.7
	Np	(c)	0.003	NpO ₂	0.31
	Pu	0.0001-0.006	0.002	PuO ₂	0.17
	Am	(c)	0.009	Am ₂ O ₃	0.96
	Cm	(c)	0.003	Cm ₂ O ₃	0.26
				Subtotal	7.4
				Total	47.0

- a. The reference HLLW is representative of a large state-of-the art commercial reprocessing plant such as BNFP.
- b. Potential soluble poisons which may be used during fuel dissolution.
- c. Depends upon burnup of the fuel being reprocessed, should not vary over a factor of two from the reference waste composition (burnup=25,000 MWd/MTU).

- fuel receiving and storage liquid wastes including,
 - ion-exchange regeneration wastes
 - cask decontamination wastes
 - cask cool-down system wastes
- solvent burner quench pot scrubber solutions
- building and equipment decontamination wastes
- building floor drains
- personnel decontamination facilities
- cold chemical wastes from the cold chemical makeup area.

Representative ILLW physical properties and chemical composition are given in Section 2.0. In discussing the flexibility of HLLW treatments, the impact of combining ILLW will be considered. Process flexibility is required because the volume and the composition of ILLW is somewhat variable. As an example, during an extensive maintenance period, large quantities of facility and decontamination wastes will accumulate at a time when no HLLW is being generated. During operating periods, solvent wash wastes, fuel receiving and storage wastes, and laboratory wastes can be expected to make up most of the ILLW. The major constituent of ILLW is sodium, but minor amounts of many constituents may appear, especially from decontaminating agents.

It is possible, although not yet demonstrated, that highly active solid wastes such as spent fuel cladding, can also be encapsulated during HLLW solidification.

6.2 FEATURES COMMON TO SOLIDIFICATION PROCESSES

Many aspects of HLLW solidification are common to all of the solidification processes. These common aspects will be discussed generically prior to descriptions of the individual solidification processes.

The function of HLLW solidification processing is to convert a liquid containing highly radioactive fission products and actinides to a stable, solid form. In the process, the volume of HLLW is decreased by a factor of 5 to 10, and secondary solid, gaseous, and liquid wastes are created. Approximate quantities of the secondary wastes are shown in Figure 6.1.

A HLLW solidification process includes the following:

- feed preparation
- solidification
- packaging of solidified HLLW
- treatment of secondary effluents.

Providing these functions requires design and construction of a major facility.

(a) THE OPERATION OF AN HLLW SOLIDIFICATION FACILITY WILL ALSO GENERATE BETWEEN 0.2 AND 0.8 m³/MTU OF MISCELLANEOUS SOLID RADIOACTIVE WASTE, INCLUDING NONCOMPACTED GENERAL PROCESS TRASH, ION-EXCHANGE AND ADSORPTION BEDS AND FAILED PROCESS EQUIPMENT.

(b) THE VOLUME OF GASES RELEASED, INCLUDING BUILDING AND CELL VENTILATION, WILL BE 2-3000 m³/min.

(c) THE DECONTAMINATED LIQUID EFFLUENTS RANGE FROM 600-1800 l/MTU AND MAY OPTIONALLY BE VAPORIZED FOR INCLUSION WITH THE GASEOUS EFFLUENTS.

FIGURE 6.1. Generalized Function of HLLW Solidification Processing

Processing Scope and Design Considerations

Before detail engineering can start on a major facility such as a HLLW solidification facility, several parameters must be fixed. This is generally done in the scoping phase of a project and is formalized by issuance of a set of design criteria. As a minimum, the following parameters, each of which has a bearing upon selection of the HLLW solidification process, must be considered.

Capacity

The capacity of the solidification facility must equal that of the nuclear fuels reprocessing facility. It may be desirable to provide 15 to 20% extra capacity, depending upon the surge capacity of the interim HLLW storage system and the operating and maintenance modes of both systems. For the discussion in this document it is assumed that the HLLW solidification process is associated with a reprocessing plant having a spent fuel capacity of 1500 MTU/year (5 MTU/day assuming 300 operating days per year).

Effluent Decontamination Factor Requirements

The design of the HLLW solidification effluent treatment systems will incorporate the regulatory requirements that all effluents discharged to the environment will be as-low-as-reasonably achievable (ALARA). The range of the decontamination factors for both gaseous and liquid effluents can be expected to be between 10⁹ and 10¹⁰.

Remote Maintenance Mode

A prime consideration is that the solidification process unit as well as closely related process support units will likely be remotely maintained. The mode of remote maintenance may vary from canyon and crane-type operations to master-slave manipulators, and will depend on the size and complexity of the equipment required for the solidification process and upon plant operating philosophy. Included in the selection of the mode of remote maintenance will be choices as to the mode of viewing the process and remote maintenance. These include viewing windows, television, and optical devices.

Support Systems

All solidification facilities will require support systems. Their size depends somewhat upon the solidification process selected, parallel processing lines requiring more support systems. The exact size and configuration of these systems is determined during detail design, but consideration must be given them during the scoping phase. These systems include, but are not limited to, the following:

1. Personnel facilities	5. Maintenance area
2. Control room facilities	6. Storage and loadout
3. Piping and instrument areas	7. Building and cell ventilation
4. Utilities, including:	8. Fire protection
• Electrical	9. Security systems
• Steam	
• Cooling water	
• Air supply systems	

Feed Preparation

A typical HLLW solidification feed preparation system is outlined in Figure 6.2. The first operation is batch transfer of HLLW from an interim HLLW storage tank (interim storage of HLLW is described in Section 19.0) to an initial feed or surge tank in the HLLW solidification facility. Because of the heat generated by the HLLW (Table 6.1), the receiving tank will have either cooling coils or a cooling water jacket. It will also have agitation, off-gas service, instrumentation, and sampling capabilities.

In most systems the HLLW will be concentrated prior to solidification to reduce the thermal energy input requirements for the solidification unit. As an example, HLLW may be stored at 1100 liters per metric ton uranium (ℓ/MTU) and concentrated to 380 ℓ/MTU or less before being introduced into the solidification unit. A thermosyphon concentrator is generally used for this service. The design of the concentrator will include features to minimize the radioactive content of the concentrator off-gas stream and process condensate.

FIGURE 6.2. Typical HLLW Solidification Head-End System

Such features include low vapor velocity in the concentrator disengaging section, baffle plates or bubble cap trays in the disengaging section, and demister pads at the off-gas exit point in the concentrator.

It may be desirable to denitrate the HLLW, i.e., reduce its nitric acid concentration, during the concentration step to achieve improved ruthenium decontamination during solidification. Denitration is an integral part of German and French HLLW solidification processes, as will be described later. Organic compounds, such as formic acid, formaldehyde or sugar, are used for denitration.

Solidification

A generic discussion of the solidification step is not feasible because of the variety of processes available for this step. Candidate processes for the solidification step will be detailed individually (Section 6.3) after completion of the generic process description.

Packaging of Solidified HLLW

Solidified HLLW will likely be encased in sealed cylindrical canisters. Stainless steel and other candidate materials are being investigated for canister construction. Design of the canisters must be compatible with requirements imposed by handling, interim storage, transportation, and Federal repository considerations.

Canister Criteria

Design criteria for HLLW canisters have not been defined in detail, but some probable limits, now in preliminary study stages for conceptual design of a final storage pilot plant, may be described:

- maximum diameter, 40 to 60 cm
- maximum length, 3 to 4.5 m
- maximum heat density, 2.9 kW/linear meter
- maximum radiation, 1×10^3 rem/hr neutron dose rate and 1×10^6 rem/hr gamma dose rate, measured 1 meter from any point on the surface of the canister.
- Surface contamination not defined, but must be low enough to maintain acceptable contamination levels at the Federal repository.

It should be emphasized that these limits are based on factors which become restrictive after the solidified HLLW leaves the reprocessing plant, i.e., during transportation and at the Federal repository. These limits on heat density and radiation, for instance, can be exceeded when the canisters are initially filled. At the time of filling, the limits are heat removal capabilities and allowable centerline and canister surface temperatures. The canisters can then be held at the reprocessing site until the heat and radiation have decayed to levels permitting receipt at the Federal repository.

Canister Post-Fill Treatment at the Reprocessing Plant

An important aspect of HLLW solidification, common to all processes, is the canister post-fill treatment. The post-fill operations are shown in Figure 6.3. The major required post-fill operations are seal-welding the canister and decontamination. Other post-fill operations, as shown in Figure 6.3, can be employed for both routine and nonroutine quality control. These include calorimetry, radiation profilometry, nondestructive measurement of wall thickness, and leak checking. Annealing of vitreous waste forms may also be included as a post-fill operation.

Double Containment (Overpacking)

The option exists of "overpacking" the primary HLW canister with a secondary canister. Overpacking is not presently required; however, the possibility that the canister criteria, as finally defined for the Federal repository, may be most easily satisfied by overpacking should be considered. Criteria which could result in decisions to overpack include canister surface contamination limits and possible coding of the canister as a pressure vessel. Thus possible reasons for overpacking include:

1. Simplified decontamination. The secondary canister will not have been exposed to the contaminated processing cell environment.

FIGURE 6.3. Typical Post-Fill Treatment of Solidified HLLW Canisters

2. Improved quality of external containment. The secondary canister will not have been exposed to the high temperatures of processing (500 to 1050°C for vitrification, depending on process; 900°C for calcine processes; and as low as 700°C for some alternative processes). Primary canisters containing vitrified product may also be stressed because the solidified waste has a lower thermal expansion coefficient than stainless steel ($8 \times 10^{-6}/^{\circ}\text{C}$ versus $17 \times 10^{-6}/^{\circ}\text{C}$). Methods are being sought to decrease the stress in the primary canisters containing vitrified product.

Disadvantages of overpacking are that it requires reducing the heat content in the canister and it adds to the cost of the waste containment.

Treatment of Secondary Effluents

Off-gas Treatment System (Gaseous and Liquid Effluents)

The off-gas treatment system is the largest and most complex system in the solidification facility. It must provide a decontamination factor (activity reduction) of 10^9 to 10^{10} .

No one type of process unit can provide the level of decontamination required. The off-gas system must therefore comprise a series of different process units, including condensers, scrubbers, filters, and concentrators. A typical waste solidification process off-gas system is shown in Figure 6.4.

- (a) ALMOST ALL HLLW SOLIDIFIER SYSTEMS HAVE A PRIMARY FILTER OR REFLUX SCRUBBER AS AN INTEGRAL PART OF THE SOLIDIFIER SYSTEM.
- (b) "FEED CONCENTRATOR" SHOWN IN FIGURE 6.2 MAY ALSO SERVE AS THIS EVAPORATOR.
- (c) DENITRATION, IF USED, MIGHT REQUIRE ADDITION OF AN ACID ABSORBER AT THIS POINT.
- (d) RUTHENIUM ADSORBER LOCATION IS OPTIONAL, MAY NOT BE REQUIRED WITH CERTAIN SOLIDIFIERS.

FIGURE 6.4. Typical HLLW Solidification Off-Gas Treatment

The off-gas treatment system copes with three different cleanup operations or design parameters:

- particulate matter in the micron and submicron regions
- volatile and semivolatile elements and compounds
- nitrogen oxides.

One of the first units in the off-gas system is a condenser. The condenser will separate most condensible components of the off-gas from most of the noncondensable components. Most of the particulate matter and much of the volatile and semivolatile components, as well as part of the nitrogen oxides, will collect in this primary process condensate. A quench scrubber may be used in place of a condenser. In this system the off-gas is directly condensed by a liquid to accomplish the same purpose as the condenser but usually with greater activity reduction efficiency.

Generally the primary process condensate will contain sufficient ruthenium so that it is either recycled to the feed concentrator or to a special ruthenium recovery unit.⁽¹³⁾ The off-gas from the feed concentrator, or the special ruthenium recovery unit still requires extensive cleanup, including the removal of NO_x , trace particulate matter, ^{129}I , and volatile ruthenium compounds. The off-gas will go to a condenser or to an acid absorber, which will be included at this point if formaldehyde or sugar denitration has been used in the feed concentrator or special ruthenium recovery unit. The off-gas and condensate and/or absorber bottoms then go to an acid fractionator where the nitric acid content is concentrated. If sufficiently decontaminated, the

concentrated recovered acid can be recycled back to the reprocessing facility dissolver unit, or it can be denitrated and returned to the evaporator. The process condensate from the overheads of the acid fractionator may require further treatment, such as ion exchange, before it can be released to the environment.

Following acid fractionation, the main off-gas stream may be passed through one or more scrubbing steps, then through an ^{129}I absorber (see Section 13.0). A ruthenium adsorber (see Section 13.0) may precede the iodine absorber. The off-gas will then probably be scrubbed before being passed through two or three stages of High-Efficiency Particulate (HEPA) filters for the final off-gas cleanup step.

Other process units that might be used in the off-gas cleanup system include:

- deep sand filters
- mercuric nitrate scrubbers
- electrostatic precipitators
- sintered metal filters
- venturi scrubbers
- peabody scrubbers
- brink deentrainment units
- dehumidifiers.

Each unit has a specific purpose and can be used to solve unique problems.

Another important item to note is that the solidification unit is not the only source of off-gas. Each process unit, vessel, and concentrator generates a flow of off-gas which must be factored into the system.

Solid Effluents

Aside from the altered primary waste, i.e., the canisters of solidified HLLW, there will also be miscellaneous solid wastes. These include spent iodine and ruthenium adsorption beds, failed process equipment, and general process trash.

Resource Demands

The principal resource demand on HLLW solidification is associated with the stainless steel if it is used in packaging the final product. For a 1500 MTU/year reprocessing plant, 60 and 30 MT of chromium and nickel, respectively, might be used irretrievably each year.

Most of the other resources used in HLLW solidification are abundant. An exception may be the zinc or lead used in certain vitrification formulations. Up to 70 MT of zinc or 100 MT of lead could be used per year for vitrifying the HLLW from a 1500 MTU/year reprocessing plant.

Process Selection

Although the high-level waste treatment plants can be scoped in a generic fashion, choice of a specific solidification process precedes detailed design. As described earlier in this section, no high-level waste solidification process has yet operated in a commercial power reactor fuel reprocessing plant. There are, however, a number of processes available for near-term implementation.

Each process has distinct, individual differences to be factored into the process selection. Examples of some of the processes and their characteristics which affect plant design are shown in Table 6.3.

Two types of processes are shown in Table 6.3, processes which produce coherent vitrified products, and processes which produce particulate calcine products. This is where the first decision on process selection would be made. In Europe and India the decision has already been made to convert all HLLW to coherent vitrified products. In the U.S. either product is acceptable under prevailing regulations.⁽¹⁾

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6.3 ALTERNATIVE SOLIDIFICATION PROCESSES

Once the fundamental decision on product form has been made, process selection will be based on the standard considerations of public health and safety, economics and projected operational reliability. The following pages describe the high-level waste solidification processes which are furthest developed. For convenience they have been divided into three categories:

Drying and Calcination

Vitrification

Other Solidification Processes

Table 6.4 lists the processes detailed in these sections and their development status. Though not all-inclusive, the listing does indicate the scope of the R&D being conducted.

6.3.1 Drying and Calcination

The first engineering-scale operational facility for the solidification of liquid radioactive wastes was the Waste Calcining Facility (WCF) which began calcining wastes from the Idaho Chemical Processing Plant in 1963. Although these wastes were generally factors of 10 to 100 less radioactive than commercial HLLW, the successful operation of the WCF demonstrates the feasibility of solidifying radioactive waste on a routine basis. The WCF product is a granular free-flowing powder which is being stored onsite in vented stainless steel bins.

The WCF uses a continuous fluidized bed calciner. A batch operated fluidized bed calciner was designed and built for operation in the Midwest Fuel Recovery Plant (MFRP), a 1 MTU/day commercial fuel reprocessing plant

TABLE 6.3. Plant Design Factors as Affected by Choice of HLLW Solidification Process

Assumptions: Solidification process is sized to handle HLLW from 1500 MTU/year reprocessing plant.
(5 MTU/day with 82% time on line).

HLLW has composition of reference waste, Table 6.2.

Liquid feed rate to solidifier = 80 μ /hr.

Waste is solidified 1 year out-of-reactor (self heat = 9.2 KW/MTU).

Process	Product Description	Additives Required, Kg/day	Throughput Considerations				Facility Considerations	
			Solidified Product				Number of Solidifiers	Important Solidifier Dimensions
			Weight, Kg/day	Volume μ /day	Max. Canister Diam, cm ^(a)	Canisters per Day ^(b)		
<u>Calcination</u>								
Fluidized Bed Calcination	Leachable oxide powder of variable particle size, surface area = 1,000-50,000 cm ² /g	0-75	325-400	160-200	13	4.2-5.2	1 fluidized bed calciner serving 2 canister furnace positions	Fluidized bed calciner barrel, 0.6 m dia. x 2.0 m tall, heated by in-bed combustion.
Fot Calcination	Leachable oxide powder of variable particle size, surface area = 1,000-50,000 cm ² /g	0-25	325-350	220-290	15	4.9-6.5	5 canister furnace positions	Canister furnaces are only heated units.
<u>Vitrification</u>								
In-Can Melting	Low leachable glass monolith, surface area = 0.05-0.5 cm ² /g	325-980	650-1300	180-390	36	0.8-1.7	1 spray calciner serving 2 canister furnace positions	Heated barrel of spray calciner, 76 cm dia. x 2.4 m long. Filter housing, 76 cm x 60 x 120 cm
Continuous Ceramic Melter	Low leachable glass monolith, surface area = 0.05-0.5 cm ² /g	325-980	650-1300	180-390	36	0.8-1.7	1 melter serving 2 canister fill positions (may not be heated)	Melting chamber holds 250 μ molten glass, 0.9 m wide, 14. m long, 0.2 m deep. Drain chamber extends 0.5 m from side
French Rotary Kiln-Continuous Metallic Melter	Low leachable glass monolith, surface area = 0.05-0.5 cm ² /g	325-980	650-1300	180-390	36	0.8-1.7	2-3 rotary kiln calciners each serving 1-2 metallic melter-canister fill positions (may not be heated)	Rotating barrel of rotary kiln calciner is 27 cm in dia. x 3.6 m long. Melter is 35 cm in dia. x 1 m long.
British Rising Level Glass Process (FINGAL/HARVEST)	Low leachable glass monolith, surface area = 0.05 - 0.5 cm ² /g	325-980	650-1300	180-390	60 with 6 cm annulus	0.3-0.7	2 canister furnace positions	Canister furnaces are only heated units. Annular canisters require center heating.
German Spray Calciner-Continuous Metallic Melter	Low leachable glass monolith, surface area = 0.05-0.5 cm ² /g	325-980	650-1300	180-390	36	0.8-1.7	1-2 spray calciners each serving 2 metallic melter - canister fill positions (may not be heated)	Reaction chamber of spray calciner, 0.6 m dia. x 2 m tall. Melter approx. 35 cm in dia. x 1 m long.

a. Canisters have 3 internal longitudinal cooling fins, centerline temperature limited to 800°C when canister is cooled only by air convection.

b. Canisters are 3 m long.

TABLE 6.4. Development Status of HLLW Solidification Processes

Treatment Category	Ready for Demonstration(a)	Requires Further Development	
		Short-Term(c)	Long-Term(d)
Drying and Calcination	Fluidized Bed Pot Calcination Rotary Kiln Spray Calcination	Wiped/Scraped Film Evaporator	
Vitrification	In-Can Melting French Rotary Kiln-Continuous Melter(b)	British Rising Level Glass German Spray Calciner-Continuous Melter Continuous Ceramic Melter	
Other Solidification Processes			Supercalcine Metal Matrix Sintering Glass Ceramics Coated Pellets Ion Exchange

a. Less than 1 year to be ready for engineering detail design.

b. Construction of a plant which will use this process to vitrify the HLLW from the Marcoule reprocessing plant is nearing completion.

c. Less than 5 years to be ready for engineering detail design.

d. Greater than 5 years to be ready for engineering detail design.

constructed at Morris, Illinois by the General Electric Company. Startup of MFRP has been postponed indefinitely, but for reasons not associated with waste treatment. A batch calcine process, the Potcal process, was developed at ORNL specifically for the solidification of commercial HLLW and demonstrated at PNL on a fully radioactive basis in the WSEP (1966-1970) program. Other calciners, developed for use with vitrification processes can also stop at a calcine, although that is not the purpose for which they were developed.

The calcines produced by all of the calciners have many properties in common, differing mainly in particle size and bulk density. Some common properties of calcine which affect process design and other considerations include thermal conductivity, leachability, and volatiles content. The thermal conductivity of calcine is generally two to three times lower than that of consolidated products. Thus, because of the high heat generation in HLW, the storage of calcine requires small diameter bins or cans or special heat removal features. Up to 20 to 25% of the constituents of a typical commercial HLW calcine produced by the Potcal process dissolve readily on contact with

water.⁽¹⁾ The volatiles content consists mainly of residual nitrates which are not completely decomposed at average calciner temperatures (350 to 550°C). The problem of volatiles in the calcine was obviated with the WCF product by venting the storage facility. The HLW canisters are required to be sealed, however, for transportation and receipt at the final storage site. During the Potcal process development at ORNL, a processing temperature of 900°C was found required to achieve complete nitrate decomposition and thus assure that sealed canisters of calcine would not pressurize. Therefore, in the following descriptions of HLLW calcining processes a "bakeout" of the loaded calcine canisters at 900°C is shown.

Following discussion of calcining, under the categories of "Vitrification" and "Other Solidification Processes," various post-treatments for calcine are described which involve consolidation to improve thermal conductivity and leach resistance.

Fluidized-Bed Calcination

Process Summary

Final Product Form: A mixture of granules and powder in the size range 0.05 to 0.5 mm and generated at a rate of ~40 l/MTU processed. The product can be stabilized (denitrated and dehydrated) for storage, or the calcine is a suitable feed to a glass melter.

Process Description: Wastes are atomized into a fluidized bed, heated by in-bed combustion, operating at a bed temperature in the range 500 to 600°C. Evaporation occurs on the surface of particles and results in a product consisting of granular bed material and powdered calcine, both of which are

removed from the calciner. Stabilized calcine product can be stored in canisters, or the calcine can be converted to other waste form (e.g., glasses, metal matrices, sintered glass ceramics).

Applicable Wastes: Wastes (liquid or slurries) consisting of HLLW, HLLW-ILLW, radioactive concentrates from evaporation processes, and organic spent solvents from fuel reprocessing.

Development Status: Process flowsheet has been verified on cold pilot-plant scale at feed rates up to 2 liters/hr; similar process and equipment operability has been demonstrated on a full radioactive scale using ERDA wastes at routine processing rates in the range 400 to 500 liters/hr. This corresponds to 2 to 3 times the projected output from a 5 MTU/day plant. The ERDA wastes for which high processing rates have been demonstrated are mainly composed of aluminum or zirconium nitrate, whereas commercial HLLW is predominantly fission product nitrates.

Process Effluents: Process off-gas can be treated by routine processing.

Process Operating Conditions and Features

Background

Fluidized-bed calcination was developed at the Idaho National Engineering Laboratory during the period 1952-1959. A demonstration plant-scale facility for solidifying aluminum nitrate wastes was constructed and began "hot" operation in 1963.⁽²⁻⁵⁾

Product

The product is a mixture of granular bed material and powdery solids removed from the off-gas system in the primary cyclone; the product is normally removed from the bed pneumatically. If glass is required, the calcined solids would be fed directly to a continuous melter. If calcine is to be stored directly, the calcined solids must be stabilized (denitrated and dehydrated) at about 900°C.

- Waste Form Composition and Volume

Calcined product density is in the range 2.0 to 2.4 g/cc; specific volume is nominally 40 l/MTU when processing combined HLLW-ILLW corresponding to the Barnwell Nuclear Fuel Plant (BNFP).

- Thermal Conductivity

The thermal conductivity of simulated commercial waste calcined solids is in the range 0.2 to 0.3 W m⁻¹ °C⁻¹.

- Leach Rate

About 60% of the ^{137}Cs and 40% of the ^{90}Sr were removed by 2000 hr of continuous leaching of fluidized-bed calcined ERDA waste. The leach rate of fluidized-bed calcine produced from typical commercial HLW waste compositions has not been determined.

- Chemical Limit

Mercury and iodine are not retained in the calcined solids; fluoride and chloride can be retained if additives are included in the feed. Sodium concentrations above approximately 0.4M may require use of additives such as iron.

- Temperature Limits of Stabilized Calcine

Stabilized calcine can be stored in practical size canisters, either in air or water storage. Both glass and calcine resulting from processing wastes as young as 1 year are difficult to store because of centerline or wall temperature limits. Annular canisters less than 60cm OD have distinct advantages in storage of young wastes. However, no annular canisters have been fabricated or tested. For 1-year old wastes, about 800 canisters (glass or calcine) will be required to store the waste output from a 5 MTU/day plant operating 300 days per year.

Processing

Fluidized-bed calcination is basically a continuous evaporation process for converting liquid radioactive HLLW and ILLW to a blend of powder and granular materials. Concentrates from the evaporation of low-level liquid wastes and spent solvents can also be processed in the fluidized bed.

Feed is transferred by air or steam jet to the feed preparation system in the calcining facility; the feed is prepared (chemical additives and mixing of HLLW and ILLW) batchwise and fed by a combination airlift and gravity system to the calciner. The feed is atomized by air through spray nozzles located on the wall of the calciner vessel.

The primary mechanism for solidification is the evaporation of atomized liquid droplets on the fluidized-bed particles; a portion of the atomized liquid also evaporates to a dry solid before striking the surface of a bed particle. Process heat is provided by in-bed combustion of kerosene, and the bed temperature can be easily maintained at any temperature in the range of 500 to 600°C.

The capacity of a fluidized-bed calciner is usually stated on the basis of liters of throughput per hour per 1000 cm² of calciner vessel cross-sectional area. The net capacity of the Waste Calcining Facility (WCF) for

processing ERDA wastes is 40/liters/hr-1000 cm². Capacities in the range 60 to 100 liters/hr-1000 cm² have been verified in the pilot plant.

Ruthenium volatility is affected by the method used to heat the calciner. With in-bed combustion about $2 \times 10^{-3}\%$ of the ruthenium in the feed is volatilized independent of operating temperature in the normal operating range of 500 to 600°C. With external heating, however, higher operating temperatures have been found to decrease ruthenium losses. At 570°C, 0.002% of the ruthenium is volatilized versus 0.02% at 500°C. There are no data available for full-level commercial HLLW; these data were obtained with simulated commercial waste solutions. Volatile ruthenium present in the calciner off-gas is removed by silica gel adsorption. Solid particulates are removed from the off-gas using conventional cyclones, a wet scrubbing system, and HEPA filters.

Fluidized-bed calciners are reasonably flexible as to the types of waste that can be satisfactorily calcined. Major properties of the waste feed affecting calcinability are feed solids concentration and constituents that cause particle agglomeration. The feed should be concentrated sufficiently to permit particle growth (maintenance of bed inventory) to properly balance particle attrition. Excessive concentrations of sodium in the feed can cause particle agglomeration. Currently expected commercial waste feed compositions do not present major problems in fluidized-bed calcination.⁽⁶⁾ However, in most tests to date a large percentage (30 to 50%) of the calcine has been in the form of fines, most of which are removed from the off-gas by a cyclone. The fines less than 10 μm, which are not collected by the cyclone, are scrubbed from the off-gas and recycled.

The fluidized bed using in-bed combustion also has the capability of accepting reasonable quantities of waste solvent for processing. Normally the annual production of waste solvent at the fuel reprocessing plant will be small compared to the quantities of high-level wastes. Thus, the waste solvent can be blended into the feed or fuel without significant impact on the process.

Limited pilot-plant runs have been made to determine fluidized-bed calciner operability with waste solvent; no insurmountable problems have been observed. However, long-term testing of the burning of waste solvents at conditions anticipated in a commercial calciner will be required to assess process operability accurately.

The process can be automated to minimize manpower requirements and to minimize the potential for human error. Based on WCF operating experience, equipment most prone to failure would be feed rate control valves, fuel and feed nozzles, and scrubbing solution pumps in the off-gas wet-scrubbing system.

The high-heat generating wastes in a collapsed bed during a shutdown would be cooled with redundant fluidizing air systems, but would have to be removed for extensive shutdowns. Redundant fluidizing air and pneumatic bed removal systems would remove the bed, if necessary, for transport to interim storage canisters.

Manpower and space requirements are as follows:

	<u>Space Requirements</u>	<u>Manpower Requirements</u>
Land Area, m ²	1400	--
Cell Space, m ³	2100	--
Manpower		
Operators	--	15
Maintenance	--	2
Health Physics	--	2
Other	--	5

Estimated Time of Readiness for Practical Design

Conceptual design can begin immediately; detailed design can begin 6 to 9 months after conceptual design starts.

Major Program Objectives

The development program discussed herein has the primary goal of verifying the applicability of the fluidized-bed calcination process to BNFP high-level wastes and generating data required for design and operation of a demonstration-scale plant facility. The basic flowsheet is based on the mixture of HLLW-ILLW currently proposed by BNFP. Except for the age of the waste and the attendant increasing requirements on the off-gas cleanup system with decreasing waste age, the specific waste composition does not significantly affect the basic plant design.

Major efforts in the program are: 1) verification of the calcinability of simulated AGNS waste at steady-state conditions in a large-scale pilot plant unit, 2) verification of the ability of the candidate off-gas cleanup system to remove particulate and volatile fission products and noxious chemicals to acceptable levels, 3) verify on a suitable scale the ability to address major safety questions, e.g., removal of a collapsed fluidized bed or heat dissipation without sintering in a collapsed configuration, 4) demonstration of a suitable calcine stabilization process, 5) design of a practical calcine storage system, 6) evaluation of the state-of-the-art in specific equipment to determine need for equipment developed, and 7) prototype equipment and remote maintenance mockup testing as necessary to minimize risks of significant process or equipment problems during plant operation.

Completion of the formal development and prototype testing program is planned for 1978; however, significant data applicable to the design of a demonstration facility are already available and will continue to be generated throughout the program. Essentially all of the data, based on cold testing, for detailed design would be available in 1977. The feed system, fluidized-bed calciner, off-gas cyclone, solids transport, calcine storage, and process support facilities could be designed with confidence beginning in early 1977.

Pot Calcination

Process Summary

Final Product Form: A porous cake of friable calcine containing about 90% HLLW and 10% additives to reduce volatilization. The calcine is readily soluble up to 20 to 40 wt%; the remaining oxides are relatively insoluble. Thermal characteristics are relatively poor.

Process Description: The process canister, which also serves as the final storage vessel, is heated in a furnace to boil and concentrate incoming HLLW and additives. When the liquid has been sufficiently concentrated, it begins to form scale on the inside walls of the canister. As the can becomes full of scale, the incoming feed addition rate continuously drops to a very low rate and is turned off. Radioactive decay heat causes the calcine temperature to rise at a fast rate so that the furnace temperature has to be steadily decreased from a 900°C temperature while the calcine in the center is increasing to 900°C, a required temperature for complete calcination.

Applicable Wastes: All liquid wastes which can be evaporated and dried or calcined to form oxides (excludes Hg, Cl, for example). Certain volatile constituents (sulfate for example) can be incorporated if additives, such as sodium or calcium, are provided.

Development Status: Fully demonstrated in both cold and fully radioactive pilot plant at feed rates of 15 to 30 liters/hr and overall total cycle rates of 12 to 15 liters/hr (equivalent to 0.75 MT/day).

Process Effluents: Liquid and gaseous effluents, including 10 to 30% of the ruthenium in the feed, can be treated by equipment routinely available in reprocessing plants.

Process Operating Conditions and Features

Background

The pot calcination process (Potcal) was developed by Oak Ridge National Laboratory in the early 1960's. References 7 and 8 present summaries of the process development. In the Potcal process, concentrated waste from an evaporator is fed into a pot (canister) heated by a furnace where the waste is denitrated and reduced to a calcine.⁽⁷⁾ Additives required to produce a desirable solid may be added to the waste or separately to the pot. Several operating modes are possible, but generally the process includes a waste evaporator to strip most of the nitric acid from the waste.⁽⁹⁾ A mathematical treatment for predicting calcine deposition in the pot and the resulting processing rate was developed by Perona.⁽¹⁰⁾ Jury at ORNL developed the theory for predicting temperature behavior in the pot during the calcining cycle in order to assure that wall temperatures could be controlled to prevent excessive calcine temperatures.⁽¹¹⁾

Radioactive demonstration of the pot calcination process was carried out in the Waste Solidification Engineering Prototypes Program (WSEP) at Hanford.^(12,13) Although the process was satisfactorily operated with fully radioactive waste, the Potcal process has not been seriously considered because of its apparent capacity limitations.

Product

The pot calcine product forms in the pots as a porous cake of friable calcine with an irregular cone-shaped void at the top center. The calcine is laid down on the pot walls and bottom in a somewhat layered fashion. The permissible canister size is highly dependent on the heat content of the waste, and the diameter is severely limited because of the low calcine thermal conductivity. For the reference waste the use of an 20-cm-diam canister would require that the waste have been aged for over 2 years. Large diameters would require older waste (i.e., over 4 years for a 30-cm-diam canister).

- Waste Form Composition and Volume

In order to prevent cesium and rubidium volatilization, the following chemical relationship must be satisfied in the aqueous feed to the process:

$$\frac{\text{chemical equivalents alkali metals}}{\text{chemical equivalents nonvolatile anions}} \leq 1;$$

Suitable nonvolatile anions are sulfate and phosphate.

For the reference HLLW: Using phosphate as the nonvolatile anion,

$$\frac{0.01 \text{ Na} + 0.039 \text{ Cs} + 0.0095 \text{ Rb}}{3(0.042 \text{ PO}_4^{3-})} = 1.14$$

Therefore additional nonvolatile anion is required.

Specific gravity 1.2 to 1.5 for Purex Waste. (8,14)

Specific volume $65.5 \text{ kg/MT} \div 1.35 \text{ kg/liter} \approx 50 \text{ liters/MT}$.

- Thermal Conductivity

In laboratory tests, the thermal conductivity of Purex pot calcine varied linearly from $0.35 \text{ W/m}^\circ\text{C}$ at 200°C to $1.0 \text{ W/m}^\circ\text{C}$ at 800°C (p. 68, Reference 7). The thermal conductivity of radioactive calcine prepared in engineering-scale equipment averaged $0.35 \text{ W/m}^\circ\text{C}$ from 100 to 700°C (p. 5.23, Reference 15).

- Leach Rate

About 25 wt% of bulk material including cesium is readily leachable. Remaining oxides, such as cerium are considerably less soluble (p. 5.51, Reference 15).

- Chemical Limits

Mercury not retained (p. 43, Reference 7). Sulfate can be retained almost quantitatively ($\geq 98\%$) if the ratio of:

$$\frac{\text{chemical equivalents (alkali metals + alkaline earths)}}{\text{chemical equivalents (SO}_4^{2-} + \text{other nonvolatile anions)}} \geq 1.1$$

Likewise, alkali metals such as sodium can be retained if the ratio:

$$\frac{\text{chemical equivalents (alkali metals)}}{\text{chemical equivalents (nonvolatile anions)}} \leq 1$$

(p. 51, Reference 7).

Fluoride and chloride unknown, but may hold fluoride by same methods used for sulfate (p. 52, Reference 7).

Limitations are summarized in (Reference 14, p. 10.8).

- Temperature Limits

General: Limit temperature to maintain below processing temperature. Assuming a 900°C centerline limit, from 6.5 kW to 8 kW can be incorporated in 38 to 50 cm diam pots with a 2.4 m fill height. However, smaller diameters are essential unless the waste is stored before calcining, assuming 50 liters calcine/MT and 25,000 MWd/MT fuel:

<u>Diam, cm</u>	<u>W/liter</u>	<u>Age of Waste, years</u>
15	145	1.5
20	90	2.5
25	60	3.5
30	45	4.5

Processing

In the Potcal process, the canister is placed in a heating-cooling furnace and connected to the off-gas system. The canister is heated, and concentrated waste is fed from the evaporator into the heated pot until the liquid is somewhat below the desired fill level (to minimize entrainment during the high boil-off period). When scaling of the pot wall occurs, the level will rise to the desired fill level and then for the duration of the filling cycle the feed is added at a continually decreasing rate to exactly balance the boil-off. The feed is terminated at about 5 liters/hr. As the calcine scale grows on the pot wall, it becomes necessary to reduce the heat input to prevent the calcine temperatures from becoming excessive due to the fission product heating. Thus the pot wall temperature is controlled by reducing heat input and finally by cooling so that a 900°C temperature wave passes through the calcine from the wall to the pot centerline. (7,13)

A special self-cleaning off-gas line is recommended to prevent line plugging. After cooling, the canister is removed for post-treatment (welding, etc.), and another canister is installed. All steps have been demonstrated. (Note that canister installation and removal times could be 2 to 4 hr each, but should be similar for all processes requiring a canister.)

- Flexibility

Pot calcination is quite flexible, but is benefited by maximum concentration of the HLLW. Flowrate changes are of no major significance. A separate additive stream may be proportionately controlled off the main feed stream.

ILLW can be combined with the HLLW, but a nonvolatile additive such as phosphate must be added. Organics will cause severe foaming in the pot if an antifoam agent is not used. (13)

- Process Reliability

Process reliability - requires self-cleaning off-gas line and emergency vent system.

Remote maintainability - very little to maintain except for the heating-cooling furnace, which is standard for most waste solidification processes. Occasional cleaning of the off-gas system is required. Occasional plugging in the canister level and pressure tubes can occur.

Remote operability - Good control of feed rate is required. Feed rate is controlled by the pot liquid level, which is sometimes difficult to determine due to boiling and foaming. Temperature control to prevent excessive temperatures requires pot centerline thermocouples at several levels in the canister.

- Process Capacity and Space Requirements

Capacity - 15 liters/hr of reference HLLW for 15 to 30-cm diam pots (Reference 12, p. 4.6, Reference 14, pp. A.10 and 4.6).

$$5 \text{ MTU/day} \times 100 \text{ gal/MTU} \times 3.78 \text{ liters/gal} = 1900 \text{ liters/day} \\ \approx 80 \text{ liters/hr}$$

$$80 \text{ liters/hr} \div 15 \text{ liters/hr} \approx \underline{5 \text{ pot cal lines.}}$$

Maximum concentration of the HLLW is beneficial to pot calcination; thus 200 liters/MTU HLLW would require less than 3 pot lines. The possible use of internal fins in the canister has never been tested but should significantly increase canister diameter and process capacity.

Space - 4.8 m wide x 13.4 m long x 9.1 m high (Reference 14, p. 9.20).

Estimated Time of Readiness for Practical Design

Pot calcination has been demonstrated on a full scale in both cold and radioactive operation. Detail design of a waste treatment plant using multiple pot lines could begin in less than 1 year.

Major Development Program Objectives

The development program for pot calcination was essentially completed with cold development at ORNL⁽⁷⁾ and radioactive demonstration at Hanford.⁽¹⁴⁾ At the time work was terminated on the process it was believed that pot calcination would not be used by reprocessors for solidifying HLW. The reasons were twofold: 1) other continuous calcination processes and processes to make glass appeared to make pot calcination obsolete and 2) the limited capacity of the batch process appeared to require too many multiple pot lines.

A current evaluation indicates that pot calcination could be used to successfully calcine HLLW. Components of a development program to improve pot calcination include:

1. Calcine testing to determine if the calcine is sufficiently stabilized.
2. Methods to increase process capacity to minimize the number of multiple lines required. This could include the use of finned canisters. (Another option would be to age the waste before processing so that large diameter canisters could be used.)

3. Calcination tests to determine operating characteristics with current low-salt, high-fission product waste compositions.

Testing for 1 year should provide sufficient answers to allow detailed design of the process to start at that time.

Rotary Kiln Calcination

Process Summary

Final Product Form: A relatively free flowing finely divided oxide powder.

Process Description: The rotary kiln calciner is an externally heated (500°C) rotating cylinder operating at a slight angle so that deacidified HLLW introduced at the upper end is dried and almost completely denitrated before it exits the lower end. A loose bar keeps the calcine free-flowing and prevents deposits sticking to the wall. The off-gas is scrubbed with water to remove entrained particulates, which are recycled by combining the scrub solution with incoming HLLW. The calcine product is heat treated to assure total decomposition of nitrate.

Applicable Wastes: All aqueous wastes which can be evaporated and dried or calcined to form oxides (excludes Hg, for example). The alkali metal content of the waste should be stabilized by the addition of stoichiometric amounts of a stable anion such as sulfate or phosphate.

Development Status: The process has been in development for over 10 years in France for use with a continuous HLLW vitrification process. For much of that time an engineering scale unit has been in use with simulated nonradioactive waste. There has been no radioactive experience.

Process Effluents: Liquid and gaseous effluents can be treated by equipment routinely available in reprocessing plant.

Process Operating Conditions and Features

Background

The French CEA has developed the rotary kiln calciner specifically for close coupling with a continuous melter to convert HLLW to glass. This development is described in more detail in Section 6.3.2.

Product

No data on rotary kiln calcine is available since the French always have fed the calcine directly to a vitrification unit. The calcine should have a bulk density of 1.0 to 1.3 g/cm³.

Processing

The process would differ from the vitrification operating mode only in that the calcine product would exit to a diverter system leading to at least two canister stations. This would permit continuous operation of the calciner, by diverting the product calcine to a new empty canister as soon as the calcine level in the canister being filled reached a preset level.

Estimated Time of Readiness for Practical Design

The French are scheduled to have a radioactive engineering-scale rotary calciner in operation in their vitrification facility in 1977. Much of the technology from this installation could be applied to a calcine product facility.

Major Development Program Objectives

Development which would be required for a calcine product facility include:

- Methods of increasing the bulk density of the rotary kiln calcine.
- Methods of increasing the thermal conductivity of the calcine product.
- Engineering design of the calcine diverter valve.

Spray Calcination

Process Summary

Final Product Form: A very fine powder. Most particles have a diameter in the range of 2 to 5 μm .

Process Description: The HLLW is pumped to an internal mixing pneumatic atomizing nozzle in the top of the heated (700°C wall temperature) spray calciner barrel. The atomized droplets (nominally <70 μm in diam) are flash dried and calcined as they fall through the hot barrel. The finely divided powdery product is separated from the off-gas by sintered stainless steel filters.

Applicable Wastes: All aqueous wastes which can be evaporated and dried or calcined to form oxides (excludes Hg, for example). Any pumpable waste concentration can be calcined. Wastes containing 2M Na can be readily calcined.

Development Status: The process has been in development at PNL for over 15 years. Thirteen fully radioactive engineering-scale runs (about 50 hr each) with the spray calciner were made in the Waste Solidification Engineering Prototypes (WSEP) program. Over 1000 operating hours with simulated waste at feed rates up to 75 liters/hr have shown spray calcination to be a simple reliable operation. A large-scale calciner is currently under construction to demonstrate spray calcination at higher feed rates.

Process Effluents: Liquid and gaseous effluents can be treated by equipment routinely available in a reprocessing plant.

Process Operating Conditions and Features

Background

Except in the very initial stages of development, the spray calciner has been used in conjunction with calcine post-treatment processes, producing either phosphate melt products or borosilicate glasses (see Section 6.3.2). There is apparently no reason that spray calcines could not be loaded directly into the final storage canister if the decision is made that calcine is an acceptable product.

Product

The calcine produced in the spray calciner is very finely divided and has the lowest bulk density of the products from any calciner described in this section. The bulk density may range from as low as 0.5 g/cm^3 to 1.3 g/cm^3 , depending upon the composition of the HLLW.

Processing

The process would differ from the vitrification operating mode only in that the calcine product would exit to a diverter system leading to at least two canister stations. This would permit continuous operation of the calciner by diverting the product calcine to a new empty canister as soon as the calcine level in the canister being filled reached a preset level.

Estimated Time of Readiness for Practical Design

The spray calciner, as coupled to an in-can melter, is essentially ready for preliminary design. Much of the technology from this installation could be applied to a calcine product facility.

Major Development Program Objectives

Development required for a calcine product facility would include:

- methods of increasing the bulk density of the spray calciner product
- methods of increasing the thermal conductivity of the calcine product

Wiped/Scraped Film Evaporator

Process Summary

Final Product Form: A dry oxide cake.

Process Description: Liquid or slurry wastes are evaporated to a thick, flowable slurry, or to a free flowing solid, and discharged to a receiving canister. After filling, the canisters are baked to complete the dehydration and denitration. Additives to control the characteristics of the final product and the operation of the evaporator may be added to the inlet end of the evaporator with the feed stream.

Applicable Wastes: Any liquid or slurry.

Development Status: Evaporation of simulated HLLW to a 50% slurry product has been demonstrated at 150 liters/hr/m² of heat transfer surface using 120 psig steam as a heating medium. Evaporation to a free-flowing solid has been demonstrated at about 110 liters/hr/m². No radioactive demonstrations have been made. The process of following the filling of canisters with a post-treatment bake is conceptual only, not demonstrated. The direct conversion of the slurry concentrate to a borosilicate glass has been demonstrated with the metallic melter, the in-can melter, and with the ceramic melter.

Process Effluents: The only process effluent, the off-gas stream, will contain condensable water and nitric acid, noncondensable gases, and volatile or entrained solids, all of which can be routinely treated with standard chemical processing equipment.

Process Operating Conditions and Features

Background

The application of wiped film evaporators to reduce a wide variety of simulated high-level, intermediate-level, and mixed liquid waste formulations to slurries containing up to 55 wt% solids has been studied at PNL.⁽¹⁶⁾ Other recent studies at PNL⁽¹⁷⁾ with wiped film evaporators operating at higher temperatures have reduced high-level liquid wastes to a free-flowing solid product in a single pass. Use of wiped-film evaporators has been studied at the Savannah River Laboratory⁽¹⁸⁾ to learn whether they can successfully reduce underground stored nuclear waste solutions to a product that solidifies on cooling.

Possibilities for using a wiped film evaporator to reduce the volume of residual liquors resulting from vacuum crystallization of Hanford underground stored nuclear wastes have been studied by the Atlantic Richfield Hanford Company.^(19,20) The use of wiped film evaporators to reduce the volume of low-level liquid nuclear wastes (e.g., laundry wastes, reactor cooling water blowdown, decontamination wastes, laboratory wastes) has been studied at the Ballistic Research Laboratory.⁽²¹⁾

Industry utilizes the machine's low retention time characteristics in processing heat-sensitive materials like catsup, concentrated fruit juices, and instant coffee. Also, the plastics industry uses the evaporator's efficient processing of high-viscosity solutions to remove organic solvents from crude plastic materials. As a result of their wide industrial use, wiped film evaporators are available from several manufacturers in a wide variety of designs and in almost any structural or process-contact metal or alloy desired.

Product

Wiped film evaporators can yield products of all concentrations and consistencies from dilute solutions through slurries and pastes to free-flowing powders, depending upon design of the unit and the operating mode. There is, however, very little experience in converting HLLW compositions to dry powder. Most of the development has centered around the production of slurries. In the case of ILLW, these are allowed to cool to a solid crystalline salt material. In the case of HLLW, the slurries are fed to a vitrification unit (see the section on the continuous ceramic melter, for example). It is also conceptually possible to fill a heated canister directly with wiped film evaporator-concentrated HLLW and bake out to form in the canister a calcine cake equivalent in properties to other calcine products, especially the Potcal product.

Processing

A waste solution, or slurry, is introduced into one end of a heated cylinder, vertical or horizontal. Multiple paddles, rotating within the cylinder with a tip speed of from 6 to 12 m/sec, wipe the waste on the heated surface in a thin, highly agitated, film. Partial evaporation takes place rapidly from the thin film and the concentrate is respread quickly over the heated surface by the following paddle. The solids move to the opposite end of the cylinder and drop as a slurry, or as a solid, through a discharge nozzle on the bottom of the evaporator to a receiver below. Additives to control the operating characteristics of the evaporator, or the characteristics of the final product, are added to the evaporator with the feedstock, or to the receiver with the concentrate.

Estimated Time of Readiness for Practical Design

The practical design for a facility to concentrate underground stored wastes from past nuclear fuel reprocessing operations is currently available. Prototype units, with 3.7 m^2 of heat transfer surface, are currently being built, and design verification tests will be started as soon as the prototype units become available. (18)

Only minor modifications to the design of standard industrial evaporators (to enable them to be remotely operated and maintained) are needed if high-level, or mixed level wastes are to be reduced only to a slurry for feed to an in-can or to a ceramic-type melter. These modifications could be implemented and tested on simulated wastes in 1 to 2 years. If a free-flowing solid product is desired, 2 to 3 years of design modification, implementation and testing of high-temperature equipment, off-gas cleanup, and volatile materials behavior with simulated high-level waste solutions will be required.

Major Development Program Objectives

The optimum product form will need to be determined, i.e., slurry or solid product, and the post-treatment required to realize the optimum product characteristics.

It will be necessary to determine the most appropriate configuration of the various vertical and horizontal evaporators available, consistent with the product form chosen. This step includes considering the ease of remote operation and maintenance, decontamination capabilities, and the movement of the product from the evaporator into the solidifier.

A typical evaporator would be acquired and operated with simulated waste solution to identify operating characteristics and the paths of volatile materials through the equipment and to develop instrument sensors to aid in remote operation.

The design would be modified to improve remote operation and maintenance, and to minimize points of possible contamination buildup.

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6.3.2 Vitrification

Glass or glasslike forms are being emphasized internationally in development programs for the near-term immobilization of power reactor wastes. Development of glass waste forms began more than 20 years ago. Initially the investigations emphasized relatively high melting formulations (operating temperature 1250 to 1400°C) resembling those of common glasses.⁽¹⁻³⁾ As development began on an engineering-scale, emphasis shifted to lower melting formulations (operating temperature 950 to 1150°C) that allowed melting in metal containers. The lower operating temperatures also significantly reduced volatility, permitting a higher waste loading in the glass.

Several waste vitrification processes, using batch or continuous metallic melters, have now been carried through various degrees of development, including two major radioactive pilot plant operations. In the U.S. in the years 1966 to 1970 the Waste Solidification Engineering Prototypes (WSEP) program demonstrated waste fixation in glass at radiation levels equivalent to less than 1 year out-of-reactor for fuel with a 45,000 MWd exposure.⁽⁴⁻⁵⁾ The WSEP equipment was scaled to handle HLLW for a 1 MTU/day reprocessing plant. In France, the PIVER pilot plant began vitrifying HLLW from the Marcoule Purex plant in May 1969.⁽⁶⁾ Because of progress in waste vitrification, several nations have chosen to convert their HLLW arising from nuclear power generation to glass. International waste solidification plans are shown in Table 6.5.

TABLE 6.5. International Plans for Solidification of HLLW

<u>Country</u>	<u>Product Type</u>	<u>Process</u>
England	Borosilicate Glass	Rising level glass
France	Borosilicate Glass	Rotary kiln calciner and continuous metallic melter (Marcoule), rotary kiln calciner and continuous ceramic melter (La Hague)
Germany	Borosilicate or Phosphate Glass	Spray calciner and continuous metallic melter
Russia	Phosphate Glass	Unknown
India	Borosilicate Glass	Rising Level Glass
Japan	Undecided	Undecided

Glass has the advantage of being a very inclusive material. Although only a few of the waste constituents are glass formers by themselves, much of the periodic table can be incorporated in glass, either as network formers or modifiers, and thus be immobilized in the glass. Typical borosilicate glass compositions and other characteristics are shown in Table 6.6.

TABLE 6.6. Borosilicate Glass Characteristics

Composition	
SiO ₂	25-40 wt%
B ₂ O ₃	10-15 wt%
Alkali metal oxides	5-10 wt%
ZnO	0-20 wt%
Waste oxides	20-35 wt%
Typical volume	60-80 l/MTU
Density	3.0-3.6 g/cm ³
Thermal conductivity	0.9-1.3 w/m-°C
Leach rate	10 ⁻⁴ -10 ⁻⁷ g/cm ² -day
Processing temperature	1000-1400°C

Glass formulations have been developed which provide low leachability and high integrity when solidified and yet permit trouble-free processing. Properties important during processing include low viscosity, corrosivity, and volatility and good homogeneity. Current melt compositions have the following:

- A viscosity of 200 poise or less at processing temperatures (950 to 1150°C) allows melt draining and/or complete gas evolution.
- Corrosion of both the canister and melter is within acceptable limits.
- Radionuclide volatilization from borosilicate melts has been shown to be within operational limits.
- To minimize sludge buildup in continuous melters, solution of all waste constituents in the melt is maximized.

Some compounds frequently found in ILLW, which may be incompatible with current melt compositions, include iodine, chloride compounds, sulfate compounds, and mercury compounds.

It is planned that radioactive waste glasses be cast in sealed canisters to give an additional level of isolation. Due to the low rate of glass corrosion during normal filling and storage conditions, it is generally agreed that external factors will govern the lifetime of the canister.

If the canister is breached, the most probable mechanism for release is by dissolution or leaching of the waste. Although the leaching of constituents from glass is a complex phenomena, a simple comparison can be drawn by stating that glass formed in a refractory type melter has a leach rate about equal to that of Pyrex in neutral or basic solutions. Glasses formed in metallic melters have a somewhat higher leach rate.

The quantity of radioactivity released if the glass product contacts water is a function not only of leachability but also of surface area exposed. For large canisters of glass the surface exposed per weight of glass is very

low. But accident conditions such as physical and thermal shock may increase the surface area due to breakage. Experimental data⁽⁷⁾ show that an impact at 21 m/sec the surface area increases by a factor of 10. Thermal shock produced by plunging a 15-cm diam, 1000°C canister of glass in water increases surface area by a factor of about 20.⁽⁸⁾

A major advantage of the glass form is a thermal conductivity which allows containment of relatively large amounts of high heat generating waste. Based on the following conditions:

- reference waste composition
- one year out-of-reactor
- glass composition incorporating 25 wt% waste oxides
- canister, 30 cm diam filled to a depth of 2.4 m
- maximum centerline temperature, 800°C
- free convection air cooled,

a canister of glass can contain the waste from about 2.5 tonnes of fuel. Addition of eight drop-in, stainless steel fins allows a diameter of about 50 cm, which can store waste from up to 6 tonnes of fuel.

In-Can Melting

Process Summary

Final Product Form: Borosilicate glass containing about one part HLLW oxides and two parts glass-forming additives by weight, a low leachability, stable product, meeting current 10 CFR 50 requirements. Most waste oxides are accommodated in the glass structure, but a few occur as separate phases that are dispersed in the glass.

Process Description: In-can melting is a batch process for vitrifying HLLW. The storage canister is placed in a multi-zone furnace and coupled directly to a HLLW calciner. Glass-forming frit is fed to the canister at a rate proportional to the calcine production rate, and the blend is melted at 1000 to 1100°C in the canister. As the melt level rises, the furnace zones below the level are turned off and cooling is started to remove heat generated by the

waste. The off-gas from the melting is vented through the calciner off-gas system. The canister of glass is cooled, sealed, decontaminated, and inspected.

Applicable Wastes: HLLW can be processed. Volatiles such as Hg or I cannot be maintained in the glass structure.

Development Status: Demonstrated in a fully radioactive pilot plant at 7.5 kg glass/hr, and in a nonradioactive pilot plant in 20 and 30-cm diam canisters at melting rates as high as 29.5 kg glass/hr (~ 3 MTU/day equivalent). Pilot plant operations essentially complete. Ready for design of a full-scale facility.

Process Effluents: The gaseous and condensable process effluents can be treated by equipment normally available in a reprocessing plant. Less than 2% ruthenium and 0.5% of all other waste oxides escape into the calciner off-gas.

Processing Operating Conditions and Features

Background

Vitrification of HLLW using a spray calciner for drying and the storage canister as the melting crucible was demonstrated at PNL in 1970 during the WSEP program. Two fully radioactive engineering-scale runs were made.⁽⁹⁾ "Pot vitrification" processes based on somewhat similar principles have also been developed in England, France and India.

Some advantages of in-can melting are:

- simplicity of the processing vessels and heaters
- no internal moving parts
- no process equipment between the calciner and glass storage container
- no transfer or valving of melt required
- elimination of melter deterioration and disposal problems.

Because of the success with the in-can melting process in the WSEP program,^(4,5) further development was initiated at PNL in 1974. Between October 1974 and October 1975 13 engineering-scale, nonradioactive, in-can melting campaigns were completed. Direct coupling of an in-can melter to a spray calciner, to a fluid-bed calciner, and to a wiped-film evaporator was demonstrated. Various internal fin designs were evaluated, melting rates were established, and processing details were resolved. Presently equipment and canister designs are being verified in preparation for further hot cell demonstration, and equipment is being prepared for full-scale (5 MTU/day capacity) remotely operated processing demonstrations. A comprehensive canister development program being conducted includes materials selection, thermal and stress analyses, closure and fin design, economics, and reference design and specification preparation.

Product

The product of the in-can melting process is a vitrified, slightly fractured monolith sealed in a metal canister. Because the melting is done in the metallic storage canister, processing temperature restraints prevent complete assimilation of all waste oxides into the glass matrix. The result is a glass matrix in which minor amounts of several different crystalline phases are dispersed. Cerium dioxide is the most prevalent crystal phase observed. The leachability of the glass is not significantly increased by the crystalline phases.

Recently installation of internal, longitudinal fins in the canister for increased thermal conduction has increased processing capacity as well as about doubled the heat producing radioisotopes allowable in the canister. The maximum canister diameter is a function of the number of fins used and of the heat generation rate of the glass, which is a function of the waste loading in the glass and the age and burnup of the reprocessed fuel. Maximum diameters may vary from 20 cm in a can with no fins containing a product having a heat generation rate of 150 W/liter to 60 cm for a glass containing 5-year-old waste.⁽¹⁰⁾ Cracks in the glass monolith observed after rapid cooling are the result of differences in thermal expansion between the glass and the fins, and of stress in the glass caused by rapid cooling. The glass can be annealed to obviate cracking if desired.

Processing

Vitrification by in-can melting involves two steps, HLLW calcination and melting. The melting step is flexible and can accommodate a wide range of calcine characteristics. Spray calcination has been developed most completely for coupling to an in-can melter; fluidized bed calcination has been studied less extensively for this purpose.

Spray Calcination. The heated-wall spray calciner has proven a simple, reliable unit for remote calcination of a wide variety of nuclear wastes. Over 1500 operating hours have been logged processing simulated high-level wastes in both remote maintenance hot cells and contact maintenance areas.

In the spray calcination process HLLW is pumped to an atomizing nozzle located at the top center of the heated-wall spray calciner. The waste is atomized by pressurized air, producing small droplets which are dried and calcined in flight through the 700°C wall temperature vertical spray chamber.⁽¹¹⁾ Calcination time is extremely short, thus inhibiting radionuclide volatilization and providing essentially zero calcine holdup in the calciner. Periodic operation of wall-mounted pneumatic vibrators prevent scale accumulation in the calciner. Atomizing air, steam, and oxides of nitrogen leave the calciner through sintered stainless steel filters which are periodically

cleaned by a reverse-direction pulse of air. Less than 0.1% of the nonvolatile radionuclides pass through the filters, thus significantly reducing the load on the effluent treatment system and reducing the amount of liquid recycled to the calciner from the treatment process. Calcine from the spray chamber and filters drops directly into the in-can melting canister. The fine spray calcine particles react rapidly with the glass frit in the melter.

Tests with recently developed ceramic atomizing nozzles show less than 0.01 mm wear on the 6.3-mm nozzle orifice after 1000 hr of operation.⁽¹²⁾ It is anticipated that in service the remotely replaceable feed nozzles will last many months.

Heated-wall spray calciner operation is relatively simple. Startup is accomplished as rapidly as the calciner furnace can be heated to temperature. Shutdown requires only discontinuation of liquid feed followed by a 1-min nozzle flush.

Since spray calcination does not rely on physical contact with a hot surface, waste concentration is not a process concern. Wastes containing from 0 to 250 g of solids per liter are easily calcined without process or equipment changes. Moreover, large amounts of ILLW can be incorporated with the HLLW. Wastes containing 2M sodium have been processed without requiring feed additives or process changes.

Pilot-scale equipment has been operated at feedrates of over 75 liters/hr (80 liters/hr required for a 5 MTU/day plant) and full-scale equipment under construction is expected to process 100 to 200 liters/hr of waste.

Fluidized Bed Calcination. Fluidized bed calcination provides an alternative means of feeding an in-can melter. The section on calcination describes conventional fluidized bed operation and equipment designed to produce a stable calcine as a final product. Modified techniques developed at PNL^(13,14) would use equipment similar, if not identical, to that described in that section, but with a different operating mode.

Operation for use with the in-can melter would be as follows: A temperature-resistant, granular, glass-forming material such as SiO_2 , would be continuously added to the fluidized bed where it would be coated with calcined waste. This coated material would overflow and/or be elutriated from the calciner vessel to an adjacent filtering vessel directly coupled to the in-can melting canister so that the material drops into it. A separate addition to the canister of the other glass-forming additives (B_2O_3 , CaCO_3 , etc.) is required. The modified operating technique results in a low calcine and fission product inventory in the bed at all times, reducing the potential overheating consequences of loss of fluidization.

The bed can be operated at temperatures ranging from 400 to 800°C using in-bed combustion heating. A single fluidized bed calciner can handle the waste from a 5 MTU/day reprocessing plant.

The in-can melter could also be supplied with calcine from a rotary kiln calciner or a drum dryer.

Melting. The HLW calcine generated by the spray calciner or any of the other calciners mentioned above is dropped directly from the calciner into the storage canister located in a multi-zone furnace below the calciner. Because calcining is a continuous operation while in-can melting is a batch process, two melting furnaces are located below the calciner, and a diverter valve is placed in the duct connecting the calciner to the melters. The glass-forming frit is added to the calcine above the diverter. While the batch is being diverted to one canister, an empty canister is exchanged for a filled one in the other furnace position. Calcined waste and frit are fed to the canister being filled at a rate not exceeding the melting capacity of the furnace.

A melting rate of 29.5 kg/hr has been demonstrated with an 20-cm-diam canister containing eight internal fins.⁽¹⁵⁾ Computer modeling of the in-can melting process indicates the melting rate in a 30-cm-diam canister to be 51 kg/hr. A melting rate about 45 kg/hr is required to support a 5 MTU/day reprocessing plant.

The glass-forming frit is metered continuously to the melter at a rate proportional to the calcine generation rate. Because the HLLW flow rate to the calciner is known and because the total oxide content of the HLLW is known, the frit flow rate is easily established. The frit flow rate is also easily maintained because the hopper and metering equipment are located outside the hot cell. The metered frit then passes through an airlock into the cell and flows by gravity into the cone below the calciner. Because the calcine and frit do not come together until just before entering the melter, the potential for batch sintering in processing equipment due to self-heating of the waste is minimized.

As the melt begins to fill the canister, the temperature below the melt level rises above the processing temperature because of the heat generated by the waste. Therefore, the furnace zones are turned off after the melt level rises above them, and cooling is initiated in those zones.

After the canister is filled to the desired level, the feed mixture of HLW calcine and frit is diverted to the other melting station. The unfixed material on the inside canister surface above the melt level is either removed or melted in place. The canister is maintained at temperature for several hours to assure complete melting. Then the canister is cooled, capped and removed from the furnace. The canister is seal welded, leak checked, decontaminated and integrity checked prior to removal to storage.

An advantage of the in-can melting process is that it does not use a separate melter unit. The need for melt draining and valving, probably the most troublesome and difficult-to-engineer operation associated with the use of a separate melter, is avoided. With melt draining not required, the in-can melting process is relatively insensitive to melt viscosity. Wide variations in waste composition and frit-to-calcine ratio are tolerated. Laboratory tests have shown that calcine agglomerates even above 1 cm in diameter dissolve readily in the melt.

Melter corrosion problems are minimized since a new melter is used for each run. The corrosion rate of the standard in-can melting canister (i.e., melter) material, 304 L stainless steel, in waste glass melts at 1050°C is less than 0.1 mm/day.

Estimated Time of Readiness for Practical Design

Experience with the spray calciner is complete enough that practical design may be initiated immediately. Development with the pilot-scale melter is essentially complete, and full-scale testing will provide the additional information desired for practical design within a year.

Major Development Program Objectives

Major development objectives in the current in-can melting program include: 1) finalization of canister design, 2) process procedures optimization using a multi-zone furnace, and 3) full-scale, remote demonstrations. The canister development program includes fabrication and testing of designs which eventually will meet all the criteria for processing, handling, shipping, storage, and disposal of the waste.

The in-can melting development program requires procurement of a near full-scale multi-zone furnace in which developmental canister designs can be used to evaluate and demonstrate various processing techniques, cycles, hardware, etc. Beyond this a full-scale totally remote system may be required to demonstrate long-term reliability and maintenance of the process.

Continuous Ceramic Melter

Process Summary

Final Product Form: Inert borosilicate glass containing about one part by weight HLLW oxides and two parts by weight glass-making additives.

Process Description: Glass frit is slurried with the HLLW and fed directly to the melter (optionally the feed may be preconcentrated or calcined). Water, nitric acid and nitrous oxides escape through the off-gas system, while the waste oxide residue and frit are fused into a homogeneous vitreous glass at temperatures ranging from 1100 to 1200°C. The glass is then drained into the storage canister.

Applicable Wastes: All liquid wastes which can be calcined, all waste oxides (incinerated ash) and all nonpyrophoric solids which can be added to the canister. Most chemical species which volatilize (Hg, I, Cl) below the glass melting temperature cannot be incorporated into the glass matrix.

Development Status: Demonstrated at 30 liters/hr while feeding simulated HLLW (11 kg of glass/hr) and 60 kg of glass/hr while feeding powdered calcine. Current engineering prototype was held at temperature (1000 to 1300°C) continuously for 11 months. During intermittent operation within this period 4 MT of glass was produced.

Process Effluents: Liquid and gaseous effluents can be treated by equipment routinely available in reprocessing plants.

Process Operating Conditions and Features

Background

During the past decade joule-heated, ceramic-lined melters have been gaining broader use in the glass industry in the U.S. and throughout the world. Selection of this type of melter by the glass industry has been based on low off-gas effluents, high capacity, long life, and superior glass quality. Since all these characteristics are desirable for a HLLW vitrification system, development programs have started in the U.S. and abroad.

The first known application of a joule-heated ceramic melter for vitrifying simulated HLLW was by the Danes.⁽¹⁶⁾ The melting energy was provided by passing current between a special electrode arrangement through a thin layer of glass. Direct feeding of simulated HLLW was demonstrated. More recently the French have been investigating a joule-heated, ceramic melter using induction coupling to the glass to provide the needed melting energy.

Development of a joule-heated ceramic melter at PNL was started in 1973.⁽¹⁷⁾ Four laboratory-scale melters were assembled and tested during 1974.⁽¹⁸⁻²¹⁾ In 1975 an engineering prototype was held at temperature (1000 to 1300°C) continuously for 11 months. Intermittent operation during this period produced a total of 4 MT of glass.⁽²²⁻²⁵⁾ The design of the PNL melters is based on conventional glass industry melting technology, which employs submerged power electrodes in a rectangular tank.

Product

The capabilities provided by a continuous ceramic melter allow for broad flexibility in glass composition and final form.

Waste Form. The controlled draining of glass from a melter can permit possible future changes in the waste form package. For the current procedure of storing the waste as a monolith in a canister, the continuous ceramic melter would allow periodic filling of even a water-cooled canister. However, a continuous ceramic melter would not be limited to filling canisters. A continuous stream of glass draining from the melter could be coupled to a glass shape-forming device which could produce marbles, for example. In this process configuration the melter would be compatible with alternative solidification process schemes discussed later, e.g., metal matrices and coated pellets.

Waste Form Composition. The high-temperature melting capability of a ceramic melter allows for improvement in the chemical durability of HLW glass. Generally stated, the chemical durability of glass is most readily enhanced by high silica concentration in the glass. Higher concentration of silica implies a higher melting temperature for the glass. Although not limited to high temperature glasses, a ceramic-lined melter may be the only practical system for processing higher temperature glasses if they are desired.

Certain constituents (Fe, Cr and Ru) in waste absorb infrared radiation and lower the thermal conductivity of the glass melt. In radiant or heated-wall type melting systems this characteristic can result in poorly or incompletely melted glasses. In an ionically heated melter the heat is dissipated within the glass itself, assuring thorough melting of the glass. Glasses with iron oxide content as high as 12 wt% have been melted with ease.⁽²⁶⁾

Processing

System Description. The fundamental components of HLW, joule-heated, ceramic melter are: 1) glass contact refractories, 2) electrodes, and 3) molten glass.

1. Glass Contact Refractories. Corrosion testing of many of the commercially available refractories using the current reference HLW glass has been completed by Bates.^(27,28) The results have shown that several refractories are suitable for a long melter life.
2. Electrodes. Positioned at both ends of the tank, the electrodes transmit alternating current to the molten glass. The electrodes must be resistant to glass attack and be electrically conductive. The primary materials used as electrodes in the glass industry are molybdenum, tin oxide, and platinum. For low-temperature (1000 to 1100°C) glasses chrome-nickel alloys can be used.
3. Glass. Molten glass is a fundamental component of a joule (ionically) heated melter, because it is used as the "heating element." The alternating voltage between the electrodes force mobile ions (primarily sodium) to migrate through the molten glass. Resistance to this migration causes the dissipation of energy known as joule-heating.

System Operation

Startup. For an ionically heated melter to operate, the glass must be brought to a temperature at which the glass becomes adequately conductive. Several techniques are possible. A sacrificial element technique for both initial startup and restart with a frozen tank is being developed at PNL.⁽²¹⁾ The sacrificial element startup technique employs a temporary set of electrodes placed just in front of the main power electrodes. A resistance heating element spans between the startup electrodes. For initial startup the heating element is buried in glass frit; for restart the heating element is laid on top of the frozen glass. Power metered to the heating element raises the melter temperature until continuity through molten glass between the main electrodes is established. When the glass becomes molten, the sacrificial element is rapidly consumed by the glass.

Production Melting. After the melter has been started up and the tank is full of molten glass, the system is ready for operation. HLLW is transferred to a mix tank where frit is slurried into the waste liquid. The slurried waste is then fed directly into the melting cavity. Pressurized feeding is not required; simple gravity feeding through an open-ended pipe may be used. The transfer of heat from the molten pool flashes the liquid to steam. Further heat transfer denitrates the metal nitrates, leaving an oxide residue which melts into the molten pool. Steam, nitrous oxides, and entrained particulates are vented to a standard off-gas cleaning system. The molten glass

is drained off periodically, or continuously, into a receiving canister through an overflow drain. Testing of liquid feeding at PNL has indicated that the capacity is more than 6 liters of HLLW/hr/1000 cm² surface area.

If boosting of the capacity by preconcentration is desired, the wiped film evaporator may be used. The wiped film evaporator, described in an earlier section, has been demonstrated capable of concentrating the HLLW solution to a flowable 50 wt% water slurry. Since evaporation of the solution requires the most energy, this preconcentration would increase melter capacity by more than 25%.

If even higher capacity is desired, the HLLW could be calcined prior to melting. In this scheme the melter could be direct coupled to any calciner. With calcined HLLW and frit fed to a ceramic melter, capacities higher than 20 kg of glass/hr/1000 cm² of surface area have been demonstrated.

Shutdown. Frequent shutdown of a joule-heated ceramic melter is not required, nor is it desirable. Should it become necessary to interrupt processing temporarily, the ceramic melter can be placed in an idling status. If shutdown is desired, the bottom freeze valve is allowed to thaw and the contents of the melter are drained into the standby canister.

Containment of Molten Glass. The refractories, water-cooled backup plates, and metal container provide redundant assurance that escape of glass to the hot cell is very unlikely. Although glass melting is a high-temperature process, this type of melting system confines the high-temperature region to the melting cavity. The cooling plates surrounding the melter assure a cool exterior. Thus confinement of the glass is an inherent characteristic of this type of melter.

Estimated Time of Readiness for Practical Design

Calciner Coupled Ceramic Melter. Practical design by mid 1977. (The French plan to begin detailed design of a direct induction ceramic melter in 1976.)

Liquid Fed Ceramic Melter. Practical design by 1978.

Major Development Program Objectives

Calciner Coupled Ceramic Melter. Experience with the present operating melter while feeding calcined waste indicates that an operable HLW system could be developed by 1977. The design would be remotized and operated under simulated remote conditions. Demonstration of a rapid on-off glass drain would be the primary area for development. To tilt the entire melter less than ± 5 degrees from horizontal will allow rapid on-off control while not interrupting production melting in the melting cavity. Emphasis would be placed on long-term operation (~ 30 days).

Direct Liquid Fed Ceramic Melter. A two-stage program is needed to develop a direct liquid-fed ceramic melter for use in vitrifying HLLW. First, a half-scale system (50 liter/hr) would be designed and constructed. The major design improvements would be a rapid on-off melt drain design, use of tin oxide (rather than Inconel) for the power electrodes to gain refractoriness, and an electrically less conductive brick material than the Cr_2O_3 presently in use at PNL.

The first-stage direct-fed melter design would be based solely on the heat transport from the molten pool to the liquid solution. Certain alternative systems promise to boost the capacity of the system without increasing the size of the melter. The operability of these techniques will be examined with the 50 liter/hr design. If they prove successful, the larger stage two design will incorporate these features. If the boosting techniques are unsuccessful, the stage two design will be scaled up from the information obtained from stage one.

The stage two design would be a full-scale liquid-waste-to-glass system with all the remote features needed for remote operations. Greatest emphasis in the stage two design would be placed on system verification testing through long-term, continuous, remote operation (greater than 30 days). From these tests a refined system design could be developed for immediate application in an operating reprocessing plant.

French Vitrification Processes

The French have been developing vitrification processes for HLLW at least since 1959. A batch process⁽⁶⁾ and a continuous process have been developed. The continuous process utilizes a rotary kiln coupled to either a continuous metallic melter or a continuous ceramic melter. Since the continuous process utilizing the metallic melter is scheduled for use first, it will be described in detail.

French Rotary Kiln - Continuous Metallic Melter

Process Summary

Final Product Form: Borosilicate Glass.

Process Description: The process unit is a rotary kiln calciner closely coupled to a vitrification furnace. The HLLW is fed to the upper end of the rotary kiln with the resultant calcine exiting the kiln into a vitrification furnace. Glass frit is concurrently introduced to the vitrification furnace with the calcine. The vitrified product is allowed to flow from the vitrification furnace to a product container in predetermined batches.

Applicable Wastes: HLLW can be processed. Volatiles such as Hg and I cannot be maintained in the glass structure.

Development Status: Nonradioactive pilot plant operations are essentially complete. There has been no radioactive experience. Construction of 1000 MTU/year equivalent plant is nearing completion at Marcoule.

Process Effluents: Both liquid and gaseous effluents can be treated by routinely available equipment.

Process Operating Conditions and Features

Background

The French Commissariat A L'Energie Atomique (CEA) started a major program to solidify high-level liquid waste in 1959.⁽²⁹⁾ The first laboratory studies were conducted at Saclay and Fontenay Aux Roses. These studies were continued at Marcoule using pot vitrification processes.⁽³⁰⁾ A production-scale pilot plant known as PIVER started hot operation in 1969 solidifying high-level liquid waste generated by the spent nuclear fuel reprocessing facility at Marcoule.⁽⁶⁾ The PIVER process was a pot vitrification process producing a borosilicate glass product. An extensive laboratory complex known as Vulcain was constructed in support of the PIVER process. The main function of Vulcain was the evaluation of various product formulations tested during the hot operation of PIVER. The PIVER facility was designed by Saint-Gobain Techniques Nouvelles (SGN).

The PIVER demonstrated the feasibility of vitrification of HLW. However, because of being a batch process its capacity was limited. Thus the French decided to develop a continuous process using the rotary kiln for use in their full-scale reprocessing plants.

After 5000 hr testing of a prototype rotary kiln calcination unit, a full size industrial rotary kiln was designed and manufactured for coupling with a continuous melter in 1971. Extensive testing of this unit was started in 1972 and is continuing today.

Engineering design of a full size production vitrification facility, for Marcoule, was started in 1973 by SGN and CEA. This facility is scheduled to

start radioactive operation by the middle of 1977 and will use the continuous rotary kiln calcination-metallic melter vitrification process.

Product

The French have been very active in the development of glass compositions for radioactive waste immobilization and have developed glass compositions for several different waste compositions with burnups ranging from 1,000 to 33,000 MWd/MTU.⁽³¹⁾ Most of the glass compositions are of the borosilicate type; however, one which incorporates the molybdenum from processing of U-Mo fuels contains relatively large quantities of phosphate. The glasses for both PIVER and the continuous process are designed for melting at 1150°C. Leaching tests show that after 10 to 20 days of leaching at 25°C with distilled water the leach rates drops to about 10^{-7} g of glass/cm²-day.⁽³¹⁾

Processing

Process Capacity. One rotary kiln unit of the size tested can calcine between 40 to 50 liters/hr of concentrated high-level liquid waste. The composition and volume of the high-level waste varies among nuclear fuel reprocessing facilities. But assuming a high-level waste composition of a reasonably low content of nonfission product salts, 2 or 3 rotary kiln units could calcine the high-level waste generated by a 5 MT/day nuclear fuel reprocessing facility.

Rotary Kiln. The rotating barrel of the rotary kiln is positioned at a slight angle to facilitate the flow of material through the kiln. High-level liquid waste is fed by gravity into the upper end of the kiln. The calcined product is discharged from the lower end of the kiln directly into a vitrification furnace. The rotating barrel of the kiln is about 3.6 m long and 27 cm in diameter. The barrel is supported at each end by roller bearings. Static end-fittings provide a seal for the rotating barrel. The longitudinal expansion and contraction of the barrel caused by thermal cycling is compensated for in the design of the seals. The seals at each end of the rotating barrel are sufficiently tight so that a slight negative air pressure can be maintained inside the kiln with respect to the exterior atmosphere. A small air bleed is passed through the seal to sweep the seals clean.⁽³²⁾

The rotary kiln is heated externally by an electric resistance furnace. The electric furnace has four independently controlled heating zones. The first 2 zones facilitate the evaporation of the high-level liquid waste and have a heating capacity of 20 kW each. The last 2 zones have a heating capacity of 10 kW each. This provides a total of 60 kW heat to the rotary kiln.⁽³³⁾

Average processing time for conversion of HLLW to calcine in the rotary kiln is 30 sec. This short holdup time helps minimize volatility problems.

The off-gas from the rotary kiln exits through the upper end of the kiln. The off-gas is first passed through a small wet scrubber for preliminary particulate matter control. The scrubber solution is recycled from the bottom of the scrubber to the top and allowed to cascade downward through the scrubber countercurrent to the flow of the off-gas. The recycle rate and temperature of the scrubber solution are controlled to provide an equilibrium evaporation rate from the scrubber. A continuous small bleed is taken from the bottom of the scrubber and routed to the feed head pot of the rotary kiln to control the specific gravity of the scrubber solution. Makeup water is added to the top of the scrubber.

Following the wet scrubber the off-gas is routed through a normal off-gas cleanup train. The first unit in such a train would be a condenser. After the majority of the condensables are removed from the off-gas stream, less than $1 \text{ m}^3 \text{ gas/hr}$ remains which requires cleanup.

Vitrification. The vitrification furnace is connected directly to the lower end-fitting of the rotary kiln by an expansion bellows. The heat is supplied to the furnace by induction heating of the Inconel furnace vessel. The furnace vessel is about 35 cm in diameter and 1 m tall. Glass frit and calcine from the kiln are continuously added to the furnace. When the molten product in the furnace reaches a predetermined level, the vitrified product in the furnace is allowed to flow through a freeze valve into a product container.

Two vitrification units are connected to each kiln. The vitrification furnaces have the capacity to produce about 20 kg of vitrified product per hour. The off-gas from the vitrification units is routed through the rotary kiln and becomes part of the rotary kiln off-gas. The operating temperature of the vitrification unit is 1150°C .⁽³²⁾

Pilot plant testing of a vitrification furnace designed to heat by inductive coupling to the molten glass product is now in progress. The vitrification furnace vessel is constructed of a refractory material which does not interact with the induction heating. The advantages of this type of vitrification furnace over the first type of furnace include high furnace temperature, longer furnace life, and a larger product throughput. It is planned to install an inductive heated ceramic melter, fed by a rotary kiln, to vitrify HLLW from the La Hague reprocessing plant.

Remote Maintenance. The design and construction of the pilot plant calcination-vitrification unit included all of the features required for complete remote maintenance. All major sections of the rotary kiln, vitrification unit, and the first wet scrubber can be removed and replaced separately within 12 to 16 hr by remote handling techniques. These major sections include kiln furnace components; kiln end-fittings including seals; kiln barrel; kiln support frame; vitrification furnace vessel; and vitrification induction coils.

Estimated Time of Readiness for Practical Design

A rotary kiln-continuous metallic melter facility is being constructed in a new building beside the Marcoule reprocessing plant which will handle the entire output of HLLW from the plant. The facility, known as Atelier Vitrification Marcoule (AVM), is scheduled for cold testing in 1976 and radioactive operation in 1977.

Major Development Program Objectives

The development program objectives remaining center around radioisotope behavior. Radioactive testing is planned, with the behavior of Ru, Te, Tc and Mo of particular interest. Techniques are being developed for denitration of the HLLW feed to reduce ruthenium volatility.

British Rising Level Glass Process (FINGAL/HARVEST)

Process Summary

Final Product Form: Inert borosilicate glass containing about one part by weight HLW oxides and two parts by weight glass-making additives.

Process Description: Liquid waste and glass former are fed directly into a heated canister where drying, calcination and melting occur at 1000 to 1050°C. The waste constituents thus melted are completely dissolved or dispersed in the glass matrix. Solids entrained from the melter and volatile constituents are removed from the off-gas and returned in the feed stream. The process canister, either cylindrical or annular in shape, is the final storage container.

Applicable Wastes: All liquid wastes which are compatible with the glass formulation and solid wastes which can be comminuted.

Development Status: Operated in nonradioactive facilities at a melter feed-rate of 13.8 liters/hr and in the radioactive FINGAL pilot plant under remote operating conditions at up to 5 liters/hr. Current development efforts are directed toward use of annular canisters to improve melting capacity.

Process Effluents: Liquid and gas effluents can be treated by equipment routinely available in a reprocessing plant.

Process Operating Conditions and Features

Background

Development of the rising level glass vitrification process named FINGAL started in the late 1950s at Harwell, England.⁽³⁴⁾ Since that time both non-radioactive and radioactive engineering-scale testing has been conducted in waste canisters 15 cm diam by 1.5 m long, and nonradioactive tests were conducted in canisters up to 30 cm^(35,36) in diam. To increase melter capacity, annular canisters are being considered along with other improvements in a process termed HARVEST.⁽³⁷⁾

A rising level glass process has been selected for immobilization of HLLW from the Tarapur reprocessing plant in India.⁽³⁸⁾ Development work on a rising level glass process has also been conducted in the U.S., in nonradioactive studies at ORNL,^(39,40) and in one fully radioactive engineering-scale demonstration run at PNL.⁽⁴¹⁾

Product

Both phosphate and borosilicate glass formulations have been developed for use in rising level glass processing. Generally borosilicate glass formulations are preferred because they are less corrosive to the stainless steel processing vessel which also serves as the final storage vessel. For HLLW containing sulfate, phosphate glass formulations are preferred because sulfate forms an immiscible, water-soluble, phase in borosilicate glass.⁽³⁸⁾

A typical glass composition for the HARVEST process is:⁽⁴²⁾

SiO ₂	43 wt%
Borax	32 wt%
Waste Oxides	25 wt%

Processing

The proposed HARVEST⁽³⁷⁾ process is a batch vitrification process in which an annular canister up to 1.2 m diam by 2.4 m long is used as the melting crucible. During operation, the canister is lowered into a cylindrical multi-zone furnace and another small furnace is inserted into the canister annulus. An annular shaped cover containing feed inlet ports and off-gas discharge ports is placed on the canister, and the entire furnace is heated to 1050°C. Coincident with HLLW feed introduction, glass formers are added either dry or as a slurry. As the waste and glass formers dry and melt, the level in the canister rises and the furnace power is automatically adjusted to provide heat to the melting zone until the canister is filled. Two or three parallel

melts will be required to process the HLW from the reference plant. Additional melts may be required if prolonged refining or annealing is necessary.

Process Flexibility.

- Probable that any material compatible with the glass formulations can be processed.
- Can process wide range of waste concentrations. Maximum glass production rate is roughly proportional to feed solute concentration.
- ILW addition is limited only by glass formulation.
- Processing easily automated, canister operations likely manual.

Process Reliability.

- Simplest proven vitrification concept--no moving in-cell parts required.
- Melter replaced with each canister, thus major equipment life is that of the melter furnace.
- Operating variables to be controlled:
 - liquid feedrate
 - glass former feedrate
 - furnace zone temperature
 - primary deentrainment system.
- Possible pressurization due to liquid flowrate surge or excessive feedrate.
- Startup, restart, and shutdown require only feed line flushing prior to beginning and after terminating feed.
- Likely failure modes
 - furnace failure
 - blockage of feed, glass former, or off-gas lines
 - instrumentation failure
 - canister sealing or handling failure.

Process Capacity. It is estimated⁽⁴³⁾ that three parallel 30-cm diam melters could vitrify the waste from the reference 5 MTU/day fuel reprocessing plant. However, fewer large annular canisters will be required.

Estimated Space Requirements.⁽³⁷⁾

cell height - 2 1/2 times canister length
 Floor space - 4.5 m x 13 m

Estimated time of Readiness for Practical Design

Currently ready for design of low-capacity melters. Practical design for reference plant likely could begin in late 1976.

Major Development Program Objectives

Two basic areas of development are under way to prepare the HARVEST process for commercial use, 1) increased capacity and 2) improved primary deentrainment. Increased capacity is being sought by use of a large annular canister. New technology is needed to allow casting and welding of the large partial toroidal shaped head and in developing the annulus interior heating furnace and cooling assembly. Operating experience with an annular canister is needed.

Primary deentrainment capability is sought which can return the entrained and volatilized radionuclides to the melter in a form readily assimilated homogeneously into the melt. Use of a spray condenser or a conventional tube and shell condenser is being evaluated.

Further development may also be required to assure vitrification of the dust coating in the canister neck area. Stress generated in the canister during cooling caused by unequal thermal expansion rates between the glass and stainless steel may also necessitate further development to assure canister integrity during water storage.

German Vitrification Processes

Research and Development on the vitrification of radioactive wastes has been under way in Germany for about 10 years. R&D is being conducted at three sites, Gesellschaft für Kernforschung (GFK, Karlsruhe), Hahn-Meitner-Institute für Kernforschung (Berlin), and Kernforschungsanlage (KFA, Julich). The process being developed in Karlsruhe for use at the WAK reprocessing plant is the most well developed and will be discussed in detail. Other German vitrification processes will be discussed in less detail.

German Spray Calciner--Continuous Metallic Melter

Process Summary

Final Product Form: Inert borosilicate glass containing about 30 wt% HLW oxides in a metal canister.

Process Description: Liquid HLLW is first denitrated to reduce the volatility of ruthenium then solidified in a spray calciner. The calciner produces a calcined powder which when combined with glass frit forms molten glass in an Inconel melter at 1100°C. Molten glass is drained from the melter via a freeze-drain valve into a metal canister.

Applicable Wastes: System will handle all liquid wastes which can be calcined and all solid wastes which can be comminuted. Certain chemical limitations exist due to volatility (Hg, Cl, for example) or formation of immiscible phase in glass (SO₄ for example).

Development Status: Demonstrated with nonradioactive wastes in pilot-scale plant and with HLLW in discontinuous, lab-scale equipment.

Process Effluents: CO₂ and N₂O make up about 95% of the off-gas. Radioactive effluents are recycled to the fuel reprocessing plant for routine treatment.

Process Operating Conditions and Features

Background

West Germany's spray calciner--continuous metallic melter is being developed at the Karlsruhe Nuclear Research Center. During the late 1960s a waste solidification process for calcining of high-level liquid waste from the WAK (40 tonnes/year prototype) spent fuel reprocessing plant was proposed, which mixed the calcine with glass formers and melted it to form glass. The process was named VERA. To demonstrate the technical feasibility of this process, and to gain operation experience, a pilot-scale VERA facility for nonradioactive tests was built. It began operation in 1970.⁽⁴⁴⁾ Since then, numerous runs have been made in the VERA facility, resulting in several significant design improvements and considerable operating experience. Laboratory-scale experiments using simulated waste spiked with radioactive ⁵⁴Mn began in 1971.^(44,45) These tests led to further work using waste containing fission products in 1974.⁽⁴⁶⁾ Current plans call for construction of a remotely operated, production sized prototype, incorporating the improvements made on the existing equipment. The prototype, though nonradioactive, will serve to demonstrate operability by remote control for a large-scale plant.

Product

The product is a borosilicate glass cast in a stainless steel canister 20 cm in diameter and 1 m deep. Borosilicate glass compositions are being developed. A representative glass composition is, in wt%:

SiO_2	35
B_2O_3	10
Na_2O	19
CaO	2
Al_2O_3	1
TiO_3	3
HLW oxides	30

The WAK plant HLLW contains about 35 wt% Gd_2O_3 after calcination; therefore, glasses which will incorporate relatively large amounts of gadolinium have been developed.⁽⁴⁶⁾ Glass-ceramic compositions are also being investigated.

Processing

The VERA process involves three steps:

- liquid waste denitration
- spray calcination
- melting and casting.

Denitration. The denitration step uses formic acid to destroy the free nitric acid and as much fission product nitrates as possible before calcining.^(47,48)

By controlling the calciner feed nitrates to less than 0.5 moles of NO_3^- per liter, ruthenium volatilization is reduced to 0.01 wt% (of the total ruthenium) during calcination and melting. Most heavy metal nitrates are completely denitrated.^(44,48)

Calcination. The VERA spray calciner is similar to conventional spray driers used in the chemical industry. Waste is pumped to the top center of the 2-m tall by 0.6-m diam calciner, where it is steam atomized then dried and calcined in flight by superheated (600°C) steam. Calcine is swept along by the steam velocity into the filter chambers, where the calcine is removed by sintered metal filters with 3- μm pores. To reduce filter clogging, 20 wt% of the required amount of (SiO_2) glass additive is mixed with the liquid waste prior to calcining.

The off-gas steam is condensed, decontaminated and recycled. Noncondensable gases are returned to the fuel reprocessing plant for routine treatment. Very little radioactive or toxic gases appear in the off-gas because the pre-calcining denitration not only reduces the formation of NO_x but also reduces the oxidation potential of the waste solution, resulting in formation of less volatile fission product compounds.^(44,45)

Melting and Casting. After calcination, the calcine along with a prescribed amount of borosilicate glass frit is metered into an induction-heated Inconel 600 crucible. The crucible is heated to about 1150°C and held at that temperature for 2 hr to homogenize the melt. The induction field (2000 Herz) creates

sufficient stirring of the low viscosity (<50 poise) melt to assure melt homogeneity.^(44,48) Atmosphere control inside the melter is not required.⁽⁵¹⁾ The melter is drained via a freeze valve located in the melter bottom when it becomes about 2/3 full. A small induction coil is used to open and close the freeze valve.⁽⁴⁸⁾ An induction-heated waste canister receives the melt and provides for annealing. After annealing, the filled canister is welded shut and inspected prior to storage.

Process Reliability. A pilot-scale, nonradioactive facility has been operated at Karlsruhe since 1970. Recently the system has operated continuously for 1-week periods with planned shutdowns. All major components, the denitrator, the spray calciner, and the induction-heated Inconel 600 melter, are conventional designs, modified somewhat for use in the VERA process.

At present the Inconel 600 melter has a life expectancy of 1000 hr limited by warping and corrosion. An Inconel 690 melter used in lab tests has shown superior corrosion resistance, but as yet no pilot-plant experience has been obtained using Inconel 690.

Control of the melt level by an Inconel conductance probe causes problems: melt and calcine buildup on the probe, electrically insulating it from the melt. Development of an improved level control is under way.

Estimated Time of Readiness of Practical Design

Waste solidification facilities will be required in the Federal Republic of Germany in the early 1980s, and development is proceeding to that end. It is estimated that the steam-heated spray calciner could be ready for practical design in 2 years.

Major Development Program Objectives

A full-scale remotely operated demonstration plant is scheduled for completion in 1980. Operation of this facility will provide long-term reliability and maintainability information.

Further development of the steam superheating system will proceed, and improved designs will eliminate calcine depositions. Improved melter life and capacity will be sought.

Other German Vitrification Processes: Thermite Process

A thermite process for solidification of HLW is being developed at Karlsruhe as a potential alternative for the glass melting step in the VERA process. A typical thermite mixture prior to reaction, is given below:⁽⁴⁵⁾

23 wt%	Calcine
16 wt%	SiO ₂
40 wt%	MnO ₂
21 wt%	Al

The reaction is carried out in a ceramic crucible preheated to 1000°C to prevent cracking. A small amount of the material to be reacted is placed in the crucible and ignited. The remaining material is continuously added as the reaction proceeds. A 2-kg batch of material is completely reacted in about 3 min. Temperatures of over 2500°C are reached during the reaction, and 60 to 80 g of solids are collected in the off-gas filter for each 2-kg batch. Used filters are disposed of by placing them in the reaction chamber.⁽⁴⁵⁾

The thermite reaction produces a very rugged, two-phase, ceramic-metal material. The product is at least equivalent to glass.

Most developmental work has been conducted in a semi-continuous 2-kg laboratory-scale facility. A semi-continuous 15-kg pilot-scale facility was scheduled to start operation in late 1975.⁽⁴⁵⁾

Other German Vitrification Processes: Glass-Ceramic

The Hahn-Meitner Institute is conducting experiments involving the fixation of fission products in glass-ceramics. To date, experimental work has been carried out on a laboratory scale utilizing the compositions listed below:⁽⁴⁸⁾

30-70 wt%	SiO ₂
≤30 wt%	Al ₂ O ₃ , B ₂ O ₃ , C ₂ O, CaO, ZnO
≤20 wt%	Li ₂ O, Na ₂ O, K ₂ O
≤13 wt%	TiO ₂
≤30 wt%	fission product oxides

Glass-ceramics are discussed in more detail later in this section.

Other German Vitrification Processes: Julich Borosilicate Glass

Most of the development work at Julich has been directed toward perfecting a denitration, drum drier, in-can melting process for borosilicate glass. Early work used an induction-heated graphite crucible which would later be canned in mild steel, rather than in-can melting.⁽⁵⁰⁾

Liquid HLW is deacidified with formaldehyde to a pH of about 3.0, then glass-forming additives (e.g., CaCO₃, SiO₂) are introduced which raise the pH further to form a viscous slurry. The slurry is pumped to a drum drier and converted to a solid cake which is continuously scraped off the drier and dropped into a canister, where it is melted.⁽⁵⁰⁾

The Julich process has been demonstrated on a laboratory scale for both nonradioactive and radioactive glasses.

Other German Vitrification Processes: Pamela Phosphate Glass Process

The Pamela Process is being developed by the Gelsenberg Company at Julich. The goal of the program is to convert thorium-containing wastes to

glass. Phosphate glasses have been chosen to achieve higher waste loading. The process is designed to avoid devitrification of the phosphate glass by assuring that the glass is maintained below 500°C in storage. This is done by forming the glass in small granules (about 3 mm diam) which are incorporated in a metal matrix.⁽⁵¹⁾

Liquid HLW is denitrated with formaldehyde and concentrated with sufficient H_3PO_4 to form phosphate glass when the slurry is heated to about 1000°C in a platinum melter. The melt is drained to a special container with orifices in the bottom. Drops are formed as the melt flows through the orifices. The drops are cooled on a rotating plate and scraped off into a canister.

A platinum melter is required to contain the corrosive phosphate melt; however, tests of a special ceramic coating that will allow the use of steel instead of platinum are going on at Julich. The granulated glass is encapsulated in a lead alloy using technology developed at Eurochemic. The hot cell demonstration equipment at Julich has a throughput of about 7 liters of waste solution/hr, producing 150 to 200 ml of glass/hr. It is planned to transport some of the radioactive granules to hot cells at Eurochemic, where they will be incorporated in metal blocks having a volume of about 3 to 5 liters. Vitrification off-gas is fed back into the reducing atmosphere of the denitration unit, which guarantees retention of any ruthenium volatilized and leads to only one off-gas stream (from denitration) for the whole process.

The Pamela process has been demonstrated in both active and inactive modes.

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6.3.3 Other Solidification Processes

Alternatives to calcination and vitrification are being investigated for one or more of four reasons:

1. Reduce the cost of solidification and/or storage and thus the total cost of power.
2. Simplify the operation, making the processing more reliable.
3. Produce inert forms from wastes not readily compatible with vitrification.
4. Allow production of a waste form which has greater inertness and lower dispersibility than the major options have.

Waste forms in the last category generally increase complexity of operations, adding to the operating risk and cost, which must be weighed against the benefits of a more stable product.

Numerous alternative methods have been suggested for solidification. Some of these, involving direct disposal, are covered in the section on Alternatives for Final Storage and Disposal. However, most are processes that would be installed at the reprocessing plant. The major alternative processes are described in this section. Some processes are grouped for this report. For example, for ion exchange many procedures have been proposed; however, it is covered in detail for only one specific procedure, representing the most recent investigations. Other processes can draw from developments described in several sections to produce the final waste form. For example, a process could form a pellet of supercalcine, encase the pellet in a durable coating, and then incorporate the coated pellets into a metal matrix in a canister. Alternatives such as the latter can continue to increase in complexity, with additional barriers and coatings, until any desired degree of product safety is obtained. Each increase, however, brings increased cost and process complexity with decreased plant reliability.

The alternatives have not received the attention and development that vitrification and calcination have. They are, therefore, less well developed, and the best combinations and options have not necessarily been tested. This implies that further improvements are possible with the processes and products. It also means that the limitations and potential problems have not necessarily been identified. Longer lead times will generally be required before alternative technology can be applied to full-scale plants since alternative development has been mostly limited to the laboratory.

The alternative solidification processes described are not all-inclusive, but a representative listing of alternative waste forms and processes currently under investigation for HLLW immobilization. Examples of waste forms not described in detail include:

Ceramic sponges^(1,2)

Concrete⁽³⁻⁵⁾

Waste oxide in glassy carbon⁽⁶⁾

Supercalcine

Process Summary

Final Product Form: "Supercalcine" is a term for a "tailor-made" crystalline ceramic waste form prepared by modifying the high-level waste stream with selected additives (35 to 45% by weight) so that when it is calcined and given additional heat treatment, an assemblage of thermodynamically stable crystalline phases will be formed which are more refractory and leach-resistant than ordinary oxide calcine formed without additives. Supercalcine is a potentially superior calcine product as it stands; it can also be used as the core for a composite multibarrier waste form.

Process Description: Additives, (usually including Ca, Sr, Al and Si), selected according to the waste composition are solution mixed with HLLW. The additive:waste solution can be calcined by any of the HLLW calcination procedures described previously. Heat treatment at 900 to 1100°C is required to fully develop the desired crystalline species. Processes which could use supercalcine as part of the composite waste form are described in subsequent pages.

Applicable Wastes: HLLW can be processed. Volatiles such as Hg or I cannot be maintained in the calcine structure.

Development Status: Supercalcine formulations have been under nonradioactive laboratory-scale development since late 1973 at Pennsylvania State University. One nonradioactive engineering-scale run has been made in a spray calciner at PNL.

Process Effluents: No special gaseous or liquid process effluents result; i.e., they can be treated by equipment normally provided for HLLW solidification effluent treatment.

Process Operating Conditions and Features

Background

Work was begun in the fall of 1973 at Pennsylvania State University (PSU) on development of supercalcine and is continuing.⁽⁷⁾ The first step was a study of the oxide crystal chemistry of combinations of HLLW cations. This was followed by an extensive evaluation of crystalline phases suitable for Cs fixation, which concluded that an aluminosilicate, $\text{CsAlSi}_2\text{O}_6$, was the best available phase. Recently, supercalcine formulations have been developed which fix most major HLLW species in stable, inert crystalline phases. (The waste species Ru, Te, U, Tc and Pd and several other minor and trace constituents have not yet been added to these formulations.) One of the formulations has undergone engineering-scale processing at PNL by spray calcining. Adequate crystallization of the preselected phases and good sinterability have been demonstrated on a laboratory scale using temperatures in the 900 to 1100°C range.

Product

Supercalcine is meant to be only the first barrier in a multibarrier waste form. Thus one cannot specify all the relevant bulk properties of a composite product which may include coatings on pellets, metal matrices, etc. Only those pertaining to the crystalline phases are presented here.

Cesium is the greatest problem in supercalcine design. Few of its oxide crystalline phases are both leach-resistant and thermally stable in the 900 to 1100°C range. The most suitable phase for Cs fixation has been found to be pollucite, $\text{CsAlSi}_2\text{O}_6$, the mineral in which Cs is found in nature. It is highly resistant to water leaching of the Cs⁽⁸⁾ and possesses good thermal stability.⁽⁹⁾ The concept of atomic scale isolation of radioactive nuclides is illustrated by the Cs coordination polyhedron in pollucite. The Cs ion is surrounded by 12 oxygen ions which are part of a three-dimensional network of aluminosilicate tetrahedra. When a Cs ion is incorporated into this framework during crystallization of pollucite from supercalcine, it is locked into these sites because it is too large to migrate.

In a similar fashion each long-lived nuclide is fixed in a selected crystalline structure. Often more than one waste species is contained in a crystalline structure. For example, all the trivalent rare earth ions ($\text{RE} = \text{Nd, La, Pr, Sm, Pm, Eu, Gd}$) plus Sr and PO_4 are fixed in the apatite structure solid solution phase, $\text{Sr}_{2+x}\text{RE}_{8-x}(\text{SiO}_4)_{6-x}(\text{PO}_4)_x\text{O}_2$. It is likely also that the actinides may be included on the rare earth sites in this phase, but this has not yet been studied. In addition to pollucite and apatite, other crystalline phases selected for atomic level fixation include scheelite type $(\text{Sr, Ca, Ba})\text{MoO}_4$, fluorite type $(\text{Ce, Zr})\text{O}_2$, perovskite type $(\text{Ba, Sr})\text{ZrO}_3$ and spinel type $\text{Ni}(\text{Fe, Cr})_2\text{O}_4$. Each of these crystalline phases is a high thermal stability solid at 1200°C and, based on the known behavior of chemically simpler isostructural phases, this temperature stability should extend to at least 1400°C .

To prepare these crystalline phases about 35 wt% of additives must be mixed with a high fission product type waste. Current formulations require that Ca, Sr, Al and Si be added to the wastes. It is estimated that 35 to 40 wt% of additives will be required for the reference waste.

Thermal conductivity has not been measured, but it should differ little from that of glass, if the supercalcine is consolidated.

Leaching experiments have not yet been performed on either the individual phases or the composite supercalcine. The molybdate scheelite structure phase is expected to show the greatest leachability, but even this is expected to be below $10^{-5} \text{ g/cm}^2/\text{day}$ based on some precipitation reactions involving SrMoO_4 .

It is obvious that certain additives are required to make certain crystalline phases. Since it is anticipated that the waste stream will not be of constant composition, excess quantities of the additives required to fix the most troublesome species (e.g., Cs, Mo) are included in the supercalcine formulation. When these excess components are not needed, they react together to form an inert stable matrix (e.g., strontium aluminosilicates).

Processing

To prepare supercalcine, selected chemical solutions are added to the HLLW liquid stream. Current formulations require nitrate solutions of calcium, strontium and aluminum plus a stabilized colloidal suspension of silica (SiO_2). The liquid mixture is then calcined by either the spray or fluidized bed techniques described previously. At this point the product is granular and largely x-ray amorphous. It must be heated in the range 900 to 1100°C to become crystalline. Heating times as short as 30 min are satisfactory. The atomic scale mixing obtained by rapidly drying solutions decreases the amount of solid state diffusion required for crystallization. This is one important reason that such relatively small energy inputs (i.e., temperature and time) yield good crystallization.

The diagram of the supercalcine process shows two out of a number of options for processing a waste form in which supercalcine provides atomic level fixation of nuclides. The simplest process would be to place the product of calcining directly in the canisters and use either external heating or self-heating from radioactive decay to crystallize the supercalcine. This, however, gives a weakly consolidated, low-density product, which could be physically dispersed in case of a breach of canister.

A higher-density product results from pelletizing before the usual crystallization step. The subject of pelletizing is discussed in other sections.

Estimated Time of Readiness for Practical Design

If an unconsolidated calcine continues to be an acceptable waste form, supercalcine formulation concepts can be introduced into the flowsheets immediately which will improve the stability and insolubility of some of the radioactive waste constituents. It is estimated that several more years will be required to develop the full potential of the supercalcine concept, i.e., to be able to incorporate all HLLW constituents in optimally stable crystalline forms.

A composite product utilizing supercalcine requires the development of several integrated processing steps, examples of which are pelletizing and application of coatings. It is estimated that it will be 10 years before a process producing a multibarrier waste form using supercalcine as the core is ready for practical design.

Major Development Program Objectives

Laboratory work is continuing in several areas:

- Refinement of additives and formulations.
- Consideration of the potential volatilization losses of Ru, Te, Tc, etc. during crystallization heat treatment (900 to 1100°C) and, where necessary, design of suitable crystalline phases of these species to prevent volatilization losses.
- Consolidation methods for supercalcine.
- Characterization of granular and consolidated supercalcine for leachability and thermal stability.
- Radiation effects and fission product retention.
- Crystal chemical role of selected nuclides in supercalcine (e.g., ^{137}Cs , ^{90}Sr , ^{99}Tc , actinides).

Sintering Process

Process Summary

Final Product Form: The product is a glass and crystalline phase prepared by sintering a 50 to 67 wt% calcined waste-flux mixture at temperatures between 850 and 1070°C. The products are leach-resistant, have high impact strength, are resistant to thermal shock, and remain a solid at temperatures of 800°C. The product can be formed as pellets or as large thick disks.

Process Description: Calcine is mixed with a flux and a binder-lubricant, which can be water. If large disks are desired, the mixture is pressed to a low-profile, thin-walled steel container. If smaller pellets are to be formed, the powder is fed to a pelletizer. The shaped mixtures are then sintered with the large disks, requiring a low-pressure pressing while still hot to conform the product to the container. After cooling, the disks could be loaded directly into the canister. The pellets would require a matrix and could be coated.

Applicable Wastes: All calcinable HLLW and HLLW-ILLW are applicable. Volatile anions such as Hg and Cl would not be incorporated.

Development Status: Products have been formed and tested at the laboratory scale. Long-term and detailed characterization has not been completed, but engineering-scale development of specific options could begin within about 1 year. Detailed design of a demonstration facility could be started in 1979 and 1980.

Process Effluents: All projected liquid and gaseous effluents could be treated by routinely available equipment.

Process Operating Conditions and Features

Background

Sintered calcine-flux products have been developed at both INEL⁽¹⁰⁾ and PNL.⁽¹¹⁾ The processes are similar in that calcine wastes and a flux or frit are mixed, formed into the desired shape, and sintered to react the calcine with the additives and to increase product density, strength, and durability. The products have both a glass and crystalline phase and have been called sintered glass-ceramics (SGC) by INEL.

Product

The properties of the sintered products can be varied over wide ranges, depending on the choice of the frit or flux and the calcine addition. By high-temperature sintering (875 to 1070°C) a high calcine loading (50 to 70%) can be used. The products have good stability at temperatures near 800°C, which can be encountered with the high heat generation rates of young wastes.

An aluminosilicate flux used by INEL for the fluidized bed calcine is composed of 3.9% Na₂O, 2.0% K₂O, 9.7% Al₂O₃, 52.1% SiO₂, 2.4% CaCO₃, 19.6% BaCO₃, 3.5% ZnO and 6.8% TiO₂. The frit 75-10 used by PNL is composed of 6% Na₂O, 6% K₂O, 47% SiO₂, 7.5% CaO, 2.5% MgO, 15% ZnO and 16% B₂O₃. The additives have been tested with several synthetic calcines. Product densities range from 2.4 to 3.3 g/cm³, and specific volumes of the reference waste would be 30 to 55 liters/MTU. The products have residual porosity of 8 to 25 vol%, with a thermal conductivity of ~0.7 W/m°C. Small-diameter pellets exhibit good thermal shock resistance by remaining intact after dropping from an 800°C furnace into room temperature water.

The leach rates of well sintered products are similar to glass. INEL has tested their materials at 25°C and have found initial leach rates of ~10⁻⁵ g/cm²-day, with the rate decreasing to ~6 x 10⁻⁸ g/cm²-day after 35 days. Good high temperature stability has also been demonstrated with about 0.1 wt% loss after 30 days at 800°C in air.

Processing

The processes for sintered products involve a common high-temperature heat treatment where the products are reacted and densified. The preparation of the material for sintering and its post-treatment vary according to process goals. Sintering processes have been developed at the laboratory scale only. Thus these descriptions are conceptual rather than engineering demonstrated.

The INEL product is prepared by mixing 50 to 67 wt% calcine with unfritted flux. From 5 to 8% water is added to increase the mix density, eliminate dusting, and serve as a binder. The mixture will be fed to thin-walled (~0.5 mm) steel containers (10 to 15 cm high x 30 cm diam), then leveled under light

pressure (700 to 3500 g/cm²) to conform to the container. The temperature of the contained mix will be slowly raised over a 4 to 6-hr period to the sintering temperature. During this period, volatile compounds (NO_x, CO₂, H₂O), present either in the calcine or flux, will be released. Sintering temperatures are between 970 and 1070°C, depending upon the type of calcine, flux, or mixing ratio used. Sintering time is 4 to 6 hr. Since additional densification occurs on sintering, the hot (950 to 1000°C) semisolid product is pressed at low pressure (1400 to 3500 g/cm²) to assure uniform contact between the product and container wall near the end of the sintering cycle. The sintered product is gradually cooled (2 to 4 hr) and loaded into the final storage canisters, which have not been subjected to processing temperatures.

At PNL several methods are being investigated for preparation of pellets for sintering.⁽¹²⁾ These include extrusion, cold pressing, and disk pelletizing. Disk pelletizing, the simplest, is discussed here. A disk pelletizer is simply a shallow, circular, inclined pan which is rotated about its center. Calcine and frit are metered into the pan, and a solution of water or binder is sprayed onto the powder. The damp powders begin to snowball, and spherical pellets form and overflow the pan as it fills with material. The pellet size is controllable from ~1 to 10 mm by varying operating parameters. The pellets are then subjected to a heat treatment cycle for drying and sintering at about 900°C. The sintered product could then be coated or directly incorporated into a metal matrix. Further details on coatings and matrices are included in their specific sections.

The sintering processes will produce a gaseous effluent of NO_x, CO₂ and H₂O. A small amount of radioactive ruthenium and cesium may also be volatilized. Off-gas filtering and entrapment equipment typical of other solidification systems will provide adequate decontamination since the off-gas volume is expected to be less than 10% of that from calcination.

The processes will require equipment for monitoring mixing ratios, temperature, gaseous effluents, product quality, canister integrity, and heat generation rates. Design of the in-cell equipment would be modular for easy replacement and remote maintenance. Standard plant utilities will be required; these include plant air, steam, electricity, decontamination and general plant maintenance facilities. General space requirements would include the in-cell remote operating area, remote repair and decontamination areas, and remote canister loading and storage areas. An out-of-cell loading area and chemicals makeup and materials storage areas will also be required.

Estimated Time of Readiness for Practical Design

The INEL process could be ready for design engineering of a full-scale demonstration plant in 1979.

The PNL process including the coating and metal matrix development work could be ready for design engineering in 1980.

Major Development Program Objectives

Process equipment development and design verification is the major effort remaining for SGC development. The process would be developed through testing and evaluation of equipment for each operating stage, and verification would be through nonradioactive pilot-plant operation. Stages of the process which may require experimental development include product forming, moving the containers through the sintering furnaces, and off-gas cleanup. The type of sintering furnace to use, batch or continuous, should be evaluated. Operational reliability of mixers, or pelletizers, furnaces and the off-gas system, etc. need to be established, and equipment would be modified for efficient remote operation and maintenance.

Additional product characterization is needed using radioactive elements, such as cesium and ruthenium. This would determine more precisely the extent of volatilization during product formation and the effect of uranium on product properties. More precise determination of long-term high-temperature product stability using radioactive products is also needed. Heating rates required for sintering 20-cm-diam or larger products must be determined.

Time requirements for INEL pilot-plant facility design and preliminary evaluation of equipment are expected to be 6 to 9 months, plus an additional 6 months to fabricate equipment and erect the facility. Pilot plant operation could begin in the second half of 1977. Product evaluation can be completed concurrently with the pilot plant development and operation.

The section on coatings includes additional PNL objectives.

Metal Matrices

Process Summary

Final Product Form: Metal matrices are high thermal conductivity monolithic forms composed of calcine, vitreous beads, or pellets cast in molten metal or embedded in sintered metal. Alloys of lead, zinc, aluminum or other low melting metals are used in casting; iron, iron alloys, or copper are used in sintering. Waste constitutes up to 65 vol% of the matrix.

Process Description: The waste is formed into particles, beads, or pellets. Cast matrices can be formed by either introducing the formed waste near the bottom of the canister and letting it displace molten metal or by forcing molten metal by pressure or vacuum through a canister of waste particles. Sintered matrices can be formed by either mixing wastes and metal powder, compacting the mixture into a pellet and sintering, or by vibrating a metal powder throughout a canister loaded with a formed waste and sintering the total canister into a coherent mass.

Applicable Wastes: All wastes which can be produced in the form of granules, beads, or pellets.

Development Status: Products have been formed and tested on a laboratory scale. Casting of vitreous beads by molten metal displacement has been verified on a cold pilot plant scale.

Process Effluents: The off-gas contains particulate metal oxides which can be filtered.

Process Operating Conditions and Features

Background

High-level waste less than 5 years old has high heat generation rates. When such fresh waste is solidified as calcine, or as vitrified or crystalline ceramic bodies, the low thermal conductivities and high heat generation rates require restrictions on the canister diameter to avoid excessive centerline temperature in the solidified waste canisters. Metal matrices are being developed to provide a high-conductivity form for lowering product centerline temperatures and increase impact resistance. Molten metal cast matrices have been made using either granular calcines^(10,13,14) (0.1 to 0.5-mm diam) or vitrified waste beads⁽¹⁴⁾ (3 to 10 mm), although other small forms of solidified wastes are castable.^(15,16) Sintered metal matrices have also been made using powdered or granular waste forms.^(10,16)

Product

The product consists of waste particles uniformly distributed in a metal matrix. The metal matrix may be high-density, as solidified from a melt, or porous, as sintered from powder. Molten metal and metal sintered matrices have been prepared using several types of solidified wastes and metals.

The waste form may be calcine particles, beads or pellets. In molten metal casting, the particles should be larger than 0.1 mm granules. Particles finer than 0.1 mm and present in amounts greater than about 10% are difficult to cast in molten metal. Fine particles do not allow sufficiently large void spaces for the molten metal to penetrate the calcine matrix. Hence a process step to pelletize fines prior to incorporating in the metal matrix may be needed.

Aluminum, zinc, or lead alloys are most commonly used for molten metal castings, although higher melting point materials such as bronze may be used. Temperatures for casting are 50 to 100°C above the melting point of the metal used. To fill the void spaces between the waste particles 30 to 40 vol% metal is required.

In sintering processes copper alloys, iron or iron alloys are typically used. Processing temperatures of 0.6 to 0.9 of the metal melting point are required to bond the metal powders together. Generally, the higher the sintering temperature and the finer the metal powder used, the stronger the metal matrix.

Metal matrices have impact and thermal shock resistance consistent with the metal. Thermal stability may be limited to temperatures below the metal melting point to minimize slow oxidation, or reaction of the metal with the waste or the canister. Metal matrices vary in leach resistance, depending on the form of the waste incorporated. If untreated calcine wastes (which are quite leachable) are used, the leach rate for the metal matrix is 10^{-3} to 10^{-4} g/cm²/day. But if leach-resistant vitreous beads are used, the leach rate is expected to be much lower. Thermal conductivities of metal matrices are high, ranging from 5 to 35 W/m°C for lead alloy and aluminum matrices, respectively. Thermal conductivities of metal matrices vary little with the waste form or method of matrix formation.

Processing

Molten Metal Casting

Two basic methods are used for molten metal casting of wastes. In one, the solidified wastes are metered into a container having a retaining grid to hold the particles in place. The particles are heated to the proper temperature, and molten metal is forced by inert gas pressure and/or vacuum through the waste to fill the void spaces and form the matrix. A variation is to force the metal down through a central tube embedded in the waste and up through the granules. In the second method, a heated container is filled with molten metal, and waste granules or beads are metered into the container through a central tube using inert gas to force the particles to percolate up through the metal until the container is full. A retaining grid prevents the

granules from floating on top of the metal while the displaced metal flows to another container. This method, developed by Eurochemic,⁽¹⁴⁾ has been successfully tested in a nonradioactive pilot-plant using 15-cm diam x 50-cm high canisters, vitreous beads, and a lead-alloy metal.

Powdered Metal Sintering

Powdered metal sintering processes are being investigated at INEL and PNL. In the INEL sintering process calcine, as produced or stabilized, is mixed with the metal powder of less than 0.15 mm size in a slowly rotating drum mixer for 1 to 3 hr to provide a uniform mix and to coat the calcine with the fine metal powder. The mix is then fed to a compacting press where it is compacted under about 1400 kg/cm². These fairly high pressures are used to produce good metal interparticle contact to assure that the metal will sinter together well. The mix may be compacted in dies or in the storage canister. Low-profile compacts (8 to 10 cm high) may be needed to assure uniform density throughout the compact. Compacted samples are rapidly brought to sintering temperature and sintered for 15 to 30 min. An atmosphere of dry nitrogen or argon is needed in the sintering furnace to prevent metal oxidation. Sintering temperatures are 600 to 620°C for aluminum and about 980°C for iron.

In the PNL gravity sintering process the waste pellets or beads are loaded directly into the canister. The metal powder would be loaded into the remaining void volumes by simply pouring the powder with some vibration of the container to assist in packing. A screen may be required at the container top to retain the HLW particles. The required matrix metal particle size is dependent on the HLW particle size and shape. The matrix will be 30 to 65% dense, depending on the shape and size of both the matrix and HLW particles. After loading and welding of the end closure, the canister would be heated to the desired sintering temperature (maximum temperature would be the previous sintering/outgassing temperature of the HLW particles or 100°C or more below the melting point of the matrix material). This heating would occur with the stagnant air atmosphere left in the can after seal welding.

To avoid possible pressure buildup in storage canisters, the solidified waste should be pretreated to remove volatile components, primarily nitrates. Calcines can be denitrated by heating them to 800 to 900°C, or by adding phosphates prior to calcination to form granules free of nitrates, or by converting the calcine to vitreous beads.

Metal cast product volumes remain essentially the same as those occupied by the solidified waste whereas sintered product volumes increase with decreasing waste content. Product volumes can therefore vary from about 30 to 80 liters/MTU. For casting, aluminum is the least costly metal to use. It is abundant and also has high thermal conductivity and temperature stability.

On the other hand, lead alloys are easiest to cast and the most corrosion resistant. Iron and alloy steels which could be used for sintering would cost less than aluminum and be more temperature resistant, but would have lower thermal conductivity.

The gaseous effluent released during casting or sintering contains a small fraction of entrained metal-oxide vapor resulting from the processes and is readily filterable. Small amounts of metal waste may also occur.

Facility operation would be batch or semicontinuous, and plant shutdown or startup is not expected to be difficult or time-consuming. Process equipment requirements include: solidified waste-metering devices; furnaces for sintering or casting the product; connecting mechanisms between feeders and casting containers for gas, waste and molten metal; and an off-gas filtering system. Monitoring devices to measure and regulate waste amounts used, furnace temperature, off-gas product quality, and product heat-generation rate will also be required.

Estimated Time of Readiness for Practical Design

Design for a full-scale facility could begin in late 1978 or early 1979.

Major Development Program Objectives

The matrix formation properties of new waste compositions with different metals should be evaluated and a conceptual process verified through cold pilot plant operation. Several experimental methods have been used to prepare metal matrices, but the method most suitable for the various waste forms under remote conditions remains to be determined. Because high percentages of fines in calcines are difficult to cast and hinder the formation of strong metal matrices, methods for casting the fines or reducing the fines percentage should be investigated.

Methods for metering particles and molten metal to the casting container should be verified. Since metals can form slags in air, reliable inert-gas, metal transfer and casting systems should be tested. General process techniques for receiving waste, canister hookup and removal from the matrix forming apparatus, etc., remain to be determined. Special dies and the pressures required for compacting mixes for the sintering process should be developed. Additional product characterization, such as determination of possible slow metal oxidation (waste-metal interaction) on long-term storage at temperatures near the metal melting point, remains to be determined.

Glass-CeramicProcess Summary

Final Product Form: A glass-ceramic results from a glass being subjected to a controlled crystallization which produces a fine grained crystalline body with some residual glass phase. The glass-ceramic would be formed in thin cross sections and may be contained in a metal matrix. A glass-ceramic is stronger than glass, would not be as susceptible to uncontrolled devitrification at high storage temperatures, and would have leach resistance similar to glass.

Process Description: Liquid HLW is calcined and melted with the addition of glass frit. The melt is cast in small blocks or plates sized so that temperature gradients will be small. The blocks are cooled rapidly so that they remain completely vitreous and are then taken through a carefully programmed thermal treatment to promote controlled nucleation and crystallization. The blocks are stacked in a canister and the annulus filled with metal for enhanced heat transfer.

Applicable Wastes: HLLW can be processed. Volatiles such as Hg or I cannot be maintained in the glass structure.

Development Status: Limited work at the laboratory scale has been completed. Several years of additional laboratory work remain to identify optimum compositions and characterize behavior.

Process Effluents: Liquid and gaseous effluents could be treated by routinely available equipment.

Process Operating Conditions and Features

Background

The glass-ceramic concept utilizes the metastable nature of glass to control the "devitrification." The glass-ceramic concept is relatively new to the ceramic field with the first commercial patent issued in 1960.⁽¹⁷⁾ The term glass-ceramic is sometimes applied to various combinations of glass and crystalline material. However, as used here and throughout the ceramic and glass industry, it applies specifically to a homogeneous glass which has been subjected to a controlled temperature cycle in which crystals are nucleated throughout the body, then the temperature increased and the crystals allowed to grow until the body is no longer a glass, but mainly a very fine grained crystalline material. Some residual glass phase may remain, but composition must be controlled carefully so that the residual continuous glass phase is not highly leachable.

Application of the glass-ceramic concept to HLLW solidification is known to improve the thermal and mechanical stability of the waste product and is currently under development in Germany.^(18,19)

Product

The glass-ceramic waste form will require a thin cross section (3 cm or less) to allow rapid cooling and to maintain uniform temperatures during processing for control of the nucleation and crystal growth periods. A disk waste form is one acceptable geometry which could be formed, treated, then stacked into a canister with a filler (probably metal) added to aid heat transfer between the disks and canister walls. The radial thermal gradient in the canisters may initiate some cracks in the disks.

An optimum composition for each waste may need to be developed. However, a composition VC 15K mod has been suggested⁽¹⁹⁾ which may be applicable to the reference waste composition. It contains 38.9% SiO₂, 3.9% TiO₂, 4.6% Al₂O₃, 3.9% B₂O₃, 3.9% MgO, 9.8% Li₂O, 3.9% K₂O, 20% waste oxides and 11.1% Gd₂O₃. The crystallized product has a density of 2.85 g/cm³ and would have a specific volume of about 77 liters/MTU with the given waste and Gd₂O₃ loading. The thermal conductivity of the product is 2.2 W/m°C at 400°C.

The leachability of glass-ceramics will generally be similar to that of the parent glass. With the proper composition the residual glass phase will be low in alkali and durable. The glass-ceramic will not be subject to increases in leachability due to uncontrolled devitrification.

The ideal glass-ceramic starts from a completely homogeneous glass. This may be difficult to obtain since the solubility of elements such as Ru, Rh, and Pd in silicate glasses is very low. These elements plus Zr, Ag and P, also found in the waste, are used as nucleating agents in glass-ceramics. Addition

of other nucleating agents should not be required. The halogens Cl and I, and Hg are very volatile at glass melting temperatures and cannot be incorporated into the glass even at moderate levels. Fluorine is also volatile, but of a lower magnitude and can be incorporated into the glass-ceramic with some recycle. Sulfate can be used as a nucleating agent at low levels ($\sim 1\%$); however, it can lead to a major phase separation in high concentration.

The maximum allowable storage temperatures will be similar to the crystallization temperature used during processing, or about 700 to 800°C.

Processing

The development of the process has been limited to laboratory scale. Therefore, a concept must be described rather than an operating process. The flow diagram is shown in the summary section. The liquid waste is calcined and then fed into a continuous melter where it is melted with the proper additives. After sufficient residence time to form a homogeneous mass, the glass is fed to a mold or forming device which produces disks of glass. The disks are then rapidly cooled to avoid devitrification. These disks are then subjected to controlled nucleation and crystal growth periods in a tunnel kiln which moves the disks through the appropriate temperature cycles. The temperature cycles are very dependent on the compositions and on the thickness of the disks since thermal shock must be avoided.

Glass-ceramics will not be as flexible in compositions such as glass, since each atom will form only certain types of crystals and there must be specific ratios between the various constituents. Sodium can be incorporated into many glass-ceramics and should allow some intermediate-level waste to be incorporated.

The various operations required in a glass-ceramic process are currently automated in industry. However, they have not been operated remotely, and maintainability in a remote facility has not been demonstrated. Equipment such as tunnel kilns may require major development to operate under the proposed conditions.

The effluents from the process are generally similar to those from glass melting, discussed in other sections. Volatiles may be somewhat higher because of the need to form a homogeneous glass, which requires higher temperatures. Resource demands are anticipated to be similar to those of the glass making process discussed previously.

Estimated Time of Readiness for Practical Design

The technology is not well developed, and many questions remain to be answered. It is estimated that design of an operating facility could not begin until after the 1980 period.

Major Development Program Objectives

There is not currently any major effort in the U.S. to develop this option. To allow use of this waste form, 2 to 5 years of major laboratory research would be required to develop the best compositions and characterize their behavior during the waste fixation and storage process. Engineering development of the glass casting and heat treating process would also require a major effort.

Coated Pellets

Process Summary

Final Product Form: Stable pellets of solidified HLW oxides completely sealed within a nonradioactive coating of a leach-resistant material, which provides complete protection of the waste from leaching or vaporization for long periods. The pellets are imbedded in a metal matrix which provides increased strength, impact resistance and high thermal conductivity.

Process Description: Stable pellets would be formed from calcine, supercalcine or as a sintered product. The pellets would be coated by chemical vapor deposition (CVD) in a fluid bed or drum coater, by a plasma spray or by an enameling process. Large pellets could then be added to a canister, and a metal powder vibrated between the pellets to fill the voids. Smaller 1-mm type pellets may require premixing with the metal before addition to the canister. The powdered metal and pellets are then reheated to sinter the metal to provide increased strength and thermal conductivity. It may also be possible to cast the pellets in a molten metal matrix.

Applicable Wastes: All wastes which can be formed into stable pellets.

Development Status: The process is in early laboratory development. The coating material, its thickness, and the process for applying it are currently being selected and optimized.

Process Effluents: Effluents from calcining and pelletizing are covered in their respective sections. The CVD coating process could produce HCl gases which could require special off-gases handling. Fine oxide powders which are generated in the equipment but do not become part of the coating would require recycle.

Process Operating Conditions and Features

Background

The coating of a waste form was first patented by Bixby,⁽²⁰⁾ who suggested that an enamel coating could be applied to a waste-containing clay body. More recently Gray⁽¹⁵⁾ has suggested using HTGR fuel technology and applying coatings of pyrolytic carbon with possibly a second coating of SiC over waste particles. Gray and Browning⁽²¹⁾ have also tested other oxide and carbide coatings and are currently considering the high-durability oxides SiO_2 and Al_2O_3 .

Loose pellets have poor thermal conductivity, and their coatings could chip during handling and transport. To eliminate these problems, the pellets will be incorporated into a metal matrix. The section on metal matrices reviews casting technology which could be applied to this area. Sump⁽¹⁶⁾ has begun investigating the concept of gravity sintering of metal powders containing waste pellets.

Product

The optimum combination of waste form, coating type and method, and metal matrix composition and form is still being determined, and many options are available. The waste form should be an inherently stable product such as supercalcine or a sintered product. The coating materials such as SiO_2 and Al_2O_3 are the most durable of the oxides, whereas carbon products are even more resistant to water leaching and attack by salt, but are susceptible to oxidation at high temperature. The coating of a waste with a separate inert material has several advantages, including 1) selection and control of the surface to be exposed to weathering, 2) complete protection of the radioactive atoms from water leaching for long periods, allowing decay of most β and γ emitters, 3) option of applying quality assurance to each pellet, and 4) high waste loading within the canister.

Tests of both pyrolytic carbon and chrome carbide have shown them to have leach rates as measured by the Soxhlet test which are at least 100 times lower than pyrex glass. Calcine wastes coated with pyrolytic carbon with and without SiC overcoat have shown good thermal stability at temperatures up to 1200°C in an inert atmosphere.

The thermal conductivity of the final waste form will depend on the metal selected and its final density and its weight ratio to the coated pellets. The thermal conductivity can be expected to be much higher than that of glasses or powder oxides. The heat loading will probably be limited by final storage considerations rather than by waste form.

The gravity sintering approach allows selection of metal such as stainless or alloy steels, copper, or bronze with higher melting points and therefore increased stability at high temperature and with lower reactivity toward the waste or its coating.

Processing

The total processing requirements have not been completely determined. Thus processing related questions can only be indicated.

High-quality coatings can be applied by CVD (Chemical Vapor Deposition) techniques in either a fluid bed or a drum coater, as has been demonstrated with HTGR fuel. The CVD coatings are formed from reactions such as:

in the presence of H_2 and He. The reactions occur within the heated coater, and the coating, in this case Al_2O_3 , is deposited on the pellets. The coatings build slowly, $\sim 20 \mu\text{m/hr}$. Some of the Al_2O_3 formed will coat the process equipment and require recycle of that material back into the waste.

Carbon coatings are formed by the thermal decomposition of hydrocarbon gases at temperatures above 800°C . The process residues, principally carbon, can be disposed of by burning and do not require recycle as waste.

The coating process will allow considerable variations in the chemical makeup of the waste pellet without affecting the properties of the coating and its behavior in the environment. With large pellets the effects of thermal expansion mismatch must be considered. Coating with a material of lower thermal expansion can increase the strength of the coated pellets by the surface being in compression.

The process will involve movement of material from calciners to pellet formers to coaters and finally to the canister. The additional processing steps will increase the complexity of the system and may adversely affect reliability of the process.

The effluents may contain HCl and could require special considerations. Use of enamels for coatings may simplify the off-gas treatment and the total process.

The gravity sintering process would involve loading of the canister with large pellets and vibrational feeding of metal powders into the voids, followed by a heat treatment to sinter the metal into a monolithic matrix.

Estimated Time of Readiness for Practical Design

Two to three years of laboratory-scale experiments would be required prior to beginning pilot-scale development. Another 2 years would be necessary before conceptual design could begin.

Major Development Program Objectives

The two most crucial steps in the development are the selection of the pelletizing and the coating processes. Several alternatives in materials and processes are being explored and should be selected by 1977.

Matrix optimization and detailed characterization of the product is needed and should be completed in 1978.

Equipment development for remote operation may be required. However, ORNL has done remote setup of the HTGR fuel fabrication process, which may have many similar features.

Ion Exchange

Process Summary

Final Product Form: The product is a tough ceramic with low leachability and high thermal stability. It has a density of $\geq 4.5 \text{ g/cm}^3$ and contains $\sim 25 \text{ wt\%}$ fission product oxides for a concentration factor of $\geq 1.1 \text{ g fission product oxides/cm}^3$.

Process Description: HLLW is neutralized to $\text{pH} = 1$ with NaOH and clarified by centrifugation. The clarified waste is then almost completely decontaminated ($< 10^{-5} \text{ Ci/ml}$ total activity, mostly ruthenium, cesium, and technetium, and $< 10^{-10} \text{ Ci/ml}$ α -emitters demonstrated on a laboratory scale) by ion exchange with sodium titanate (ST). Cesium is subsequently removed by ion exchange with a zeolite, and the remaining trace wastes such as ruthenium and pertechnetate ions are removed with an anion exchange material and other

reagents. The exchanged ST and zeolite are removed as slurries and combined in slurry form with the suspended solids which were removed in the clarification step. This mixture of slurries is dewatered and dried on a pan filter, then consolidated by pressure sintering, the only high-temperature step in the process.

Applicable Wastes: HLLW streams containing fission products from a Purex solvent extraction fuel reprocessing plant can be decontaminated by this process.

Development Status: The decontamination of actual HLLW with ST and a zeolite has been demonstrated on a laboratory scale. All critical process steps in a first baseline flowsheet have been verified feasible by laboratory-scale measurements.

Process Effluents: Low-level dry sodium salt solids and tritiated water are the major process effluents. A small quantity of trace cleanup solids is also expected.

Process Operating Conditions and Features

Background

The phenomenon of ion exchange, as the name implies, is simply the exchange of ions occurring across a boundary between two phases. In its most common form, this definition applies to exchange between a liquid phase and a solid phase across the boundary separating them, and in the special case of a liquid phase containing ionic radionuclides the ion exchange process by definition accomplishes solidification of these nuclides. If the exchange capacity per unit volume of the ion exchanger is high with respect to the concentration of exchangeable ions in the waste solution, volume reduction comparable to evaporation methods can be realized. Therefore, it is not surprising that ion exchange materials and processes have been extensively investigated and widely applied in the nuclear industry.⁽²²⁻²⁷⁾

An ideal exchanger for high-level waste would be an inorganic material which provides high decontamination factors for process effluent, high capacity for radionuclides, and which when spent, could be directly processed to a form suitable for either interim or final storage. A variety of inorganic exchangers have been developed, but fall short in one or more of the above areas. Clay materials generally have low exchange capacities (in the range of 0.03 to 1.5 meq/g), lack stability in acid solution, and have variable purity with respect to ion exchange properties.^(22,28,29) Zeolites have substantial capacities, but they are generally very selective and work poorly when it is desired to solidify a broad range of cations.^(30,31) Heteropoly acid and insoluble salt inorganic exchangers may have potential but have not been investigated for solidification of a broad range of radionuclides.^(22,32)

A solidification process based on inorganic exchangers of the hydrous oxide type is currently being developed at Sandia Laboratories.⁽³³⁾ The experimental program includes investigation of the effectiveness of the ion exchanger, consolidation of the solidified waste, evaluation of the physical and chemical properties of the resulting waste form, and a modest engineering effort directed at defining a usable full-scale process.

Product

The quantity of solidified waste from this process is about $0.05 \text{ m}^3/\text{MT}$, corresponding to a tenfold reduction in waste volume. This solid is a ceramic with a density of $\geq 4.5 \text{ g/cm}^3$, containing $\sim 25 \text{ wt\%}$ fission product oxides for a concentration factor of $\geq 1.1 \text{ g/cm}^3$, and has a low leach rate and high temperature stability.

Processing

The HLLW is neutralized with 50 wt% aqueous NaOH solution to $\text{pH} \sim 1$. Suspended solids are then removed by centrifugation. The separated sludge is washed with water inside the centrifuge, extruded from the centrifuge by means of a screwfeed device, and transferred by gravity to a slurry mixer tank, where it is suspended in a slurry mixture of exchanged titanate and zeolite. The wash liquor is combined with the clarified liquid waste to make up the feed for the exchange step with sodium titanate (ST).

The solids-free liquid feed is to be stored in surge tanks with cooling and pumped batchwise through ST ion exchange beds during the ion exchange part of each process cycle. Two ST ion exchange columns operated in parallel would provide the required ion exchange capacity for a 5-MT/day plant based on the following ion exchange bed properties:

Geometry:

Cylinder: 30 cm x 3 m long
Volume: 220 liters

Composition:

Sodium Titanate: -80 +200 Tyler Mesh particle size

Pressure drop:

$< 3500 \text{ g/cm}^2$ at $\sim 3.05 \text{ m/hr}$ superficial velocity, based on measurements of pressure drop in beds up to 30 cm deep at full-scale process linear flow velocities

Cycle time:

3 hr ($\sim 1 \text{ hr}$ exchange, $\sim 1 \text{ hr}$ wash, $\sim 1 \text{ hr}$ turnaround)

Ion exchange efficiency:

90% saturation of each batch in the ion exchange bed.

After the ion exchange step in the cycle is complete, the bed is washed with ~ 1.5 bed volumes of deionized water. The almost completely decontaminated feed and wash streams (all radionuclides except cesium, ruthenium, technetium, tritium, and other noncationic species near MPC) leaving the ST ion exchange columns are mixed in a holding tank, then pumped through zeolite ion exchange beds for cesium removal.

The effluent liquid stream from the zeolite beds (consisting of nearly completely decontaminated feed combined with wash water from both ST and zeolite columns) is fed to a cleanup decontamination process for technetium and ruthenium. Technetium (as TcO_4^-) removal is expected to be accomplished by anion exchange with a commercially available anion exchanger using established process techniques. A ruthenium removal step will be defined pending identification of the ruthenium species present at this stage of the overall decontamination process.

Water is separated from NaNO_3 (and other sodium salts) in the decontaminated stream from the cleanup steps by means of an evaporator-drier. The water vapor can be condensed and recycled in the plant. Sodium nitrate solids at $\sim 0.1 \text{ m}^3/\text{MT}$, relatively dry and very low level in radioactive contamination, are removed from the evaporator-drier and treated as low-level solid waste from the plant. The volume of NaNO_3 yielded by SSP would be only a small fraction of the total low-level solids emanating from a fuel reprocessing plant.

After the ST ion exchange step, the exchanged titanate and zeolite beds are transported out of the columns as slurries. The exchanged ST and zeolite slurries are combined in a holding tank with suspended solids removed from the feed. This mixture of slurries in the mixer tank is fed batchwise by gravity to a horizontal pan filter where it is dewatered and dried with hot air drawn through the solids to the vacuum side of the filter medium. Water (or slurring solution) from the filter-drier is returned with a small quantity of makeup to a holding tank where it is available to slurry out the next batch of loaded ST or zeolite.

The dewatered and dried solids are dumped from the pan filter by gravity into a hopper below the filter by rotating the horizontal pan through 180° . Positive release of the solids from the filter medium can be assured by a pulsed backflow of air. They fall by gravity through the hopper and into a press where sintering under pressure consolidates the material. Monolithic cylinders $\sim 0.3 \text{ m}$ in diam and $\sim 0.3 \text{ m}$ long are generated in this step and are to be suitable for stacking into a storage capsule.

Any traces of radioactive volatiles released during consolidation are trapped with filters or other entrapment devices and treated as low-level

solid wastes. It is unlikely that this solid stream will be a large fraction of the total solid waste leaving a fuel reprocessing plant.

Heat transfer calculations have demonstrated that no serious engineering problems should be caused by the self-heating of 1-year-old waste.

Estimated Time of Readiness for Practical Design

This process is in bench-scale demonstration and should be ready for the practical design of a full-scale plant during 1981. This time scale assumes a substantial development effort during CY 1976-77, 1 year of cold pilot plant demonstration, and 2 years of hot, remote pilot plant studies and demonstration.

Major Development Program Objectives

By late 1977:

1. Demonstrate a bench-scale physical operation of the ST ion exchange process step.
2. Establish the optimum process chemistry for ST and zeolite ion exchange steps.
3. Establish the process chemistry for the tail-end cleanup (for Tc, Ru, and nonionic trace contaminants).
4. Develop and demonstrate a complete and practical bench-scale process, including solids consolidation.
5. Establish the optimum process chemistry for ST synthesis.

By early 1978:

6. Design a pilot plant for synthesis of ST.
7. Design a pilot plant for HLLW decontamination.

By early 1979:

8. Demonstrate pilot plant operation with simulated HLLW.

By 1981:

9. Complete development and demonstration of a remotely operated pilot plant with radioactive feed.

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6.4 EXISTING COMMERCIAL HIGH-LEVEL WASTE

Presently stored at the West Valley, New York, plant owned by Nuclear Fuel Services are 600,000 gal of neutralized high-level Purex waste (570,000 gal of supernate, 30,000 gal of sludge) and 12,000 gal of acid thorium waste. The neutralized waste is stored in a single 750,000-gal carbon steel tank, and the acid waste is contained within a 15,000-gal stainless steel tank. Each tank has a duplicate into which the liquid wastes can be transferred if necessary.

A number of alternatives for managing the waste stored at the West Valley plant are discussed here. These alternatives are limited to concepts presently under active investigation by ERDA for managing Federal radioactive waste. Each waste management option is briefly described and is considered as to:

- status of the technology
- its applications to managing NFS waste
- its advantages and disadvantages
- the research and development needed to implement the option
- safety considerations
- estimated time to implement the process.

Other alternatives to, and hybrids and combinations of processes are potentially applicable to managing NFS waste. However, they are not considered here because they are not currently under development by ERDA. One example would be to utilize any future NFS waste management facilities for processing the existing waste. Such potential alternatives may be considered in future specific follow-on studies for the management of existing NFS waste.

Common to each alternative is the need to remove some or all of the waste from the storage tanks for treatment. A suggested method for removing the neutralized waste includes these steps:

1. removing most of the supernate by pumping or jetting
2. dispersing the sludge using a hydraulic jet
3. pumping the dispersed sludge to a holding tank
4. removing as much of the remaining sludge as practicable using a chemical flush.

No sludge is expected in the thorium waste, and the waste can likely be pumped readily from the tank.

The tanks for neutralized waste contain a number of internal obstructions which impede complete removal of the sludge. A preliminary estimate indicates up to 70% sludge removal, assuming that no major modifications are made to the tank and that a high-pressure sluicing technique developed at the Savannah River Plant (SRP) is used. A single chemical flush following the sluicing

operation might be expected to remove an additional 80% of the remaining sludge (total of 94% of the original quantity of sludge in the tank). Subsequent sluicing and chemical flushes would be required to remove the remaining 6% of the sludge. Because of the obstructions and limited tank access, the amount of sludge that will be removed cannot be ascertained until field application is completed.

6.4.1 Waste Management Alternatives

Table 6.7 summarizes the characteristics of the waste management alternatives considered in this study. Throughout the study it is assumed that the acid thorium waste is amenable to managing by the same processing alternatives as the neutralized waste.

TABLE 6.7. Characteristics of Waste Management Alternatives

<u>Alternative</u>	<u>Final Form</u>	<u>Storage Location^(a)</u>	<u>Waste Container</u>
Liquid storage	Liquid & sludge	NFS site	Tank
Conversion to cement	Solidified cement, crystallized salt	NFS site, Federal Repository	Canister
Shale fracturing	Solidified grout	NFS site	Geologic formation
Shale cement	Solidified grout	NFS site, Federal Repository	Canister
Calcination	Calcine	NFS site, Federal Repository	Canister
Aqueous silicate	Aluminosilicate mineral	NFS site, Federal Repository	Tank, Canister
Conversion to glass	Glass	NFS site, Federal Repository	Canister
Salt cake	Crystallized salt	NFS site, Federal Repository	Canister

a. Storage facility at NFS site would be Federally operated.

Permanent liquid storage, the waste management option presently licensed for the West Valley plant, is included as a reference alternative. In this option a storage tank would be placed in a catch pan located within an underground concrete vault. The supernatant liquid and sludge would be periodically pumped into a new tank for continued storage. The frequency of pumping was assumed to be 40 years but could be required sooner or be postponed, depending on the condition of the tank.

The supernate is in retrievable form for further treatment; the sludge exhibits more difficulty, especially if more than 95% of the sludge must be recovered.

Past experience has provided a well founded technology for design of storage tank systems.⁽¹⁻⁴⁾ A catch pan or double wall storage tank makes it possible to apply corrective action before waste inadvertently leaking from the tank reaches the surrounding soil.

For conversion to cement the sludge and supernate would first be separated by centrifuge. Sludge would be exposed to a series of drying and washing steps before it is finally incorporated into a cement and placed in steel containers. Liquid discharged from the centrifuge would be treated by ion exchange to remove cesium, concentrated by evaporation, and placed into steel containers where the resulting salt hardens to monolithic form when it cools. The cesium-bearing ion-exchange zeolite would be periodically combined with the dried sludge and incorporated into a cement matrix. Alternatively, the sludge and/or zeolite might be incorporated into a glass. This option is presently under active development for application to ERDA neutralized waste.

In shale fracturing, a grout consisting of waste mixed with a blend of cement and other additives is pumped down a well and injected into a shale formation isolated from the surface environment. The shale is first fractured by pressure from a small volume of water. Waste grout is then injected into the initial fracture. As the crack propagates, it is filled with grout. Injection continues until the batch of waste-grout is depleted. A few hours after injection the grout sets, permanently fixing the radioactive waste in the shale formation. Subsequent injections form sheets parallel to and a few feet above the first. The shale fracturing option is a waste disposal process currently used at Oak Ridge National Laboratory for permanent disposal of locally generated intermediate-level waste solutions.

The shale cement process is an outgrowth of the shale fracturing alternative. The process is carried out at ambient temperature and involves combining waste with an appropriate mixture of cement and additives, including Conasauga shale, to form a grout. The grout is then pumped into drums where it solidifies, and the drums are stored in a retrievable manner. At present the shale cement option is a conceptual process.

Calcination is a process for converting liquid high-level radioactive waste into a solid form.^(5,6) Currently there are two candidate approaches for calcining liquid waste: fluidized bed and radiant-heat spray. In both approaches liquid waste is evaporated to dryness and the remaining solids are converted to oxides in the calciner. Although not treated in this study, the resulting calcine can be incorporated into a glass to provide a low-leaching, readily retrievable monolithic solid.

Fluidized bed calcination consists of spraying liquid into a bed of heated fluidized particles. Evaporation occurs primarily on the surfaces of the particles. Resulting off-gases are treated to remove entrained particulate solids and volatile fission products prior to discharge through the stack. Fluidized bed calcination has been demonstrated and is fully operational for solidifying acid and low-concentration sodium wastes.

Solidification by spray calcination is based on atomizing the liquid waste into fine droplets. As the droplets fall through a heated chamber, waste is evaporated and converted to a fine suspension of oxide particles. The oxide particles are generally separated from the off-gas by filters. After passing through the filters the off-gases are further cleaned prior to discharge to the atmosphere. Simulated and radioactive acid wastes have been solidified on a pilot scale using a spray calciner.

With additives (e.g., sugar and stable anions such as sulfate or phosphate), direct calcination of the 8M sodium NFS waste using either candidate process appears potentially feasible.

The aqueous silicate process provides means of converting radioactive wastes to solid, relatively insoluble, aluminosilicate minerals.⁽⁷⁾ Powdered clays such as kaolin or bentonite are mixed with, and allowed to react with, aqueous solutions or slurries of caustic wastes at temperatures ranging from 30 to 100°C. The reaction produces a moderately hard, salt-filled sodium aluminosilicate with radioactive isotopes trapped in the aluminosilicate framework structure. Excess clay acts as a binder and also adsorbs unreacted salts and radionuclides. The technical feasibility of the aqueous silicate process has been verified in the laboratory on radioactive and nonradioactive wastes. Solidification of NFS waste supernate by the aqueous silicate process appears technically feasible; sludge waste might be similarly immobilized.

Conversion to glass of radioactive waste provides a form with properties of low dispersibility, low leachability, and relatively high thermal stability. In one conceptual application, supernatant solution, salt cake or sludge waste is dewatered and mixed with glass-forming additives. The mixture is melted by heating to 1025 to 1400°C. When cooled, the melt solidifies to form a glass which can be contained in an easily retrieved steel canister. Boro-silicate glasses have been formed for simulated and actual wastes near the composition of the high-level neutralized waste at NFS, but with lower concentrations of Na_2SO_4 than present in NFS waste.⁽⁸⁾

Salt cake (mostly NaNO_3) results from evaporation of supernate from neutralized high-level waste.⁽⁹⁾ Sludge could likely be processed in a similar manner and treated separately or incorporated into the salt cake but is not treated as an option herein. Methods for producing a salt cake include: forced-circulation evaporation, wiped-film evaporation, and spray drying.

A forced-circulation evaporator can achieve a large degree of concentration with waste containing high concentrations of caustic. The evaporator is designed to produce a slurry containing 25 to 30% solids, which is routed to a series of settling tanks. The supernatant liquid is removed from the settling tanks and returned to the evaporator for additional concentration. Atmospheric type evaporators (at Savannah River) and vacuum type evaporators (at Hanford) are fully operational.

Neutralized Purex waste can be concentrated in one pass through a wiped film evaporator to a product that solidifies upon cooling to room temperature. At storage temperatures approaching 100°C, however, only partial solidification can be achieved, and thus the system would require salt-supernate separation and recycle similar to that of the vacuum evaporator method. For intermediate storage temperatures (e.g., 40 to 50°C) one-pass evaporation and solidification may be possible. Pilot-scale equipment testing using synthetic waste is in progress at the Savannah River and Pacific Northwest Laboratories.

Pilot-scale spray drying equipment using a single synthetic NFS waste formulation has had limited testing. Results show that wastes of the composition studied can be satisfactorily spray dried. However, the testing program was too narrow in scope to reliably apply the results to other cases such as NFS wastes.

For application to NFS wastes, shale fracturing, shale cement, or salt cake alternatives will probably require only relatively minor technical alterations if NFS wastes behave like ERDA wastes, as is assumed. The remaining options (conversion to cement, calcination, aqueous silicate, and conversion to glass) have not been sufficiently demonstrated for detailed application to NFS waste. However, implementation of any of the potential alternatives appears technically feasible. Although apparently feasible, any decisions should await the outcome of current ERDA research and development programs.

6.4.2 Advantages and Disadvantages

Table 6.8 summarizes the advantages, disadvantages, and current technological status for each alternative.

TABLE 6.8. Advantages, Disadvantages and Status for NFS Waste Management Alternatives Based on ERDA Processes

Alternative	Advantages	Disadvantages	Current Technological Status
Liquid Storage	No offsite shipping Fair retrievability <i>Amenable to change in form if necessary</i>	Potential for leakage Tank life short compared to necessary storage time <i>Higher probability for dispersion during natural acts, e.g., flood and earthquake, than for monolithic solid</i> Continuous surveillance, active control, and emergency response capabilities are required for centuries	Fully operational for storing neutralized high-level radioactive waste
Conversion to Cement	Low-leaching solid product Good retrievability Easily transported	Difficult to change to alternative form if necessary Technology has not been demonstrated Need to store large volume of residual salt Potential for container to pressurize Salt product would contain significant quantities of water (up to 20%)	Process is under active laboratory development and conceptual design of facilities for application to ERDA neutralized high-level radioactive waste.
Shale Fracturing	Low-leaching solid product No offsite shipping Immediate placement in geologic formation Process has been field tested using intermediate-level radioactive waste Not susceptible to natural acts on earth's surface, e.g., glaciation, denudation, flood, tornados	Site verification required Criteria for disposal of long-lived alpha emitters not established Waste is not retrievable Not possible to change to alternative form Requires pipeline transport of liquid high-level waste for distance of about 1 mile Technology has not been demonstrated for NFS waste	Full-scale demonstration for ERDA neutralized low- and intermediate-level radioactive wastes at Oak Ridge National Laboratory
Shale Cement	Low-leaching solid product Key portions of process use state-of-the-art technology Good retrievability Easily transported	Large volume of waste-grout mixture must be stored Potential for container to pressurize <i>Difficult to change to alternative form if necessary</i> Technology has not been demonstrated	Process is in the conceptual stage
Calcination	Good retrievability Easily transported Product would be thermally and radiolytically stable	Technology has not been demonstrated for NFS waste Difficult to change to alternative form if necessary Without glassification, calcine product is quite leachable	Fully operational using acidic, low-sodium ERDA high-level radioactive wastes.
Aqueous Silicate	Reasonably low-leaching solid product Good retrievability when stored in canisters Easily transported	Product would contain significant quantities of water (up to 35 wt%) Canisters must resist internal corrosion associated with high water content Difficult to change to alternative form if necessary Large volume of aqueous silicate product must be stored Potential for canister to pressurize Technology has not been demonstrated	Aqueous silicate product has been produced on a laboratory scale using ERDA neutralized high-level radioactive wastes
Conversion to Glass	Low-leaching solid product Glass product would be thermally and radiolytically stable Good retrievability Easily transported	Technology has not been demonstrated Difficult to change to alternative form if necessary	Glass product has been produced on a laboratory scale for ERDA neutralized radioactive high-level waste. Has been demonstrated on pilot plant scale for acidic high-level waste
Salt Cake	<i>Amenable to change in form if necessary</i> Fair retrievability	High leach rate Limited thermal and radiolytic stability Product would contain significant quantities of water Potential for container to pressurize Containers must resist internal corrosion Technology has not been demonstrated for NFS waste Sludge is not treated	Fully operational units now processing ERDA neutralized high-level radioactive wastes

6.4.3 Research and Development

All potential alternatives will require successful completion of research and development programs before they can be implemented. Table 6.9 summarizes the estimated research and development needs and timing to routine operation of the processing facility. These needs are in addition to current ERDA programs, which are assumed to provide much information applicable to managing existing NFS wastes. Common to each potential alternative is the need to determine the physical and chemical characteristics of the NFS wastes and to establish waste removal and decommissioning procedures (Section 15.0).

TABLE 6.9. Estimated Research and Development Activities and Timing to Routine Operation

<u>Alternative</u>	<u>Major Activities</u>	<u>Total Time to Operation,^(a) years</u>
Liquid storage	Materials selection and development; leak repair techniques; leak detection systems; tank flaw detection; thorium and neutralized waste blending; characterize NFS waste supernate and sludge; decommissioning.	0
Conversion to cement	Characterize NFS waste supernate and sludge; salt "decontamination" achieved by the ion-exchange processing step; salt concentrating parameters; sludge washing and drying procedure; concrete formulation; radiolytic gas generation in concrete; applicability of commercially available equipment to processing NFS waste; decommissioning; container corrosion rates.	10
Shale fracture	Disposal criteria; characterize NFS waste supernate and sludge; verify suitability of West Valley shale beds; cement mix for NFS waste; sludge handling problem; decommissioning.	5.5
Shale cement	Characterize NFS waste supernate and sludge; define cement mix for NFS waste; determine storage drum life; develop process equipment; sludge handling problems; decommissioning; container corrosion rates.	9
Calcination	Demonstrate calcination using NFS waste; verify flowsheet; establish the ability of off-gas treatment system to conform with release limits; characterize NFS waste supernate and sludge; decommissioning.	13
Aqueous silicate	Demonstrate process for sludge and chemical immobilization; heat transfer studies; characterize NFS waste supernate and sludge; decommissioning; container corrosion rates.	13
Conversion to glass	Demonstrate pilot-scale vitrification process; develop applicable glass formulation; characterize NFS waste supernate and sludge; decommissioning.	14
Salt cake	Container corrosion rates; demonstrate wiped film evaporation with NFS waste; characterize NFS waste supernate and sludge; heat transfer studies; decommissioning.	6

a. Includes research and development time.

Technology and procedures for permanent waste storage in tanks are considered to be largely developed and the alternative considered operational.

The research and development activities for tank flushing assumes that investigations currently under way at ERDA sites will continue and will substantially benefit sludge removal technology.

Conversion to cement will require additional research and development work before it can be applied to managing the existing NFS wastes. Principal investigations should include studies to determine 1) if adequate salt decontamination can be achieved using NFS wastes, 2) the effectiveness of the SRP-developed sludge washing and drying procedure using NFS wastes, 3) the suitability of cement for fixation of the NFS waste, and 4) the ability of the process to treat a mixture of neutralized and thorium waste. The present SRP research and development program is assumed to continue and to provide much technology to managing NFS wastes by a similar process. The estimated time to the start of routine operations is 10 years.

Shale fracturing and shale cement options will need programs to establish suitable waste-cement formulations for use with NFS waste. Some additional geologic investigations will likely be required for the shale fracturing option. A program of equipment development is anticipated for the shale cement process. Time to operation for shale fracturing is projected to be 5.5 years; for shale cement 9 years.

The calcination alternative would require an extensive research and development program to attain an integrated process for managing the NFS waste. The program would comprise flowsheet verification, requiring 6 months to 1 year, followed by pilot plant demonstration. Process development would stop at the end of this period if the process was judged inapplicable to managing the NFS waste. The time required to provide an operational facility is estimated at 13 years.

Research and development needs for the aqueous silicate option would include heat transfer studies and a demonstration of the ability of the process to immobilize sludge and chemical flush solutions. It is assumed that the present ERDA aqueous silicate program will continue and that most data collected will apply to the NFS process. It is estimated that about 13 years will be required to achieve commercial operation for managing NFS wastes.

Fixation of the NFS waste by conversion to glass would require considerable research and development effort. Of prime importance is demonstration of

the process, including developing an acceptable glass product and proving the operating reliability and lifetime of key reprocessing equipment such as the melter. An estimated 14 years are necessary before commercial operation can be started. As in previous options, continued research and development by the ERDA is assumed.

The major needs in salt cake research and development are to demonstrate a wiped film evaporator for concentrating NFS wastes and to establish corrosion rates of metal tanks containing the resulting concentrate. About 6 years may be required to bring the facility into operation.

6.4.4 Safety

Safety is presented as a qualitative discussion based on the characteristics of the various final forms. In the absence of data for NFS Wastes, characteristics of stored forms of solidified ERDA Wastes are summarized in Table 6.10. For this document, processing operations (radionuclide immobilization by solidification) are assumed to be conducted over a relatively short period and to be performed under closely controlled conditions in vaults or cells which provide equivalent containment. This approach assumes that all the facilities can be designed to meet equivalent accident and chronic release criteria and thus are equally "safe." Also, except for salt cake formation, the waste will be removed from the tanks in the same way for processing for each option under consideration, making the safety of the removal portion of the process the same for each option. When detailed designs become available, more complete safety analyses will be required.

TABLE 6.10. Summary of Characteristics of Stored Forms for ERDA Wastes

<u>Alternative</u>	<u>Leachability (g/cm²-day)</u>	<u>Volatility</u>	<u>Particle Size</u>	<u>Impact Resistance</u>	<u>Thermal and Radiolytic Stability</u>	<u>Containment</u>	<u>Container Stability (Corrosion)</u>
Liquid storage							
Supernate	∞	high	liquid	--	poor ^(a)	tank	poor
Sludge	medium	medium	wet powder	--	poor ^(a)		poor
Acid	∞	high	liquid	--	poor ^(a)		poor
Conversion to cement	<10 ⁻³ (cement) high (residual salt)	medium	monolithic	high	fair	canister	good
Shale fracturing	<10 ⁻³	medium	monolithic	high	poor ^(a)	geologic formation	--
Shale cement	<10 ⁻³	medium	monolithic	high	poor	canister	fair
Calcination	<10 ⁻¹	low	powder	--	fair to good	canister	good
Aqueous silicate	<10 ⁻²	medium	monolithic	low	poor	canister	fair
Conversion to glass	<10 ⁻⁵	low	monolithic	high	good	canister	good
Salt cake	high	medium	solidified melt	--	poor	canister	poor

a. Not necessarily a problem in these storage alternatives.

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7.0 TREATMENT AND IMMOBILIZATION OF CHOP-LEACH
FUEL BUNDLE RESIDUES

7.0 TREATMENT AND IMMOBILIZATION OF CHOP-LEACH FUEL BUNDLE RESIDUES

In current fuel reprocessing technology, fuel bundles are sheared in short lengths, without disassembly, for acid leach of the fuel pellets in a dissolver. The residue from the acid leach includes short lengths of fuel cladding, fuel bundle support rods, poison rods, and massive end fittings; fuel support grids; assorted springs; and spacer elements. The materials used and the fuel bundle design will depend on the reactor type and the fuel fabricator.

Fuel bundle residues constitute a high-volume waste, in weight about 22% of the fuel bundle processed. Without compaction, the fuel hardware constitutes a substantially higher volume than the high-level waste calcines or glasses. Recovery of the fuel hull material from the dissolvers in metallic form creates possibilities for beneficial use within the fuel cycle.

In this section, the characteristics of the fuel bundle waste stream are discussed first, followed by the details of alternative treatment technologies. Except for fluoride dissolution of fuel cladding all the alternative technologies are pilot plant, laboratory, or conceptual processes needing development. Interim storage of fuel bundle residues is discussed in Section 18.

7.1 CHARACTERISTICS OF CHOP-LEACH FUEL BUNDLE RESIDUES

This waste stream is originally composed of all the undissolved fuel bundle hardware produced in fuel reprocessing. The composition of this stream will vary as fuel manufacturers change their materials of construction. The stream currently consists mostly of Zircaloy, with lesser amounts of stainless steel, Inconel, and other materials. The fuel cladding, chopped into short lengths and acid leached, contains about 0.05% to 0.5% of the original fuel.

All materials have been exposed to a neutron flux and thus activated to some degree. The extent of activation versus position can be estimated from Figure 7.1. All of the alloying and impurity elements are subjected to activation and transmutation. After heavy irradiation, impurity uranium (less than 3.5 ppm in the Zircaloy) can yield more than the proposed limit of 10 nci/g of TRU elements. These TRU elements are uniformly distributed in the metal and not removed by surface decontamination.

The average density of untreated fuel hulls is estimated to be 1 kg/liter, or a volume of 0.3 to 0.4 m³/MTU.⁽¹⁾

FIGURE 7.1. Axial Burnup Distribution

7.1.1 Source

The source of the fuel bundle waste stream, its projected volume, and average properties have been described in Sections 2 and 3. The average expected values from Section 2 for a reference LWR fuel are:

Zircaloy, kg/MTU	287.0
Stainless Steel, kg/MTU	29.0
Inconel, kg/MTU	8.0
Density, kg/liter	1
Volume/MTU, M ³ /MTU	0.3
Fuel Assemblies, FA/MTU	3.2
Fuel Oxide wt,* MT/MTU	1.13
Total wt, MT/MTU	1.46
Typical Exposure, MWd/MTU	25,000

These average values for a hypothetical fuel element are useful in considering large waste accumulations or material usage. The values used in this section are either for a specific fuel element type or for a range of values readily applicable to treatment of a single type of fuel element.

* In Section 2 the residual fuel adhering to the clad hulls was assumed to be 0.05% of the input fuel.

The fuel bundle residue waste stream originates with the disassembly and shearing of the fuel element. Some fine materials resulting from shearing remain in the dissolver effluent. The bulk of the larger material is removed from the dissolver, rinsed, and checked for undissolved fuel. This larger material, any previously removed fuel bundle hardware, and the fines remaining in the dissolver solution constitute this waste stream.

7.1.2 Mass

Anticipated ranges of weights of various fuel bundle materials are discussed in the following fabrication material categories.

Zircaloy

In a typical pressurized water reactor fuel assembly, the total weight of Zircaloy in the clad, end plugs, and guide thimbles (variable) approximates 230 to 290 kg Zircaloy/MTU. The BWR fuel elements do not have guide thimbles; their spacers are Zircaloy (Zr), the rod tubes are thicker and longer than in the PWR, and the channels (reusable fuel bundle covers) are Zircaloy. In estimating quantities of fuel channels which may require disposal as TRU-contaminated waste, it would be reasonable to assume an average life of 4 years for 80-mil channels and 8 years for 100-mil channels. This translates to 149 and 93 kg Zr/MTU, respectively, which will be an additive to the expected 290 kg Zr/MTU from other parts of the BWR fuel bundle.

In general, the PWR elements have utilized Zircaloy-4 while the BWR elements have used Zircaloy-2. If this trend continues, the BWR elements will have a trace of nickel and cobalt not present in the PWR Zircaloy.

The oxide-coated Zircaloy is present as thin-walled (0.6 to 0.9 mm) tubing or sheet. Shearing generates some (probably less than 0.1%) fines. Some of the fines adhere to the fuel tube surface and some remain in the dissolver solution. An accurate description of the fines formed during shearing of irradiated fuel is not available.

Stainless Steel

Stainless steel, Type 304, is the material chosen for those portions of the fuel assembly regions located outside the high-flux region of the core. Stainless steel members include the upper and lower tie plates and nozzles which attach to the end of the tube bundle and direct the flow of water and steam within the assembly, the lock washers and nuts which secure the upper nozzle to the tube bundle, and sometimes the plenum springs which hold the fuel pellets in place in the fuel rod. In total, about 30 kg of stainless steel/MTU is present in the reference fuel assembly (see Section 2.3). Older fuel assemblies contain about 45 and 65 kg of stainless steel/MTU for BWR and PWR assemblies, respectively.⁽²⁾

Nickel Base Alloys

Inconel-718 is the material choice for the PWR spacer grids in older fuel elements, the tube expansion springs on the upper tie plates, the finger springs on the lower tie plates, and on some fuel assemblies, for lock washers and nuts on the upper tie plates. The total quantity of Inconel in a fuel assembly varies considerably from one fuel manufacturer to another and also with fuel for different reactors from the same fuel manufacturer. On the lower end of the range only about 2 to 3 kg of Inconel per MTU are present; on the upper end of the range about 16 to 18 kg of Inconel per MTU are present. Section 2.3 assumes 8 kg/MTU Inconel as the average value for the reference fuel element. Some Inconel spacer grids are brazed.

Other Materials

A small portion of the fuel and fission products contained within the Zircaloy tubes does not dissolve in the acid solution during the dissolution operation. The acid-leached hulls are likely to contain between 0.05 and 0.5% of the original fuel present, equivalent to about 30 to 150 g fissile material/MTU. In this section a conservative value of 0.5% residual fuel content is assumed. Section 2 assumes a value of 0.05%.

Small amounts of other materials may occur in the waste stream. These may come from oxide insulator pellets, brazing material, and other metals or oxides not dissolved during the leaching.

7.1.3 Radiation Characteristics

Radioactivity of fuel bundle residues includes activation products of stainless steel, Inconel, and Zircaloy, fission products and transuranic nuclides from the undissolved fuel materials. The split of radioactivity between Zircaloy, stainless steel, and Inconel varies with the quantities of each metal in the fuel assemblies, and with the neutron exposure history of that metal. The radiation characteristics of the cladding waste from the reference fuel elements are presented in Section 2.

Actual analyses of two Zircaloy-4 fuel hulls after exposure in PWRs followed by leaching have been reported.^(3,4) They indicate that about 50% of the residual fuel (0.01%) can be leached from the surface, about 50% is incorporated in the inside surface corrosion product layer, and less than 0.1% is induced in the metal from the irradiation of impurity uranium in the original fuel cladding.

The heat generated by radioactive decay and the shielding required must be considered in storing and processing the fuel bundle residues.

Figure 7.2 shows typical fractions of the total heat as a function of decay times attributable to each of the materials of construction as well as

FIGURE 7.2. Fraction of Heat from Hulls Clad Constituents

the contribution from 0.5% undissolved fuel in the cladding wastes. The exposure history in this plot is for higher burnup, lower specific power, and higher enrichment than the worst case fuel.

To calculate these numbers, the following relative burnup values were selected from Figure 7.1, which shows expected axial distribution of flux within the reactor.

1. Stainless steel end fittings would have seen ~ 0.4 of the core neutron flux, and stainless steel in springs would have seen ~ 0.6 .
2. Inconel receives a 0.95 fraction of core flux (conservative because some Inconel will be displaced from core center).

The Inconel and stainless steel dominate radioactivity on a unit weight basis. Corrected for the amounts of metal present in typical cladding waste (Zircaloy:stainless steel:Inconel 20:2:1), radioactivity attributable to Zircaloy dominates for the first 6 months after removal from the reactor. The radioactivity attributable to stainless steel then dominates out to about 2 years, and after about 3 years the Inconel radioactivity is dominant. Results of another computer simulation⁽¹⁾ are shown in Figure 7.3. The simulation does not include the contribution from actinides and fission products. Calculated activation and fission products in the cladding hulls are reported elsewhere.^(2,5,6)

FIGURE 7.3. Induced Radioactivity in Waste Zircaloy Cladding and Inconel Spacers(1)

Figure 7.4 shows maximum calculated heat release from the BNFP hulls container for fuel from different reactor manufacturers. Based upon typical relationships between enrichment and specific power, the plot shows output of total watts as a function of time at the maximum burnup expected. In actual practice, the heat generation from a large array of containers should be based on the blend of fuel, not the maximum worst case for each container in the array.

7.1.4 Pyrophoricity

Self-heating of Zircaloy resulting in rapid oxidation requires a high proportion of material having a high surface-to-mass ratio. It is also a function of surface condition (activation versus oxidation), decay heating, and rate of heat loss. The specific surface area-mass ratio and quantity of fines necessary for auto-ignition are not readily predictable. This is true even where decay heat and heat loss rates can be estimated, because of the variable effects of surface condition.

The Zircaloy hulls have surface-to-mass ratios of $3.7 \text{ cm}^2/\text{g}$ and $4.9 \text{ cm}^2/\text{g}$ for the BWR and PWR hulls, respectively. Fines generated in shearing, sawing, and other handling have much higher surface-to-mass ratios. The corrosion of Zircaloy in reactor service together with corrosion product deposition coats the Zircaloy surfaces with 10 to 100 μm of oxides.

Because zirconium fines have a history of generating fires and explosions, the pyrophoricity characteristic of Zircaloy has been recently investigated for unirradiated material (Table 7.1).^(1,2) It is not known whether

FIGURE 7.4. Typical Maximum Heat Releases Expected from 1 MTU Cladding (includes 0.5% undissolved fuel)

TABLE 7.1. Apparent Effects of Selected Factors on the Pyrophoricity of Zirconium⁽⁷⁾

Factor	Trend of Factor Tending To Increase Pyrophoricity
Particle size	Decrease
Surface-to-Volume ratio ^(a)	Increase
Specific surface (area/mass)	Increase
Moisture content of environment	3-25% maximizes pyrophoricity, as does alternating wet/dry conditions
Temperature	Increase
Total mass of zirconium	Increase
Geometry of mass ^(a)	Reduce (toward minimum surface/volume)
Gaseous environment	Increasing oxidizing power
Impurities, alloying agents	Complex relations
Energy of ignition source	Minimum required for ignition; not directly related to pyrophoricity.

a. Geometry of mass relates to dissipation of heat once reaction has been initiated. The surface-to-volume ratio refers to the individual particles or pieces of the mass.

irradiated Zircaloy will prove more reactive than unirradiated material. In general, no major hull fires have occurred in the handling of commercially irradiated oxide fuel hulls. However, the amount of fuel handled has been limited, and the hulls were buried. Thus, if fires occurred after burial, they would likely be undetected. Irradiated Zircaloy cladding wastes contained in 115-liter (30-gal) drums have been stored at Nuclear Fuel Services (NFS), West Valley, New York, in a cell prior to burial for up to 3 months without fires.

7.2 ALTERNATIVE TREATMENTS AND IMMOBILIZATION TECHNOLOGIES

The decision areas for chop-leach fuel bundle residues are diagrammed in Figure 7.5. In general, the treatment methods shown result in either metallic or nonmetallic products. The complex nature of the processing of fuel bundle residues is diagrammed in Figure 7.6 for processes resulting in nonmetallic products. The following text details these various processes, first those producing mostly metallic products, followed by those producing nonmetallic products. The only commercial treatment used in the U.S. to date is burial of barrels containing untreated hull residues. In that this practice is "no treatment," it will not be discussed here. However, it is presented in the discussion on storage of hull residues (Section 18). Except for storage (no treatment), covered in Section 18, and dissolving of Zircaloy in aqueous fluorides, all the treatment technologies are in the small pilot plant, laboratory scale, or conceptual process stages requiring further development.

FIGURE 7.5. Decision Areas in the Management of Fuel Bundle Residues

FIGURE 7.6. Chop-Leach Fuel Bundle Residue Conversion to Nonmetallic Products

The volume of untreated waste involved, the high associated TRU activity, and the potential for reaction and leaching do not represent a totally satisfactory or low-cost final waste form for storage. Alternative processes can, however, be identified which lead to much reduced volume and lowered reactivity. The technology required in these alternative processes is more complex and is in a much less advanced state of development or demonstration. Active development programs are under way on the most promising of the advanced technologies. If progress continues in these advanced fuel hull processes, they may prove candidates for the demonstration plants of the 1980s.

The process characteristics, the status, and the product description for each treatment alternative are summarized in Tables 7.2 and 7.3. Some areas of comparison are more meaningful than others. One can confidently select an optimized product form, but judgments about reliability of partially explored processes are necessarily tentative.

Sorting (material segregation) and surface cleaning are the principal pretreatment activities with the potential for application to fuel bundle residues. Simplified storage and treatment of metal wastes from irradiated LWR fuels provide incentives for size and materials segregation and for surface cleaning of metallic residues. Although used primarily for pretreatment, the following discussion considers both sorting and methods for cleaning the surface of zirconium, stainless steel, and Inconel components of an irradiated fuel bundle as alternative treatment options.

TABLE 7.2. Process-Product Characteristics and Status

TREATMENT ALTERNATIVE				PROCESS			STATUS OF TECHNOLOGY			PRODUCT DESCRIPTION				COMMENTS
	YES	B	LOW	YES	PLANT	YES	1/1	?	?	YES	NO	NO		
CONTAINED ONLY, NO TREATMENT MATRIX	YES	B	LOW	YES	--	YES	1+1	YES	YES	YES	NO	NO		CONSTITUTES PRESENT PRACTICE
MECHANICAL COMPACTION	YES	C	?	NO	--	YES	1/3	?	?	NO	NO	NO		WHILE NOT DEMONSTRATED ADDITION OF CONCRETE OR LOOSE SAND APPEARS TO BE WELL WITHIN CURRENT TECHNOLOGY
MECHANICAL COMPACTION AFTER DECONTAMINATION	YES	B, C	?	NO	--	NO	1/3+	?	YES	YES	NO	NO		CONCEPTUAL ONLY - MECHANICAL PROPERTIES OF IRRADIATED FUEL HULLS LARGELY UNKNOWN
DENSIFICATION BY MELTING	YES	B	?	YES	LAB	NO	1/6	YES	YES	NO	NO	YES		AS ABOVE
DENSIFICATION BY MELTING WITH DECONTAMINATION	YES	B	?	?	LAB	NO	1/6+	YES	YES	YES	?	YES		MELTING DEVELOPED THROUGH PROOF OF PRINCIPLE STAGE
DENSIFICATION BY MELTING WITH DECONTAMINATION SEGREGATION	YES	C	?	NO	LAB	NO	1/6+	YES	YES	YES	YES	YES		DECONTAMINATION DEVELOPED THROUGH PROOF OF PRINCIPLE STAGE
DISSOLUTION IN SULFURIC ACID	YES	B	?	NO	LAB	YES	1/1	YES	?	YES	NO	NO		SEGREGATION OF FUEL HULL RESIDUE METALS HAS NOT BEEN DEMONSTRATED
DISSOLUTION IN AQUEOUS FLUORIDES	YES	B	LOW	YES	PLANT	YES	1/1	YES	?	YES	NO	NO		CAN HYDROLYZE TO OXIDE AND INCLUDE IN GLASS
FUEL HULL VOLATILIZATION	YES	B		NO	LAB	YES	1/1	YES	?	YES	YES	NO		CAN HYDROLYZE TO OXIDE AND INCLUDE IN GLASS
BURNING FUEL HULLS TO OXIDES	YES	C	?	NO	LAB	?	1/1	YES	?	YES	NO	NO		CONVERSION TO HLW ABSORBENT
CONVERSION OF SIDE WASTE STREAMS	YES	B	?	NO	LAB	?	1/1	YES	?	YES	NO	NO		CAN BE INCLUDED IN GLASS
														PROOF OF PRINCIPLE, TECHNIQUES FOR HANDLING SIDE WASTE STREAMS NOT DEMONSTRATED

TABLE 7.3. Densification Process--Mass Volume Summaries

TREATMENT	PROCESS ADDITIONS			IMPORTANT PRODUCTS				SIDE STREAMS			REMARKS
	INPUT	CHEMICALS	THEORETICAL MASS	PRODUCT	1	2	RECYCLE POSSIBLE	THEORETICAL MASS OF STREAM			
					THEORETICAL MASS + VOLUME	PRODUCT			THEORETICAL MASS + VOLUME		
CHEMICAL CONVERSION											
● BURNING TO OXIDE	260 kg Zr/MTU 0.24 m ³ Zr/MTU	HF (CATALYST) O ₂	91 kg O ₂ /MTU			ZrO ₂	350 kg ZrO ₂ /MTU 0.06 m ³ ZrO ₂ /MTU	H ₂ O ₂ HF H ₂ O	NO YES YES YES	EXCESS ONLY ~40% OF GAS VOLUME	
● DISSOLUTION IN H ₂ SO ₄ + HNO ₃	"	H ₂ SO ₄ HNO ₃	560 kg H ₂ SO ₄ /MTU	Zr (SO ₄) ₂	810 kg Zr(SO ₄) ₂ /MTU 0.24 m ³ Zr(SO ₄) ₂ /MTU	ZrO ₂	"	H ₂ SO ₄ HNO ₃ NO _x SO _x	YES YES YES YES	560 kg H ₂ SO ₄ /MTU	
● VOLATILIZATION	"	HCL OR ZnCl ₂ H ₂ O	416 kg HCL/MTU OR 777 kg ZnCl ₂ /MTU	Zr Cl ₄	665 kg ZrCl ₄ /MTU 0.24 m ³ Zr Cl ₄ /MTU	ZrO ₂		HCl H ₂ Zn	YES NO YES	416 kg HCL/MTU 11 kg H ₂ /MTU 370 kg Zn/MTU	
● DISSOLUTION IN AQUEOUS FLUORIDE	"	NH ₄ F NH ₄ NO ₃ H ₂ O	630 kg NH ₄ F/MTU	(NH ₄) ₂ Zn F ₆	690 kg (NH ₄) ₂ ZrF ₆ /MTU 0.60 m ³ (NH ₄) ₂ ZrF ₆ /MTU	ZrO ₂		NH ₃ N ₂ NO _x HF	YES NO YES YES	360 kg NH ₃ /MTU 340 kg HF/MTU	
● SURFACE CLEAN	260 kg Zr/MTU 0.24 m ³ Zr/MTU	HF (GAS) AMMONIUM OXALATE AMMONIUM CITRATE AMMONIUM FLUORIDE H ₂ O ₂ H ₂ O	10 kg/MTU 25 kg/MTU 16 kg/MTU 1.6 kg/MTU 5-390 kg/MTU	METALLIC Zr HULLS	≥ 210 kg Zr/MTU 0.24 m ³ Zr/MTU	ZrO ₂	≤ 50 kg ZrO ₂ /MTU ≤ 0.01 m ³ ZrO ₂ /MTU	HF CO CO ₂ ZrO ₂ (Fe, Ni, Cr)O _x H ₂ O	YES NO NO NO NO YES	10 kg/MTU 390 kg H ₂ O/MTU	
METAL PRODUCTS											
● MATRIX FORMATION	260 kg Zr/MTU 0.24 m ³ Zr/MTU	CEMENT BITUMEN SAND	150-390 kg/MTU	(260 kg Zr/MTU) Zr-MATRIX	410-650 kg Zr MATRIX/MTU 0.24 m ³ Zr MATRIX/MTU					Zr - MATRIX DENSITY CAN INCREASE TO 420 kg Zr MATRIX/MTU BY INCREASING Zr DENSITY TO 50% OF MAX 0.08 m ³ Zr MATRIX/MTU	
● MECHANICAL DENSIFICATION				Zr COMPACT	260 kg Zr/MTU 0.06 m ³ Zr/MTU					~70% THEORETICAL DENSITY	
● MELT				Zr INGOT	260 kg Zr/MTU 0.04 m ³ Zr/MTU			CaF ₂	YES	8 kg CaF ₂ /MTU	

7.2.1 Sorting

The extent of the segregation possible or desirable depends on the treatment technology being applied. Table 7.4 summarizes the sorting criteria to be considered for each treatment technology. Pyrophoricity may be a prime reason for sorting for several of the treatment technologies. Sorting by alloy type could enhance the efficiency or product quality of the treatment process. Sorting by size may be required to meet the limits of treatment process equipment. Sorting by alloy type and/or size could result in fractions having high and low TRU contamination and radioactive intensities, thus affecting shielding, shipping and disposal designs and procedures.

TABLE 7.4. Summary of Sorting Criteria

Technology	Sorting Criteria				
	Pyrophoricity	Alloy Type	Size	TRU Contamination	Shielding Requirement
No treatment	X	0	NR	0	0
Matrix forming	?	NR	NR	0	0
Mechanical densification	X	NR	X	0	0
Melting	X	X	X	0	0
Surface cleaning	X	0	X	0	0
Dissolution in sulfuric acid	X	0	0	0	0
Dissolution in aqueous fluorides	NR	0	0	0	0
Volatility processes	NR	?	?	0	0
Oxidation with HF-O ₂	NR	NR	X	0	0
Conversion to zirconate for use in HLW ion exchange	NR	?	NR	0	0

X = Probably required by process

0 = Economic decision

? = Uncertain

NR = Probably not required by process.

The sorting of fines may be required for safe operation. Argonne National Laboratory has studied⁽⁷⁾ the pyrophoricity of zirconium and its impact on the handling of cladding wastes. This study concludes that it is desirable to separate fines from the hulls after the fuel is dissolved and to retrieve fines routinely from the dissolver so that they may be deactivated by oxidation.

Segregation, however, adds to capital cost and to the operating complexity of the reprocessing plant. Thus the benefits from such segregation would have to outweigh the costs.

The first commercially operated U.S. reprocessing facility, NFS, simply buried all metallic fuel assembly waste. However, the fuel assembly nozzles or end boxes were removed from the fuel bundle prior to chopping and burying

in separate containers. Thus the end boxes, containing no appreciable U or Pu, were loaded out separately without going through the leaching process. The cladding wastes, including hulls (2.5-cm to 5-cm-long tube sections), fines, and grids were processed through the leaching cycle, placed in drums, and buried like the end boxes. With the prospect of the proposed regulations on TRU wastes, which would require shipment of the hulls to a Federal repository, a sorting program which would allow the continuation of onsite burial of end boxes might be considered.

In the Barnwell Nuclear Fuel Plant (BNFP), owned and operated by Allied-General Nuclear Services, at Barnwell, South Carolina, the dissolver has sufficient capacity to permit combining the 5-cm to 13-cm-long fuel tube sections and the whole end fittings into the dissolver basket. Suspended fines having a maximum diameter of less than 0.4 mm will probably pass through the 40-mesh screen located in the dissolver product stream. These particles then settle in the vessels or collect in the centrifuge downstream.

The design of future chop-leach systems within reprocessing plants could provide a separate diverter mechanism in the discharge chute of the shear to dump the stainless steel nozzles, or end fittings, directly into a waste container. Onsite burial of these wastes might then be possible if the end fittings are not transuranic element-contaminated.

Sorting of potential nontransuranic materials, such as the Inconel bolts, springs, and grids, from the Zircaloy cladding may not be justifiable because they represent only about 4 wt% of the total structural materials in the assembly.

If pyrophoricity studies indicate that segregation of Zircaloy fines is desirable, the most available technology would probably be to separate all the fines below a certain size, regardless of the material composition, from the remaining cladding materials. Adapting size segregation equipment to remote operations may require development before such techniques could be applied to fuel cladding residues.

The chief reasons for sorting fuel cladding by size or materials are considerations of safety, simplified processing, and storage. The reprocessor could benefit economically by separate disposal of the transuranic materials and nontransuranic end fittings, flow channel, and any other material not normally in contact with the fuel materials. The reprocessor could give the transuranic portions further pretreatment if desirable and provide final off-site storage for a minimum volume of waste.

If an overall evaluation of safety and economics indicates a need to sort the cladding wastes, then three size classifications are indicated. In the

massive group would be the end fittings and the grid sections; in the intermediate group the hulls segments and the plenum springs; and in the third group would be the remaining materials. Undissolved fuel would be in the intermediate or fines groups. The fines could be rendered safe to handle by casting in a matrix or by conversion to a more stable compound by controlled oxidation or chemical change. Levitz⁽⁷⁾ suggests that Zircaloy particles above 0.085-cm diam are safe to handle.

The segregation of fuel bundle residues by materials was included in the General Electric Midwest Fuel Processing Plant at Morris, Illinois. Equipment was designed, built and installed in the plant mechanical hot cell to withdraw fuel rods from the bundle. The removed fuel rods were aligned and run through a shear. The hulls were rinsed to remove fines material after the leach step. The operation was demonstrated on cold fuel bundles, but was not demonstrated using irradiated materials over an extended period. This disassembly process, while impractical for retrofitting in existing fuel reprocessing plants, does represent a possible alternative for successor plants.

7.2.2 Surface Cleaning

Surface cleaning provides a pretreatment option that will either reduce the radioactivity of the major volume stream or enhance the physical characteristics of the final waste form, e.g., melting. If materials are not seriously contaminated with uranium and thorium prior to irradiation, surface cleaning might provide sufficient treatment for direct disposal. Surface cleaning requirements for specific treatment processes are discussed in later parts of this section.

The roughly sorted hull stream consists of massive stainless steel end fittings and Inconel springs and spacers in one fraction, 2- to 13-cm-long pieces of Zircaloy tubing in another fraction and fines in another fraction (see Section 7.1). The stainless steel and Inconel pieces of the fuel bundle have an iron, nickel, chromium oxide scale on the outside surface of 5 to 50 μm thick from operation in the reactor. If these pieces have been through the dissolver, they will have adsorbed a substantial amount of TRU elements from the dissolver solution. If they have not been through the dissolver, they are probably very low in TRU elements unless exposed to fuel ruptures in the reactor. Actual TRU element concentrations in Inconel spacers and stainless steel end fittings have not been determined but can be calculated⁽⁸⁾ from the original uranium and thorium concentration of the metal. The Zircaloy fuel cladding contains as a residue about 0.1% of the original fuel. About 50% held is leachable and 50% nonleachable and integral with the corrosion product oxide on the ID fuel surface clad.⁽³⁾ Usually less than 0.1% of the TRU element contamination of the cladding is found in the metal. Thus surface decontamination factors of 10^3 to 10^4 are attainable by cleaning the zirconium

dioxide corrosion product from the surface. Satisfactory decontamination factors for stainless steel and Inconel are anticipated, but not yet demonstrated.

7.2.2.1 Zircaloy

The surface cleaning of zirconium alloys with a substantial oxide layer is usually accomplished by mechanical removal, which is clearly impractical with hulls. Fluoride compounds attack the oxide, but most aqueous fluorides usually attack the metal much faster than the oxide. Nonaqueous molten fluoride salts quickly attack the oxide and metal,⁽⁹⁾ but it is difficult to control corrosion and the adherence of fused salt (dragout) on the high surface area piece when removed from the bath. Other laboratory methods have been developed using a gaseous HF-Ar mixture at 600 to 650°C followed by an aqueous stripping solution. All products of this reaction except the removed oxides and metal can be volatilized for decontamination and recycling of HF and H₂O.

Modified Aqueous Process

This process for decontaminating the Zircaloy cladding has been tested on a mini-scale; scaled-up laboratory tests are in progress. The process involves the treatment of dry Zircaloy hulls with a gaseous mixture of HF and argon at 600 to 650°C for about 30 min. The gas phase treatment apparently penetrates small imperfections in the corrosion film and builds a self-limiting zirconium fluoride layer between the corrosion film and the metal. The cooled hulls are removed from the argon and placed in an aqueous decontaminating solution. This solution attacks the metal more slowly than it removes oxide and puts TRU contaminants in solution. Thus far, the solution found best suited is one developed for gas reactor decontamination.^(3,10,11) It consists of 0.4M ammonium oxalate, 0.16M ammonium citrate, 0.1M ammonium fluoride, and 0.3M hydrogen peroxide in a solution heated to 95°C. Zircaloy placed in this solution after gas treatment quickly loses much of its oxide and fluoride coating, developing a bright metal surface in as little as 30 min. The metal loss during decontamination is usually less than 25 μm. Overall metal loss involves the thickness of the reactor-formed corrosion layer plus decontamination losses, probably less than 50 μm total. The cleaned Zircaloy can be dried, flushed with inert gas (Ar or He), and melted. The side stream of corrosion product oxides and fluorides can be dehydrated, pyrohydrolysed, and calcined to metal oxides. The volatilized fluoride and H₂O can be used as solution makeup; the CO and CO₂ can be treated as gaseous effluent.

Plant equipment materials have not been completely tested at this point. Evaporation equipment must withstand HF vapor, and thus will require a high nickel alloy. The current scale-up of process is expected to produce more valid material tests and recommendations.

The modified aqueous treatment process splits the Zircaloy hull waste into two streams, one a relatively clean metal with small TRU element content

consisting of 80 to 95% of the total material, and a second consisting of highly TRU contaminated zirconium oxide and other corrosion product oxides consisting of 5 to 20% of the total input. The side streams may generate a small amount of excess water which will be tritium contaminated. Equipment waste can generally be treated by the process and incorporated in the metallic or oxide waste stream. Gaseous waste streams will be contaminated with particulates, volatiles, and radioactive gases. These contaminants have not been well characterized, but will include the cesiums, antimony, and tritium. Most of the gas streams will be low volume.

Fused Salt Process

This process for zirconium oxide film removal has been explored^(11,12) using a 37 mole % lithium fluoride--37 mole % sodium fluoride--26 mole % zirconium fluoride bath at about 700°C. This process was selected because data developed for a fuel dissolution process indicated it would attack the oxide more rapidly than the metal.⁽⁹⁾ Corrosion rates on the metal are variable and depend on impurities in the salt or gas stream. The adherence of salt to the Zircaloy surface appears proportional to the corrosion experienced.

The process involves drying and preheating the oxidized Zircaloy in a hot argon stream, immersing the piece in the salt at 700°C while continuing the slow argon or Ar-HF flush through the salt. The piece is removed after an appropriate time and cooled in an argon flow. The cooled piece is further treated using an aqueous decontaminant.

Laboratory test apparatus, constructed of Hastelloy N, held up well to the fused salt. Inconel entrance and exit tubing also appeared relatively uncorroded. Pilot plant tests in the fuel dissolution studies⁽¹³⁾ established materials for handling the fused salt system.

This process will generate three streams; fused salt, aqueous decontaminant and residual metal. The fused salt will contain TRU elements, zirconium oxide, and deposited corrosion products. The aqueous stream from the salt removal process will contain the salt adhering to the Zircaloy together with any impurities in the salt. The residual metal makes up the third stream. The refining of waste streams has not been studied. Replacement of salt adhering to the high surface area waste will probably keep the fused salt to within the desired chemical purity; however, purity standards have not been established. The high solids content aqueous waste stream will pose a difficult recovery problem and will be too large to ignore. Although the fused salt process does remove zirconium dioxide corrosion products, substantial improvement in lowering the metal corrosion rate, reducing the dragout and recycling the salt will be required before the process is acceptable.

7.2.2.2 Iron-Nickel-Chromium Alloys and Other Materials

Stainless steel and Inconel materials undergo corrosion and deposition of reactor corrosion products during reactor irradiation. If they are adjacent to a fuel rupture, they will become contaminated with irradiated fuel. If they are placed in the dissolver with the fuel, they will become contaminated with TRU elements.

Reactor decontamination solutions^(14,15) will clean the stainless steel and Inconel surfaces for PWR exposure. Exposure in BWRs produces a film which is more difficult to strip with mild reagents but is subject to removal by commercial practice if corrosion is not a major consideration. The use of the ammonium oxalate-citrate-fluoride-peroxide bath of the Zircaloy process will probably strip the alloys satisfactorily. In fact, these alloys may be satisfactorily processed with the Zircaloy with the advantages of minimizing side stream treatments and waste volumes.

The nonaqueous processes such as fused salt fluxing or sodium hydroxide hydride-baths can be used to clean stainless steel alloys in conjunction with an aqueous etch. These processes all have the problem of viscous dragout and consequent high side stream waste volume. In general, corrosion product oxides can be removed from the iron-chromium-nickel alloys more easily with other processes. However, fused salt processes are available if desired.

Current fuel element materials selection (UO_2 , stainless steel, Zircaloy, and Inconel) may change as fuel designs advance. For example, insulator pellets will include Al_2O_3 or ZrO_2 . Many of these new materials will not be removed by mechanical sorting or dissolved in the dissolver and will be present in the surface cleaning processes. The inertness of Al_2O_3 or ZrO_2 pellets will cause them to persist until the melting operation unless a fused salt process has been employed. During melting, zirconium will react with essentially everything, while the melting operation for stainless steels will slag off oxide-type impurities. The separation of these other materials will be necessary only if a high-purity Zircaloy melt is desired.

7.2.2.3 Status of Surface Cleaning Technology

The surface cleaning of Zircaloy fuel hulls has been demonstrated on a mini-laboratory basis. Equipment is currently being tested to develop the process for 100-ml batches of cladding hulls. This testing and the following pilot hot cell equipment should be processing kilogram quantities by early 1978. A parallel development of side stream treatment and melting may be pursued.

The surface cleaning of stainless steel and Inconel can now be accomplished by standard reactor decontamination techniques. Procedures applicable to zirconium alloys appear to work well with Fe-Cr-Ni alloys. A common aqueous cleaning step will minimize contaminated side-streams and equipment.

7.2.3 Matrix Forming

Incorporation of the hulls waste into an enveloping neutral matrix likely would reduce pyrophoricity, leachability, and shielding and improve heat dissipation. While pyrophoric fines may be removed at the reprocessor's plant, the generation of additional fines is possible during subsequent handling and shipping operations. A matrix binder or diluent will eliminate formation of fines by immobilizing the fuel hulls and also reducing reactive oxygen. The matrix technology is virtually in place. Concrete and bitumen are currently being used for some radioactive wastes. A disadvantage is that later recovery of metal is complicated. Some form of precompaction or flattening may be desirable prior to matrix casting. This could result in an increased hulls to matrix ratio. Mechanical densification of hulls is described in Section 7.2.4.

7.2.3.1 Casting in Concrete

The use of concrete as a matrix material for Zircaloy hulls has been considered in connection with hull storage. Limited experience with concrete matrices for low- and intermediate-level wastes is available in the U.S. NFS has had some experience using concrete as a matrix material for hulls. The Stock Equipment Company has demonstrated casting of hulls, applying their grouting process which is presently used for solidifying low- and intermediate-level wastes.

The conceptual process includes mechanical compaction by rolling of hull wastes, followed by vibratory mixing with the grouting materials. Hulls are added to the grout. Stock showed that a 50% grout--50% hulls mixture could hold together when removed from the mold. Mechanical strength may not be necessary; if true, this suggests that a higher ratio of hulls to grout is practical which would result in economic advantages. Maintenance of equipment required for concreting may be a major problem because of the highly radioactive environment and the need for remote maintenance. Any process that requires significant material handling will require substantial equipment maintenance and possibly a system backup. Assurance of a high-reliability system requires considerable checkout before facility startup. Concreting systems currently being used by some nuclear power stations have had problems with over-filling drums and with malfunction of equipment which, in one case, allowed solidification of concrete in the mixer.

7.2.3.2 Casting in Bitumen

Bitumen has been used in a rad-waste disposal system for handling low- and intermediate-level wastes. The process does not appear to be applicable to solid metal waste materials of high radiation content due to radiolytic decomposition of the matrix. In one case, the potential decomposition problem along with flammability has prevented serious consideration of the use of a bituminous matrix material.

7.2.3.3 Casting in Glass

Section 6 describes the technology for converting liquid high-level wastes into glass. It is conceivable that at some later time these glasses could be used as the matrix material for hulls. In so doing, two waste forms could be combined, resulting in considerable volume and weight savings.

7.2.3.4 Sand as a Matrix Material

Sand is more fluid than the other matrix materials mentioned. Because of its ability to flow, it can easily fill in or be vibrated into the voids of cladding waste dumped into a waste container. NFS is presently considering sand as a matrix material because of its ease of handling, its flexibility for pre- and post-storage treatment of cladding wastes, and because it has the capability to reduce fines concentrations through mixing, thus reducing the possibility of fines ignition.

The equipment required for sand distribution appears less sophisticated than that required for concrete, glass, or bitumen. Therefore, the capital investment for sand dispensing and mixing equipment probably decreases while the reliability of the equipment, because of its relative simplicity, likely increases. Sand also offers the potential for easy metal recovery if desired.

7.2.3.5 Waste-Matrix Interactions

Consideration must be given to the storage process relative to the heat content, radioactivity levels, and radionuclide composition. This information can be calculated using the ORIGEN code.⁽⁸⁾ Thermal and radiolytic decomposition of the matrix material should be evaluated before committing it for use.

Zircaloy. The addition of most matrix materials will increase the weight of waste to be disposed. This increased weight will vary, depending on the matrix material selected and the method of application. For example, sand may be selected as a matrix material to dilute the Zircaloy fines in a mixture of fines and hulls, or a smaller quantity could be added to the fines alone.

Stainless Steel. Since stainless steel is not pyrophoric, there is little incentive for stainless steel fuel hardware to be placed in a matrix. At NFS, the stainless steel end boxes were sorted from the rest of the fuel assembly materials and buried onsite. Although the proposed regulation defining TRU waste as 10 nCi/g could affect the burial of hulls, it does not necessarily affect the stainless steel end fittings. However, if the end fittings have to be individually monitored before burial, it becomes a matter of economics whether it is preferable to sort, monitor, and bury onsite, or ship to a Federal repository.

Inconel. The total quantity of Inconel in a fuel assembly averages 8 kg/MTU; however, the amount varies considerably among fuel types. The Inconel is not sorted out in the NFS processing, and since such small

quantities are involved, there is little incentive to do otherwise. Inconel activates after irradiation and, in fact, radiates high-energy gamma which will require more shielding than otherwise required.

7.2.3.6 Status of Technology

The technology for matrix forming is for the most part available. The use of a glass matrix needs developmental work.

Information on the benefits of incorporating fuel bundle residues in matrix materials should be collected. Matrix technologies should be evaluated on the basis of necessity, cost, and benefits in order to establish their selection and use.

7.2.4 Mechanical Densification

The void fraction of untreated hulls, end adapters, grids, etc., is 80 to 90%. Densification by compaction and flattening can at least triple the amount of unfueled metal that can be stored in a given space. Thus, there is an economic incentive for densification in the handling, transport, and storage of fuel bundle residue.

Surface cleaning may be required if particle-to-particle bonding within the compact is required. See Section 7.2.2 for surface cleaning procedures. Surface cleaning of hulls is not practiced at NFS, and the BNFP will not include surface cleaning when their plant becomes operable. Both plants, however, wash their hulls with nitric acid and water to recover dissolver solution, but this does not constitute decontamination or oxide removal.

7.2.4.1 Compacting

It has been estimated⁽¹⁾ that the accumulated waste hull volume by the year 2000 will be $3.1 \times 10^4 \text{ m}^3$. If the hulls are compacted (assuming a compaction factor of 4.5), the volume would be about 6900 m^3 . More detailed volume projections can be obtained from Section 3.

Zircaloy-4 tubing has been compacted commercially.⁽⁷⁾ Compacts or briquettes (27.9 cm diam x 12.7 cm high) of 3.6 kg were produced at about 72% of the theoretical density of Zircaloy. This does not mean, however, that irradiated and embrittled hulls will deform and lock together to produce a briquette that will not fall apart. On the contrary, embrittled hulls are expected to break in half and produce platlets when flattened. In so doing, small Zircaloy particles may be produced at the broken faces, tending to increase pyrophoricity. However, if the irradiated hulls are annealed, they should retain enough ductility to lock together when compacted.

Commercial compacting equipment of proven performance is presently available. Assuming a downtime as high as 50%, a 10 MT/day unit of standard design

which could handle the hulls from a 5 MT/day spent fuel reprocessing plant can be obtained commercially. Densification of 70% of the theoretical density of Zircaloy is probably obtainable.

7.2.4.2 Flattening

Zircaloy hulls can also be flattened. The most commonly suggested method for doing this, but as yet undemonstrated, is passing them through opposing rollers. This technique is used for consolidation of scrap metal. Irradiated hulls would be expected to flatten and break in two, slightly cupped as they emerge from the rollers. Small pyrophoric particles of Zircaloy-4 may be dislodged from the broken faces, but there is no information available on this phenomenon.

7.2.4.3 Other Methods

Other techniques of the densification of hulls are not readily apparent. High energy compaction and extrusion have been suggested, but no industrial experience is available on these techniques for compacting hulls.

7.2.4.4 Containment of Densified Products

Blomeke and Perona⁽¹⁶⁾ have studied the "Storage, Shipment and Disposal of Spent Fuel Cladding," and suggest steel pipe container(s) for briquetted and flattened cladding (3.25 m long x 25 cm ID x 0.71 cm thick wall) or (3 m long x 61 cm x 0.64 cm thick wall). The small container is for briquettes and the larger one for flattened cladding.

7.2.4.5 Waste Process Interactions

The general properties of input waste are described in Section 7.1. The mechanical properties have also been described by Levitz et al.,⁽¹⁾ especially as affected by irradiation.

The size and mass of stainless steel end fittings will require very large presses for compacting in excess of 50% of theoretical density.

The absorption of hydrogen by the Zircaloy cladding and irradiation will render it brittle at low temperatures, causing fragmentation during compaction.

The mechanical densification of fuel bundle residues could achieve a maximum theoretical densification of six-fold (1.1 to 6.6). However, densification to density of 4.6 is considered the practical limit, and even that will take large presses and high pressures. The compaction of oxidized material will produce unbonded (noninterlocked) compacts which will fall apart if not compacted within a packaging container. The irradiation and hydrogen embrittlement of the Zircaloy cladding will tend to produce a highly fragmented product with compaction at room temperature.

The leachability of mechanical compacts is related to the available surface area which, in general, will be increased somewhat by broken surfaces. The corrodibility will be related to the available water, surface area, and temperature and will be similar for all compacts of uncleaned residues. Cleaning the residues will promote metallurgical bonding, a lower internal temperature, a high initial corrosion rate of available surface, and much lower levels of leachable radioactivity. Zircaloy cleaned by the process described in Section 7.2.2 will be substantially annealed and fairly ductile, which will promote surface bonding and reduced heat generation.

The compaction of uncleaned fuel bundle residues will seal some internal surfaces and thus preclude surface decontamination to remove residual fuel. If the mixed waste stream (stainless steel, Inconel, and Zircaloy) is compacted it will rule out future mechanical separation of the alloys unless the compact falls apart.

The pyrophoricity of the Zircaloy tube sections is decreased by the presence of a large heat sink but simultaneously increased by the lack of thermal conductivity of the uncleaned compact. If fines are produced by fracture during compression, the Zircaloy will become more pyrophoric. The cleaned hulls would be less pyrophoric because of metallurgical bonding, heat dissipation, and reduced surface area.

7.2.4.6 Status of Technologies

Metal compacting, flattening, and densifying processes are available. The application of these processes in cell to highly irradiated fuel bundle residues has not been demonstrated. R&D effort may be required to produce and demonstrate equipment systems suitable for sustained remote operation.

7.2.5 Melting

Densification by melting can reduce the chop-leach fuel hull waste volume by a factor of about 6. Melting can be accomplished using cold crucible or hot crucible processes. Some degree of decontamination may result during the melting process. Tonnage quantities of Zircaloy, stainless steel and Inconel are currently produced using well established melting technologies. These production processes routinely recycle large quantities of scrap with virgin melt stock. The melting of irradiated and contaminated fuel hulls has yet to be demonstrated.

Some degree of sorting will be required, depending on whether the ingot is intended for storage or for reuse. Fuel channels and end fittings will require chopping to match the crucible size and transfer system. For direct storage fuel bundle residues will be rough sorted into two fractions, 1) Zircaloy with small amounts of stainless steel and Inconel and 2) stainless steel and Inconel with small amounts of Zircaloy.

For reuse, sorting into 1) Zircaloy and 2) stainless plus Inconel with small amounts of Zircaloy will be required.

7.2.5.1 Cold Crucible Melting

The chemical activity of zirconium at its melting point ($\sim 1850^{\circ}\text{C}$) requires that it be melted in vacuum or inert atmosphere. Conventional crucible materials react vigorously with molten zirconium. For example, zirconium melted in graphite crucibles, picks up excessive carbon. Consequently, cold crucible processes were developed for producing zirconium.⁽¹⁷⁾ These processes have also been used for the melting of iron, nickel and cobalt alloys.

A number of cold crucible melting options are available for consolidating metallic fuel bundle residues into ingot form. The selection among the possibilities is based on the process adaptability to the following requirements:

- A cold crucible melting process for the consolidation of hulls should be capable of producing 100 to 150 kg per 8-hr day in a diameter range of 8 to 15 cm. Single melted ingots should be made directly from cladding hull fragments without an electrode preparation step. Furnace capabilities should be based on the remelting of the zirconium base materials; however, the ability of the furnace to remelt stainless steel and Inconel and mixtures of these three should also be considered. Hot cell space requirements should be kept at a minimum consistent with high-quality zirconium remelting practice that results in low oxygen, hydrogen and nitrogen pickup.
- A remotely operable materials transport and weighing system should be considered to provide separated melt stock to the melting furnace feeder.
- Consideration should be given to a chamber within the vacuum system that will allow for tritium fixation, i.e., hot zirconium.
- Closed loop cover gas and cooling systems should be used.
- Furnace preparation, charging, melting, stripping, cleaning and maintenance operations must be performed remotely from the floor of a hot cell. Critical maintenance items should be identified and procedures for component cleaning, removal and replacement investigated. Safe operation and maintenance shall be a prime consideration during all phases of design. Mechanical and electrical interlocking devices will be installed, assuring automatic shutdown in the event of operator and/or component and systems failures.

Cold crucible melting techniques have been evaluated in the context of fuel bundle residue densification and with regard to the selection criteria cited above.⁽¹⁸⁾ Conclusions from this evaluation resulted in selecting the Inductoslag process as the most promising process for this application.

Inductoslag melting (Figure 7.7), a development of the U.S. Bureau of Mines located in Albany, Oregon,⁽¹⁹⁾ consists of induction melting in a segmented, water-cooled, copper crucible. This system, developed for the melting of reactive metal scrap, requires the use of a high-purity slag, such as calcium fluoride, when applied to melting of materials such as titanium and zirconium. To date this equipment has produced ingots to 13 cm in diameter and up to 107 cm in length, at power levels to 100 kW. Dimensions could probably be increased without major problems. Melting to date has been performed by evacuating the furnace chamber and backfilling with helium or argon to about 240 mm of mercury absolute pressure.

FIGURE 7.7. Inductoslag Melting Process⁽²⁰⁾

The Inductoslag process has been demonstrated for the experimental melting of simulated chop-leach cladding hulls.⁽¹²⁾ Clean unirradiated Zircaloy-4 cladding tubing was chopped into 2.5-cm-long pieces and melted into a 41-kg, 10-cm-diam ingot. This ingot was still within the nuclear grade chemical and hardness specifications for cladding tubing. Portions of the ingot were refabricated into cladding tube size and successfully met ASTM corrosion testing standards.⁽⁴⁾

The Inductoslag process has also successfully melted unirradiated chopped fuel bundle end fittings of Grade CF3 (casting grade of 304 stainless steel) as well as chopped sheet of Inconel 718.⁽⁴⁾ These materials appear suitable for refabrication or storage. Inductoslag melting of an 85 wt% Zircaloy-4, 10 wt% 304 stainless steel, 5 wt% Inconel 718 ingot resulted in an ingot suitable for storage. This ingot contained unmelted Zircaloy-4, 304 stainless steel, and Inconel 718 potted in a matrix of eutectic mixture.⁽¹¹⁾

This process also has produced an ingot of 67 wt% of chopped fuel bundle end fittings of Grade CF3 and 33 wt% of Inconel 718 chopped sheet. The ingot contains some unmelted Grade CF3 material potted in a mixture of melted Grade CF3 and Inconel 718.⁽⁴⁾

This melting system is complex mainly because of the crucible's design and configuration. Although the crucible is more complicated and perhaps more fragile than other cold wall crucibles, no complicated electrode and/or electrode suspension system is required. Advantages of the Inductoslag melting system are related to a clean melt with a minimum of splash and splatter. The geometry of the equipment provides maximum room for feeding of material, and the resultant ingot on a one-melt basis is of excellent quality.

Disadvantages are related to a relatively low production rate and the problems associated with slag handling and recycle. From time to time problems may be encountered with bridging, dependent upon size and density of feed stock. However, bridging problems can be minimized by a supplemental heating source if required.

7.2.5.2 Hot Crucible Melting Methods

Two hot crucible processes are included in this survey of melting methods. We include hot ceramic crucible melting for completeness, graphite crucible melting because it is applicable to special situations.

Ceramic Crucible Melting. Conventional induction melting of the stainless steel and Inconel or their mixtures can be performed either in air or vacuum. The technology for this type of melting is well established. Ceramic crucibles are used (normally MgO), and their relative life is partially dependent on how they are imbedded in the backup insulation of the coil assembly. Applying this type of melting to hulls presents remote crucible replacement problems and adds significantly to the waste stream in the form of ceramic insulation and crucibles. Zirconium cannot be melted by this process because of its severe reaction with the crucible and air. Stainless steel and Inconel or their mixtures containing upwards of 10 wt% zirconium would have a deleterious effect on crucible life.

Graphite Crucible Melting. Early zirconium melting was performed in graphite crucibles.⁽¹⁷⁾ Crucible reaction resulted in carbon contents in the range of 3000 ppm in the zirconium. Damage to the crucible was not extensive, and multiple remelts could be made in the same crucible. The hot strength of graphite and its relative immunity to thermal shock allows one to use a slip-fit replaceable liner type of crucible assembly, simplifying crucible replacement. Melting stainless steel and Inconel or their mixtures in graphite crucibles results in excessive crucible reaction because of formation of iron and chromium carbide.

Iron, chromium and nickel each form binary low melting eutectic mixtures at about 85 wt% zirconium composition. Laboratory experiments have shown⁽²¹⁾ that pre-alloyed 85 wt% Zircaloy-2, 15 wt% 316 stainless steel will start melting at about 925°C and complete melting at about 1100°C. Ten-kilogram ingots of 85 wt% Zircaloy-2, 10 wt% 304 stainless steel, 5 wt% Inconel 718 have been melted in graphite crucibles and poured into graphite molds at 1300°C.⁽²²⁾ Clean chopped sheet was used as charge material, and the vacuum during melting was below 5 μ m. Carbon pickup in the ingots was not detectable,⁽³⁾ and crucible reaction was very slight, indicating that the crucibles were reusable.

Graphite crucible eutectic melting offers advantages for melting hulls:

- a) The percentage of Zircaloy in the chop-leach hulls is conveniently near the desired eutectic composition.
- b) The eutectic composition eliminates the need to melt at the extremely high temperature melting point of zirconium, ~1850°C.
- c) Low temperature reduces carbon pickup and extends crucible life.
- d) Slip-fit easily replaceable crucible liners can be employed.
- e) Spent crucibles can be burned to an ash to reduce the waste stream.

Disadvantages are:

- a) Crucible life will probably be less than that of cold crucibles.
- b) Reuse of the ingot would not be possible.
- c) Maintenance of the backup crucible and coil assembly will be required.

7.2.5.3 Molten Metal Refining Processes

Traces of uranium and thorium impurities in the original Zircaloy, stainless steel or Inconel will transmute to TRU elements under irradiation and be distributed within the metal and thus not available to surface decontamination. Additionally, small amounts of TRU elements surface fuel contamination remain on the metal when it is melted and thus become intermixed with the melt. Molten metal refining processes provide the potential to reduce the minute amounts of TRU elements contained in the melt.

Molten metal refining has some industrial status, but very little of the technology is directly applicable to molten hull decontamination. A recent survey⁽²³⁾ of removing uranium from several steels and other metals gives encouragement that some small decontamination factor (DF) can be obtained from the hull melts, especially the stainless steel and Inconel. The basic methods for purifying molten melts involve adsorption, slag extraction, vaporization, and precipitation. Many of these techniques involve a change in oxidation state for the impurity to be removed. Because the metal is in an unoxidized

condition, the impurity must be oxidizable without affecting too much host metal. The TRU elements are all very electropositive and thus could be oxidized in the presence of the hull waste stream. Zirconium closely approaches the TRU elements in electropositive character, which means that the impurities will be more difficult to selectively oxidize in the presence of zirconium.

Slag Extraction Methods. The extraction of impurities into a slag or flux depends on converting the impurity into a salt which is insoluble in the metal and soluble in the flux. The distribution of the impurity between the metal and the flux can frequently be predicted by free energy considerations of the impurity atom in the metal and in the slag. The establishment of an equilibrium between flux and melt means that the flux must be very pure (with respect to the extractable impurity) or that the distribution strongly favors the flux. The reduction of the 10 ppb plutonium level in the zirconium metal to about 1 ppb will require a very pure flux. This flux might be purified by electrolytic extraction or impurity volatilization. Impurity control in the flux by replacement will in general create too large a waste stream.

The use of a slag or flux to extract TRU elements from the hull waste stream requires a suitable container to avoid severe corrosion problems. The stainless steel and nickel alloys can generally be melted in oxide crucibles with oxidizing slags. Both materials can be melted in a cold crucible process with frozen flux or metal acting as the crucible material. Alloys of Zircaloy, stainless steel, and Inconel can be melted in graphite. In general, all melting processes are under inert gas at a reduced pressure.

The potential decontamination of the alloys from TRU elements by melting processes has not been determined to date. A decontamination factor of 10 is probably all that could be hoped for in the case of Zircaloy, based on free energy consideration, removal of uranium from stainless steels, and the extremely low level of TRU impurities to be removed. Stainless steels will decontaminate easier, and a factor of 10^3 may be obtainable.

Adsorption on Solid Surfaces. The presence of a high surface area solid in the molten metal such as the crucible wall may adsorb impurity atoms directly or after some chemical interaction. This type of purification would be a potential method for hull melts because of the extremely low level of impurity that must be removed. The adsorption will saturate the solid surface quickly and thus would not be applicable if substantial amounts of impurity had to be removed.

For solid surfaces to act as adsorbents they must be reasonably compatible with the molten metal. For zirconium this excludes practically everything except graphite and possibly Y_2O_3 . Stainless steels are compatible with many oxides. The zirconium-stainless steel-Inconel alloy might be compatible with more crucible materials than zirconium because of the lower melting temperature,

~1100°C. It has been observed that the graphite crucible after a uranium melt will contain a concentrate of highly radioactive decay products. It is conceivable that certain radioactive isotopes from hull melts would collect on or in the wall of a crucible.

Potential decontamination by this method is very difficult to predict because very little work has been done. If an absorbent quite specific to TRU elements could be found which was stable to the molten metals, a very high DF might be achieved.

Vaporization Decontamination. The volatilization of impurities from the molten metal as a method of decontamination is a well known method for such atoms as iodine or tritium. The TRU elements, as a group, are not volatile, and thus it is necessary to convert them to compounds which are more volatile. A flux will be chosen to help volatilize the TRU elements as fluorides.

No data applicable to the low level of TRU impurities are available. Distribution studies currently being planned will determine volatility as well as distribution between the salt and metal phases.

Precipitation of Impurities. The removal of TRU impurities from a melt by adding a precipitant has not been explored. Some of the crucible interactions produce insoluble compounds such as the zirconium carbide when melting Zircaloy in a graphite crucible. The very small amount of precipitated material expected would require the use of some carrier material so it could be extracted from the metal.

Zone Refining and Liquation. In cold crucible processes with shallow molten pools the conditions exist for zone refining. Impurities that are soluble in the liquid and insoluble in the solid will tend to accumulate in the liquid phase and occur as concentrates at the top of the ingot. Low-density impurities that are insoluble in liquid may also tend to drift toward the top of the ingot.

Status of Molten Metal Decontamination. The removal of impurity uranium from stainless steel, copper, aluminum, and nickel has been explored in large melts. The final purity was several orders of magnitude greater than the starting material for these decontaminations. Molten metal decontamination at EBR-II and in early fuel refining research achieved substantial DFs, but were effective on percentage level impurities, not ppb. It may be possible to attain DFs of 10 in the "Inductoslag" melt, but no data are available at the TRU element concentration level of interest.

7.2.5.4 Metal Reworking Processes

Ingots melted from cleaned and completely separated material are suitable for reuse. Their fabrication from ingot to useful shapes can be accomplished by a variety of conventional metal working processes such as forging, extrusion,

rolling, swaging, drawing, machining, and welding. The choice of the fabrication route is dictated by the design of the finished part. Because of the cost of metal working tools, it is likely that reuse will be confined to objects of simple shape. Shapes requiring a single forging or extrusion operation can be considered. Applications such as brackets, baskets, handles, extensions, stirrers, pedestals, and simple containers may be found in basins or reprocessing plants. All reprocessed, irradiated metal wastes will be radioactive. Applications must reflect that fact. (See Section 18.3.)

7.2.5.5 Waste Process Interactions

Waste stream metal feed size and crucible size with its attendant feeding system will have to be compatible. Waste will be remotely fed from a storage hopper through a transfer system and dropped into the crucible. Bridging in the hopper, transfer system, and crucible should be avoided. Mass of the feed entities should be such that feeding does not damage the crucible. Crucible sizes now envisioned will require the end fittings, spacers, and shroud tubes be further reduced in size.

The surface condition of the hulls will have a major effect on the choice and operation of the melting system. The high surface-to-volume ratio of the hulls greatly adds to the contamination of the melt and increases the degree of off-gassing control required of the melting operation. Oxide films, crud and associated adsorbed gases and other dirt may cause eruptions and spattering as cold material is added to the molten pool, complicating furnace cleaning. Arc control becomes difficult with material having high dielectric coatings. Slagging operations become of prime importance, and in all probability the ratio of slag to metal will increase significantly, thus adding to the waste stream. Eutectic melting will probably not be as effective in lowering the melting point because of the diffusion barriers presented by the oxide films. The reuse of material melted from uncleaned hulls is not possible. Some surface treatment of hulls may be required prior to melting if the hulls are not cleaned for decontamination reasons.

Melting will reduce the bulk volume of the hull waste stream by a factor of about 6. It is anticipated that ingots 10 to 15 cm in diameter, 50 to 100 kg each will be produced. Ingot sizes can be varied within limits to meet constraints imposed by hot cell design, packaging, shipping, and storage.

Pyrophoricity is not a problem with ingots. Leachability and other properties will depend to some extent on whether the materials were cleaned or sorted prior to melting. Also properties will probably differ with hot and cold crucible melting. Leachability and other properties of surface cleaned and completely segregated materials will be nearly the same as the virgin alloy, e.g., negligible.

Small amounts of most other metallic materials will mix with the Zircaloy, stainless steel, and Inconel upon melting. Problems may occur with widely different melting points and high vapor pressure materials.

Nonmetallics can interfere with the melting process by decomposition and violent evolution of gaseous products. Refractory materials will occur as inclusions in the ingot. Other materials will affect the properties of the ingot.

7.2.5.6 Status of Technology

The technology for the melting of Zircaloy, stainless steel, and Inconel exists. It remains to be demonstrated that this technology can be safely applied to the melting of chop-leach cladding hulls. Inductoslag melting can produce ingots of a quality suitable for reuse and/or storage. Selected mixtures of Zircaloy, stainless steel and Inconel can be melted in graphite at temperatures substantially below the melting point of the individual components of the furnace charge. Areas that need additional developmental effort are:

1. Perfect sorting procedures that will insure a pure enough product for reuse.
2. Develop size reduction processes that will meet feed material criteria.
3. Determine the minimum surface treatment requirement for melting hulls.
4. Determine the effect of the melting process on TRU removal.
5. Develop slag treatment and recycle procedures.
6. Demonstrate the reliability of melting system equipment for sustained remote operation.
7. Demonstrate the melting of irradiated chop-leach hulls.

7.2.6 Dissolution in Sulfuric-Nitric Acid

The use of concentrated sulfuric acid-nitric acid mixtures to dissolve cladding hulls has been investigated on a laboratory scale. The mixture provides adequate penetration rates of the Zircaloy cladding in well controlled reactions but does not dissolve Inconel or stainless steel.

7.2.6.1 Dissolution Process

In the dissolution process, Zircaloy cladding and nitric acid are added to a batch of concentrated sulfuric acid at 150 to 250°C. Zircaloy metal readily dissolves in the sulfuric-nitric acid mixture, with dissolution rates as high as 79 mils/hr (1400 mg/cm²/hr) having been measured at 150°C. Penetration of any zirconium oxide layer is readily accomplished after an initial induction period. Dissolution of stainless steel and Inconel in the system is relatively slow, with measured dissolution rates of 0.7 mils/hr (12.9 mg/cm²/hr) and 0.1 mils/hr (1.4 mg/cm²/hr) for the stainless steel and Inconel, respectively.

A conceptual process for sulfuric-nitric acid dissolution of cladding is shown in Figure 7.8. Fuel bundle residues could be sorted into their respective components and the Zircaloy added to a mild steel vessel containing sulfuric and nitric acid at 150°C. The Zircaloy is dissolved in the hot acid and is converted to water soluble zirconium sulfate. The mixture is then heated to 250°C to 350°C to evaporate the excess acid. Zirconium sulfate remains in the mild steel pot and is ready for shipment and/or storage in the same vessel. The zirconium salt is available for rework at a later date when sufficient amounts accumulate to justify processing for ultimate disposal. Since transuranics associated with the residues are converted to leachable sulfates, nitric acid leaching of the sulfate salt residue either before or after evaporation of the excess sulfuric acid would convert the plutonium and zirconium to ionic forms which could be separated using standard ion exchange or solvent extraction techniques.

7.2.6.2 Waste-Process Interactions

The process does not dissolve the iron-chrome-nickel alloys and thus these must be sorted from the waste stream or handled with the zirconium sulfate salt or solution.

The product formed from sulfuric-nitric acid dissolution of Zircaloy is water soluble zirconium sulfate. Differential Thermal Analysis (DTA) of the dried zirconium sulfate showed it to be inert when heated to 800°C in air. Conversion of the zirconium sulfate to an oxide has not been investigated, but

FIGURE 7.8. Conceptual Process for Zirconium Hulls

presumably could be converted to some other inert form (e.g., to a cement). The reaction rate of the acid mixture or its vapors with zirconium fines and with substantial quantities of Zircaloy hulls remains to be determined. The volume ratio of Zircaloy to zirconium sulfate is about 1.

7.2.6.3 Status of Technology

Sulfuric-nitric acid dissolution of Zircaloy cladding residues is in the conceptual stage of development and not available. Currently no work is being done on the process. The preliminary laboratory data indicate that rapid and complete dissolution of Zircaloy can be accomplished in hot (150 to 250°C) concentrated sulfuric acid containing nitric acid oxidant with the formation of water-soluble salt for disposal. The dissolution rate is high enough to provide rapid penetration of cladding. The resulting residue is readily isolated from the dissolver acid by evaporation of the excess acid. Transuranic elements are converted to nitric acid leachable sulfates and are potentially available for recovery. The zirconium sulfate residue is also readily soluble in nitric acid and is potentially available for cleanup and possible use as an HLW absorbent.

7.2.7 Dissolution in Aqueous Fluorides

The dissolution of fuel bundle residues in fluoride is primarily a process for zirconium alloy dissolution. Although stainless steels can be corroded at substantial rates in the process, it is not a dissolution process for stainless steel. Inconel would be even less attacked; thus stainless and Inconel would collect in the dissolver.

7.2.7.1 Dissolving

The Zircaloy cladding has been removed from fuel in several chemical processes employing HF or NH_4F . One of the better known processes, the Zirflex process, outlined in the following paragraphs, could be used to dissolve Zircaloy residues produced from a chop-leach process or it could be used as the decladding mechanism.^(24,25) The following discussion is mainly concerned with residue dissolution.

The oxide film found on Zircaloy cladding has a major retarding effect on the dissolution rate in Zirflex dissolvent. The film dissolves slowly if at all. However, it is penetrated in localized areas followed by pitting and undercutting to expose unoxidized zirconium. The sheared ends of Zircaloy would be immediately available for attack. In a normal Zirflex dissolution run, any residual flakes of oxide would be expected to remain in suspension in the terminal solution during transfer for further processing or to storage. No study of the dissolution rate of ZrO_2 in Zirflex dissolvent has been made.

Zirflex dissolvent ($6M \text{ NH}_4\text{F} - 0.5M \text{ NH}_4\text{NO}_3$) at the boiling point is quite corrosive to the 300 series stainless steels (corrosion rate 20 to 30 mpm). However, the dissolvent is only mildly corrosive in the presence of dissolving Zircaloy due to the evolution of ammonia.

The Purex facility at Hanford successfully reprocessed Zircaloy-clad fuels from N Reactor using the Zirflex process to declad the fuel elements. Decladding with $\text{NH}_4\text{F} - \text{NH}_4\text{NO}_3$ solution and core dissolution with nitric acid solution occurred in the same stainless steel (304L) dissolver. During the decladding operation, the surfaces of the metallic fuel cores react with fluoride ion to form insoluble UF_4 ; thus addition of aluminum nitrate to the core dissolvent solution is required to complex fluoride and reduce the corrosiveness of the system during core dissolution. It is of interest to note that decladding and core dissolution in the same dissolver leads to fluoride contamination throughout the separations facility. The Zirflex process has been used on a production basis only at the Hanford Purex facility.

Dissolution of cladding hulls via the Zirflex process may best be accomplished in a separate relatively inexpensive stainless steel dissolver rather than in the fuels dissolver in order to: 1) prevent fluoride contamination throughout the reprocessing facility, 2) conserve dissolver capacity, 3) eliminate the potential for serious corrosion of large and expensive fuel dissolvers, and 4) permit dissolution to a residual heel, thus increasing the average dissolution rate and reducing corrosion of the dissolver. This concept also permits the use of a dissolver made of an alternative material. For example, if 100% dissolution of ZrO_2 is deemed necessary, dissolution by HF in a Monel dissolver would be possible.

The complete solution of the cladding and residual fuel will allow the development of TRU extraction processes by solvent or ion exchange practice.

In considering the dissolution of Zircaloy via the Zirflex process, it is of interest to note that it may be feasible to reduce the volume of final waste by recycling the ammonium fluoride. It has been reported⁽²⁶⁾ that the addition of ammonia to ammonium fluoro-zirconate solution regenerates ammonium fluoride with simultaneous precipitation of hydrous zirconia. The reaction appears to be as given in the equation:

If feasible, this procedure could be used to reduce the amount of fluoride sent to ultimate storage.

7.2.7.2 Waste-Process Interactions

The input waste stream has been described in Section 7.1. The separation of Inconel and stainless steel is desirable to avoid buildup in the dissolver. The storage of the wastes should have little impact on this process.

The volume ratio of hydrous zirconia to Zircaloy hulls is 0.6. The product is absorptive but is noncombustible. It will lose water if heated to form zirconium oxide, which is insoluble and unreactive. The ammonium zirconate originally formed is soluble and will volatilize ammonia on heating as well as some HF.

The stainless steels will be etched and the Inconel relatively unaltered. Ceramic materials and zirconium dioxide will be slowly dissolved.

7.2.7.3 Status of Technology

The application of this process to dissolving hulls needs some verification and process development; however, the process has been employed at plant-scale in Hanford and Idaho Falls for fuel clad removal. The dissolving technology for Zircaloy is essentially available. The treatments of the dissolved waste will require development.

7.2.8 Volatilization of Fuel Bundle Residue Zirconium

In this alternative process the chopped, leached fuel hulls are treated with a chlorinating agent, gaseous HCl or molten ZnCl_2 , disintegrating the hulls and hardware and converting them to metal chlorides. Since the zirconium product of this reaction, ZrCl_4 , is volatile, it can be separated by distillation from most of the other constituents of the primary waste, including structural metals, fission products, and actinides. The ZrCl_4 would be accompanied, however, by the chlorides of tin, a significant constituent of Zircaloy, and a few of the other structural metals and fission products which are also volatile. The ZrCl_4 can be converted subsequently by a pyrohydrolysis reaction, to ZrO_2 , a compound that is very stable thermally and chemically. Removal of the massive end pieces would reduce the time required for complete conversion of the materials to chlorides. The decision on sorting will depend on the purity and radioactivity criteria selected for the chloride end product.

7.2.8.1 Treatment with HCl of ZnCl_2 to Form ZrCl_4 Gas

Residues from the chop-leach operation would be dried before being fed to the chlorination operation. Chlorination with HCl would be carried out at about 400°C , probably with a mixture of HCl in an inert gas. The reaction is represented by the equation,

Hydrochlorination has been carried out in equipment of ^{200}Ni .⁽²⁷⁾ The reaction can be carried out in a fluidized bed of some inert, granulated solid, such as alumina, or in an open tube reactor. Entrainment of nonvolatile solids in the gaseous product stream bearing ZrCl_4 may result in an undesirable level of transuranium compounds in the zirconium product. To remove entrained solids, the gaseous product stream is filtered. Passage of the gas stream

through sintered metal filters and a packed bed of granulated solids, e.g., alumina, of the appropriate particle size can probably be developed to provide adequate filtration.⁽²⁷⁾

Chlorination at about 500°C with ZnCl_2 , on the other hand, offers the advantage of incorporating the residue constituents in a medium that is not easily dispersed. The quantitative volatilization of ZrCl_4 from the solution in the molten ZnCl_2 , however, may offer some difficulty.^(28,29) With either method of chlorination, anhydrous conditions must be maintained inside the equipment to avoid the hydrolysis of ZrCl_4 , depositing immobile ZrO_2 at sites other than those in which collection is intended. Also, the temperature of all containing equipment must be maintained at 350 to 400°C to avoid the condensation of ZrCl_4 at sites other than the condenser. The reaction with ZnCl_2 might be carried out in a tungsten crucible in an atmosphere of inert gas. The reaction can be represented by the equation,

The ZnCl_2 might be regenerated by reaction of the zinc with chlorine:

Two potential problems associated with the chlorination by ZnCl_2 need to be solved by development of appropriate techniques, i.e., the inhibition of the reaction by the deposition of zinc on the surfaces of the Zircaloy and also the quantitative vaporation of ZrCl_4 out of solution in molten ZnCl_2 .

7.2.8.2 Conversion of ZrCl_4 to ZrO_2 and HCl for Recycle

The conversion of ZrCl_4 to ZrO_2 would be carried out by pyrohydrolysis with steam at about 350°C. The reaction can be represented by

Similar pyrohydrolysis reactions have been carried out in a fluidized bed of granulated solids contained in equipment of 304 stainless steel.⁽²⁷⁾ A fluidized bed can be used in order to promote effective heat transfer and the formation of free-flowing solid product. If the dilution of ZrO_2 with other solids is to be avoided, depending on its eventual disposition, then a bed of granulated ZrO_2 can be used as the fluidizing medium.

The ZrCl_4 can also be used as a feed for the HLW absorbent process (see 7.2.1.1).

7.2.8.3 Waste-Process Interactions

The waste properties are not expected to greatly affect the basic reactions used in this process, i.e., the hydrochlorination and the pyrohydrolysis or the feasibility of storing zirconium as ZrO_2 . The options that include

utilization of the zirconium as a zeolite may be affected by metal impurities with volatile chlorides, e.g., tin, silicon, titanium, niobium, and aluminum. The effect of such impurities on the ion exchange properties of the ZrO_2 prepared to absorb HLW or on the ductility of zirconium metal prepared for container construction remains to be investigated.

When considering previous storage, perhaps the most significant interaction on the waste properties is the decrease of radioactivity with time of the zirconium recovered from the volatilization process. Radioactivity associated with fuel residues has been tabulated in detail,^(2,5,6) and the change of radioactivity is illustrated by Figure 7.4. The curves indicate that most of the radioactivity associated with the zirconium, the major-volume waste fraction of this process, has decreased greatly after about 600 days. However, for the minor volume fraction, i.e., the residue from the hydrochlorination, although the radioactivity of chromium and iron have become relatively insignificant after 7×10^3 days, the total radioactivity, associated mainly with nickel and cobalt, remains at a significant level.

Previous storage may also have chemical effects on the outcome of the volatilization process. Fuel residues are stored hot and wet for long periods before processing. The oxide film formed on the metal may initially act as a barrier to the reaction between HCl and the underlying zirconium metal. On the other hand, the hydrogen formed in the reaction of the metal with HCl can be expected to react with the oxide film, producing water vapor inside the equipment. This can in turn hydrolyze some of the $ZrCl_4$ before it has been distilled into the collection vessel and thus create materials-transport problems.

7.2.8.4 Status of Technology

This technology is not yet available. The basic reactions of hydrochlorination and pyrohydrolysis have been demonstrated in work involving other zirconium alloys on a pilot plant scale.⁽²⁷⁾ Developmental work with Zircaloy specifically has been tested at ANL on a laboratory scale involving the hydrochlorination of nonradioactive Zircaloy.^(28,29) The value of further development of this process could be determined from laboratory-scale experiments to test the separation of transuranium elements from zirconium by the hydrochlorination reaction.

7.2.9 Oxidation with $HF-O_2$

Still another way for managing cladding wastes involves burning the zirconium and stainless steel materials to oxides. The resulting oxides can be stored as such or, preferably, converted to dense, immobile glasses. Technologies important to this alternative are discussed in this section.

In the presence of HF gas both the Zircaloy and stainless steel components of cladding waste can be burned in oxygen at 500 to 600°C to oxides. Behavior of Inconel to HF-O₂ mixtures at elevated temperatures is not known; because of its high nickel and chromium content, however, Inconel would not be expected to be appreciably attacked by HF-O₂ mixtures. Mechanical separation of massive stainless steel and Inconel fittings from the other cladding wastes can be done before oxidation. Such separation is desirable to avoid problems associated with handling massive pieces of metal in the subsequent HF-O₂ treatment in a fluidized bed.

7.2.9.1 Treatment in High-Temperature Oxygen or Air

No direct experience in burning irradiated Zircaloy cladding residues and/or fines in air or oxygen has been reported. Recent⁽⁷⁾ experience with tests on a variety of unirradiated Zircaloy materials showed that fines could be ignited with a relatively low energy source, such as a match, depending on particle size. Tubing segments simulating cladding could not be ignited even at 1600°C with a gas-oxygen torch. This experience contrasts with earlier reported⁽³⁰⁾ results in that in dynamic systems where samples are shaken continuously to remove the oxide film, massive unirradiated Zircaloy burns in air at 1000°C at a rate of 0.26 mg/cm²-min (40 mils/hr).

Cladding-type stainless steels are probably more resistant to oxidation by hot air than is massive Zircaloy. Accordingly, the use of hot air or oxygen to burn stainless steel cladding wastes is restricted to cladding fines.

7.2.9.2 Treatment in Hydrogen Fluoride Catalyzed Oxidation

Both stainless steel and Zircaloy are smoothly, rapidly, and completely converted to oxides by exposure for 1 to 4 hr at 500 to 625°C to gas mixtures containing 30 to 65% HF and 70 to 30% O₂. Successful oxidation of these cladding materials was demonstrated in laboratory-scale work performed in both the United States⁽³¹⁻³³⁾ and Europe⁽³⁴⁾ as part of efforts to develop and demonstrate nonaqueous procedures for decladding and processing of power reactor fuels.

At the Brookhaven National Laboratory effects of both temperature and gas composition on the rate of oxidation of Type 348 stainless steel by HF-O₂ mixtures were determined in 3.8 to 7.6-cm-diam fluidized bed reactors (Figure 7.9). Experiments were also carried out on the decladding of 38-cm lengths of unirradiated Yankee Reactor fuel rods; these fuel rods consisted of 0.86 cm OD x 0.053 cm wall, Type 348 stainless steel tubing containing sintered UO₂ pellets. Using a 40% HF-60% O₂ gas mixture at 600°C, complete disintegration of the fuel rod had taken place within a 2-hr period. Examination of the bed after each run showed that it contained Fe₂O₃ scale and uranium reaction products (U₃O₈, UO₂F₂, and UF₄). In other experiments simulated fuel rod

FIGURE 7.9. Reaction of Type 348 Stainless Steel with HF-O₂ Mixtures in a Fluidized Bed⁽³¹⁾

assemblies consisting of nine, 30-cm-long sections of end plates were completely disintegrated by exposure in a fluidized bed at 625°C to a 40% HF-60% O₂ mixture.

Applicability of HF-O₂ mixtures to oxidation of unirradiated Zircaloy in fluidized beds was demonstrated in two tests conducted in 1966 at the Oak Ridge National Laboratory.⁽³²⁾ Simulated fuel assemblies were made by placing four Zircaloy tubes (1.0 cm OD, 0.07 cm wall thickness, 30.5 cm long) containing UO₂ pellets (0.95 cm OD, 1.27 cm long) in 2 x 2 square array, 1.33 cm apart on centers. The assembly was held together by two spacers made from Type 304 stainless steel, each spacer being 2.54 cm from the end of the assembly. Alcoa T-60 alumina (-48+100 mesh) was used as the fluidized bed material in both experiments. Oxidation of the Zircaloy to ZrO₂ was easily accomplished at 550°C by passage of 40% HF-60% O₂ for 1 hr followed by passage of 20% HF-80% O₂ for 2 hr. The cladding residue in both runs consisted mainly of ZrO₂ fines, but some massive ZrO₂ shards were also present.

Apparently, reaction of HF-O₂ mixtures with irradiated Zircaloy and/or stainless steels has not yet been studied. Information is thus lacking on the fate and disposition during the oxidation step of the radionuclides

associated with the cladding hulls; some of the radionuclides would probably be converted to nonvolatile oxides, but others (e.g., uranium) may be at least partially converted to fluoride compounds while others (e.g., ^{137}Cs , ^{106}Ru , ^3H) will volatilize. Provision will thus have to be made for trapping these volatilized materials and for their ultimate disposition.

In all the studies reported to date, HF-O_2 oxidations of stainless steel and Zircaloy materials have been performed in fluidized bed reactors employing alumina as the fluidized medium. It would be desirable to eliminate dilution of the oxidized cladding with inert alumina. To avoid the need to size-reduce stainless steel and Inconel fittings, it is desirable that these massive chunks of metal be sorted from the other cladding materials prior to the HF-O_2 treatment.

7.2.9.3 Waste-Process Interactions

The particular properties of the waste stream--i.e., the nonreactivity of Inconel with HF-O_2 mixtures and of massive Zircaloy and stainless steel in hot air--important to burning of cladding wastes to oxides have already been cited.

The HF-O_2 oxidation process is intended for converting both Zircaloy hulls as well as fines to zirconia. (Fines alone can be burned in air.) One liter of zirconium residues will theoretically yield 0.25 liter of ZrO_2 .

The HF-O_2 oxidation process will successfully convert all the stainless steel cladding components, including end fittings, to oxides. Size-reduction of massive end fittings would be desirable to permit rapid oxidation in fluidized bed reactors. One liter of stainless steel residues will theoretically yield 0.29 liter of (FeNiCr) oxide. Inconel will be relatively unaffected.

7.2.9.4 Status of Technology

This technology is not available. A cladding waste management scheme which involves HF-O_2 oxidation of the Zircaloy and stainless steel components and glassification of the resulting oxides is largely in the conceptual state of development. On the basis of very limited and isolated scouting studies, however, such a burning-glassmaking process appears a technically feasible way for direct and positive conversion of cladding wastes to a storage form. Laboratory and pilot-plant tests with irradiated and simulated cladding wastes of key process elements are needed to better determine if an oxidation-glassmaking process is an economically viable alternative.

7.2.10 Conversion of Oxides to Glass

Both zirconium and iron-chrome-nickel alloy oxides are inert and thermodynamically stable materials and may be suitable terminal storage forms. An

objection to the storage of oxides is the large surface area they present to possible leaching solutions. Conversion of the oxides to a monolithic glass more resistant to leaching of radionuclides, particularly actinides, is a process alternative although it increases waste volume.

Schulz, Dressen, and Hobbick⁽³⁵⁾ have reported scouting studies on conversion of oxidized cladding materials (resulting from prior HF-O₂ treatment) to silicate glasses. In the conceptual glassmaking scheme (Figure 7.10) devised by these investigators, oxidized cladding is melted at 1200 to 1400°C with appropriate amounts of sand (or basalt), Na₂CO₃, and B₂O₃ to yield a dense, immobile silicate product.

Glasses result when charges containing 10 to 15 wt% ZrO₂, 38 to 60 wt% sand or 10 to 20 wt% stainless steel oxides, 50 to 60 wt% sand (or basalt) are melted for an hour at 1200 to 1400°C. Glass-like materials containing some crystalline zirconia result when charges containing 10 to 30 wt% ZrO₂, 40 to 60 wt% basalt are melted at 1200 to 1400°C; similarly charges containing 30 to 50 wt% stainless steel oxides, 20 to 40 wt% basalt (or sand) when melted at 1200 to 1400°C yield glassy silicates containing some unidentified crystalline substances. Irrespective of their nature, all the silicate products prepared

FIGURE 7.10. Conceptual Process for Conversion of Cladding Wastes to Silicate Glasses⁽³⁵⁾

by Schulz et al.,⁽³⁵⁾ including some from irradiated Zircaloy and types 304L and 316 stainless steel, were very resistant to attack by water; leach rates in deionized water at 25°C were in the range 10^{-8} to 10^{-5} g/cm²/day.

Detailed discussions of glassmaking processes for fission product oxides are presented in Section 6.

7.2.11 Conversion of Zirconium to HLW Absorbents

The processes in making HLW absorbents of zirconium have not been extensively investigated. They are currently being explored at Sandia.⁽³⁶⁾ The ability to minimize leaching by absorption and fixation of HLW ions on hydrous zirconium oxide is as yet poorly defined. Processes selected for the formation of an absorbent obviously will rest on the properties the absorbent must have. One can postulate that many of the processes which produce zirconium compounds (i.e., the sulfates, fluorides, and chlorides) would be adaptable to making an absorbent of suitable properties, but this has not yet been established. One sequence of processes proposed to produce the HLW absorbent is shown in Figure 7.11.

FIGURE 7.11. Zircaloy Conversion Process

The basic sorting technology has been discussed in 7.2.1. Some elements which form volatile chlorides may interfere with the properties of the zirconium absorbent and thus might need to be removed mechanically prior to zirconium volatilization. Materials not reacting or forming nonvolatile chlorides would be removed from the reaction chamber periodically.

7.2.11.1 Volatilization of Zirconium

Refer to 7.2.8 for a similar process description. Several chlorinating agents can be used to produce the volatile metal chlorides of zirconium, tin, etc. However, ammonium chloride^(37,38) is considered in this flow diagram because of its lower heat of reaction and better controllability compared to HCl.^(39,40)

7.2.11.2 Alkoxide Conversion

The volatile chlorides are distilled into isopropyl alcohol (iPrOH), where they react in the presence of NH₃ to form isopropoxides.⁽⁴¹⁻⁴³⁾ For zirconium the reaction is

Solid NH₄Cl would be regenerated in the reaction, and in the presence of NH₃ should be quite soluble⁽⁴³⁾ in the alcohol solution. However, addition of benzene to the system limits the NH₄Cl solubility so that it can be effectively removed from the alkoxide converter by dissolution⁽⁴³⁾ in formamide (HCONH₂). The final formamide/NH₄Cl solution is immiscible in the alkoxide/alcohol/benzene solution. The use of formamide as a second liquid phase avoids a potentially costly and difficult large-scale filtration process to remove and recycle NH₄Cl.

7.2.11.3 HLW Absorbent Formation

The tetraisopropyl zirconate and other alkoxide impurities would be readily recovered from the volatile solvent and converted to the ion exchange material by hydrolysis using methods already demonstrated. For zirconium, the hydrolysis reaction is

and the isopropyl alcohol could be recovered and recycled. The overall reaction is

The only other products would be the nonvolatile chlorides that remain behind in the chloride converter. In principle, all the reagents are recycled in the process so that no major new radioactive waste stream is formed. In actual practice, some losses would be expected to occur, resulting in some waste streams.

The absorption of HLW radioactivities and the previously generated non-volatile chloride wastes appears possible. The fixation of ions and problems inherent in the process will be discussed in Reference 36. See also Section 6.0.

7.2.11.4 Waste-Process Interactions

Materials which will not react to form chlorides must be separately handled either before or after treatment to volatilize the zirconium. This could amount to a substantial side stream. The presence of elements which form volatile chlorides which are objectional from an absorbent formation standpoint might have to be separated prior to chlorination. No information is currently available on either possibility.

The conversion of the fuel bundle residues into the equivalent zirconate will result in an estimated volume change of 1 into 0.4 for the zirconium. If this material can also hold the high-level waste liquid in this reduced volume, it represents one of the minimum volume storage alternatives. See Section 6.0 on Ion Exchange for the potential of this material in HLW absorption.

7.2.11.5 Status of Technology

This technology is not available. The usefulness of this HLW absorbent storage form together with the processes to produce the form are being investigated but require substantial development even to be evaluated (refer to Section 6.0, Ion Exchange). The promise of volume reduction for the total waste picture is a primary motivating force for its evaluation. However, the volume of HLW calcine will be increased by adding the hull waste.

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8.0 TREATMENT OF NONCOMBUSTIBLE SOLID WASTES

8.0 TREATMENT OF NONCOMBUSTIBLE SOLID WASTES

The solid noncombustible wastes discussed in this section comprise those non-high-level wastes generated by the operation of reactors, fuel reprocessing plants (FRPs), and mixed oxide (MOX) fuel fabrication plants. High-level waste and chop-leach fuel bundle residues are covered in Sections 6.0 and 7.0, respectively, and are excluded from this section.

8.1 CHARACTERISTICS OF AS-GENERATED WASTES

The primary constituent of the waste covered in this section is metal, but other noncombustibles such as glass and concrete are also present. Incidental quantities of combustible material such as grease, plastic, and floor sweepings are also included with the noncombustible waste. Sections 2.0 and 3.0 provide formal discussions of the various waste classifications and quantities.

Most failed or obsolete process equipment eventually becomes noncombustible waste. It is normally flushed and decontaminated prior to removal from service and has combustibles removed whenever it is practical to do so. Reprocessing plant canyon operations provide the largest and most radioactive pieces of failed equipment. Typical large items consist of dissolvers, columns, and concentrators which might be up to 3 meters in diameter and 10 meters in height. Such items may be disassembled at predetermined joints to permit removal from their operating positions. Further disassembly may be required for movement beyond the confines of the reprocessing facility. As an alternative to removal from the reprocessing facility, failed equipment may be stored temporarily in unused cells or in specially designed storage areas such as the plutonium-uranium extraction (Purex) equipment tunnel at Hanford.

Reactor noncombustible waste also includes large components that require size reduction before removal from the reactor containment system. Both the FRP and reactor wastes may be highly radioactive, requiring personnel shielding equivalent to several feet of concrete.

Mixed oxide fuel fabrication plant failed equipment includes large items such as glove boxes. Direct radiation levels may be low enough to permit contact work or work with light shielding; however, the presence of plutonium requires elaborate systems to prevent the spread of plutonium to the environs.

Failed equipment provides the more difficult problems due to size and radiation problems; however, there also is a steady stream of miscellaneous noncombustible waste from each type of plant. Typical items in this category include glass, filters, concrete, scrap metal, and trash. Depending on the type and size of a production facility, the combustible and noncombustible waste may be mixed and require sorting prior to packaging for final storage.

Ion exchange materials or like chemicals constitute a significant percentage of the solid noncombustible waste from each type of facility. Such material can normally be handled as a fluid by pumping or sluicing, arriving at its destination as a wet powder or granular material. The waste treatment system must either provide for drying the material or be designed to cope with the high moisture content.

8.2 TREATMENT OPTIONS

Since the start of the nuclear industry the simplest and least expensive treatment for solid wastes has been burial in the soil. Packaging was designed to contain the waste during transit and burial. Failure of containers after burial due to soil loading, decay, or corrosion was of no great concern because the layer of soil was considered to provide adequate confinement.

In recent years, disposal by burial has lost favor for a variety of reasons but is still acceptable for selected materials. A comprehensive discussion of waste burial is given in Section 24.0 of this document.

8.2.1 Alternative Treatments

Alternatives for treatment and storage of non-high-level solid wastes range from direct burial as described above to sophisticated treatments such as meltdown of metals to ingots that are very stable and can be stored in a relatively small space.

Figure 8-1 is a flow chart which gives a graphic presentation of the alternative treatments of non-high-level noncombustible solid waste. Relative volumes are also given on the chart with the primary waste assigned 100 units of volume. Because of the heterogeneous nature of the primary waste, it is not practical to try to determine rigorous unit values as a result of application of each treatment to each type of waste. The volume numbers assigned are indicative of trends rather than absolute numbers. Significant observations regarding volume trends are (1) pretreatment will not affect volume appreciably, (2) mechanical disassembly will reduce volume to about 80 units, (3) melting will reduce the volume to approximately 10 units, while dissolution, crushing, or chemical reduction will decrease volume by intermediate amounts, and (4) packaging of the treated waste will increase volume by about 50 percent to give final volumes ranging from 15 to 150 units.

The purely mechanical size reduction treatments produce negligible amounts of secondary wastes and such wastes are easily controlled by filtration. However, the operations involving high temperatures or aggressive chemicals will produce gaseous, particulate, and liquid streams that require sophisticated treatment to prevent losses to the environs. Secondary wastes

consisting of filters, ion exchange resins, and other solids will, after treatment, range from 10 to 25 percent of the primary waste volume (see Section 8.5).

8.2.2 Technology Development

A large portion of the noncombustible waste to be treated for storage is equipment that has failed in service or has become obsolete. Over the years techniques have been developed for the decontamination, maintenance, and repair of such equipment.

FIGURE 8-1. Noncombustible Solid Waste Flow Diagram

The first steps in waste treatment of large equipment are apt to be decontamination and disassembly and it must be assumed that the maintenance techniques for such work are directly applicable to the waste treatment operation. The maintenance practices have a goal of returning equipment to service, while the goal of waste treatment is to reduce the equipment to a dense, unleachable mass of noncombustible material. This difference in goals will be reflected in the method of applying the technology. Specific differences are as follows:

- If a piece of equipment is to be returned to service, it must not be damaged excessively by decontamination or disassembly efforts.
- More exacting work in the repair operation is likely to require the close approach by craftsmen, therefore, lower radiation levels must be attained.
- High radiation exposures may be justified in special cases where minor repairs are to be made on a complex and expensive component; such exposures cannot be tolerated for personnel operating continuously in a waste treatment facility.

8.3 AVAILABLE WASTE TREATMENT TECHNOLOGIES

There is no sharp line of distinction between technologies that are available and those that require development. A number of technologies such as sorting and decontamination are routinely practiced in nuclear facilities and are generally classed as "available waste treatment technologies." However, development work is still underway in these areas and there is room for improvement. Conversely, there are a number of technologies such as scrap equipment disassembly and metallic melters that are routinely used in the nonnuclear industry but have not been fully adapted to the nuclear industry. Technologies requiring large amounts of development and adaptation for use by the nuclear industry have been classed as "treatment technologies requiring development."

8.3.1 Sorting

Sorting is one of the waste pretreatment steps that is sometimes necessary prior to the major waste treatment operations such as size reduction, melting, or compaction. The need for sorting is minimized by (1) requiring that waste producers segregate waste at the point of origin and (2) providing major waste treatment facilities that can handle appreciable percentages of foreign material. These efforts are not always successful and enough unsegregated waste will arrive at the waste treatment facility to make it necessary to have sorting capability.

A comprehensive discussion of sorting technology is given in Section 9.0 of this document. The basic sorting operation for noncombustible waste is essentially a visual-manual operation using a shielded work area equipped with windows or periscopes for viewing and manipulators to handle materials. Glove boxes may also be used for sorting noncombustible waste if the radiation level is low.

8.3.2 Decontamination

Decontamination is one of the pretreatment operations that may be required to make noncombustible solid waste acceptable for major treatments

such as size reduction or melting. The decontamination of radioactive equipment is commonly practiced by currently operating nuclear facilities using well developed and well documented technology.^(1, 2) The goal of conventional decontamination is to reduce the radiation level of equipment to permit the performance of routine work on the equipment or in its vicinity. This same goal applies to the decontamination of waste; however, more destructive procedures can be used on waste because it is not necessary to return the equipment to an operating condition.

Technology exists to perform almost any desired degree of surface decontamination including levels that would permit release of material for unrestricted public use. However, the materials to be released must be limited to simple items where all surfaces can be monitored to check the effectiveness of decontamination. Porous materials or items with concealed surfaces are more difficult or impossible to monitor with the accuracy required to ensure that the decontamination has been successful. Monitoring problems, plus high cost, make decontamination unattractive as a means of obtaining release of low value materials such as waste.

8.3.3 Plutonium Recovery

Plutonium recovery is covered extensively in Section 11.0 of this document and will be minimized in this section. The recovery of plutonium may be necessary as a pretreatment for noncombustible solid waste under unusual or infrequent conditions. Normally plutonium is recovered by processing operations prior to the time that the material is declared to be waste. Plutonium remaining after the completion of process operations and decontamination is generally considered to be unrecoverable for technical or economic reasons. The plutonium/waste problem then becomes one of plutonium containment rather than one of plutonium recovery.

Under certain conditions plutonium may be trapped in inaccessible portions of glove boxes or other equipment and can be recovered only after partial disassembly of the equipment. At the proper time in the disassembly sequence of such items, steps are taken to recover the plutonium using the appropriate procedures described in Section 11.0.

8.3.4 Compaction

Methods used for compacting small noncombustible wastes such as glassware, ceramics, metal containers, and light equipment are the same as used for compacting combustible solid wastes and are described in Section 9.0 of this document. Larger items such as heavy equipment, hoods, and structures are generally mechanically disassembled if treated at all. There have been no significant efforts or studies to use large-scale shredders or compactors, such as are used on automobiles, for crushing large pieces of radionuclide

contaminated equipment. Crushing is well developed in the commercial, non-nuclear metal scrap industry; but areas requiring special consideration in adapting this technology include: remote operability, maintenance, contamination control, pretreatment (sizing), and defining applicable wastes (some wastes may be too large, of too complex configuration, or too radioactive to be subjected to crushing techniques).

8.3.5 Fixation in Concrete, Bitumen, or Urea Formaldehyde

The alternative of placing noncombustible waste in concrete, bitumen, or urea formaldehyde can be used for waste that has been cut up into small pieces. These processes serve to reduce the potential for contamination spread and take the place of such processes as melting and chemical dissolution. It is also possible to include small quantities of combustible materials or ash with the noncombustible wastes.

Descriptions and comparisons of the concrete, bitumen, and urea formaldehyde processes are given in Section 12.0 of this document.

8.4 TREATMENT TECHNOLOGIES REQUIRING DEVELOPMENT

The technologies described in the preceding section (8.3) are commonly used in the nuclear industry and are considered to be available for use. The technologies described in this section are less well developed or have not been fully adapted to nuclear services. The required development in some cases consists of the scale-up or adaptation of existing technology, but solution of the problems to be encountered may prove expensive and time consuming.

MECHANICAL DISASSEMBLY

Process Summary Process Description

Solid wastes, comprised mainly of metallic equipment, are dismantled to reduce the volume and/or simplify handling. A variety of techniques may be employed, such as using hand tools, cutting torches, saws, shears, or explosives.

Development Status

Basic techniques exist as an extension of techniques used in maintenance operations. Improved techniques are being developed to increase facility capacity and reduce radiation exposure.

Applicable Waste

Waste items that are too large for standard packaging or that require size reduction to fit subsequent processing equipment.

Volume/Weight Change

Volume change is highly variable ranging from a 25 percent decrease to a 200 percent increase. Weight will not change.

Prior Treatment Required

The equipment may be decontaminated to lower radiation levels, to remove plutonium, and to remove materials not compatible with the disassembly process.

Potential Problem Areas

Material handling of large equipment into the process area and the handling of irregular, heavy parts as removed from the large equipment pieces.

8.4.1 Mechanical Disassembly

Failed or obsolete mechanical equipment may be too large to move to storage without partial disassembly. In other cases it may be necessary to reduce metallic items to small pieces in preparation for melting or packaging.

8.4.1.1 Process Description

The technologies for mechanical disassembly operations exist in maintenance practices as noted earlier in this section. The technologies have also been used on a small scale at ERDA facilities,⁽²⁾ at foreign facilities,^(3, 4) and on a larger scale at the Elk River Reactor decommissioning.⁽⁵⁾ These operations employ the commonly used tools such as saws, shears, impact tools, and cutting torches. The operations tend to be slower than desired and require excessive amounts of labor with the potential for radiation exposure to personnel. However, the job can be done if the need exists.

8.4.1.2 Development Status

Development programs are underway to provide better mechanical disassembly systems by providing facilities and disassembly equipment especially designed for the purpose of disassembly.

A typical program of this type is currently underway at Atlantic Richfield Hanford Company (ARHCO), and calls for the development of a prototype facility for the disassembly of contaminated process equipment in a remotely operated facility. Basic criteria for the facility require major equipment such as large vessels and heat exchangers be cut to pieces of about 30 cm maximum dimensions. These pieces may be packaged for storage or may be further processed by melting to ingots.

The facility is expected to be a shielded area operated by personnel outside the cell using remote viewing and remote operation of the disassembly equipment.

In addition to the use of the more conventional disassembly equipment, the facility will also be used to develop and test less conventional equipment such as arc saws and special plasma cutting torches.

The development program is expected to provide nonradioactive demonstrations during FY 1977, adaptation to low contamination equipment in FY 1978, and adaptation to highly contaminated equipment in FY 1979 or 1980. The program may continue for several more years to improve the technology if it appears warranted.

Development work has also been performed by Battelle, Pacific Northwest Laboratories on the use of explosive shaped charges for dismantling large pieces of equipment.⁽⁶⁾ The capability of the shaped charge was demonstrated but considerable work would be required to adapt the concept to remote operation in shielded facilities.

MELTING

Process Summary Process Description

Sized metallic waste is melted in a furnace and cast into ingots for long-term storage.

Development Status

Only limited melting studies have been performed on radionuclide-contaminated stainless steel samples. There is significant industrial experience on nonradionuclide-contaminated metals and metallic scrap melting.

Applicable Waste

All metallic scrap is candidate material for this method of treatment.

Volume/Weight Change

Volume will be reduced by an average ratio of 10/1 but may range from 5/1 to 15/1. Weight will not change except for slag losses or gains.

Final Product Form

Metal ingots and a slag.

Prior Waste Treatment Required

Size reduction and sorting, as required.

Potential Problem Areas

Process development required to select melting process and construction materials. Operability, maintainability, off-gas treatment, and fission product behavior require demonstration.

8.4.2 Melting

Metallic waste materials, after treatment to provide an acceptable feed for a melting furnace, are melted and cast into ingots. The ingot represents the minimum volume for the waste and provides a means of fixation for the radionuclides.

8.4.2.1 Process Description

The melting furnaces under consideration are modelled after small metallurgical furnaces currently used in industry. They will accept pieces of metal with maximum dimensions up to about 30 cm and may operate on either a batch or continuous basis.

The radionuclides contaminating the metal or equipment are generally surface contamination. Melting the metal incorporates the radionuclides into the metal matrix, where they are immobile. Some radionuclides such as strontium and plutonium will be preferentially included in the slag covering the melt.⁽⁷⁾ The slag would be a radioactive waste byproduct.

The furnace, depending on the type used and off-gas system design, could also combust or pyrolyze small amounts of organic wastes included in the feed scrap. The ash or carbon would be included in the slag or metal. This would represent a greater than 95 percent organic waste volume reduction without impairing metal melting processing. To ensure that all pyrolyzed carbon dissolves in the melt, the combustible fraction should be kept under 10 weight percent of the total charge. There is the possibility that ceramic materials could be added to the furnace to convert them to a more compact and consolidated state, but this would depend on furnace design and the slag handling method.

Process operating conditions cannot be specified at this time due to the development required to define the melting process, off-gas handling, construction materials, system operability, system maintainability, and ingot and slag handling.

8.4.2.2 Development Status

- Estimated Time of Readiness for Practical Design

At this time, programs are getting started to demonstrate the utility of equipment meltdowns as a large-scale production process. Only very limited laboratory meltdown on small samples has been performed to assess the behavior of radionuclides in the process. No highly contaminated large pieces of metal have been melted. Atlantic Richfield Hanford Company plans to set up a test vacuum furnace. Preliminary nonradioactive demonstrations will be conducted during 1977-1978. Initial radioactive melt tests will begin in 1979. A full-scale production plant could follow by about 1984.

Pacific Northwest Laboratory is conducting a program to solve similar problems but is concentrating on the treatment of chop-leach fuel bundle residues as described in Section 7.0 of this document. Argonne National Laboratory⁽⁸⁾ and other ERDA laboratories are performing development work related to molten metal technology, and Atomics International is adapting a molten salt process to the treatment of contaminated metals as described in Section 8.4.2.3 of this document. The timing of these programs is comparable to the timing of the ARHCO program.

- Major Development Programs - Objectives and Status

The technology for metal scrap meltdown and the production of ingots is well developed in nonnuclear industries; however, the behavior of radionuclides in such processes is not fully understood. Areas under development at present include: definition of radionuclides that will vaporize at molten metal temperatures; distribution of radionuclides in the molten metal, slag, and furnace structure; mobility of radionuclides in the final ingot and slag; and development of adequate off-gas treatment methods. The timing of these development programs is consistent with the timing of the practical design needs. The complex problems of remote operation and maintenance of such facilities should also be demonstrated in this time frame.

8.4.2.3 Alternative Melting Technologies

Alternative furnace concepts considered for these processes and the status of the technology are as follows:

- Vacuum Furnace

Vacuum furnaces are widely used in specialty metals manufacture. They are most suitable for off-gas and ventilation control, and also appear to be most amenable to remote operation and maintenance. This type furnace appears to be well suited to melting radionuclide contaminated metals.

- Induction Heating

Induction heating appears to offer many advantages over other heat sources. Energy is transferred by an electromagnetic field in a manner which allows the working coils to be separated from the molten metal. This could simplify operation and maintenance. There is no transfer of material in induction heating, and the only source of gas evolution is from the melt. Induction heating energetically is the most efficient heat source, and has been the choice in industrial vacuum furnace operations.

- Autogenous Melting

An autogenous melting system large enough to accept scrap without prior size reduction, fueled by some form of oxidant and metal powder has many conceptual advantages. Such a system was tested using a thermite reaction as the autogenous heat source, but safely controlling the heat source proved to be impractical. The continuous addition of gaseous oxygen and powdered metal has many of the same problems of any electrical heat source (complexity, expensive probes, lances, leads, etc., operating near molten steel temperatures). Batch operation, using a solid oxidant and metal powder, is potentially explosive. Any of the exothermic reactions generate copious volumes of fumes in a short time, which would make containment very difficult.

- Electric Arc

A method which avoids size reduction as a preliminary step would be a drip-melt system. Power could easily be supplied by electric arc. The large open volume complicating off-gas control, the poor control over the resulting molten product, and the problem of working with large objects at high temperatures in the presence of a complex and cumbersome power source discourage this approach.

- Plasma Arc

A plasma arc powered furnace operated at atmospheric pressure instead of in vacuum may have advantages over the vacuum furnace. It may be easier to process nonconductors in greater volume than in a vacuum induction furnace. Most of the problems, however, will be common in either system.

- Purification and Decontamination by Electroslog Methods

This method would convert the metallic scrap to a slag mass. It is also known that such a technique can be made to work. However, the volume of contaminated slag generated would approach or exceed the initial volume of contaminated metal.

8.4.2.4 Applicable Wastes

Melting may be applied to any metallic waste that can be reduced to a size that will fit into the furnace. Pretreatment to segregate metal types may be of advantage if an attempt is made to salvage the resulting ingots. Incidental quantities of combustible wastes may also be included.

CHEMICAL REDUCTION

Process Summary Process Description

At about 850 °C, molten sodium carbonate and air will oxidize metals and retain them in the salt along with ash, sodium chloride, and fission products.

Development Status

Demonstrated on bench-scale at 0.5 kg/hr contaminated waste and 50 kg/hr with uncontaminated waste.

Applicable Waste

Applicable to both combustible and noncombustible wastes. Currently limited to thin-wall metallic components.

Volume/Weight Reduction

Volume will reduce by about a factor of 5 as compared to fabricated metal components and weight will increase by the amount of sodium carbonate used.

Prior Waste Treatment Required

Metallic components must be reduced to a size that will enter the combustor.

Potential Problem Areas

Corrosion of the materials of construction will be a serious problem as will the handling of the molten salt process material.

8.4.3 Chemical Reduction

Any of the noncombustible solid waste components could be chemically dissolved by proper choice of solvents and process conditions. Dissolution and subsequent solidification provide a means of reducing complete structural items to a uniform solid which might approach the density of melted and cast metals, but the overall product of the dissolution process would increase by the amount of chemical salts used in dissolution.

During the time the waste is in solution, there is an opportunity to perform chemical separations treatment and an opportunity to produce clean metals that can be returned to industry. These possibilities are being studied and some development work has been started. A typical program of this type is underway at Atomics International Division of Rockwell International and a brief description of the program follows.

8.4.3.1 Process Description

At 850°C in molten sodium carbonate, air combines with combustible wastes to form carbon dioxide and water and with acidic substances such as sulfur, phosphorus, or chloride in the waste to form sodium salts. Inorganic combustion and reaction products such as metallic oxides, ash, sodium chloride, and fissile material are retained in the melt. The system is remotely operable, therefore, both transuranic (TRU) and fission product wastes can be processed.

The development program indicates that the process will also dissolve glass and light gage metals. Glass reacts quite rapidly with the sodium carbonate. Carbon dioxide is evolved, indicating the silica reacts with the sodium carbonate to form silicate. At 1000 °C thin-walled (<1.5 mm) steel containers dissolved within an hour while thick-walled (9 mm) carbon steel containers required about 24 hours to completely dissolve. At higher melt temperatures, the dissolution rate increases.

In a large-scale (90-cm diameter) combustor, 5 cm Schedule 80, Inconel 600 pipe dissolved in about 24 hours, whereas 5 cm Schedule 80, stainless steel (304) pipe would not dissolve in one week. The mechanism of corrosion for the nickel alloys involved the formation of nickel sulfide intermediates which did not inhibit corrosion, whereas a sodium chromite, corrosion-inhibiting film formed on the stainless alloys. Thus, it would appear from these tests that silica-based glasses, carbon steel, and nickel-based alloys could be dissolved in the melt, but that stainless steels would require considerably longer to completely dissolve.

8.4.3.2 Development Status

Combustion of TRU wastes has been demonstrated on a bench-scale (0.5 kg/hr) with plutonium contaminated waste and on a pilot plant-scale

(50 kg/hr) with uncontaminated waste. Destruction and volume reduction of metallic components have been tested on a bench-scale. Some preliminary design and testing on a large-scale unit have been completed. Further testing of specific wastes would be required during preliminary design of a large-scale unit. Pilot-scale tests with depleted uranium or tracer-quantity fission product contaminated wastes could be made in an existing pilot-scale combustor (50-100 kg/hr). Molten salt technology is a commercial technology utilized in mineral recovery from dry lake beds.

8.4.3.3 Applicable Waste

The process is applicable to all combustible solids and liquids, and thin-walled metallic components. It is not recommended for thick-walled (>2 mm) cobalt based alloys or for high chromium (>10 percent) alloys, unless dissolution times of several days can be allowed. It is especially applicable to nickel based alloys and silicon based glasses. Heavy or bulk metallic components would pose a feed problem. Friable or shreddable inorganic solids, such as HEPA filters, glass labware, and stainless fuel cladding can be accepted by the system.

8.4.3.4 Final Product Form

Disposal product consists of drums of solidified fused salt containing metal oxide ash.

8.5 SECONDARY WASTE TREATMENT

The basic goal of the treatment of primary waste is to produce an altered primary waste that can be safely stored for long periods of time. Desirable additional goals are the reduction of waste volume and cleanup of contaminated materials to permit release to the environs or recycle by industry. Incidental to the accomplishment of these goals is the production of secondary waste streams such as contaminated off-gas and liquid. It is essential that the secondary wastes also be confined and reduced to a form that is suitable for long-term storage, or clean enough for release to the environs or for recycle.

8.5.1 Process Description

Figure 8-2 shows a simplified flow diagram for the secondary wastes from the noncombustible waste treatment system. All of the treatments are performed in an area that is maintained somewhat below atmospheric pressure to control airflows and this requires an exhaust fan and filter system. Treatments requiring high temperatures (melting, torch cutting, etc.) release vapors or fumes containing radioactive material. This necessitates the use of a scrubber to remove most of the vapors and fumes before they reach the

filter. Off-gases leaving the filter must be suitable for release to the environs. A more complete discussion of off-gas treatment is included in Section 13.0 of this document.

The off-gas scrubber generates a liquid waste that contains the materials scrubbed from the off-gas. This liquid is combined with the decontamination liquid stream and diverted to the non-high-level liquid waste stream (Section 10.0).

FIGURE 8-2. Noncombustible Solid Waste--Handling of Secondary Wastes

HEPA Filters used for final treatment of the off-gas stream will require replacement when they become loaded with particulate material. They will be treated as described in Sections 12.0 and 13.0.

8.5.2 Secondary Waste Quantities

The treatment of solid noncombustible waste results in secondary streams such as contaminated air and contaminated water. At times the quantities of these streams might equal or exceed the volume and weight of the primary waste. However, the contaminated streams are cleaned by such equipment as ion exchangers and HEPA filters. The results are clean effluent streams of air and water that are released to the environs. The contaminated materials from these streams are concentrated in ion exchange resin, evaporator bottoms, and partially plugged filters to comprise the secondary waste streams from

the solid noncombustible wastes. The volume and weight of these concentrated secondary waste streams are small by comparison to the original primary waste stream; the quantity that must be stored might range from 10 percent to 25 percent of the primary waste.

8.5.3 Development Status

The concentration of radionuclides in the noncombustible solid waste stream is orders of magnitude lower than in the high-level waste system. This is because the radioactive material available for release from the noncombustible waste stream is only incidental contamination from surfaces that have been partially decontaminated, while the high-level wastes are concentrated fission products. Technology exists (Section 6.0) for treatment of these high-level wastes and it is reasonable to assume that the same technologies will provide a large factor of safety when applied to the treatment of the much less concentrated secondary wastes from the noncombustible waste system.

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9.0 TREATMENT OF COMBUSTIBLE WASTES

9.0 TREATMENT OF COMBUSTIBLE WASTES

A material is considered combustible if it can be ignited or if it can react exothermically with air by any physical or chemical means. The combustible wastes considered in this section are largely composed of organic materials (paper, plastics, rubbers, ion exchange resins, solvents, etc.) but may contain noncombustible materials as integral or admixed components.

Primary objectives of recent waste management programs have been to reduce the as-generated and stored volumes of combustible wastes. Several volume reduction options are being investigated, including minimizing waste generation at the source, mechanical compaction, and various conventional and specialized combustion methods. Combustion serves not only to reduce the volume but also to convert the waste to inert or less reactive forms, thereby reducing possible problems associated with transportation and storage of these wastes.

9.1 CHARACTERISTICS OF AS-GENERATED WASTES

Combustible solid radioactive wastes include a large variety of items such as paper, rags, plastic sheeting, protective clothing, gloves, rubber shoes, wood, organic ion exchange resins, filter aids, etc. Much of the combustible waste materials generated in nuclear facilities is collected as general trash, which usually consists of a mixture of combustible and noncombustible items. Therefore, treatment options generally include sorting prior to treatment of the wastes.

Waste compositions vary depending on the operations involved. General trash, or non-glove box waste, includes primarily cellulosic materials such as paper, wood, cardboard, absorbent cotton, cotton clothing, and rags. Usually these materials burn readily to release water vapor and carbon dioxide. Glove box-generated wastes, on the other hand, primarily contain rubber or plastic materials since cellulosic materials are mostly excluded from glove box operations. Some examples of plastic and rubber materials used in the nuclear industry are listed in Table 9-1.

Knowledge of the constituents to be burned is important in combustion system design. For example, nonhalogenated plastics, when burned in air, give combustion products similar to those obtained from cellulose but can also generate substantial quantities of soot. Halogenated plastics and rubbers also generate corrosive, acidic vapors such as HCl and SO_2 . Combustion of lead-loaded rubber gloves can result in deposition of PbCl_2 in the off-gas duct and formation of a low-melting eutectic that can attack the furnace refractory.

TABLE 9-1. Plastic and Rubber Materials Commonly Found
in Combustible Solid Radioactive Wastes

CHLORINATED PLASTICS

Polyvinylchloride or PVC (Geon, Koroseal)
Polyvinylchloride acetate (Vinylite V)
Polyvinylidene chloride (Saran, Geon, Velon)
Chlorinated polyether (Penton)

FLUORINATED PLASTICS

Polytetrafluoroethylene (Teflon)
Polyvinylidene fluoride (Kynar)

NONHALOGENATED PLASTICS

Polyethylene
Polypropylene
Polystyrene (Styron, Lustron, Styrofoam)
Polymethyl methacrylate (Plexiglas, Lucite)

CHLORINATED RUBBERS

Chlorosulfonated polyethylene (Hypalon)
Polychloroprene (neoprene)

NONHALOGENATED RUBBERS

Butadiene-styrene (GR-S, Duradene)
Polyisoprene (natural rubber, latex)
Butene-diene (butyl rubber)

Organic ion exchange resins constitute a special class of combustible solid wastes. Resin types most frequently used in radioactive service are strong-acid cation and strong-base anion exchange resins.⁽¹⁾ The resins consist of organic matrix materials such as styrene, styrene-divinylbenzene, epoxy polyamines, phenolic and acrylic compounds, etc., which contain amine and sulfonic active groups with exchangeable ions such as sodium, hydrogen, nitrate, chloride, or hydroxide. Combustion of ion exchange resins can, therefore, yield corrosive gases such as SO₂, which contribute to the off-gas cleanup problems, and metallic salts that can attack the refractory furnace lining. Radioactive ions loaded on the resin can also present a shielding and containment problem.

Typical combustible liquid wastes consist of process solvents (tributyl phosphate diluted with a refined hydrocarbon diluent), laboratory solvents, cleaning solvents, and lubricants. These may contain sulfonic, amine, halogen, and phosphate groups that yield acidic gases on combustion. Spent process solvent can also contain sufficient radioactivity to require shielding during treatment.

The amount of waste generated at a nuclear facility will vary depending on the operations performed. The amount and characteristics of these wastes

have been discussed in Section 2.0. Typical quantities of combustible solid wastes for nuclear fuel cycle facilities are summarized in Table 9-2. Combustible solid waste compositions used in combustion process development studies have contained 20-50 wt% cellulose, 10-40 wt% rubbers, and 20-40 wt% plastics.⁽²⁻⁴⁾ These composition ranges are considered to be representative of the wastes generated in nuclear fuel cycle facilities.

9.2 TREATMENT OPTIONS

Various treatment options are available for application to combustible wastes, ranging from simple storage in boxes or steel drums to compaction, encapsulation in cement, or combustion. The waste treatment applied will be influenced by the cost of waste storage, the status of waste treatment technologies, and possible regulations relating to storage of combustible radioactive wastes.

Examples of treatment options for mixed combustible wastes, ion exchange resins and organic liquids are shown in Figure 9-1. For mixed combustible solid waste materials, four treatment options are currently practiced: (1) no treatment at all, (2) compaction, (3) sorting and shredding of the wastes followed by immobilization in cement or other solid matrix, and (4) sorting and shredding of the wastes followed by incineration (or other combustion process) to convert the waste to a noncombustible residue. When incineration is used, the resulting residue (or ash) can be processed for plutonium recovery prior to immobilization and storage. These four treatment options are discussed in more detail below.

The simplest treatment option for mixed combustible nuclear wastes is no treatment at all, e.g., the wastes are simply packaged in metal drums for storage. However, as waste storage costs increase, there is an increasing economic incentive to reduce the volume of wastes before storage.

Compaction is the most widely used volume reduction technique in the nuclear industry. The volume reduction obtained by compaction depends on the composition of the waste and on the force applied but generally is of the order of three to five-fold. While compaction significantly reduces the volume of combustible wastes, it lowers but does not eliminate the possibility of fire occurring.

Immobilization of shredded combustible wastes by mixing them with a non-combustible matrix, such as cement, has been accomplished (see Section 12.0). This method normally eliminates the possibility of fire and reduces the possible mobility of radioactivity in the waste.

TABLE 9-2. Characteristics and Source of Combustible Wastes

FACILITY	WASTE SOURCE	TYPE OF WASTE	ESTIMATED AS-GENERATED VOLUMES, M ³ /GWe-yr
Reactor	General trash	Protective clothing, plastic sheets and bags, rubber gloves, shoe covers, paper, rags, towels.	280
	Water cleanup	Ion exchange resins, filter aids, filters	100
	Off-gas cleanup	HEPA filters	7
Fuel Reprocessing	General trash	Protective clothing, plastic sheets and bags, rubber gloves and mats, shoe covers, paper, rags, towels.	80
	Water cleanup	Ion exchange resins, filter aids, filters	2
	Off-gas cleanup	HEPA filters	6
	Solvent extraction	Waste solvent	0.5
Fuel Fabrication (MOX)	Glove box waste	Rubber gloves, plastic bags, paper wipes, lead-loaded gloves.	10
	Process area wastes (Non-glove box)	Protective clothing, plastic sheets and bags, rubber and plastic gloves, shoe covers, paper, rags, wipes.	6
	Off-gas cleanup	HEPA filters	1

FIGURE 9-1. Treatment Options for Combustible Radioactive Wastes

Incineration of combustible nuclear wastes has been practiced in the United States and in foreign countries for over 25 years. A list of incinerators used at various sites for burning radioactive solid wastes is shown in Table 9-3. Waste incinerators have exhibited a variety of problems, including excessive corrosion of off-gas equipment, incomplete combustion of organics, formation of tars and soot which clog filters and other off-gas treatment devices, inefficient off-gas cleaning, and mechanical problems associated with operation of the incinerators in a radioactive environment.

To alleviate these problems, an extensive program is underway in the United States to develop incinerators and/or other combustion devices specifically for treating radioactive combustible wastes (transuranic-contaminated wastes in particular). The objective of this program is to gain practical experience with demonstration-scale units using radioactively-contaminated wastes. The combustion processes being developed include both conventional and advanced types of incineration, pyrolysis, molten salt combustion, and chemical digestion. General characteristics of these combustion processes are summarized in Table 9-4. Specific details of the processes, including a discussion of the current status of development, are presented in Section 9.5.

The various combustion processes reduce the volume of combustible wastes by factors of 20 to 50*, depending on the process, the composition of the waste, and the assumed as-generated waste density. In general, volume reductions obtained for the various treatment processes will be quite similar since all of the processes completely oxidize the organic materials in the wastes leaving the inorganic materials as residue. The resulting residues may be packaged as the final product or treated further by one of the immobilization techniques described in Section 12.0. The residues can also be treated for recovery of plutonium by methods described in Section 11.0.

As shown in Figure 9-1, three treatment options are being practiced for ion exchange resins and organic liquids: (1) drying or dewatering of the resins, evaporation of volatile solvents; (2) immobilization (by cementation, for example); and (3) combustion or chemical digestion to produce a non-combustible residue. When combustion or chemical digestion is used, the resulting residues can be treated for plutonium recovery. Of these three options, only the third will be discussed in this section; option 2 is discussed in Section 12.0.

*The volume reductions quoted are for primary treatment of the waste to a residue or ash and do not include other secondary wastes generated by the processes themselves.

TABLE 9-3. Incinerators Used for Combustion of Radioactive Solid Wastes

INCINERATOR INSTALLATIONS	LOCATION	YEAR BUILT	OPERATIONAL STATUS	CAPACITY kg/hr	OPERATING FEATURES	COMBUSTIBLE WASTE TYPE	WASTE ACTIVITY	REFERENCES
Knolls Atomic Power Lab.	N.Y.	1949	Not in operation	9-18	Single chamber; pure O ₂ ; 550°C	Cellulosic	Low	5
Argonne Nat'l Lab.	Ill.	1951	" " "	68	Single chamber; 450-600°C; vibrating grate; gas fired	"	Low	5
Bettis Atomic Power Lab.	Penn.	1953	" " "	—	Single chamber; cyclone air feed	"	Low	5
Shippingport Atomic Power Station	Penn.	—	" " "	18	Cyclone air feed	"	Low	6
United Nuclear Corp.	Conn.	~1960	" " "	95	—	"	U	7
Metals and Controls	Mass.	~1960	" " "	90	—	"	U	7
Pratt and Whitney Aircraft	Conn.	~1960	" " "	270	—	"	U	7
Douglas United Nuclear	Wash.	1967	" " "	—	Natural draft incinerator for open pit burning	"	Low	8
Yankee Rowe Atomic Elec. Co.	Mass.	~1968	In operation	18	Cyclone air feed	"	Low	9
Bradwell Power Station	U.K.	1967	" "	—	Rocking grate; afterburner	"	Low	10
Berkeley Nuclear Lab.	U.K.	1965	" "	—	—	"	Low	10
Hunterston "A"	U.K.	1967	" "	—	—	"	Low	10
Cadarache Nuc. Study Center	France	—	" "	30	Dual chamber; 1000-1100°C	"	Low	11
Fontenay-Aux-Roses Center	France	1967	" "	50	Dual chamber; 800-1000°C; oil or propane fired	"	Low	11
Bhabha Atomic Research Center	India	1966	" "	45	Dual chamber; 500-1000°C; Kerosine fired	"	Low	11
JAERI - Tokai	Japan	1966	" "	50	Dual chamber; 1000°C, oil fired	"	Low	12
JAERI - Oarai Research Establishment	Japan	1973	" "	30	Four chambers; 600-900°C; Kerosine fired	"	Low	13
Chalk River Nuc. Lab.	Canada	~1960	Not in operation	200	Dual chamber; 815-1200°C; tilting grate; propane fired	"	Low	5
Bruce Nuclear Complex	Canada	(1976)	Under construction	—	—	"	Low	14
Chalk River Nuc. Lab.	Canada	—	" "	—	—	"	Low	—
Nat'l. Lead Co. of Ohio	Ohio	1954	In operation	1000	Dual chamber; 980°C; gas fired	"	U	15
Union Carbide K-25	Tenn.	1972	" "	—	Dual chamber; 930-1100°C; gas fired	"	U	—
Union Carbide-Paducah	Ky.	—	Not in operation	—	—	"	U	—
G.E. Atomic Power Equipment Department	Calif.	1960	" "	45	Triple chamber; 760-820°C; gas fired	"	U	16,17
Goodyear Atomic Corp.	Ohio	1971	In operation	68	Dual chamber; 815-1000°C; gas fired	"	U	18
Gulf Gen. Atomics	Calif.	1963	" "	20	Dual chamber; 900-1200°C; gas fired	"	U	—

TABLE 9-3. Incinerators Used for Combustion of Radioactive Solid Wastes (cont'd.)

INCINERATOR INSTALLATIONS	LOCATION	YEAR BUILT	OPERATIONAL STATUS	CAPACITY kg/hr	OPERATING FEATURES	COMBUSTIBLE WASTE TYPE	WASTE ACTIVITY	REFERENCES
Nuclear Fuel Services	Tenn.	—	In operation	270	Dual chamber; gas fired	Cellulosic	U	—
Union Carbide Y-12	Tenn.	1955	" "	20	Single chamber; 870°C; gas fired	"	U	19
Babcock and Wilcox	Va.	1972	" "	80	Single chamber; 1090°C	"	U	20
LASL Pu recovery incinerator	N.M.	1952	" "	<1	Single basket; 800°C; electrically heated	"	Pu	5
Mound Lab. Pu recovery incinerator	Ohio	~1972	" "	23	Single basket; 800°C; electrically heated	"	Pu	—
U.S. Army Nuc. Defense Lab.	Md.	1963	Not in operation	23	Dual chamber; cyclone air feed	All (No Cl or S)	Low	21
Marcoule Center of Pu Prod.	France	1964	In operation	60-70	Triple chamber; 700-1100°C; propane heated	"	Pu	11
Center of Nuc. Studies - Grenoble	France	1961	" "	30	Dual chamber; 1000-1100°C	"	U	22
Kerr-McGee Nuc. Corp.	Okla.	1972	" "	70	Dual chamber; gas fired	"	U	—
Harwell Nuc. Research Center	U.K.	1962	" "	27	Dual chamber; 800°C	All	Low	11
Nat'l Center of Scientific Research - Strasbourg	France	1970	" "	15	Dual chamber; 700-800°C; moving grate; gas fired	"	Low	23
Nuc. Research Center (Pilot Plant) - Karlsruhe	Germany	1963	Not in operation	—	Single chamber; 900-1100°C; rotating bottom grid; electrically heated	"	Low	24
Nuc. Research Center - Karlsruhe	Germany	1971	In operation	50-70	Single chamber; 1000°C; rotating bottom grid; electrically heated	"	Low	25
Belgium Nuc. Center - Mol	Belgium	1960	Not in operation	200	Triple chamber; 900°C; gas fired	"	Low	11
Belgium Nuc. Center (Pilot Plant) - Mol	Belgium	1970	In operation	10	Single chamber; 900°C; tilting grate; propane fired	"	Low	26
LASL (Development)	N.M.	(1976)	Under construction	45	Dual chamber; 500-800°C; controlled air	"	Pu	3
Mound Lab. (Development)	Ohio	1975	In operation	35	Single chamber; cyclone air feed; 1100°C	"	Pu	—

TABLE 9-3. Incinerators Used for Combustion of Radioactive Solid Wastes (cont'd.)

INCINERATOR INSTALLATIONS	LOCATION	YEAR BUILT	OPERATIONAL STATUS	CAPACITY kg/hr	OPERATING FEATURES	COMBUSTIBLE WASTE TYPE	WASTE ACTIVITY	REFERENCES
Rocky Flats Plant (Development - Agitated Hearth)	Colo.	(~1980)	Under construction	70	Agitated hearth; 800-1000°C; diesel fired	All	Pu	4
G. E. Nuclear Fuel Plant	N.C.	1972	In operation	450	Vortex burner; 815-980°C; gas fired	"	U	27
Westinghouse Nuc. Fuel Div.	S.C.	1974	" "	—	Dual chamber; 650-1200°C; excess air burner	"	U	—
United Nuclear Corp.	R.I.	1967	Not in operation	45	Single chamber; gas fired	"	U	—
Windscale (Pilot Plant)	U.K.	1973	In operation	5	Pyrolysis unit; 1000°C electrically heated	"	Pu	28
Marcoule Center (Pilot Plant)	France	1970	" "	1	Dual chamber; 700-1100°C; electrically heated	"	Pu	29,30
Rocky Flats Plant (Development - Rotary Kiln)	Colo.	(~1980)	Under construction	40	Rotary kiln; 600-800°C; diesel fired	"	Pu	4
Rocky Flats Plant	Colo.	1959	In operation	16	Dual chamber; 1200-1400°C	"	Pu	11,31
Babcock & Wilcox Nuclear Materials Div.	Penn.	1969	Not in operation	9	Batch burner; dual chamber; gas fired	"	Pu	32
ARHCO Pu recovery incin.	Wash.	1961	In operation	2	Dual chamber; 700-800°C; moving grate	"	Pu	33

TABLE 9-4. Processes Under Development for Combustion of Radioactive Combustible Solid Wastes

PROCESS	PROCESS DESIGN FEATURES	VOLUME REDUC-TION FACTOR*	PRODUCT	PRODUCT REMOVAL	PLUTONIUM RECOVER-ABILITY	DEVELOPMENT STATUS					REFER-ENCES
						SITE OF DEVEL-OPMENT	TESTED CAPA-CITY kg/hr	RADIOACTIVE UNITS		COMMER-CIAL AVAIL-ABILITY	
								DESIGN CAPA-CITY kg/hr	SCHEDULED STARTUP		
Controlled Air Incineration	Dual combustion chamber; primary chamber 500-800°C; secondary chamber 800-1100°C	30-50	Non-combustible, highly refract-ory oxide	Batch	Difficult; HNO ₃ -HF leach	LASL	45	45	1977	1978	3,34,35
Cyclone Incineration	Vertical combus-tion chamber; air swirls and cools the wall. Temperature 1100°C.	30-50	Non-combustible, highly refract-ory oxide	Batch	Difficult; HNO ₃ -HF leach	Mound Labo-ratory	35	35	1978	1980	
Fluid Bed Incineration	Preheated gas mix-ture, fluidizes waste in Na ₂ CO ₃ salt bed; primary bed 550-600°C; in situ neutralization of HCl	20-40	Non-combustible refractory oxide	Semi-contin-uous	Difficult; HNO ₃ -HF leach	Rocky Flats	9	82	1977	1980	36,37
Rotary Kiln Incineration	Inclined rotating horizontal cylin-der; rotary hearth increases oxida-tion by exposing new waste; primary chamber 600-800°C; afterburner 1000°C	30-50	Non-combustible refractory oxide	Semi-contin-uous	Difficult; HNO ₃ -HF leach	Rocky Flats	2	40	1980	1982	4

TABLE 9-4. Processes Under Development for Combustion of Radioactive Combustible Solid Wastes (cont.)

PROCESS	PROCESS DESIGN FEATURES	VOLUME REDUCTION FACTOR*	PRODUCT	PRODUCT REMOVAL	PLUTONIUM RECOVERABILITY	DEVELOPMENT STATUS					REFERENCES
						SITE OF DEVELOPMENT	TESTED CAPACITY kg/hr	RADIOACTIVE UNITS		COMMERCIAL AVAILABILITY	
								DESIGN CAPACITY kg/hr	SCHEDULED STARTUP		
Agitated Hearth Incineration	Stationary circular hearth with rabble arms rotating periodically to discharge ash. Primary chamber 800°C; afterburner 1000°C	30-50	Non-combustible refractory oxide	Batch	Difficult; HNO ₃ -HF leach	Rocky Flats	4	70	1980	1982	4
Controlled Pyrolysis	Limited air combustion in a vertical retort distills volatile materials which burn in a second air-rich zone; primary zone 600°C, secondary zone ~1200°C	30-50	Non-combustible refractory oxide	Semi-continuous	Difficult; HNO ₃ -HF leach	PNL	15	**	**	**	38-40
Molten Salt Combustion	Air oxidation in molten Na ₂ CO ₃ - Na ₂ SO ₄ salt combustion medium at 800°C; <u>in situ</u> neutralization of HCl	30-50	Non-combustible salt-ash or an oxide if salt is leached	Semi-continuous	HNO ₃ (HF) leach	AI	50	50	1978	1978	41-42
Acid Digestion	Sulfuric-nitric acid oxidation of waste at 250°C; liquid system	30-50	Non-combustible sulfates and oxides	Semi-continuous	Good recovery with HNO ₃ leach	HEDL	5	5	1977	1980	43-46

*Assumes the same mixed waste for each process and initial processing only (i.e., no final conversion of residue nor secondary waste generated by the process itself).

**Not currently funded; estimated 3 years needed to develop process for commercial application.

For scrap recovery operations, the ease with which plutonium is recovered from ash residues may become a consideration in selecting the various treatment options. With the exception of acid digestion, which converts the plutonium to a sulfate, all processes yield plutonium oxide as a final product. The recoverability of the plutonium oxide is normally dependent upon the temperature of the process, with more refractory oxides (less soluble) being produced at the higher combustion temperatures. The refractory forms of plutonium are normally recovered from the residues by leaching with boiling nitric-hydrofluoric acid mixtures. However, nitric acid leaching alone may be satisfactory for recovery of plutonium from acid digestion or molten salt combustion residues.

9.3 MECHANICAL SORTING AND VOLUME REDUCTION TECHNIQUES

The available technologies for mechanical processing of combustible solid wastes prior to combustion or storage include hand sorting, shredding, air classification, and compaction/baling. Sorting is used to separate wastes into constituents which are amenable to treatment by a particular technology.

9.3.1 Hand Sorting

Sorting by hand is the simplest method of separating mixed waste. This may best be done at the point of origin. Frequently, however, the wastes are hand sorted after collection as part of a waste treatment operation. The sorted categories are determined by the available treatment options. Hand sorting may be used to assure separation of combustible from non-combustible materials; it may also screen against introduction of hazardous material (e.g., pyrophoric or explosive substances) into the processing area. Hand sorting is also used to separate leachable combustibles from nonleachable combustibles and, in some applications, halogenated combustibles from non-halogenated combustibles.

Hand sorting involves close contact with the waste and thus requires appropriate personnel protection from radiation exposure. Protective clothing and radiation shielding are used as appropriate. Sorting of plutonium-contaminated waste is accomplished in glove boxes or in walk-in rooms using pressurized suits.^(11,47,48) This latter operation is used at some sites for preparatory mechanical operations (e.g., cutting, shredding, etc.). Although the levels of radioactive contamination in combustible wastes vary considerably, there is little advantage in sorting waste according to radiation levels except where considerable reduction in volume of transuranic waste may be obtained.

Examples of sorting operations which have been applied at ERDA operating facilities are briefly discussed below.

Sorting of Line-Generated Combustibles at Rocky Flats Plant

At the Rocky Flats Plant, all line-generated combustibles are routinely sorted as pretreatment to subsequent physical volume reduction by compaction.⁽⁴⁹⁾ These wastes consist of paper, rags, plastics, etc., which are generated inside the drybox system and removed by a bag-out technique. The wastes are placed in drums and the full drums are assayed using a sodium iodide detector for measuring gram quantities of plutonium. Drums counted and found to be below the economic discard limit are declared waste and sent to sorting. The drums are put into a compactor drybox system where the wastes are sorted to remove noncompactible items and passed over a gamma survey probe. The wastes with excessive activity are returned to the generator for further treatment. Acceptable wastes are moved to the compactor and fed in slowly, using a variety of feed mix rather than feeding in only one type of waste at a time. This operation was installed in March 1973 and has proven successful in reducing the number of drums of waste generated at Rocky Flats by a factor of about 2.5. Its potential applicability to fuel cycle facilities is primarily for plutonium-contaminated wastes.

Sorting of Wastes According to Radioactivity at LASL

Room trash from plutonium laboratories at LASL is hand sorted to detect and separate those few contaminated items containing more than 10 nCi/g of alpha activity.⁽⁵⁰⁾ The room trash boxes are first screened by the MEGAS (Multi-Energy Gamma Assay System) to identify those boxes containing TRU-contaminated wastes. As a rule, less than 10 percent of the trash boxes assay at >10 nCi/g of alpha activity. Sorting of the individual waste items within the high assay boxes is then done by hand using a FIDLER (Field Instrument for the Detection of Low-Energy Radiation) - Pancake counter to detect and count the highly contaminated items. Problems arise with high density trash since this restricts the detectability and accuracy of the MEGAS counter. A discussion of the radioactive assay methods is given in Section 11.0.

Sorting Recyclable from Low Transuranic Wastes at LASL

Mixtures of plutonium process solid wastes arising from R & D activities at LASL are hand sorted to separate and recycle those with high plutonium content, and to separate wastes with low plutonium content into combustible and non-combustible fractions for retrievable storage.⁽⁵⁰⁾ Approximate assay is obtained with a hand held beta/gamma counter followed by the application of more precise nondestructive assay methods using segmented gamma scan or neutron counters.

9.3.2 Shredding

Shredding of combustible or potentially combustible waste materials into small pieces is sometimes desirable for subsequent processing or storage. A survey and an evaluation of shredding equipment available for application to low-level wastes has been made by Atomics International.^(34,51) The principal types of shredding equipment are hammermills, knife cutters, and variations or combinations thereof.

Hammermills consist of pivoted or rigidly mounted hammers on a vertical or horizontal shaft or rotor. The hammers may be rectangular or chisel shaped. Crushing or shredding takes place by impact between the hammers and a breaker plate.

Commercially available knife cutters used for size reduction fall into three broad categories: (1) fly knives mounted tangentially on a rotor to work against stationary bed knives; (2) finger knives mounted axially on a rotor to work against stationary anvils; and (3) finger knives mounted axially on two counter-rotating rotors. The first type is used for shredding plastics, rubber, and cellulose, including paper. The second type is used in rubber, pulp, and food industry applications. The third type is used for volume reduction of mixed refuse. For a given type and size of feed, knife cutters generally require less power than do hammermills. Knife cutters have the disadvantage of being susceptible to damage from tramp metal in the feed and of requiring the knives to be re-ground or replaced periodically.

Shredders with two-stage operations, which combine features of both hammermill and knife cutter, are also available. For example, a knife-cutter may be used in the first stage while the more rugged hammermill serves as a second stage.

The shredded product which emerges from both hammermills and knife cutters lends itself readily to air conveying. The air serves as a cooling medium for heat-sensitive materials, such as plastics, and thus prevents their sticking in the mill.

At Rocky Flats, a series of shredding tests was performed on typical waste materials using the following four shredders:⁽³⁶⁾

- a vertical-shaft hammermill with ring-type hammers;
- a horizontal-shaft hammermill with fixed hammers;

- a rubber chopper which cuts the material between rotating hammers or blades and stationary anvils. The material is forced through a stationary orifice plate and is cut again by rotating knives as it comes through the plate,
- a low-speed shredder which cuts the materials between cutters mounted on two parallel horizontal shafts rotating at different speeds and in opposite directions.

The waste materials tested included paper, plastics (PVC and polyethylene), and items less commonly found in wastes, such as surgeon's gloves, leaded gloves, HEPA filters, water filtering cartridges, etc.

The most acceptable shredder was the low-speed cutter unit (the last unit above) which could be installed in a glove box for operation. (Each of the other units would require installation in a canyon or hot-cell to provide adequate operating space.) This shredder was equipped with an over-torque device to prevent damage by tramp metal which might be in the waste. A similar shredder has been satisfactorily tested at HEDL.

The rubber chopper gave superior performance but was eliminated from consideration mainly because it was not protected from damage by tramp metal. The vertical-shaft hammermill was satisfactory in all respects except that it was quite large and would require disassembly for nuclear safety inspections. The horizontal-shaft hammermill was rejected because it did not satisfactorily shred large-size packages.

9.3.3 Air Classification

Air classification of waste materials by density differences is feasible following size reduction by shredding. The principal application is in the separation of combustible (low-density) from noncombustible (high-density) wastes. Closed system pneumatic sorting has not been demonstrated for handling nuclear process wastes. However, air classification is used for separating municipal wastes into noncombustibles (glass, metal, etc.) and combustibles (paper, plastics, etc.), the latter then being used as a source of energy.⁽⁵²⁾ Other than radioactivity and the operating scale of the treatment facility, no major differences exist between nuclear fuel cycle wastes and municipal wastes.

A schematic representation of an air classification system for feeding combustibles into a combustion system is shown in Figure 9-2. It is estimated that hand sorting should remove about 75 percent of the tramp metal from the trash fed into the classification system. The waste is then shredded and introduced to the classifier. By control of air flow rate, separation

FIGURE 9-2. Air Classification System for Introducing Combustible Feed into a Combustion System

is achieved with minimal mechanical hazard. The air classifier should operate under a slight negative pressure and at room temperature. An air velocity of about 500 to 600 meters per minute can be used to separate combustibles from tramp metal and other noncombustibles. The combustible material is then carried by the air stream to a cyclone separator where it is removed and the air recycled to the classifier. The material of greater density drops counter to the air stream and is collected in a hopper for periodic removal.

Systems for air classification are under development at Rocky Flats. Two units are planned in support of the fluid bed incinerator process, one for the pilot plant and one for the demonstration plant under construction. Tests have been made with simulated (but nonradioactive) waste materials. Both of these units will operate on actual production plant scrap or trash. Satisfactory pilot scale operation should be established in 1976 and production scale in 1977.

9.3.4 Compaction and Baling

Compaction is a process for mechanically reducing the volume of waste such that the waste package can be subsequently handled without risk of expanding. The subject has been reviewed in detail.^(11,53) Because of varying terminology in the industry, baling is sometimes considered to be synonymous with compacting. In compaction the waste is compressed inside of a container (such as a 200-liter drum) which then is closed. Baling, however, usually involves compressing the waste and then banding it so that it cannot expand; the bale may subsequently be packaged for further disposition.

Much of the low-level solid waste from nuclear fuel cycle facilities is compactible. Paper, fragments of plastic or rubber, rags, glassware, and small metallic items typically make up this category. Compaction methods should not be applied to the following:

- items so dense or so hard that there would be negligible or insignificant reduction in volume,
- items capable of damaging the presses (e.g., very long metal items which might jam between the ram and the bottom of the press) or penetrating the container,
- pyrophoric or explosive substances,
- wastes containing free liquids.

Presses with either a horizontal or a vertical ram can be used, depending on the application and the space available. The pressure used will vary between 30 and 150 kg/cm² according to the reduction factor required. Each waste exhibits a threshold pressure region which is limiting for volume

reduction. Thus, compaction pressures above the threshold region lead to only small additional decreases in volume when compared with compaction in the working pressure region. Systematic experiments have shown that for average materials the maximum volume reduction requires a pressure of about 65 kg/cm^2 .⁽¹¹⁾ In general, a pressure of $30\text{-}50 \text{ kg/cm}^2$ is adequate.

For typical waste materials, a pressure of 30 kg/cm^2 gives a reduction in volume of 2 to 5, while a pressure of 50 kg/cm^2 yields a 5- to 15-fold reduction in volume. The volume reduction obtained from compacting waste depends on the applied force, the bulk density of the waste material, and the springback of the material when the pressure is released. Springback results from the elasticity of the compressed waste. The more elastic wastes have greater springback and lower final volume reduction factors. Volume increase resulting from springback is most pronounced in the first few minutes after the pressure is released. Springback can be significantly reduced by baling or by putting the waste in thin-walled cans prior to compaction. The springback from compacted paper or other waste which behaves as a semi-elastic material also can be reduced by applying higher pressure or applying pressure for a longer period of time.

Compaction forces out the air contained in the wastes, creating a risk of airborne contamination. Precautions must therefore be taken to contain the expelled air. For TRU wastes or wastes containing toxic materials such as beryllium, the compacting equipment must be placed in a ventilated enclosure. In less serious cases, a ventilation hood will satisfactorily remove aerosols produced by the compaction process.

A typical dry waste compactor is shown in Figure 9-3. It consists of a hydraulic system with a ram operating vertically downward, a contoured support plate, frame and safety enclosure with loading table, vent, and filter system with fan, gages, and controls. The drum extension space is evacuated by a built-in fan which draws the air through a roughing filter and then through a HEPA filter.

A special application combining shredding and baling is being tested at the Rocky Flats Plant. The shredder-baler system will shred and compact non-line-generated combustible, compressible wastes. Combustible wastes which are collected outside the dryboxes are placed in 200-liter drums. These drums are then counted using sodium iodide detectors for measuring gram quantities of plutonium. All drums containing nondetectable amounts of plutonium are sent to the shredding operation. The drums are emptied onto a sorting table where tramp materials are removed to avoid damaging the shredder. The wastes are then fed by conveyor belt to the shredder where they are reduced to an assortment of particles averaging 5 mm in size. These

FIGURE 9-3. Drum Compactor for Dry Wastes
(Courtesy Stock Equipment Company)

particles pass out of the shredder chute directly into the baler, which is capable of baling particles as fine as sawdust. Bales are wire-tied before being bagged. The bales measure about 50 cm x 60 cm x 120 cm and weigh about 90-180 kg. Eight of the bales will fit in a standard 120 cm x 120 cm x 210 cm fiberglass-coated plywood box used for waste shipments and storage.

9.4 FEATURES COMMON TO COMBUSTION PROCESSES

Although incineration is simple in principle, it presents a number of technical difficulties, especially in connection with the performance of the auxiliary support systems. A 1970 report prepared by the AEC lists the following problems encountered in the operation of incinerators (note that these are technical problems and not basic faults):

- organic material in the effluent from incinerators clogs filters and other effluent treatment devices
- use of inadequate scrubbers requires very rapid replacement of HEPA filters
- spread of contamination results from improper handling of input waste material and output solids from the incineration process.

Generally, incinerator systems have not provided the desired performance and have been expensive to maintain. To alleviate these problems, a number of alternative combustion systems are being developed in the United States; and several technical alternatives should soon be available for safely and efficiently incinerating radioactive combustible wastes.

9.4.1 Functional Description of Combustion Systems

The application of combustion or incineration to the treatment of combustible solids requires the coupling of several processes or unit operations into a total waste treatment system, as illustrated in Figure 9-4 and discussed in the following sections. Waste composition and the degree of radionuclide contamination are the primary factors determining combustion system design. The effects of these compositional factors can be summarized as follows.

Cellulosics

Pure cellulosic feeds present the least demanding requirements with respect to system design and operation. Sorting of feed materials to assure that other undesirable materials do not enter the system is a prerequisite. In general, presently available technology can be directly applied to incineration of low-level cellulosic waste of fairly uniform composition. Incinerators can be sized for almost any required throughput.

Plastics and Rubbers (Non-Halogenated)

Plastic melting can cause plugging problems in both the feed system and the furnace. Melted plastics can jam the feeder and present a fire hazard in the feed system. Thus, a waterspray or inert gas system is required for most feed systems. Melted plastics can clog furnace grates if small mesh grates are used; larger meshed grates may allow the unburned plastics to drop into the ash below. If grates are not used, the melted plastics may clog openings on the bottom of the furnace. Stair- or dish-type grates may be used, or the waste can rest on the bottom of the furnace if all openings are elevated above the floor.

Plastics and rubbers have higher heating values than do most cellulose; therefore, they should be uniformly mixed with the waste (even shredding has proved ineffective at times) to avoid pressure surges during combustion. If adequate oxygen is not available, pyrolysis and cracking of the lighter hydrocarbons may occur, producing heavy tars and soot that are difficult to oxidize. Soot entrained in the off-gases may lead to clogging the off-gas cleanup system and to filter fires.

Incomplete combustion, need for frequent replacement of filters, and danger of filter fires must be considered in incineration of mixed wastes. Two obvious approaches are improvement in furnace design and use of a device in the off-gas train designed especially to remove soot. Multi-chambered incinerators, adequate residence time, high operating temperatures, and adequate oxygen are used to achieve good combustion while feeding plastics and rubbers. Some facilities use baffles or beds of silicon carbide in the final combustion chamber in order to promote oxidation.

Halogenated Plastics and Rubbers

Additional precautions are required to minimize corrosion when burning wastes containing halogenated materials because of the generation of acidic off-gases (HCl, HF). Wet systems are normally used to remove the acids from the off-gases. They require corrosion-resistant materials such as graphite, fiberglass-reinforced plastic, titanium, glass, polyethylene, etc. Many of these materials will not withstand high temperatures; therefore, the gases are cooled before coming in contact with them. Dry systems, with beds of Na_2CO_3 pellets to remove HCl, are also used. They require that the gases be kept at temperatures above their dew points.

Miscellaneous Waste Materials

Several less frequently incinerated waste materials may require special design or operational considerations. Tributyl phosphate generates a P_2O_5

aerosol that is very difficult to remove. Sodium and vanadium salts can attack the refractory lining of the furnace. Leaded rubber gloves contain filler materials (Pb_3O_4 , MgO , Al_2O_3 , SiO_2 , ZnO , TiO_2) that form a eutectic at about 650°C . Incineration of sulfonated polystyrene ion exchange resins releases SO_2 , an acidic gas. Solid waste incinerators can be used to dispose of small amounts of laboratory liquids (both aqueous and organic) of highly variable content. While liquid and solid wastes can be burned in the same combustion chamber, the resulting operation is rarely optimum for either waste type.

Radioactive Contamination

Operation of the combustion equipment for radioactive wastes will, of course, cause it to become radioactively contaminated. Equipment design involves appropriate consideration of the potential radiation problems associated with both maintenance and routine operations with the intent to minimize personnel radiation exposure through adequate shielding and confinement of aerosols.

Some wastes generated in fuel reprocessing and fabrication operations can contain significant amounts of fissile materials such as ^{239}Pu . In the processing of these wastes, criticality considerations are an integral part of safe design. Criticality safety is assured by strict inventory control, use of safe geometric configurations, radiation warning devices, and neutron poisons.

9.4.2 Feed Preparation

Wastes scheduled for combustion are characterized and inspected to assure that hazardous materials and items generally incompatible with the system are eliminated from the process feed stream. Hand sorting, shredding, air classification, etc., discussed earlier, are all options.

Prior to its introduction into the combustion system, feed material must be conditioned to make it acceptable for burning. The type of combustion system selected and the compositional makeup of waste fed into the combustor are primary factors which must be considered in specifying feed preparation systems. Size reduction by shredding is a general prerequisite for most combustion systems. Sorting and shredding techniques have been discussed in Section 9.3.

9.4.3 Feed Systems

Feed systems vary widely from a simple manual batch feed charge to continuous systems incorporating automatic feed sorting and classification, blending, shredding, and pneumatic feed charging. The feed charging system is selected after careful review of feed characteristics and combustion

system operational and design requirements. A few of the options commonly used are summarized below with specific applications described in the later technology summaries.

Batch Feed (Manual)

In the simplest feed system, commonly used with scrap from uranium operations, a large batch of material suitable for several hours of burning is manually charged to a large combustion chamber where it is put through a complete burn cycle. The cycle is restarted by charging a new batch and reinitiating the cycle.

Semi-Continuous Feeders

A semi-continuous process can be obtained by charging small batches of feed into the combustion chamber on an incremental basis. This method provides better control of the combustion process, optimizes ash properties, and reduces the fluctuations in combustion gas flows which make effluent treatment more difficult.

The most common way of charging feed on a semi-continuous basis is by a gravity drop airlock from above or by a side-charging ram-type feeder. These systems are commonly provided with a double door airlock to minimize air surges through open doors and to reduce the chance of flashback into the feeder. Air surges make stable operation within the combustion chamber and off-gas train difficult. Semi-continuous feed systems are readily adaptable to operation with radioactive materials since feed can be handled in pre-packaged units.

Continuous Feed

Combustion control and stability can be further improved by going to a continuous feed system. Continuous feed may be combined with feed shredding and blending to minimize variations in feed composition and further improve system stability. The feed is generally introduced into the combustion chamber by a conveyor, screw feeder, or pneumatic transport. The pneumatic system may also result in increased capacity per unit volume and improve combustion efficiency. With this approach, the advantages of a contained prepackaged feed are lost, however, and mechanical complexity of the feed handling system is increased. Sorting to remove tramp metal and other objects which might damage equipment is generally required.

9.4.4 Ash/Residue Removal Systems

Ash/residue handling and removal systems vary from simple manual raking to complex, fully-automated mechanical systems. The ash removal system is

tailored to the specific characteristics and requirements of the total system. Some of those commonly used for contaminated ash handling are described below.

Manual Removal

Removal of ashes from the primary combustion chamber or an ash pit into a container with a shovel or rake is the simplest means of ash handling. This method is usually adequate for low throughput systems. Containment (glove boxes or similar barriers) is required to assure personnel protection.

Pneumatic Removal

A standard "vacuum cleaner" or modification thereof is an effective way to handle ashes, particularly where cleanout of a unit between runs for inventory purposes or criticality control is required. A pneumatic system requires the treatment of discharged gases; however, existing systems provided to handle combustion gases may be used for this purpose. Pneumatic systems are limited by their inability to handle large or heavy objects (e.g., clinkers) which may be present in the ash residue.

Automatic Removal

Moving grate, rotary grate, and rotary kiln incinerators are self-cleaning units and are more mechanically complex options for handling high activity materials. Ram feeders may also be used to automatically displace ashes into a drop box or receiver on a semi-continuous basis.

9.4.5 Off-Gas Treatment

Waste composition, combustion process design, and type and level of contamination dictate off-gas treatment requirements. Materials of construction are affected by feed composition and the corrosivity of the resultant combustion products. These materials problems, in turn, affect selection of cleanup equipment. The type and extent of feed contamination affects combustion gas contamination levels and defines the decontamination factors required prior to combustion gas release to the environment.

Both wet and dry off-gas cleanup systems are used. The wet systems use aqueous scrubbers in combination with de-entrainment devices to remove fly ash and acidic vapors. Dry systems use cyclone separators, electrostatic precipitation, filters, and similar devices to remove fly ash and aerosols. Special filters are available to remove soot and tars not burned in the primary or secondary combustion chambers. Typical components are described in the following sections.

Wet Systems

Packed towers and spray chambers are frequently used as off-gas scrubbers to remove acidic vapors and fly ash. Water is most often used as the scrub liquid, but alkaline solutions are more effective for removing acids through neutralization. The effectiveness of the scrubber is greatly increased by adding a de-entrainment device to remove aerosols from the exiting gas stream. The Brink Mist Eliminator, developed by Monsanto Company, is one of the more effective devices tested for this service; however, its ability to handle fly ash without plugging must still be demonstrated. A spray scrubber followed by a Brink Mist Eliminator is being tested in conjunction with Mound Laboratory's cyclone incinerator development program.

More effective scrub contact for aerosol removal is obtained by the use of high-energy scrubbers, such as the venturi scrubber. These devices effectively remove micron- and submicron-sized particles, the efficiency being proportional to the energy expended in the contact process. Several of the combustion units under development in the United States use venturi scrubbers as the primary off-gas treatment.

A discussion of available wet scrubbers, together with a discussion of theoretical and practical considerations, is provided in Reference 54.

Dry Systems

Totally dry systems offer the advantage that they do not produce a secondary liquid waste requiring treatment as the wet systems do. However, the more efficient dry systems are subject to plugging, and they generally cannot remove acidic off-gases. Many systems, therefore, use a combination of wet and dry components to gain the advantages of both. Typical hybrid systems include cyclone separators to remove the bulk of the fly ash, wet scrubbers to remove the acid vapors, condensers and heaters to dry the gas, and absolute filters to remove residual aerosols. Typical dry system components in radioactive service include the following:

Cyclone Separators. Cyclonic separators utilize centrifugal forces acting on denser solids to separate particulate matter from a gas vortex. Cyclones are economical, especially for removal of large particles (>10 microns), and are widely applied in industrial systems. Because of their economy, cyclone separators are often used as a pretreatment to reduce the particulate loading on subsequent off-gas treatment systems. Due to their limited efficiency when handling submicron particles, cyclones in radioactive systems are used in conjunction with more efficient aerosol removal systems. A detailed description of cyclone design theory and applications may be found in Reference 55.

Electrostatic Precipitators. Electrostatic precipitators are commonly used to remove aerosols from the flue gases of large coal-fired power plants and metallurgical smelting plants.⁽⁵⁶⁾ They are quite efficient (95-99%) in these services. They are well suited for large capacity service ($3000 \text{ m}^3/\text{min}$) due to low pressure drop and low energy requirements. Other advantages of precipitators are: 1) high efficiency on small particles, 2) dry product recovery, 3) ability to operate effectively at elevated temperatures ($>550^\circ\text{C}$), and 4) low operating cost.

Disadvantages of these units are: 1) they must be designed for a specific set of conditions, 2) their efficiency may degrade rapidly as operating conditions vary from those for which they are designed, 3) initial capital requirements are high relative to other gas cleaning systems, and 4) the high voltage electrical systems present possible safety problems.

The near term use of electrical precipitators in radioactive waste service is uncertain due to the variability of off-gas composition in incinerators, high initial cost, and lack of system flexibility. The high efficiency on small particles makes use of the electrostatic precipitator in conjunction with a coarse material separator (cyclone, etc.) a possibility for future considerations, however. Efficiencies as high as 99.99% have been reported in radioactive service.⁽⁵⁷⁾

Bag Filters. The standard commercial bag filter can give very good aerosol removal efficiencies. With their relatively large surface area (0.3 to 3.0 m^2 per m^3/min flow), they can accommodate some tars. The large physical size of these units, maintenance requirements on blowback systems, need for bag replacement, and potential for bag failure are disadvantages in radioactive service.

Filter Candles. Filter "candles" made of ceramic material or asbestos-lined metal have been developed to remove soot from incinerator off-gases. The trapped soot can subsequently be burned off harmlessly. Further development work on these units is being done in Europe and Japan.⁽²⁴⁾

Sintered (Porous) Metal Filters. The porous metal filter is a candidate for use in radioactive combustion gas cleanup.⁽³⁷⁾ Its rugged construction, good flow capacity (comparable to a bag filter), and high temperature capability ($>500^\circ\text{C}$) are a significant improvement over the standard bag filter. They have also been used to remove soot, but they tend to become plugged with tars from incomplete combustion.

Sand Filters. Sand filters are another option for removing soot and tars from incinerator off-gases. A moving bed system, being installed by Belgonuclaire, will recycle the sand through a calciner for reclamation.⁽²⁶⁾

HEPA Filters. HEPA filters will remove 99.95 to 99.97% of 0.3 micron diameter particles. They serve as a standard for comparison of other high efficiency filtration devices. The primary shortcoming of the HEPA filter is that it plugs up with high inlet dust loadings and it is not regenerable (i.e., cannot be cleaned). These filters must be replaced before excessive pressure drop allows pressurization of the combustion chamber.

Where high radioactive particle decontamination factors are required, the HEPA filter is the system of choice as demonstrated by its wide acceptance and use by the nuclear industry. In the presence of high dust loading, or where frequent changeout is hazardous or inconvenient, a preliminary cleanup system or roughing filter is used in conjunction with the HEPA.

Further information on dry filter applications is presented in Section 13.0 and Reference 58.

9.5 COMBUSTION TECHNOLOGIES

The necessary conditions for achieving complete combustion in any incinerator are: 1) adequate residence time; 2) adequate temperature (to promote complete combustion); 3) turbulence (to promote good mixing); and, 4) sufficient oxygen. Problem areas in the past have included spalling and warping of construction materials, incomplete combustion (leading to excessive carbon in the ash and creating problems for the off-gas cleanup system), clogging, fires outside the furnace chamber (including flashback in the feeder and soot fires in the off-gas cleanup system), inadequate ash handling and off-gas cleanup systems, and corrosion (particularly if sulfur or halogen-containing compounds are part of the waste).

An extensive development program is currently underway in this country to demonstrate and apply specific improvements to alleviate the problems that have been identified. Summaries of the combustion concepts under development in the U. S. are presented in the following discussion, along with a discussion of three operating units (General Electric's vortex incinerator, ARHCO's moving grate incinerator, and the pyrolysis incinerator used at Windscale, UK) which have unique features for burning radioactive wastes. In addition, two incinerators designed specially to burn contaminated waste solvents are described.

9.5.1 Incinerator Types

Numerous types of furnaces are used for incineration. They range from single-chambered systems to complex multi-chambered units and include fluidized bed, moving grate, and rotary kiln designs.

Incinerators are classified by various characteristics which have no common basis. For example, they are classified according to shape, such as open pit or multiple chamber; to the amount of air used, such as controlled air or excess air; and to moving parts, such as rotary or moving grate. A given incinerator is commonly identified by referring to only one of these classifications. A general discussion of the types of units that have been used in the nuclear industry follows.

Excess Air (Firebox) Incinerator

Older single-chamber incinerators supply excess air in addition to that required for combustion. The use of surplus air results in lower burning temperatures and more fly ash carryover than are obtained in the more modern controlled air incinerators.

Controlled Air Incinerator

Controlled air systems use the concept of multiple-chamber burning to achieve complete combustion of solid waste. Charges of waste enter the first chamber where they burn in the presence of substoichiometric quantities of air. The products of partial oxidation and volatilization flow into a secondary heated combustion chamber where excess air provides complete combustion. This mode of operation produces a nonturbulent combustion environment in the first chamber and minimizes the entrainment of fly ash.

The most frequently used configuration consists of two stacked, horizontal cylinders. Smaller units do not have a secondary chamber and use the stack for secondary, or gas-phase, burning. Most designs have multiple natural gas burners for maintaining temperature control in the chambers.

Pyrolysis-Incinerator

In a pyrolysis-incinerator, combustible material is thermally decomposed in an oxygen-deficient atmosphere to yield a volatile gas which is subsequently combined with excess air and burned in a secondary combustion chamber. A pyrolysis-incinerator depends on accurate control of the amount of air fed to the burning chambers for efficient operation.

Vortex Incinerator

The vortex, or suspended burning, incinerator consists of a stationary, refractory-lined cylinder into which the finely ground waste is pneumatically fed. Excess air ($\sim 300\%$ of the stoichiometric requirement) is introduced tangentially, giving a spiral burning pattern to the suspended waste as it passes through the incinerator. The excess air coupled with its high velocity through the chamber causes much fly ash carry-over and may require a correspondingly large gas treatment system. Primarily designed for high

burning rates, this incinerator is used in the lumber industry to burn bark and scrap. Its primary success has been in applications using only one type of feed which can be easily shredded or ground to a fine consistency for pneumatic transport.

Fluid Bed Incinerator

Shredded wastes are introduced into a vertical, fluidized bed of inert material. The highly agitated fluidized system improves mixing and combustion efficiency. It also provides improved temperature control due to the heat dissipation properties provided by the fluidized inert material. Substitution of pelletized sodium carbonate for the inert bed material provides additional benefits through neutralization of acidic combustion products, such as HCl, thus permitting use of less expensive construction materials in the incinerator and off-gas treatment system.

Rotary Kiln Incinerator

The primary combustion chamber is a tilted horizontal cylinder that rotates on its longitudinal axis to provide a tumbling action for improved combustion efficiency. The unit also provides positive ash removal from the combustion chamber, which is a definite advantage for assuring plutonium inventory control. Off-setting these advantages are the complicated mechanical drives and the need for effective seals. The seals represent a containment problem and cause difficulties in control of the combustion air.

Moving Grate Incinerator

The moving grate or rotating grate incinerator uses the motion of the grate to move waste material and constantly expose new unburned material for combustion. The moving grate also provides positive ash discharge for improved plutonium inventory control. This system, due to its internal moving parts, presents greater maintenance problems than other types of incinerators.

Development Status: Demonstrated in cold pilot plant at batch rates in excess of 35 kg/hr and with materials spiked with ^{238}Pu (<100 nCi/g waste). The gaseous effluent has shown no detectable radioactivity after filtration through a deep bed fiber filter. Technology should be available in 1978 for commercial plants.

9.5.2 Cyclone Incinerator (Mound Laboratory)

In 1965 the incineration of combustible waste was begun at Mound Laboratory for the recovery of plutonium. In 1973 efforts were directed toward developing an incinerator for reducing the volume of low activity combustible wastes. Detailed design of a pilot plant unit began in 1974 to provide information required for design of the incinerator. The pilot plant was completed in early 1975 and has processed nonradioactive waste at rates in excess of 35 kg/hr.

Process Operating Conditions and Features

The incinerator burns waste in a vertical chamber with air forming a swirling movement in the burning chamber. The swirling air serves to cool the outer walls of the incinerator as well as providing intimate contact with the waste. Combustible materials such as cloth, paper, polyethylene, polyvinylchloride, and rubber are incinerated at approximately 1100°C. The combustible waste may be hand-loaded into a stainless steel burning chamber or, alternately, a preloaded 0.2 m³ drum may be used as the burning chamber. In either method the incinerator system does not require expensive materials of construction or supplementary fuels. The system also lends itself to a modularized design. A number of burn chambers and in situ drum stations can be serviced by a central off-gas handling system.

The off-gas from the incinerator is first cooled and neutralized in a deluge chamber. The off-gas is then filtered by an irrigated, self-cleaning, deep bed fiber filter with a particle removal efficiency approaching that of a HEPA filter. The spent scrub liquid from the deluge and deep bed filter is cleaned of residual solids by conventional filtration and recycled. The filtered solids, along with the ash remaining after incineration, may then be treated for plutonium recovery or immobilized and sent to storage.

Status of Development

The system has been successfully tested with materials spiked with ²³⁸Pu. Optimization of the process is being pursued. Tests have progressed to where batches containing varying percentages of cellulose, rubbers, and plastics have been incinerated at rates in excess of 35 kg/hr.

Major Development Objectives

The primary objective is to develop a turbulent air incinerator system for significantly reducing the quantity of waste requiring storage. A modularized, remotely operated, turbulent air incinerator pilot plant will be designed

and built during 1977. Installation of the pilot plant, including waste collection drum recycling, will be completed by early 1978. The pilot plant will then be operated for the next nine months to a year to identify unexpected problem areas and to accumulate the engineering data needed for the design of a commercial plant. The pilot plant will be tested with radioactively contaminated wastes.

9.5.3 Controlled Air Incinerator (LASL)

Process Summary

Process Description: Combustible solid wastes are combusted in a starved air incinerator operated at 500-800°C. Volatile components and entrained solids are further oxidized in an air-rich secondary chamber operated at 1000-1500°C.

Applicable Waste: All combustible solid wastes.

Waste Pretreatment Required: Sorting, shredding, and blending of feed to improve stability of combustion.

Final Product Form: Dry ash which is both thermally and radiolytically stable.

Process Effluents: Combustion gases and acidic or neutralized off-gas scrubber solutions.

Principal Advantages: Limited air input to the primary chamber reduces ash entrainment while producing well-controlled reactions.

Potential Problem Areas: Corrosion of the off-gas system from acidic gases and a complex off-gas cleanup system.

Development Status: A controlled air incinerator has been installed at LASL and is undergoing testing on nonradioactive materials. Planned startup of the unit to demonstrate system suitability on a plant operational scale is planned for 1977. Design throughput of the system is 45 kg/hr.

9.5.3 Controlled Air Incinerator (LASL)

A commercially-available, starved air incinerator is being tested at LASL to identify modifications necessary for application to radioactive wastes.^(3,34,35) The incineration study is part of a development program on treatment processes for transuranic contaminated solid wastes.

Process Operating Conditions and Features

The controlled air incinerator at LASL consists of two combustion chambers located one above the other. The primary chamber consists of a 1.8 m diameter horizontal cylinder, about 2.4 m long. The secondary chamber is about 1.7 m in diameter and about 2.1 m long. Wastes are fed by a ram feeder into the primary chamber which is operated under starved air conditions at 500 to 800°C.

The incinerator chamber shells are carbon steel. High-density, 2000°C plastic-type refractory (more easily repaired and more resistant to thermal cycling than castable refractory) lines both chambers. Mineral wool insulation between the refractory and the shell reduces exterior surface temperatures to ~120°C. The inside of the incinerator shell is coated with 5 mm of an industrial mastic stack coating containing chlorosulfonated rubber to protect against combustion-produced acids. Sample ports and view ports are located in both chambers. Oversize access doors were specified to provide ample clearance for remote operations.

Off-gases from combustion are mixed with additional air as they pass into the secondary chamber where the unburned volatile components and entrained solids undergo further oxidation at 1000-1500°C. Both chambers are heated with auxiliary natural gas burners. Off-gases from the secondary chamber can exit directly to a refractory-lined stack if no radioactive materials are burned, or can be diverted through various test off-gas cleanup systems. The first off-gas cleanup system to be tested includes, in order of position in the train, a quench chamber, a variable throat venturi scrubber, a packed column, a water-cooled condenser, a heater, a roughing filter, and two HEPA filters. The off-gas cleanup system has been designed so units can be removed or new units added. Thus, selected components can be studied to improve overall off-gas cleanup performance.

Ashes accumulated during combustion drop through an orifice in the chamber floor or are vacuumed from the combustion chamber.

Status of Development

Controlled air incineration is a demonstrated method for burning industrial wastes. The LASL R&D incinerator for radioactive wastes has been

installed in a plutonium facility and is currently undergoing nonradioactive testing. The amount of plutonium in the facility will be limited to 100 grams. The test facility includes: 1) package assay, sorting, and feeding equipment, 2) the incinerator, and 3) the off-gas train. The unit is scheduled for startup in 1977 to demonstrate full-scale incineration of contaminated wastes.

Major Development Objectives

There are several major development objectives for the LASL incinerator development program. These include determination of:

- System modifications necessary to meet radiological health and safety standards.
- Operating conditions necessary to achieve maximum possible combustion of anticipated waste components.
- Satisfactory feed introduction and continuous ash removal.
- Optimum feed preparation method.
- Off-gas cleanup requirements to provide adequate pollution control and to achieve minimal liquid effluents.
- Safe operating conditions for plutonium-contaminated wastes.

While the incinerator test program will initially use nonradioactive wastes, it will eventually use slightly contaminated transuranic wastes to demonstrate plutonium handling capabilities and equipment maintainability. Radioactive tests with transuranic-contaminated wastes are planned in 1977.

9.5.4 Pyrolysis-Incineration Unit (PNL)

Process Summary

Process Description: Combustible wastes are dried, pyrolyzed and combusted with air (about 20 percent of the stoichiometric requirement for complete combustion) in a deep, fixed-bed vertical retort. Volatile combustion products are destroyed in a secondary burner.

Applicable Wastes: Appropriate mixes of all combustible solid wastes can be processed. Capability to process combustible liquids could possibly be designed into process.

Waste Pretreatment Required: Sorting and possible shredding.

Final Product Form: Inorganic ash, thermally stable with properties suitable for conversion to other low leachable forms such as a glass.

Process Effluents: Combustion gases, possibly requiring water or alkaline scrubbing for HCl removal before discharge.

Principal Advantages: Essentially flameless combustion of carbonaceous residue occurs at the base of a deep bed of fuel which minimizes any possible loss of fire. Potential for in situ neutralization of HCl.

Potential Problem Areas: Destruction of tars in the product gas without line plugging and handling of chlorides must be demonstrated.

Development Status: The process has been demonstrated with simulated, non-radioactive waste at a rate of 15 kg/hr in a nonradioactive pilot plant facility. Further development for radioactive waste has been suspended.

9.5.4 Pyrolysis-Incineration Unit (PNL)

Development of a pyrolysis process for the recovery of silver from photographic negatives was initiated at PNL in 1969. This work was followed by development of a pyrolysis-incineration process for municipal refuse sponsored by the Environmental Protection Agency and the City of Kennewick, Washington. Advantages inherent in the process, primarily production of an essentially ash-free off-gas and simple, safe operation, led to its adaptation for processing transuranic-contaminated solid wastes.⁽³⁸⁻⁴⁰⁾ Nonradioactive studies on pyrolysis of wastes typical of the nuclear industry were initiated in 1974. The process is based on technology that has been used for many years for the continuous production of town gas from charcoal, anthracite, and coal in fixed bed gasifiers.⁽⁵⁹⁾

Process Operating Conditions and Features

Shredded combustible wastes are fed into the top of a 28 cm diameter by 2.1 m high vertical shaft retort through a lock hopper and auger feed system. The vertical retort is made of refractory-lined carbon steel. A carbon steel compactor pushes the waste material down the vertical shaft and distributes the material over the cross-section of the retort. The waste materials form a deep, fixed bed in the retort. They are dried, pyrolyzed, and converted to an ash at the base of the bed as they descend countercurrent to 1200°C gases produced by combustion of carbonaceous pyrolysis products with air in the lower reaction zone. At steady state, the bed of waste material in the reactor consists of the following zones from bottom to top:

- An ash layer approximately 20 cm deep which is continuously discharged through a rotary grate and a star valve at the base of the reactor.
- A 15 cm high combustion zone in which all the heat for the process is generated by reaction of the oxygen in air with carbonaceous residue from pyrolysis of waste in the next upper zone.
- A pyrolysis zone, approximately 50 cm high, in which the waste material is pyrolyzed by hot gases rising from the combustion zone.
- A preheat and drying zone from 40 to 80 cm high in which the waste is dried and preheated by rising hot gases as it starts its descent through the retort.

The waste is ignited initially by charging about 5 kg of ignited charcoal to the empty chamber, starting the air flow and introducing the shredded waste. Use of a heating element or external furnace at the lower end of the pyrolysis chamber would be alternative methods for igniting the waste.

Superficial linear gas velocities in the upper zones of the retort are generally less than 15 cm/sec. At these low flow velocities and with the filtering action of the upper zone of waste material, very little carryover of ash material occurs. The gases are laden with pyrolysis products (HCl, moisture, and hydrocarbons) and combustion products (H₂O, CO₂, and CO) which are burned in a low calorific gas burner. Although the gases are sufficiently low in aerosols to meet federal air quality standards for stack gas emissions, they would require treatment with absolute filters in applications to radioactive wastes.

The pyrolysis system can be altered to retain chlorides, which are currently vented with the gas stream. Solid sodium carbonate can be added to the main reactor with the combustible wastes, in which case most of the chlorides would be retained by the ash.

Status of Development

The basic pyrolysis-incineration process has been demonstrated using simulated nonradioactive wastes at a rate of 15 kg/hr in the pilot plant retort. A high-density, alumina refractory has been found suitable as the construction material for the main reactor vessel.

Major Development Objectives

Sustained, long-term operation of the demonstration unit will be completed by early 1976 to determine the following: 1) distribution of inorganic elements between the gas products and ash residue; 2) gas cleaning requirements as they relate to off-gas system design and chloride removal; and 3) quantity and characteristics of tars generated in the process. Requirements for ash fixation in a glass and properties of the glass will also be determined by 1976. Further development work on the pyrolysis-incinerator for treating TRU-contaminated wastes has been suspended.

9.5.5 Pyrolysis Incinerator (Windscale, UK)

Process Summary

Process Description: Shredded wastes are pyrolyzed in an air-deficient chamber at 900°C. Volatilized materials pass to a second chamber where they are combined with excess air and heated to 1000°C by electrical resistance elements to assure complete oxidation. Ash is displaced from the pyrolysis chamber to an ash pit by the feed charging ram.

Applicable Waste: Appropriate mixes of all combustible solid waste materials.

Waste Pretreatment Required: Sorting is advisable to remove bulky or non-combustible items. Shredding and blending of feeds is desirable to improve thermal decomposition.

Final Product Form: Dry ash suitable for further stabilization or agglomeration; ash may have high residual carbon levels.

Process Effluents: Combustion gases and HCl-containing scrub solution.

Principal Advantages: Flameless combustion which produces a safe and inert product; no supplementary fuel required.

Potential Problem Areas: Incomplete destruction of waste materials and formation of soot.

Development Status: Unit has been in operation at the BNFL Windscale plant in the United Kingdom since 1973.

9.5.5 Pyrolysis Incinerator (Windscale, UK)

Since 1950, various radioactive waste incinerators have been operated in the United Kingdom with mixed success.^(10,11) The problem of efficient combustion of heterogeneous radioactive wastes led to the development of a pyrolysis incinerator. A pilot plant test unit was constructed at Windscale and began operation with radioactive wastes in early 1973 at an average feed rate of 5 kg/hr.⁽²⁹⁾

Process Operating Conditions and Features

Shredded combustible waste materials packaged in small cardboard cartons are fed to an electrically-heated, horizontal Inconel tube 30 cm in diameter by 2 m long. A feed ram is used to push the material through the furnace and maintain a gas flow path. The wastes are pyrolyzed at about 900°C in the air-deficient tube. Volatilized materials pass to a secondary chamber where combustion of the off-gases occurs in an excess of air at about 1000°C. The secondary chamber is a brick-lined labyrinth containing electrical heating elements enclosed in aluminous porcelain tubes. The ashes which accumulate during the process are displaced from the furnace into an ash pit by the feed ram, which projects into the furnace. Ashes are manually raked down a 15-cm diameter Inconel tube into a container attached to a flanged opening. Ashes are usually removed about every four days.

Off-gases leaving the secondary combustion chamber are air-cooled and then passed through a water spray column which further cools the gas and removes about 90 percent of the HCl and some particulate matter. The gases leave the scrubber at about 100°C and pass through two water-cooled condensers which remove the water vapor and residual amounts of HCl. The gas is then passed through a polyethylene felt roughing filter, a heater, and finally several banks of HEPA filters.

Status of Development

The technology has been successfully demonstrated in plutonium contaminated waste disposal and recovery operations. Additional work to assure complete carbon burnout and to develop improved furnace materials is continuing. A scaled-up production model is planned.

9.5.6 Vortex Incinerator (G.E., Wilmington, NC)

Process Summary

Process Description: Combustible wastes are shredded and blown tangentially into a cylindrical combustion chamber by a materials handling fan. In the combustion unit, centrifugal forces provide turbulence required for complete oxidation and assist in ash separation.

Applicable Waste: Combustible, pneumatically transportable material.

Waste Pretreatment Required: Sorting and shredding.

Final Product Form: Dry ash, which is both thermally and radiolytically stable.

Process Effluents: Combustion gases and HCl-containing scrub solution.

Principal Advantages: High throughput in a relatively small furnace chamber; complete combustion.

Potential Problem Areas: Requires sorting and high maintenance shredders and materials transport systems.

Development Status: This unit has been operational since 1972 in a uranium fuel fabrication plant.

9.5.6 Vortex Incinerator (G.E., Wilmington, NC)

A commercially-available Vortex I Incinerator was installed in General Electric Company's uranium fuel fabrication plant in Wilmington, North Carolina, in 1972. The incinerator is used to recover uranium from large quantities of combustible wastes. Operating capacity of the unit is about 450 kg/hr.⁽²⁷⁾

Process Operating Conditions and Features

The Incinerator is a high-performance, gas-fired, solid waste disposal system capable of handling a very large workload. It consists of a single-stage combustion chamber, approximately 1.4 m in diameter by 2.4 m long, having combustion rates 10 to 20 times greater than that of conventional model incinerator systems of similar size. These high rates are accomplished by the unique utilization of a cyclonic burning pattern. Shredded combustible wastes enter the burning chamber tangentially and pass through the burning chamber in the cyclonic pattern until complete combustion is achieved. Combustion takes place at 1000-1100°C within the chamber. During combustion, the gas flows to the center of the chamber, and centrifugal force causes the ash particles to spin to the outside of the chamber where they are expelled out the exhaust tube.

The gases and entrained particles pass from the incinerator into a titanium scrubber where the gases are cooled and fly ash and acidic vapors are removed. The gases leave the scrubber at about 100°C, pass through a mist eliminator, a heater, a prefilter, and finally through a bank of HEPA filters before being discharged. The scrubbing liquid, saturated with fly ash, is pumped through an inline filter bag/pressure vessel system. The filtered solution is recycled back to the scrubber tank. Filled filter bags are reprocessed for uranium recovery.

Status of Development

This unit is currently operational for uranium-contaminated solid wastes at General Electric's uranium fuel plant in Wilmington, North Carolina.

Major Development Objectives

Major development programs are not underway since the present unit satisfies the uranium recovery needs for which it was built. General process improvements are continually made to the unit during routine operation and maintenance.

9.5.7 Fluid Bed Incinerator (RF)

Process Summary

Process Description: Combustible wastes are burned in a fluidized bed of Na_2CO_3 at 525°C to 625°C . Acidic gases, such as HCl and HNO_3 , are neutralized in situ by the Na_2CO_3 bed material.

Applicable Waste: All combustible solids and liquids, including small amounts of noncombustible liquids.

Waste Pretreatment Required: Sorting, shredding.

Final Product Form: Ash mixed with dry salt powder.

Process Effluents: Acid-free combustion gases.

Principal Advantages: The relatively low combustion temperature and in situ neutralization of HCl minimizes corrosion; fluidization improves combustion efficiency.

Potential Problem Areas: Control of plutonium inventory; separation of ash from salt.

Development Status: Demonstrated in nonradioactive pilot plant at 9 kg/hr; pilot plant now burning TRU nonline-generated solid and liquid wastes. Radioactive demonstration plant now being designed to handle 82 kg/hr.

9.5.7 Fluid Bed Incinerator (RF)

A fluid bed incinerator has been under development at Rocky Flats since about 1972. Early laboratory tests⁽⁶⁰⁾ demonstrated the feasibility of a fluid bed incineration process for treatment of combustible wastes, including the in situ neutralization of HCl generated from decomposition of chloride-containing wastes. Subsequent pilot plant development studies were performed using a 4.5 kg/hr fluid bed burner.^(36,37) The tests demonstrated the overall engineering feasibility of the process, including efficient operation at relatively low (550°C) operating temperatures, a minimum amount of unburned material in the flue gas, and efficient HCl neutralization.

Process Operating Conditions and Features

The Rocky Flats fluid bed combustion process uses a preheated gas mixture (air and nitrogen) at 300-500°C to combust waste in a fluidized bed of sodium carbonate. The shredded waste is introduced to the reactor by a compression screw feeder. The salt and waste materials are fluidized by the combustion gases passing through the bed. As the hot gases react with the waste, further heating occurs such that the combustion process takes place at 550-600°C. The wastes are rapidly oxidized resulting in formation of an inert residue (fly ash) and gaseous combustion products (flue gas). Most of the fly ash (about 70-80 percent) is carried from the bed and collected in a cyclone separator and filtration system. The remaining fly ash (about 20-30 percent) accumulates in the bed where it is removed periodically with the bed material.

Off-gases from the process consist of typical combustion products such as CO, CO₂, HCl, hydrocarbons, and water vapor. As the off-gases pass through the upper part of the fluidized bed, HCl generated from decomposition of chloride-bearing wastes reacts with the bed material. The remaining flue gases pass through a cyclone separator to remove particulate fly ash, then into a packed, catalytic afterburner where hydrocarbons in the flue gas are burned in contact with Cr₂O₃-Al₂O₃ catalyst. Air is blended with the flue gas in the afterburner to provide oxygen for combustion and to help carry heat away from the reactions. The gases then pass through a second cyclone separator, sintered metal filters, and finally through HEPA filters.

The primary advantages of a fluid bed incinerator are its low uniform operating temperature (~550°C) and the in situ neutralization of hydrogen chloride. The lower operating temperature eliminates the requirement for a refractory lining and also avoids converting plutonium to highly refractory plutonium oxides which are difficult to recover. In situ neutralization of the acidic gases considerably reduces the corrosion of the incinerator and

off-gas system. It also makes possible the use of a dry off-gas system, thus eliminating the need for complex aqueous scrubbing systems and the subsequent processing of contaminated scrub solution. Inconel and stainless steel are acceptable materials of construction.

Status of Technology

A pilot plant test unit with a waste treatment capacity of about 8 kg/hr has been operated using slightly contaminated room trash as a solid feed. It has also been used to dispose of various hydrocarbon solvents and discarded laboratory chemicals.

A commercial fluid bed incinerator/calclner for treatment of radioactive solid and liquid wastes is being developed jointly by Energy Incorporated, Idaho Falls, Idaho, and Newport News Industrial Corporation, Newport News, Virginia. A full-scale pilot plant incinerator/calclner at Idaho Falls has successfully demonstrated the incineration of both resins and combustible wastes and the calcining of liquids and sludges. A commercial unit capable of processing about 90 kg/hr of mixed solid waste, 45 kg/hr of ion exchange resin, or 130 l/hr of liquid sludge waste is expected to be on the market by mid-1976.

Major Development Objectives

Development work is in progress at Rocky Flats to further demonstrate the applicability of fluid bed incineration to the treatment of radioactively contaminated wastes. In particular, tests are planned on the use of the process for destruction of HEPA filters, ion exchange resins, and leaded rubber gloves. Further development work is planned on utilization of other neutralization salts and oxidation catalysts. A 82 kg/hr demonstration plant is being designed and built with operation planned for 1977. The demonstration plant will be operated using TRU-contaminated combustible wastes from the Rocky Flats operation.

Title I (preliminary) design information could be available by the end of 1977. Development of fluid bed incineration to the point of commercial application is expected to be accomplished by 1980.

9.5.8 Rotary Kiln Incinerator (RF)

Process Summary

Process Description: Combustible solid wastes, HEPA filters, ion exchange resin, and liquid wastes from analytical laboratories are burned or calcined in a diesel-fuel fired rotary kiln at 600-800°C. Off-gases pass through an afterburner operated at 1000°C.

Applicable Wastes: All plutonium-bearing combustible solid and liquid wastes, HEPA filters, and aqueous wastes from analytical laboratories.

Waste Pretreatment Required: Sorting, shredding, scarfing, and crushing.

Final Product Form: An inert, dry oxide residue.

Process Effluents: Combustion gases; acidic and spent alkaline scrub solutions containing fly ash.

Principal Advantages: The rotating action of the kiln continually exposes fresh surface of the waste, enabling a more rapid and complete oxidation of the wastes. Continuous discharge of ash minimizes criticality problems.

Potential Problem Areas: Incomplete graphite burning and possible glass formation on the refractory lining from decomposition of leaded drybox gloves; maintaining a good seal on the rotary kiln.

Development Status: Demonstrated in a cold pilot plant at 2 kg/hr. A demonstration plant is now being designed to process ~40 kg/hr. The plant will be installed in the Rocky Flats Plant and will be ready for processing plutonium contaminated wastes (>0.02 g Pu/g waste) in 1980.

9.5.8 Rotary Kiln Incinerator (RF)

Use of a rotary kiln incinerator for combustion of radioactive wastes has been under development at Rocky Flats since about 1972.⁽⁴⁾ The process has been successfully demonstrated in a cold pilot plant at 2 kg/hr. An engineering scale unit with a design capacity of 40 kg/hr is currently being designed for installation and operation at the Rocky Flats Plant for treatment of transuranic wastes containing >0.02 g Pu/kg waste.

Process Operating Conditions and Features

The rotary kiln incinerator consists of an inclined, horizontal cylindrical kiln, 1.8 m ID by 4.6 m long, rotating on its longitudinal axis at about 1 to 2 rpm. Seals for the kiln which operate at about 0.3 cm water gauge differential pressure, are made from a hard graphite material called Eel-Slip. The incinerator is normally operated at 600-800°C using three diesel-fuel burners to provide ignition, to maintain the operating temperature, and to assure complete combustion.

Waste materials will be added by means of a ram feeder to the refractory-lined steel rotating kiln where the cascading action of the kiln exposes unburned material for combustion. The slow rotation of the kiln causes the waste to move in a slowly cascading manner along the length of the combustion zone. The residence time of the waste in the kiln is about one hour.

The ashes from the incinerator are discharged into an ash cooler, through a ball mill, and into an ash collection glove box. The collected ash is assayed for plutonium prior to plutonium recovery by nitric acid leaching or total dissolution techniques. The continuous ash discharge provides assurance that plutonium nuclear safety limits will not be exceeded.

Combustible off-gases and aerosols are carried into a secondary, refractory-lined steel mixing chamber where a diesel fuel burner completes the combustion at about 1000°C. The off-gases leave the afterburner and are carried through refractory-lined ducts to a series of primary and secondary venturi scrubbers to remove HCl and fly ash. The primary scrubbers use water to absorb most of the HCl; the secondary scrubbers use a KOH solution to remove residual HCl. The gases are finally routed through four stages of HEPA filtration in the incinerator and exhaust plenums prior to discharge.

HEPA filters and lead-loaded glove box gloves will be campaigned separately through the incinerator at a lower temperature (i.e., below 700°C) in order to prevent glass formation or slagging on the refractory walls.

The rotary kiln incinerator will also be used to process ion exchange resins and analytical laboratory liquid wastes, both aqueous and organic. These wastes will be atomized through a Delavan Swirl-Air nozzle on a campaign basis.

Status of Development

Results of cold pilot plant tests at Rocky Flats are being used by C. F. Braun & Company, Alhambra, California, to design a rotary kiln incinerator capable of combusting approximately 40 kg of waste/hr. The incinerator will be built by CER/Bartlett-Snow, Chicago, Illinois, and installed at the Rocky Flats Plant by about 1980 for processing plutonium-containing wastes.

Major Development Objectives

No major development program on the incinerator is planned prior to installation of the production unit.

9.5.9 Agitated Hearth Incinerator (RF)

Process Summary

Process Description: Combustible solid wastes are burned in an oil-fired incinerator at 600-800°C. Combustibles are charged by a ram feeder onto a circular hearth and moved through the incinerator by rotating rabble arms. Ash is discharged on a batch basis following completion of combustion. Gases and fly ash are further combusted in an afterburner at ~1000°C.

Applicable Waste: All combustible solid wastes generated at the Rocky Flats Plant which contain <0.02 g Pu/g waste.

Waste Pretreatment Required: Sorting (shredding optional).

Final Product Form: An inert, dry ash.

Process Effluents: Combustion gases and spent alkaline scrub solutions.

Principal Advantages: The rotating rabble arms tumble the waste through the burner. This action continually exposes fresh surfaces of the waste objects, thus accomplishing a more rapid and complete oxidation of the wastes.

Potential Problem Areas: Moving parts in the incinerator.

Development Status: Demonstrated in a nonradioactive demonstration model rated at 4 kg/hr. A unit capable of processing 70 kg/hr of waste is being fabricated for combustion of low-level (<0.02 g Pu/g waste) contaminated wastes. The unit is expected to be ready for operation with contaminated wastes in 1980.

9.5.9 Agitated Hearth Incinerator (RF)

An agitated hearth incinerator developed by Environtech, Inc., San Mateo, California, has been successfully tested in a cold pilot plant at about 4 kg/hr with wastes typical of the nuclear industry. Results of these tests are being used by C. F. Braun, Alhambra, California, to design a unit capable of treating about 70 kg/hr of mixed waste material.⁽⁴⁾ The 70 kg/hr unit will be built by Environtech, Inc., and used at Rocky Flats to process low activity wastes containing <0.02 g Pu/g waste. Operation of the unit is expected to begin about 1980.

Process Operating Conditions and Features

The Rocky Flats agitated hearth incinerator features a stationary, refractory-lined steel circular hearth 2.6 m in diameter by 4.6 m high with rotating rabble arms to tumble waste through the combustion zones and to move the accumulated ash to a quench pot. The primary combustion zone is heated to 600-800°C using auxiliary diesel fuel burners to maintain the temperature. Wastes are campaigned through the incinerator on a batch basis using semi-continuous feed. The wastes are divided into ~2 kg portions, loaded into cardboard boxes, and fed to the primary combustion chamber via a ram feeder at the rate of one box every two minutes.

Ashes accumulated during incineration of the wastes are removed from the incinerator following a five-hour charging and one-hour burnout time. The ashes are pushed through a discharge slide gate by the rotating rabble arms into a conveyor-cooler where they are cooled prior to being loaded into plastic-lined waste drums. The collected ashes are assayed for plutonium before transfer to storage.

Combustible off-gases and suspended combustible particles are carried into a secondary chamber or afterburner where final combustion occurs at about 1000°C. The off-gases then leave the afterburner through a refractory-lined duct leading to two potassium hydroxide scrubbing units, each consisting of a wetted throat venturi scrubber followed by a gas-liquid separator, which remove acidic gases and any residual fly ash. The gases are finally discharged after flowing through several stages of HEPA filters. The scrubber solution is partially recirculated back to the off-gas cleanup system while a bleed-off stream is routed to waste recovery.

Status of Development

An agitated hearth incinerator with a design throughput of about 70 kg/hr is being built by Environtech, Inc., for use in the Rocky Flats Plant. The unit is expected to be ready to process low-level plutonium wastes in 1980. No major development program is planned at Rocky Flats prior to installation of the production unit.

9.5.10 Moving Grate Incinerator (ARHCO)

Process Summary

Process Description: Combustible wastes are burned at 700-800°C by passing them through an electrically-heated, horizontal cylindrical furnace on a moving belt grate. Volatile components and fly ash are burned in a secondary tubular furnace surmounting the primary furnace.

Applicable Waste: All combustible solids except leaded gloves; small amounts of nonvolatile, combustible liquids.

Waste Pretreatment Required: Sorting and shredding.

Final Product Form: Dry ash, slightly combustible.

Process Effluents: Combustion gases and spent alkaline scrub solutions.

Principal Advantages: Low ash inventory and excellent criticality control.

Potential Problem Areas: Incomplete combustion and high maintenance, especially with the Nichrome wire belt; clogging of the off-gas line.

Development Status: Operating more than 10 years in an industrial plant at 2 kg scrap/hr. Technology available for industry but requires some additional modifications to minimize maintenance problems.

9.5.10 Moving Grate Incinerator (ARHCO)

The moving grate incinerator was developed for use in the Hanford Plutonium Reclamation Facility and has been in use since 1961 for recovery of plutonium from combustible waste materials.⁽³³⁾ Throughput on the unit is about 10-20 kg per 8-hour day.

Process Operating Conditions and Features

The incinerator consists of two horizontal tubular combustion chambers mounted one above the other and connected with four flue tubes. The lower, primary combustion chamber is a flat-bottomed semi-cylinder, 0.2 m in diameter by 3 m long. The tube is fabricated of Incalloy 800 and 321 stainless steel surrounded by 30 cm of firebrick insulation. A continuous, Nichrome-V woven-wire belt moves along the bottom of the chamber receiving the wastes to be incinerated at the front end and discharging the ashes into a hopper at the tail end. The primary chamber is maintained at a temperature of 700-800°C by external electrical resistance heating elements. The upper (secondary) combustion chamber is a 13 cm diameter Incalloy 800 tube which is also operated at 700-800°C. The off-gases from the primary chamber undergo further oxidation in the secondary chamber. Both chambers are operated with excess air.

The gases exiting the secondary combustion chamber pass through two low-pressure-drop cyclone separators where larger particles are removed, then into a 316 stainless steel scrubber system which uses a solution of water, sodium hydroxide, and urea to remove the fly ash, HCl, and HClO. The scrubbed gases pass through a heater and several stages of absolute filtration before discharge to the main building stack.

Status of Development

The present incinerator has been used in Hanford's Contaminated Waste Recovery Facility since 1961 to recover plutonium from non-leachable combustible wastes. Plastics and rubbers are avoided whenever possible because of problems with corrosion and soot. The unit is presently down for modifications and repairs.

Major Development Objectives

There are no major development programs for the incineration system described since the present unit satisfies the plutonium recovery needs for which it was built. This incinerator presents a practical design, but is subject to further improvement to reduce maintenance problems and to assure complete oxidation of combustion products.

9.5.11 Molten Salt Combustion Unit (AI)

Process Summary

Process Description: Combustible wastes are burned with air in molten sodium carbonate and sodium sulfate. Inorganic products (metallic oxides, ash, sodium chloride, and fissile material) are retained in the melt. The salt-ash product can be cast in storage drums or processed to recover salt and transuranics.

Applicable Waste: Combustible materials (solids, liquids, resins, filter sludges). Many inorganic solids, including HEPA filters, metal tubing and glassware can also be treated.

Waste Pretreatment Required: Sorting to remove large tramp-metal and shredding.

Final Product Form: Solidified fused salt cake containing 20 wt % ash.

Process Effluents: Non-acidic combustion gases.

Principal Advantages: Since wastes are oxidized beneath the surface of the molten salt, acidic gases and particulate matter are trapped in the molten salt. This substantially reduces corrosion of the off-gas cleanup system. Metal and glass are also readily dissolved in the molten salt.

Potential Problem Areas: Particulate loading in the off-gas (primarily sodium chloride) and dissipation of heat.

Development Status: Combustion demonstrated on bench-scale (0.5 kg/hr) with Pu and beta-gamma contaminated waste and on pilot plant scale (50 kg/hr) with uncontaminated waste. Ready for preliminary design with fused-cast product; salt recovery option needs large-scale tests. Combustion of organic liquids requires additional development tests.

9.5.11 Molten Salt Combustion Unit (AI)

A molten salt process for the oxidation of combustible materials has been investigated at Atomics International since 1966. The process utilizes molten salt as a medium to burn organic materials, to trap particulate matter, and to react chemically with acidic gases produced during combustion.^(41,42,61) The process has been successfully applied to destruction of chlorinated liquid wastes,⁽⁶²⁾ destruction of toxic and lethal chemicals, and destruction of other combustible materials.⁽⁴¹⁾ It has also been used to remove pollutants such as NO_x and SO_2 from process off-gas streams,^(63,64) and has been used to gasify coal.⁽⁶⁵⁾ A molten salt combustion test facility with a feed rate of ~50 kg/hr has been operated at AI since 1971. The application of the technology to the disposal of TRU wastes was begun in 1974 with bench-scale tests and finally with simulated (nonradioactive) TRU wastes at a combustion rate of about 50 kg/hr.

Process Operating Conditions and Features

The molten salt combustion process uses a molten mixture of sodium carbonate and sodium sulfate salts, contained in an alumina-brick-lined steel furnace, as a medium for air oxidation of combustible wastes. The sodium carbonate serves as a heat transfer medium and as a neutralizing agent for acidic gases such as HCl and SO_2 formed during combustion. The sodium sulfate is used to catalyze the combustion reactions and to minimize the evolution of carbon monoxide and volatile hydrocarbons.

Shredded combustible waste materials are fed with air (100 percent excess) beneath the surface of the molten salt which is maintained at 800-850°C by the combustion process. The wastes begin to burn immediately. The particulate matter and acidic gases released by combustion are trapped by the molten salt; nonreactive gases (e.g., CO_2 and water vapor) are released from the molten salt and sent through the off-gas treatment system. Combustion residues accumulate in the salt and increase its viscosity. A portion of the salt is periodically replaced, normally when the ash content reaches 20 wt%, so that a nearly constant salt composition is maintained. If the melt becomes too viscous due to the buildup of insoluble materials, fluidity is restored by increasing the melt temperature or by addition of more salt. Temperatures above 850°C are avoided, however, in order to minimize volatilization of sodium chloride.

The off-gas cleanup problems in the molten salt process are considerably simplified due to the in situ neutralization of HCl . The non-acidic combustion off-gases pass through a mist eliminator, a water cooler, and a baghouse; then through a heater and a bank of HEPA filters before venting to the atmosphere through a stack. The particulate cake from the baghouse is recycled back to the salt reactor.

Two options have been investigated for disposal of the fused salt bed following treatment of wastes: 1) fused salt casting and 2) salt and transuranic recovery. In Option 1, a portion of salt is removed periodically from the furnace and cast directly into storage drums. The composition of the spent salt is approximately 50 wt% Na_2CO_3 , 10 wt% Na_2SO_4 , 20 wt% NaCl , and 20 wt% ash. The solidification temperature is about 720°C , and the density of the fused salt block is 1600 kg/m^3 . The volume reduction factor is about 45 for a mixed waste material containing 8 wt% ash (90 kg/m^3 bulk density).

In Option 2, the melt-ash mixture is processed to recover sodium carbonate and sodium sulfate for recycle to the combustor, and to produce an ash and sodium chloride fraction for storage. This is accomplished by leaching the soluble sodium salts from the quenched melt-ash mixture by a 1-hr refluxing followed by filtration. Fractional crystallization of the concentrated brine solution at its boiling point (106°C) produces a crystalline sodium carbonate-sodium sulfate product for recycle to the combustor and a sodium chloride brine for further evaporation, crystallization and disposal. Water removed in the salt recovery steps is recycled. Plutonium is readily dissolved from the ash (<30 min reaction time) with nitric or hydrochloric acid. However, colloidal silicic acid (gelatinous) is also formed and must be dehydrated (by evaporation to dryness) before the plutonium can be recovered by conventional techniques. Very little plutonium remains in the salt fraction. The volume reduction factor for Option 2 is about 57 using the same mixed waste basis as for Option 1.

The molten salt combustion process can be used to treat a variety of combustible materials, including dissolution of thin wall metal and glass, as well as for combustion of organic liquids, oils, and solids. These treatment options are being pursued in separate development programs.

Status of Development

Experimental verification of the process has been obtained from three different sets of experiments. A 15-cm diameter laboratory combustor with a feed rate of 0.5 kg of simulated TRU waste/hr was used initially to obtain the basic combustion parameters. A 10-cm diameter combustor with a feed rate of 0.3 kg of TRU waste/hr was then installed in a glove box and operated to determine the uranium and transuranic disposition in the system when actual TRU waste was burned. Large-scale (50 kg/hr) combustion tests of simulated TRU waste were subsequently made in the 90-cm diameter Molten Salt Test Facility. Combustion of organic liquids and oils has been studied on a 2 kg/hr scale. The dissolution of metals and glasses has been investigated in both the laboratory and pilot scale systems. A 50 kg/hr unit is undergoing conceptual design for installation at an ERDA site.

Molten salt combustion units designed for coal gasification and for disposal of toxic waste materials (e.g., DDT, herbicides, trichloroethane, chloroform, nitroethane, etc.) are currently undergoing Title I (preliminary) design.

Major Development Objectives

The development of a molten salt combustion process for the treatment of other radioactive wastes will be emphasized. This would include the combustion of wastes containing tracer quantities of radioactivity in the Molten Salt Test Facility (50 kg/hr), as well as hot cell combustion tests with higher levels of contamination. Additional feed system development tailored to the actual waste to be processed is planned. The basic combustor vessel has been developed; however, additional development of a drain control valve or overflow system is needed. The off-gas system has been developed for processing of TRU waste, but some further tests are needed to determine if the developed off-gas system is adequate for all applications. Remote casting of the salt in a storage drum may also require some development. Remote interruption of melt flow during the drain procedure with subsequent remote reinitiation of flow has been accomplished; this would be required while containers are being changed.

If the salt and plutonium recovery option, Option 2, is chosen, then additional large-scale salt crystallization and additional plutonium recovery and purification tests will be needed. Determination of the exact conditions required for optimum plutonium recovery will also need additional development tests.

9.5.12 Acid Digestion Unit (HEDL)

Process Summary

Process Description: Combustible wastes are converted to gaseous products (CO_2 , H_2O , HCl) and sulfate-oxide residues by digestion in H_2SO_4 at 230-250°C.

Applicable Waste: All combustible solids except Teflon; many combustible liquids. Not advised for HEPA filters, silicones, highly-volatile liquids.

Waste Pretreatment Required: Sorting and shredding.

Final Product Form: Dry salt cake, primarily inorganic sulfates and oxides. Product is thermally stable.

Process Effluents: Scrubbed reaction gases (CO_2 , CO , O_2 , N_2 , N_2O) and spent alkaline scrub solution containing $NaCl$ and small amounts of $NaNO_3$, $NaNO_2$ and Na_2SO_4 .

Principal Advantages: Acid digestion handles a wide variety of wastes; the reactions are readily controlled; plutonium is converted to a nitric acid soluble form; the process is a low temperature single stage combustion operation.

Potential Problem Areas: Criticality limitation on capacity; containment of volatile fission products (Ru , I_2); chloride disposal.

Development Status: Demonstrated in cold pilot plant at 5 kg/hr; laboratory demonstration of Pu behavior; radioactive pilot plant for 100 kg/day being designed. Technology should be available for industry by 1980.

9.5.12 Acid Digestion Unit (HEDL)

In the early 1960's, a chemical system using selenium-catalyzed sulfuric acid for wet oxidation of combustible wastes was tested in pilot plant equipment at Risø, Denmark.⁽⁶⁶⁾ Substitution of nitric acid as the oxidant in place of the selenium catalyst was first investigated at HEDL in early 1971. Initial laboratory tests using a combination of hot concentrated sulfuric and nitric acids showed that a wide variety of potential waste materials were readily decomposed.⁽⁶⁷⁾ The sulfuric acid serves primarily to carbonize the wastes and to provide a high temperature medium (250°C) for the subsequent oxidation of the carbonized waste by nitric acid.

Process Operating Conditions and Features

In the acid digestion process, shredded combustible wastes are added semi-continuously to a simmering sulfuric acid solution (~91 wt% H_2SO_4 at 250°C) along with concentrated nitric acid. The nitric acid is added at a rate calculated to provide 75-100 percent of the oxygen required to oxidize the waste to CO_2 and H_2O . Simulated, non-radioactive waste materials typical of the nuclear industry have been processed in all-glass test equipment at rates as high as 5 kg/hr.^(43,46) The process is readily controlled by adjusting the reaction temperature, the nitric acid addition rate, or the waste addition rate. Criticality control is attained by use of geometrically favorable equipment.⁽²⁾

In the present system, shredded waste is dumped onto a shallow tray where it is contacted with nitric acid and recirculating sulfuric acid, which is air-lifted from a heated, geometrically favorable reservoir. Solids which accumulate in the system are removed during operation by periodic transfer of a portion of the acid slurry to a separate evaporator pot, from which sulfuric acid is evaporated at 350°C and returned to the digester for reuse. The resulting dry powder is composed primarily of inorganic sulfates and oxides and is thermally stable when heated in air.

Plutonium (including refractory plutonium oxide) is converted to a sulfate precipitate during acid digestion and remains with the process residue. (The solubility of plutonium sulfate in typical acid digester solutions is about 0.1 g/l.) Following evaporation of sulfuric acid from the residue, the plutonium can be dissolved from the residue by leaching with dilute nitric acid.

Off-gases leaving the digester consist primarily of H_2O , CO_2 , CO, SO_2 , SO_3 , NO_2 , NO, N_2O , N_2 , and HCl (when chloride-containing wastes are present). Nitrogen dioxide (NO_2) readily oxidizes SO_2 to SO_3 , and addition of O_2 to the off-gas is used to convert NO to NO_2 . The NO_2 , SO_3 , and HCl are readily

stripped from the off-gases using a water or dilute acid scrub. The spent scrub can be concentrated and fractionated to return the recovered sulfuric acid and nitric acid (about 70 percent of the input) to the digester. Water, HCl, and a small amount of HNO_3 can be rejected to a low-activity waste stream for disposal during this operation. The remaining nitric acid (about 30 percent of the input) is converted to N_2 and N_2O during digestion.

Status of Development

Engineering feasibility of the acid digestion process has been demonstrated in a 5 kg/hr, nonradioactive test facility. A 5 kg/hr unit for treating radioactive wastes is being constructed at HEDL and is expected to be ready for processing plutonium-contaminated wastes in 1977. Development of acid digestion to the point of commercial application is expected to be accomplished by 1980.

Major Development Objectives

The acid digestion process will be demonstrated on an engineering scale using radioactive wastes starting in 1977. Development of general reference design criteria and parameters for a commercial unit is expected to be complete by late 1979.

Several potential problem areas in the development of acid digestion still require attention. The high corrosivity of the hot digester acid mixture and of the vapor leaving the digester severely limits the potential materials of construction for the digester. Glass, glass-lined steel, and certain ceramic materials are the most likely candidates for the digester vessel. Disposal of HCl must be demonstrated. Hydrochloric acid is readily stripped from the off-gas by the recycled water scrub, along with nitric and sulfuric acids; but removal of the HCl from the recovered acids without carryover of excessive amounts of nitric acid must be demonstrated. Handling, drying and treatment of the residue for plutonium recovery must be demonstrated.

9.5.13 Waste Solvent Incinerator (SRP)

Process Summary

Process Description: Radioactively contaminated waste kerosene-TBP solvent is converted to gaseous products and a water soluble phosphate polymer residue by two stages of incineration. Radioactivity is retained in the first-stage burning pan.

Applicable Waste: Kerosene-TBP solvent containing up to 50 percent TBP. Use is limited to relatively low-level radioactivity. Upper limits of radioactivity are not yet demonstrated and will depend on site release criteria and filtration provisions.

Waste Pretreatment Required: Batch washing with Na_2CO_3 to remove radioactivity; decanting to separate waste solvent from water.

Final Product Form: Water soluble phosphate residue will contain the bulk of the original radioisotopes.

Process Effluents: Combustion gases.

Principal Advantages: The initial quiescent pan burner retains radioactive impurities; the second stage assures smokeless burning.

Potential Problem Areas: Residue removal, soot formation in first-stage burner, operation at positive pressure, and limitations on radioactivity in the feed.

Development Status: Acceptable smoke emissions demonstrated in pilot plant tests. Radioactive emissions control and other technology should be demonstrated by 1978.

9.5.13 Waste Solvent Incinerator (SRP)

At the Savannah River Plant, approximately 570,000 liters of waste solvent (kerosene and TBP containing about 45 curies of alpha activity and 45 curies of beta-gamma activity) are stored in underground tanks. Open pan burning⁽⁶⁸⁾ was used until 1971 to dispose of this solvent but has since been discontinued because of the copious quantities of black smoke evolved.

A "smokeless" solvent incinerator which meets Federal and State emission requirements is being developed to permit disposal of the current waste solvent inventory. Because of the high decontamination factor for radioactivity with quiescent burning (DF's of 10^3 to 10^4 were reported for open pan burning), the design includes a quiescent pan burner for the first stage of the incinerator. Cold tests using 30-50% TBP in kerosene show that "smokeless" burning can be achieved by burning the off-gases from the first stage in an auxiliary fired, forced draft incinerator. A scrubber is required to remove the phosphate emissions which result from burning TBP.

Process Operating Conditions and Features

Waste solvent is fed to an open pan contained in the first stage of the refractory-lined steel incinerator where it is ignited by a pilot burner. Air provided by a blower provides the required oxygen for the reaction and controls the reaction temperature. Burning proceeds through combustion of gases volatilized from the quiescent liquid surface, thus leaving behind nonvolatile solutes and organic polymers. The gases are carried into the second stage burner, operated at 100°C by combustion of auxiliary fuel, to complete the oxidation of organic vapors and unburned carbon.

The off-gas is routed to a quench scrubber where it is cooled and the P_2O_5 from combustion of TBP is removed as phosphoric acid. The contaminated scrub water and the water-soluble residue left in the burner pan are sent to the low-activity liquid waste storage tanks for concentration by evaporation.

Radioactive material content of the feed will be limited based on the overall decontamination factor afforded by quiescent burning, scrubbing, and additional deentrainment or filtration equipment that may be added to the system. The limitations will not be established until after initial operation with radioactive solvent, but the system should handle more than the $0.5 \mu\text{Ci/ml } ^{106}\text{Ru}$ demonstrated to be acceptable in the old pan burner facilities. The major problem anticipated is removal and disposal of the residue formed in the first stage. Carbon buildup on the walls of the pan in the first stage may also occur and could affect burning characteristics.

Status of Development

Quiescent, open pan burning has been demonstrated as an effective method for burning contaminated TBP solvents. Acceptable smoke emission control has been demonstrated in pilot plant tests of the two stage system. A project for design and installation of an incinerator similar to the one described in the Process Summary has been requested using a design basis of 75 liters/hr. Radioactive emission control and other technology should be demonstrated by 1978.

Major Development Objectives

- Establishment of off-gas treatment requirements.
- Development of methods for the removal and disposal of the residue formed in the first stage.
- Determination of carbon buildup on the pan walls in the first stage and its effect on burning characteristics.

9.5.14 Waste Solvent Burner (BNFP)Process Summary

Process Description: Waste TBP solvent is sprayed into the top of a combustion chamber through a nozzle also supplying air and natural gas to provide assured combustion. Off-gases are treated in a separate quench scrubber to remove P_2O_5 and unburned carbon.

Applicable Wastes: Spent separations process solvent and other nonhalogenated combustible liquids. Will tolerate some aqueous solutions.

Waste Pretreatment Required: Batch washing with HNO_3 , Na_2CO_3 to remove fission products and actinides.

Final Product Form: Aqueous solution of dilute phosphoric acid from TBP combustion.

Process Effluents: Combustion gases.

Principal Advantages: Natural gas burner system provides smooth combustion control; safety interlock system assures safe operation.

Potential Problem Areas: Burner nozzle erosion and corrosion; pilot light ignition system failure; flame detection system failure.

Development Status: Available commercially. Installed for use at BNFP.

9.5.14 Waste Solvent Burner (BNFP)

Organic liquid wastes generated at BNFP will be burned in a solvent incineration designed by AGNS and Oxy-catalyst, Inc., of West Chester, PA.⁽⁶⁹⁾

Process Operating Conditions and Features

The waste solvent burner is a forced convection incineration unit as opposed to a passive oil burner. A simplified schematic is presented in the Process Summary. As shown in the figure, the solvent burner unit is composed of two vessels, the solvent burner combustion chamber and the solvent burner quench tower. The burner nozzle is positioned at the top of the combustion chamber directed downward. The nozzle has two sets of fuel ports, one set for natural gas, and the second set for waste solvent. The combustion air is also supplied through the burner nozzle. The combustion chamber is lined with Inconel and surrounded by 10 cm of castable refractory insulation and a 304L stainless steel outer jacket purged with air.

The operation of the solvent burner is started by bringing the combustion chamber temperature to an operating temperature of 840°C by slowly increasing the flow of natural gas to the burner. After the operating temperature has been reached and stabilized, the waste solvent flow is started to the burner nozzle. The natural gas burns as a hollow cone with the solvent burning within that cone. The flow of natural gas is controlled by the temperature of the combustion chamber. As the flow of waste solvent increases and the temperature of the combustion chamber increases, the flow of natural gas decreases down to a predetermined minimum flow of natural gas. This minimum flow of natural gas is maintained to assure that a flame would continue if the waste solvent flow is disrupted or stopped. This feature allows a mixture of solvent and aqueous solutions to be fed to the burner or even a total aqueous solution to be fed to the burner without shutting the unit down. The design capacity of the BNFP solvent burner is $\sim 0.3 \text{ m}^3/\text{day}$.

The combustion gases from the combustion chamber are passed through a quench tower to reduce the gas temperatures and to scrub the majority of the combustion products out of the gas. The scrubber solution is continuously recycled by airlift from the bottom of the quench tower to the top where it cascades downward over chevron plates countercurrent to the flow of the combustion gases. The specific gravity of the scrubber solution is controlled by a constant bleed to the intermediate-level liquid waste treatment system. Makeup water is automatically added as required to replace the solution lost by evaporation and the bleed-off. Off-gases leave the tower through a mist eliminator pad and are routed to the vessel off-gas system for further treatment.

Status of Development

The system is installed for use at the BNFP. Similar systems are available commercially.

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10.0 TREATMENT OF NON-HIGH-LEVEL LIQUID WASTES

10.0 TREATMENT OF NON-HIGH-LEVEL LIQUID WASTES

10.1 CHARACTERISTICS OF AS-GENERATED WASTES

High-level liquid radioactive wastes are defined in the Code of Federal Regulations, Title 10, Part 50 (10 CFR 50), Appendix F, as being "those aqueous wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuels." As used in this document, the term "non-high-level liquid waste" denotes any liquid waste, except high-level liquid waste (HLLW), which cannot be released as a plant effluent without further treatment for radionuclide removal. By definition, HLLW can be generated only by a fuel reprocessing plant (FRP); other nuclear fuel cycle facilities can generate only non-high-level liquid waste. The above definition of HLLW implies that any radioactive aqueous waste from an FRP can become HLLW by undergoing an unspecified degree of concentration; such wastes will be considered to be non-high-level liquid wastes in this document unless they are actually combined with aqueous wastes from the first cycle solvent extraction system, or equivalent, for subsequent HLLW treatment processes. The treatment processes for HLLW are described in Section 6.0.

The non-high-level liquid waste category encompasses a broad spectrum of radioactive liquid wastes which vary widely in their chemical content, radioactivity level, transuranic (TRU) content, combustibility, etc. Non-high-level liquid waste is commonly further classified as either intermediate-level liquid waste (ILLW) or low-level liquid waste (LLLW). The differentiation between ILLW and LLLW is based primarily upon relative radioactivity levels, but can be influenced by judgmental factors, since there are no universally accepted numerical boundaries on these two classes of liquid waste. Generally, ILLW can be considered to have relatively high dissolved solids content, sufficient radioactive material to warrant shielded and remotely operated treatment facilities, and a relatively high potential for significant TRU contamination. On the other hand, LLLW can be generally visualized as a chemically dilute liquid having sufficient radioactive material content to necessitate further treatment prior to discharge; shielding requirements for treatment facilities are minimal. Few, if any, ILLW streams, and none of the LLLW streams, generate sufficient radioactive decay heat to require interim storage tank heat exchange capability. As will be seen later in this section, the individual waste treatment processes can be roughly grouped in accordance with their primary applicabilities to either ILLW or LLLW.

Typical sources of ILLW at an FRP include scrubber solutions from process vessel off-gas treatment systems, ion exchanger regenerants from spent fuel

and solidified high-level waste storage basin cleanup systems, cask and plant decontamination solutions, waste solutions from solvent washing systems, and miscellaneous waste solutions from maintenance and laboratory operations. Potential FRP sources of LLLW can include aqueous wastes from uranium and plutonium purification cycles and product conversion systems, concentrator overheads condensates, condensates from process vessel ventilation systems, laundry wastes, etc.

The operation of a mixed oxide fuel fabrication plant generates ILLW or LLLW from washing, etching, and rinsing operations, fuel element decontamination and degreasing, laboratory operations, and, if a scrap recovery system is included, from solvent extraction system operation. The waste streams from such a plant contain only trace quantities of fission products, but may contain significant amounts of TRU contaminants.

A small amount of radioactive material can be present in the primary core cooling water and the spent fuel storage basin cooling water of a nuclear power plant. This contamination can result from neutron activation of corrosion products and chemical additions, from fission of trace quantities of uranium external to the fuel elements, or from fuel cladding failure. These coolant streams are routinely cleaned by demineralization (ion exchange) to prevent contamination buildup in the recycled coolant and to reduce the radioactive material content of the blowdown effluent to a level which is as low as is reasonably achievable. If the demineralizer beds are regenerated rather than discarded, the spent regenerant becomes a liquid waste which requires further treatment. This waste, along with miscellaneous liquid wastes (from coolant leaks, floor drains, laundry and decontamination operations, etc.) is normally evaporated to a concentrated slurry to reduce the waste volume requiring further treatment.

The typical sources of non-high-level liquid wastes identified in the foregoing paragraphs are listed only as examples. Since plant flowsheet alternatives can affect the liquid waste spectrum, a complete and definitive listing of non-high-level liquid waste sources, characteristics, and quantities would require establishment of flowsheet bases. A more detailed discussion of ILLW and LLLW sources, including estimated chemical compositions and quantities, is presented in Section 2.0.

10.2 TREATMENT ALTERNATIVES FOR PRIMARY WASTES

Proper treatment of any radioactive liquid waste stream, or combination of streams, requires development of a comprehensive treatment flowsheet to ensure that the application and sequence of the selected treatment processes are compatible with waste characteristics and capable of achieving treatment objectives. Such a treatment flowsheet may consist of a single treatment

process, or combinations of processes described in this section and Section 12.0, "Immobilization of Miscellaneous Non-High-Level Wastes." The associated treatments for any secondary wastes which may be generated by the selected primary waste treatment processes should also be identified during primary waste treatment flowsheet development.

Briefly stated, non-high-level radioactive liquid waste treatment objectives include the following:

- (1) Continued confinement of radioactive material
- (2) Volume reduction of the radioactive waste material, requiring continued storage and surveillance
- (3) Incorporation of the radioactive constituents into a less dispersible waste form or matrix.

The treatment processes described in this section have as a common objective the separation of radioactive constituents from nonradioactive materials; for a given waste composition, the practical degree to which this separation can be accomplished varies among the treatment processes. Processes for incorporating the separated radioactive constituents into a solid matrix are described in Section 12.0.

A logical first step in developing overall liquid waste treatment flowsheets is consideration of possible schemes for liquid waste recycle and reuse within the process. Such schemes can reduce the total volume and types of liquid waste requiring further treatment, and also reduce the process chemical and demineralized water requirements (see Section 5.0). Another processing option for consideration is the combining of liquid waste streams having mutually compatible compositions. Combining such streams may reduce the number and types of waste treatment facilities that are required.

The treatment processes described in this section are assumed to be performed after any processing operations for recovery of product materials (U, Pu) or process chemicals. At the end of liquid waste treatment sequences, ready capability to recover product or process materials would be inconsistent with the waste form objective of low leachability. It is recognized that occasional radioactive liquid waste batches may contain unusually large quantities of transuranics due to process upsets; in such cases, rework within the process prior to normal waste treatment operations may be desirable. Basic processes for recovery of transuranics from non-high-level wastes are described in Section 11.0.

Some typical alternative sequences of treatment processes are shown in Figure 10-1 for ILLW and Figure 10-2 for LLLW. Numerical values which are assumed to be representative of volume changes through selected treatment

FIGURE 10-1. Intermediate-Level Liquid Waste Flow Diagram

sequences are shown, based upon a liquid waste input of 100 units. However, actual volume changes can vary widely as functions of specific stream composition and subsequent treatment plans.

The information presented in Figures 10-1 and 10-2 and described in the following paragraphs is not intended to imply that the treatment processes or sequences of processes can be precisely grouped by their applicability to ILLW or LLLW. Aside from the lack of a clear-cut distinction between ILLW and LLLW, many of the treatment processes are at least technically, although perhaps not economically, feasible for either ILLW or LLLW. Therefore, the alternative waste treatment sequences identified in Figures 10-1 and 10-2 should be considered as typical, but not all-encompassing.

10.2.1 Intermediate-Level Liquid Waste

An alternative for ILLW treatment at a fuel reprocessing plant which would reduce overall waste treatment facility requirements is combination with HLLW, provided that the ILLW stream is chemically compatible with the HLLW and with subsequent HLLW treatment processes. These wastes could be combined either before or after evaporation, which normally precedes HLLW solidification and/or immobilization processes. HLLW treatment processes are described in Section 6.0.

FIGURE 10-2. Low-Level Liquid Waste Flow Diagram

The first step in the separate treatment of ILLW (i.e., not combined with HLLW) is normally evaporation, to reduce the liquid feed rate to subsequent treatment processes. Following evaporation, the concentrated solution or slurry can be further processed through a calcination step, in which its solids content is dried and thermally decomposed at high temperature into stable nonfused compounds such as oxides. Either the concentrated evaporator product or the calcined waste can then be immobilized, using one of the treatment processes described in Section 12.0. The solidified product of the overall ILLW treatment operation is then packaged in a suitable container (confinement barrier) and placed into an interim storage area to await final storage or disposal.

10.2.2 Low-Level Liquid Waste

Evaporation is typically used in treating LLLW, although other methods of solute concentration or removal, particularly ion exchange, have economic advantages for applications involving large waste volumes with low solute concentrations. The concentrated evaporator product solution then becomes an input stream for ILLW treatment processes. The overheads condensate from LLLW

evaporation is generally sufficiently low in contaminant concentration to allow its discharge as a plant effluent or reuse in process applications.

Filtration or centrifugation can be employed at virtually any point in a sequence of liquid waste treatment operations for removal of insoluble particulate material. Particulate removal is often the initial step in situations where undissolved matter would have a deleterious effect upon downstream treatment processes or equipment. In some specific applications, filtration or centrifugation may be the only step required prior to reuse or discharge of the filtered liquid. However, more generally, for liquid wastes containing contaminants which can be readily flocculated or precipitated by chemical additions, particulate removal is a secondary step in the sequence; in fact, more than one stage of precipitation/filtration may be needed to obtain the desired degree of decontamination. Filtration or centrifugation can also be used as a final "polishing" step for liquid wastes which have retained small amounts of suspended solids throughout other treatment processes.

The relatively common application of ion exchange processes has proved to be effective for decontamination of LLLW waste solutions which are relatively low in ionic contaminants. In these processes, the solid ion exchange treatment material (commonly an organic resin or inorganic zeolite) preferentially bonds with the radioactive ions to be removed rather than the similar but less hazardous ions present in the original ion exchange material. Thus, an ion exchange process can ideally generate a virtually nonradioactive liquid effluent, while trapping the radioactive feed constituents within a solid matrix (the ion exchange material). The loaded ion exchange material can either be treated by solid waste treatment methods, or chemically regenerated for further use, producing a more concentrated liquid regeneration waste for further treatment by LLLW treatment methods. Since the liquid flow rate capacity of an ion exchange bed can be reduced by particulate material buildup, a filtration or centrifugation step often precedes ion exchange processing.

Reverse osmosis and electrodialysis are both membrane processes which could potentially be used for purification of LLLW streams, although additional development work and more favorable economic incentives would be needed prior to extensive application. Basically, both these processes result in the separation of soluble constituents from solute-free liquids by selective passage through a membrane; this separation is induced by feed solution pressure for reverse osmosis and by passage of an electric current through the feed solution for electrodialysis. Either process could be used either as a sole treatment method or in combination with other treatment processes. Specific waste stream compositions may be more amenable to treatment by reverse osmosis or electrodialysis rather than the more commonly used evaporation and ion exchange processes.

10.3 TREATMENT REQUIREMENTS FOR SECONDARY WASTES

All of the non-high-level radioactive liquid waste treatment processes described in this section are capable of generating secondary wastes which require further treatment prior to discharge, storage, or disposal. Secondary waste treatment requirements which are specific to individual primary waste treatment processes are identified in Section 10.4.

10.3.1 Gases

Many of the treatment processes require an off-gas treatment system. This system may consist of nothing more than HEPA filters, or it may also include additional equipment such as condensers, scrubbers, deentrainment devices, heaters, etc. Operation of such equipment generates even more waste which requires treatment (e.g., scrubber solutions, spent HEPA filters, etc.).

10.3.2 Liquids

Some treatment processes generate secondary liquid wastes with sufficient radionuclide concentrations to warrant further treatment prior to discharge. As an example, evaporation of ILLW produces an overheads condensate which, depending upon deentrainment efficiency, may require further purification, such as by ion exchange or reevaporation. Corresponding situations may occur where primary waste treatment is performed by ion exchange, reverse osmosis, or electrodialysis, but the degree of decontamination achieved is insufficient to permit discharge of the purified stream as a process effluent. Off-gas treatment systems can also generate secondary liquid wastes, such as condensates and scrubber solutions.

10.3.3 Solids

Any treatment process generates solid wastes requiring further treatment. Such wastes include spent ion exchange resins, filter media, failed equipment, and general radioactively contaminated process trash.

10.4 ALTERNATIVE TREATMENT TECHNOLOGY DESCRIPTIONS

10.4.1 Evaporation

Process Summary

Process Description

Liquid wastes are evaporated to form a lower volume product stream containing virtually all nonvolatile constituents of the feed solution, and an overheads stream consisting of water vapor (subsequently condensed), other volatile components, and only trace amounts of other feed components.

Development Status

Existing evaporation technology has been applied and demonstrated for radioactive liquid wastes in numerous processing locations.

Applicable Wastes

The process is applicable to any liquid waste stream; it is normally used for highly contaminated or high salt content solutions.

Product Form

The concentrated product may be all liquid, a slurry, or even a solid in some applications.

Feed Treatment

Chemical adjustment for corrosion control or trace chemical additions to reduce scaling or foaming tendencies are sometimes desirable.

10.4.1.1 Background

Evaporation is a process by which a solution or slurry is concentrated by driving off solvent vapors by the application of heat. It is a unit operation that has wide application in the nuclear industry for reducing waste volumes and the amounts of radionuclides in liquid effluents. Evaporation is usually used for radioactive wastes that require the high degree of separation between volatile and nonvolatile components that it offers. It is also used for wastes that are not amenable to treatment by less costly low-temperature operations such as precipitation, filtration, and ion exchange. An evaporator consists basically of a device to transfer heat to the solution or slurry and a device to separate the vapor phase from the liquid phase. The principal elements involved in evaporator design are heat transfer, vapor-liquid separation, and energy utilization.

In the design of evaporators for concentrating radioactive liquids, vapor-liquid separation is the most important factor because decontamination of the liquid is the most important objective, and heating cost is relatively less important. A small amount of entrainment can contaminate the condensed vapor to unsatisfactorily high levels. The decontamination factor for evaporation is normally defined as the ratio of the contaminant concentration in the evaporator bottoms to the corresponding contaminant concentration in

the overheads condensate. These decontamination factors normally fall within the range of 10^4 to 10^6 for a single stage of evaporation and deentrainment. Evaporator type and design, the design and performance of associated liquid droplet deentrainment devices, and the volatilities of feed solution contaminants are the most significant influences upon the attainable decontamination factors. Radioactive iodine, ruthenium, and tritium are the most notable elements for which evaporative decontamination can be difficult.

Several types of deentrainment devices have been used in conjunction with evaporators. Such devices may be located within the evaporator vessel or in a separate piece of equipment through which the vapors pass. Impingement separators, such as baffle plates and wire mesh screens are most commonly used. Enlarged vapor flow cross-sections are sometimes provided to assist gravity settling of entrained droplets by reducing the vapor velocity. Cyclone mist separators can also be used for droplet removal by centrifugal force. For more complete deentrainment, scrubbing towers are sometimes used. The several varieties of deentrainment devices are readily available commercially, and design parameters are well established.

This section will describe several generic classes of evaporation equipment and processes but will not necessarily cover all specific options available. Additional and more detailed information on evaporation as a treatment process for radioactive liquid wastes is presented in References 1 through 5.

Evaporation is most suitable for processing liquid waste which has a high total solids concentration and which requires a high degree of decontamination from its radionuclide content. The volumes of such liquid wastes are normally low in comparison to those of lower activity liquid wastes from nuclear plants. Economic considerations generally favor methods of liquid waste treatment other than evaporation (e.g., ion exchange, flocculation and filtration, etc.) for large-volume treatment of low-level radioactive liquid wastes. In cases in which liquid wastes contain scaling, foaming, or corrosive materials, some form of pretreatment (normally by chemical addition) or combination with other waste treatment methods is often desirable.

10.4.1.2 Product Characteristics

The product characteristics of evaporation processes vary widely as functions of liquid feed characteristics and degree of evaporation performed. Since evaporation is seldom the final step in the overall liquid waste treatment process, the degree of evaporation performed is influenced by the requirements of subsequent processing operations, such as those described in Section 12.0. The chemical properties of concentrated evaporator products are basically the same as those of the nonvolatile components of the

evaporator feed material, although evaporator product solutions may contain an increased amount of precipitated components. Typical evaporator product (bottoms) solutions contain from about 10 to 50 weight percent dissolved solids, although evaporators are available which can yield free-flowing solid products.

10.4.1.3 Process Description

The process of evaporation has been in common industrial use for centuries. Specific variations of available evaporation equipment are described in the following paragraphs.

- Coil or Pot Type Evaporators

This type of evaporation equipment is one of the simplest and most adaptable of low-volume treatment applications. Used primarily for batchwise operation, this equipment is merely a vessel in which the liquid to be evaporated is contained and heated, normally by steam condensation in an internal coil or an external jacket; heating by direct fire or electrical resistance heaters has also been used. The vapors leaving the vessel are normally passed through an external vapor-liquid deentrainment device and a water-cooled condenser. An example of this type of evaporator is a moonshiner's still, in which case the condensed vapors become a product for consumption rather than a decontaminated waste liquid for recycle or disposal. This evaporation system is poorly suited for treatment of liquid wastes with severe scaling or foaming tendencies.

- Natural Circulation Evaporators

Natural circulation evaporators are generally heated by condensing steam in shell-and-tube heat exchangers, although electrical resistance heaters are also feasible. The simplest type of natural circulation evaporator is one in which the tubes, containing the condensing steam, are contained horizontally within a horizontal cylindrical evaporation vessel and are surrounded by the liquid to be evaporated. This type of natural circulation evaporator is best suited for installations in which a low vertical profile is required; it is unsuitable for liquids with scaling, salting, or foaming tendencies.

Vertical tube natural circulation evaporators are more commonly used than the horizontal tube type. These evaporators are normally heated by condensing steam in the shell side of a shell-and-tube heat exchanger. Thus liquid circulation vertically upwards in the tubes is induced by vapor formation, which results in an apparent liquid density within the tubes which is considerably lower than

X

that of the surrounding liquid. This density difference promotes high circulation rates and correspondingly high heat transfer rates. The heat exchanger serving a vertical tube natural circulation evaporator may be located either within the evaporator body or outside the vessel with necessary piping connections; external heat exchangers are normally preferred for ease of tube bundle maintenance or replacement. A sketch of a natural circulation evaporator with an external vertical-tube heat exchanger is shown in Figure 10-3.

- Forced Circulation Evaporators

In the forced circulation evaporator, liquid is recirculated by a pump through the heating tubes at reasonably high velocities with

FIGURE 10-3. Natural Circulation Evaporator With External Vertical-Tube Heat Exchanger

relatively little evaporation per pass. Circulation rate is normally maintained constant and independent of the evaporation rate. The heat exchanger is normally installed as a separate unit, rather than an integral part of the evaporator body, to facilitate cleaning, maintenance, and replacement.

This type of evaporator is suitable for processing scaling liquids, since scale deposition is decreased by the high liquid velocity through the heat exchanger tubes. By proper placement of the heat exchanger in relation to the normal evaporator liquid level, or by installing a flow restricting device in the outlet of the heat exchanger recirculation piping, boiling within the heat exchanger tubes can be prevented, thus improving the overall heat transfer efficiency and further reducing scaling tendencies.

- Vapor Compression Evaporators

Additional heat economy can be achieved by reuse of the energy of vaporization to provide a heat source for further evaporation. In vapor compression evaporators the energy potential of the low pressure vapor from the evaporator is increased by compressing the vapor, thus making the latent heat of condensation available at a higher temperature. The compressed vapor is combined with the fresh steam input and recycled to the steam side of the evaporator heat exchanger as the heating medium. The vapors can be compressed either with a mechanical compressor (driven by an electric motor or turbine) or with a steam injector.

- Multiple Effect Evaporators

Multiple effect evaporators provide another means of increasing energy utilization. This evaporator system utilizes the vapor from one effect as the heating medium for the next (more concentrated liquid) effect in the system. Vapor compression is not required, since successive effects are normally operated at lower absolute pressures. This evaporator type is normally used only for large-scale applications.

- Wiped Film Evaporators

A wiped film evaporator may be considered to be a special variant of forced circulation evaporators, since mechanical energy is used to improve heat transfer. The heating surface consists of a cylinder which contains a rotating agitating blade or series of wipers, either maintaining a fixed close clearance from the cylinder inner wall or riding on the liquid film on the wall. Common orientations include both vertical and horizontal, and the cylinder

may be tapered slightly. The cylinder is externally heated by a steam jacket or other means. A sketch of a typical horizontal wiped film evaporator is shown in Figure 10-4.

Liquid waste is fed into one end of the cylinder and agitated vigorously by the rotating blades, which wipe the waste on the heated surface in a thin turbulent film. Partial evaporation from the film occurs quickly, and subsequent blade travel continuously redistributes the concentrate film as it progresses toward the discharge end of the cylinder, from which the product is discharged through a nozzle as a liquid, slurry, or free-flowing solid. In addition to concentrate redistribution and movement, the rotating blades also serve to accomplish removal of foam and/or entrainment from the central vapor space. Advantages of this type of evaporator include high heat transfer efficiency, low product residence time (i.e., reduced thermal degradation of product), and capability to evaporate to high product concentrations.

**CUTAWAY VIEW SHOWING
ROTOR BLADES**

FIGURE 10-4. Wiped Film Evaporator

- Dryers

Dryers may be included among the evaporators, since they provide a suitable method of evaporating and solidifying waste liquid of high solids content. One example of drying equipment is a spray dryer, in which no direct contact heating surface is used; thus the process is particularly applicable to scaling or heat sensitive substances. The solution is sprayed from a nozzle or from a mechanically driven, rapidly rotating atomizing disc into a drying chamber, which is also fed a supply of heated gas (usually air and combustion products) sufficient to complete vaporization of the feed liquid. Heat is transferred to the liquid droplets by direct contact with the heated gas; alternatively, radiant heating can replace or supplement preheating of the dryer air supply. The spray dried product, consisting of small spherical particles, is collected by a system of cyclones, which is normally backed up by bag filters and, in the case of toxic substances, by a HEPA filtration system.

Other types of dryers are also available for specific applications. The primary alternative to spray drying is fluid bed drying, which is performed similarly to, but at lower temperatures than the fluidized bed calcination process described in Section 6.0. As mentioned previously, wiped film evaporators can be operated as dryers for waste compositions which are compatible with this mode of operation.

10.4.1.4 Development Status and Objectives

The technology for radioactive liquid waste evaporation is well developed, since the unit operation of evaporation has long been in use for nonnuclear applications. The adaptation of existing evaporation technology to radioactive materials processing, which requires remote or semiremote operation and maintenance, has been relatively extensive and successful. Broad background information on the use of evaporation technology in radioactive service applications is presented in references 1 and 2, which also provide references to more specific information. The results of more recent development and demonstration work are described in numerous ERDA-sponsored topical reports, as exemplified by references 3 through 5, which describe adaptation of wiped film evaporation technology at ERDA's Savannah River Plant and Hanford.

Many applications of evaporation technology have already been designed, demonstrated, and used in routine service in ERDA facilities and to a lesser extent in the commercial nuclear industry, as described in the references at the end of this section. Such applications are obviously ready for practical design. However, it is anticipated that situations could arise wherein it

appears desirable to use one of the less conventional evaporation techniques for a feed stream having unique characteristics (e.g., unusual tendency for foaming or scaling); extrapolation of existing test data may not be valid in some cases. Therefore, limited pilot-scale demonstration work on simulated (nonradioactive) waste may be warranted on a case-by-case basis. Such demonstration would be expected to require no more than a year or two, since various types of test evaporation facilities are already in existence.

10.4.2 Calcination

Process Summary

Process Description

Salts present in liquid wastes are dried and decomposed at high temperature to stable compounds, such as oxides. Water vapor and volatile reaction products are evolved as off-gases.

Development Status

Process development to date has focused on high-level waste, for which calcination processes are ready for design and installation in fuel reprocessing plants. Limited development work has indicated the feasibility of combining intermediate-level waste with high-level waste to form a feed material for calcination.

Applicable Wastes

Calcination process flowsheet development is believed to be feasible for virtually any intermediate-level aqueous waste.

Product Form

Calcination product form can range from powdery dust to free-flowing granular material to porous friable cake.

Feed Pretreatment

Chemical adjustment to control the volatility or corrosivity of certain waste components may be desirable.

10.4.2.1 Background

Calcination is a high-temperature conversion process in which liquid wastes are dried and thermally decomposed into stable nonfused solid compounds such as oxides. Calcination was one of the earliest techniques investigated for conversion process development and demonstration efforts have been aimed toward the solidification of HLLW. Several calcination processes, many of which are ready for commercial implementation on HLLW, are described in Section 6.0. The incentives for solidifying HLLW also apply to certain ILLW streams which have potential long-term radiological hazards resembling those of HLLW.

Demonstration work has indicated the feasibility of combining ILLW with HLLW as feed to a calcination process; supplemental chemical additives to control the volatility of certain waste components have been found necessary. This section will focus primarily on the similarities and differences regarding calcination of ILLW as opposed to HLLW; discussion will be general rather than specific to individual calcination processes.

10.4.2.2 Product Characteristics

The calcination product form can range from powdery dusts to free-flowing granular material to a porous friable cake. Specific product characteristics are described in Section 6.0.

10.4.2.3 Process Description

The basic calcination processes developed for HLLW are believed to be applicable to ILLW, either separately or in combination with HLLW. The chemical additions required to control the volatility or corrosivity of specific ILLW components may differ from those required for HLLW; in either case, thorough determination of waste composition is essential. Design modifications to off-gas treatment systems may also be needed to allow calcination of certain ILLW streams.

Regardless of radioactivity level, prior concentration of the feed solution facilitates calcination processes. In general, the ratio of radionuclides to nonradioactive salt compounds will be considerably higher for HLLW than for ILLW. Therefore, calcination of ILLW would yield a product of relatively low radionuclide density and thermal density. Thus the

considerations of radiolytic heat removal and product container dimensions would be more straightforward for handling and storage of calcined ILLW.

10.4.2.4 Development Status and Objectives

Several calcination processes have been developed and demonstrated to the point that they are ready for practical design. Calcination flowsheet modifications may be needed for waste compositions which are significantly different from those for which the process has been demonstrated. In such cases, flowsheet demonstration work should precede practical application.

No major development programs appear to be needed for the currently envisioned calcination processes. Application of these processes to waste compositions for which calcination has not been demonstrated would require additional flowsheet definition, evaluation, and demonstration. This work would include determination of the effects on equipment integrity, off-gas treatment system performance, and process safety.

10.4.3 Filtration

Process Summary

Process Description

A liquid waste is filtered through sand (as shown in sketch) or other porous media. The process can be operated with gravity or pressurized feed.

These porous media remove coarse solids, suspended solids, and, depending on the types of filtering media, some colloidal solids.

Development Status

The process has been thoroughly demonstrated in both radioactive and nonradioactive applications. Thus, further technology development is not required for immediate application.

Applicable Wastes

All liquid wastes containing suspended solids or colloidal material are suitable feeds to a filtration process.

Product Form

A decontaminated effluent stream and a backwash stream containing the filterable solids are the products of filtration.

Feed Pretreatment

Chemical additions are often used to promote precipitation or flocculation, thus increasing contaminant removal during filtration.

10.4.3.1 Background

Filtration is a process for removal of solids from a liquid waste stream by passage of the liquid through porous media. The porous media remove coarse solids, suspended solids, and, depending on the type of filtration media, some colloidal solids. Filtration is sometimes preceded by a chemically induced precipitation or flocculation step to maximize the recovery of radioactive pollutants. The recovered solids may be included with the filtration media as a solid waste, or removed from the filter (e.g., by backwashing) for further treatment.

The porous media used for filtration can be fabricated in a multitude of physical forms. Although granular media are most commonly used, filters can also be constructed using sieve plates, woven fibers, sintered metals, etc. Granular media which have been used in water filters include sand, crushed anthracite coal, diatomaceous earth, perlite, and powdered or granular activated carbon. Combinations of these media are also in use. A dual media filter consisting of coal over sand is widely used. Multimedia filters consisting of coal over silican sand over garnet sand are also finding increased use. Examples of filters which do not use granular media are described in the following paragraphs, and in greater detail in reference 6.

- Disposable Filters

Disposable filters are designed with replaceable elements which are thrown away when contaminated. These elements are usually constructed of pressed paper, matted fibers, or porcelain materials.

Cotton fabrics are, by far, the most common type, primarily because of their low first cost and wide availability. Disposable filters are available in pore sizes ranging from ten millimicron (membrane type) up to several hundred microns. In general, these types of elements are best suited for the removal of gross contamination from low pressure, low temperature systems.

- Metallic Non- or Partially-Cleanable Filters

These elements are constructed of woven wire or sintered metal. As in the case of disposable elements, several variations are available. Wire mesh elements are available in pore sizes down to approximately eight microns absolute. Sintered elements are available in pore sizes down to approximately five microns absolute. Backflushing does not completely clean these filters, and they are best suited for the removal of medium sized contamination.

- Precoat Filters

Precoat filters use elements designed as retainers to prevent a precoat material from being flushed downstream. The actual filtering of system contamination is accomplished by the precoat material. When the filter becomes contaminated, the precoat material is replaced. This type of filter can provide low levels of filtration, but is limited by temperature and pressure extremes. In addition, the large quantities of precoat material which must be disposed of can present significant problems in terms of handling and disposal. Diatomaceous earth is commonly used as a precoat and is useful in removing any dissolved or suspended oil in the feed.

- Metallic Recleanable Filters

These are relatively new filters for the nuclear industry and are designed to be cleaned to their original level of cleanliness. Although other types are available, the chemically etched disk type is most common. Etched disk filters can generally be cleaned by backflushing if too high a pressure drop (>100 psi) has not occurred. This method is quick, economical, and can be accomplished without handling the elements. This is especially important in radioactive service. The filtration efficiency increases rapidly after cleaning due to the formation of a crud barrier on the external surface of the element. The crud barrier is the filtration media; it becomes extremely effective at less than 1 percent of the design crud load. Use of a small amount of diatomaceous earth can provide retention initially and would absorb any oil present in the feed.

10.4.3.2 Product Characteristics

The filtration process removes undissolved solids from liquids. In radioactive liquid waste treatment, the filtered solids ideally include the radionuclides to be removed and/or compounds which could interfere with subsequent liquid waste treatment processes. No chemical or physical changes to either the solids or the filtered liquid result from filtration; however, such changes are sometimes intentionally induced in a prior precipitation or flocculation step.

10.4.3.3 Process Description

Filtration is a relatively simple process for removal of solids from liquids. Numerous options exist in the selection of a specific filtration system; the primary variables involved are the type of filtration media, pressure versus gravity operation, disposable versus cleanable filtration media, and the use of precoat or adsorbents. Activated carbon is one of the more common adsorbent materials which is sometimes used in conjunction with filtration for removal of trace soluble contaminants.

In the case of granular bed filters, an ideal filter medium should be of such size as to hold a large quantity of filtered solids, provide good effluent clarity, and be readily cleaned by backwashing. These requirements are not totally consistent with one another. A fine sand gives the best effluent clarity but does not permit much penetration of solids into the bed; thus, the storage available in the bed is not utilized. Furthermore, the heavy surface deposit which occurs with fine sand tends to compact, and is difficult to remove by backwashing. Coarser sands will lengthen runs, give lower effluent quality, and wash more readily, but require higher wash water rates to achieve comparable expansion during backwash. During backwashing, the finer gradations collect near the top of the filter bed and the coarser gradations near the bottom. This further aggravates the surface removal tendency of fine sand. To overcome these problems, there has been a gradual shift to the use of coarser sands, or to double layer filters. With proper pretreatment, acceptable effluent quality and run lengths are attained with coarser media, even with higher filtration rates. There is also a tendency to specify fairly uniform sand to minimize surface removal. However, the more uniform the specification, the higher the cost.

Precipitation or flocculation processes are commonly used as pretreatment steps prior to filtration. As an example, most actinides, including plutonium and americium, can be removed from aqueous waste by coprecipitation with iron, aluminum, and other metal ions. Iron is generally preferred as the scavenger since aluminum is amphoteric. Decontamination factors vary considerably and

are dependent on the waste. More than one stage of precipitation is therefore usually required to insure sufficient actinide removal. This process is typically carried out in a pH range between 8 and 14. Higher pH solutions (above 12) are generally more effective if the solution contains complexed actinides.

In one process, the radioactive waste stream is fed to a flash mixer where it is intimately contacted (high speed mixing) with solutions of $\text{Fe}_2(\text{SO}_4)_3$ (100-125 ppm Fe^{+++}) and MgSO_4 (200 ppm). The iron forms a voluminous ferric hydroxide floc which later acts as a scavenger for the carrier precipitation. The magnesium sulfate is added to retard colloid development. The mixture from the flash mixer overflows into the flocculator where gentle mixing allows floc growth to take place. A coagulating agent is added to aid in the floc development. The stream overflows to a clarifier where a separation of the floc, which contains the radioactive materials, from the decontaminated liquid is made. The liquid is transferred to the next stage where the decontaminating process is repeated. The underflow (sludge slurry containing the radioactive material) from the clarifier is discharged on a timed basis to a filter feed tank. Examples of other specific uses of precipitation or flocculation processes followed by filtration are described in reference 7.

10.4.3.4 Development Status and Objectives

Filtration technology is fully developed and has been successfully applied in nuclear service. No additional development work is required other than tailoring filtration media to specific intended uses.

10.4.4 Centrifugation

Process Summary

Process Description

Centrifugal separation is a process in which imposed liquid rotational motion causes relative movements of suspended materials and clear liquids and permits their separation. The rotational motion can be induced by liquid velocity tangentially into a cyclone or by mechanically drive rotating devices (centrifuges).

Development Status

Centrifugal separation equipment is commercially available and state-of-the-art technology exists. Centrifuges are sometimes used in reactor radwaste treatment systems. No additional technology development is needed.

Applicable Wastes

All liquid wastes containing suspended solids or colloidal material are suitable feeds to a centrifugal separation process.

Product Form

A clarified liquid stream and a wet solids stream or slurry are the products of a centrifugal separation process.

Feed Pretreatment

As with filtration, chemical additions are often desirable to promote precipitation or flocculation, thus increasing contaminant removal during centrifugation.

10.4.4.1 Background

Centrifugal separation is a method whereby imposed liquid fluid rotational motion causes relative movements of suspended materials and liquids and permits separation of these materials from the liquids. A hydroclone is a simple device having no moving parts and is applicable to removal of relatively dense suspended solids from a liquid stream. In this device fluid pressure energy is used to create rotational fluid motion in a shaped vessle. This motion causes relative movement of materials suspended in the fluid and permits separation of these materials from the fluid. The bulk of the fluid is removed through a top outlet while separated solids are discharged through an axially located bottom outlet. Centrifuges are mechanically driven devices having a wide variety of possible designs and operating characteristics. Solids-bearing fluids are fed into a rotating section which imparts rotational motion to the suspension. Residence time in this section is dependent on feed rate and section volume. As higher density materials are accelerated toward the periphery during traverse across the rotating section, separation of suspended particles from the liquid phase results. Separate exit points are provided for discharge of solids and clarified liquids.

10.4.4.2 Product Characteristics

Separation of solids from liquids by centrifuge results in a clarified liquid product and a wet solids stream which ideally contains the radionuclide contaminants. No chemical or physical changes to these streams occur, unless a precipitation or flocculation process precedes centrifugation.

10.4.4.3 Process Description

Centrifuges separate particles from liquids through the use of centrifugal force. Liquids containing suspended radioactive materials are continuously fed to the centrifuge; solids "settle" to and are retained at the walls of the bowl by centrifugal force while the clarified liquid overflows and passes to a tank. Periodically, the accumulated solids may be removed by interrupting the flow of feed liquid and either washing out the solids, or forcing them out by agitation and gravity into a hopper. However, this step is only occasionally needed for centrifuges which are designed for continuous solids discharge.

Aqueous waste streams which contain significant amounts of high density solids, such as grit in drainage water from grinding or cutting operations or facility floors, are candidate feeds to hydroclone separation of these solids. However, more complete separation of solids is attainable by the action of a mechanically driven centrifuge, where residence time and related rotational energy input are controllable by selection of design and operating parameters suitable to the feed characteristics. Any aqueous waste stream containing suspended solids may be processed through a centrifugation step.

10.4.4.4 Development Status and Objectives

Centrifuges are sometimes used in reactor radwaste treatment systems to "dewater" evaporator slurries and filtration sludges in preparation for packaging and shipment. Centrifugal separation equipment is commercially available and technology is essentially state-of-the-art. Nuclear industrial applications of centrifugal separations have been made since the first plutonium recovery process was operated using only this method for solids-liquid separations.

10.4.5 Ion Exchange

Process Summary

Process Description

Ion exchange resins remove radioactive material from liquid wastes through the exchange of ions between the liquid phase and the solid ion exchange resin. It is a process involving the mass transfer of ions between a polar solvent and an inert solid matrix containing highly polar groups which can be ionized.

Development Status

Although ion exchange resins have been in use for a considerable period of time, new resins are being developed. These resins have greater resistance to particulate fouling, iron fouling, and organic/oil fouling. Bed capacities, equilibrium constants for specific isotope removal, interactions with nonradioactive chemicals, and engineering design parameters have yet to be determined for some of the newly developed ion exchange resins.

Applicable Wastes

Ion exchange resins are excellent for final treatment of waste treatment effluents. As the primary process, ion exchange can be used for condensates, decontamination wastes, drains, and many other waste streams. It is capable of removing both alpha and gamma activity. Certain types of resins can remove radiocolloids.

Product Form

A decontaminated liquid waste stream and a saturated resin slurry which can be regenerated or further treated as solid waste are the products of ion exchange.

Feed Pretreatment

The use of an ion exchange process, especially as the primary treatment process, may require the liquid feed solution to be filtered to prevent plugging of the ion exchange bed.

10.4.5.1 Background

Ion exchange is a process involving the mass transfer of ions between a solvent and a solid matrix containing ionizable polar groups. Equivalent amounts of ions are exchanged between the solution and the ion exchange media. A large amount of natural and synthetic materials have ion exchange properties, but the important commercial exchangers are the zeolites and polymeric resins.

Ion exchange has been used in processing radioactive solutions in many ways, including ore processing, isotope separations and purification, decontamination, and waste treatment. Many different wastes have been treated, including reactor coolants, condensates, steam generator blowdown, etc. Comprehensive presentations of commercial applications of ion exchange processes in nuclear power plants are contained in references 8 and 9 and their associated references.

The use of unconfined soil columns, called cribs, as ion exchange media is a unique application of ion exchange which has been practiced at ERDA facilities for low level waste streams. A crib consists of a subsurface liquid distribution system over a soil area such that liquid flow rate per unit area is consistent with percolation rate through the soil. The natural ion exchange properties of the soil are utilized for radionuclide removal. Since the removed radionuclides are not readily retrievable, the practice of cribbing is now considered suitable only as a disposal method for liquid effluents not requiring treatment, rather than as an ion exchange treatment process.

10.4.5.2 Product Characteristics

The desired product of an ion exchange process for liquid waste treatment is a liquid effluent which is virtually nonradioactive. The radioactive constituents of the liquid feed remain trapped within the ion exchange material, which may be regenerated and reused, thus generating a secondary liquid waste, or further treated and packaged as a radioactive solid waste.

10.4.5.3 Process Description

Ion exchange resins remove radioactive material from liquid waste water through the exchange of ions between the liquid phase and the solid ion exchange resin. All types of waste streams can be treated. However, pre-treatment consisting of coagulation/sedimentation and/or filtration may be

required to prevent bed plugging. In a typical fixed bed ion exchange process, the resin bed is between 1 meter and 3 meters deep and is contained in a cylindrical pressure vessel. The bed rests on a bottom support which can be a granular bed or metal screen supporting the resin bed but allowing liquid flow. The resin bed fills one-half or more of the vessel height, and a free space above the bed surface allows it to be fluidized and expanded during backwash. The main inlet feed is at the top of the vessel and a second distributor system just above the bed surface ensures even flow of regenerant down through the bed. The normal mode of operation is with all flows except backwash downward from the top of the bed. During a typical treatment, the top of the bed becomes loaded first with the absorbed ions. Then, a concentration front moves slowly downward until an appreciable concentration rise of the ion to be removed occurs when the front reaches the base of the column. At this point, the treatment is complete and the resin is backwashed and subsequently regenerated or treated for disposal.

Wastes with very low ionic concentrations, such as condensates, can be economically treated with ion exchange resins and the resins discarded as solid waste. Recently, macroporous ion exchange resins have been developed which have been successfully used to demineralize raw water with appreciable organic content. The porosity allows the organics to be absorbed in the resin matrix without blocking the diffusive exchange of ions. For heavily organic-contaminated water, special absorbent resins have been developed which are used as a pretreatment to conventional ion exchangers to remove these large quantities of organics. These types of resins would, in addition, absorb colloidal metal oxides. The main advantages of these new resins are their high porosity, resistance to organic and iron fouling, ability to operate in highly oxidative environments, ability to operate in polar organic solvents, and ability to remove colloids and organically complexed species. This application differs from presently used gel resins in that gel resins foul readily, need a higher level of pretreatment, and result in high pressure drops within operating columns.

10.4.5.4 Development Status and Objectives

Ion exchange resins have been in use for a considerable period of time; recent developments have provided ion exchange resins which have greater resistance to particulate, iron, and organic fouling. The bed capacities and equilibrium constants for some isotopes have yet to be determined. Only the performance of these beds based on a composite waste stream has been measured. Interaction of various radionuclides with other chemical species and the resultant effect on ion exchange resin performance is unknown. Various engineering parameters, such as loading rates, bed capacity, residence time, and materials removed would need to be evaluated for various resins.

10.4.6 Membrane Processes

Process Summary -- Reverse Osmosis

Process Description

Reverse osmosis consists of pressurizing (above the osmotic pressure) an aqueous solution and bringing it in contact with a semipermeable membrane. The permeate is the purified solution that passes through the membrane; the remaining solution contains the concentrated solutes.

Development Status

New membranes have been developed which are not as subject to hydrolysis as are the more common cellulose acetate membranes. The new membranes can withstand a wide range of pH and many oxidizing agents. Reverse osmosis has been used mainly on nonradioactive waste streams; in radioactive service, it has been used for treatment of steam generator blowdown and, experimentally, on laundry wastes. However, additional development work would be needed before reverse osmosis systems can be designed for the treatment of radioactive liquid wastes.

Applicable Wastes

Reverse osmosis could be used for treatment of virtually any low-level liquid waste stream.

Product Form

The final product consists of a clean permeate or product stream and a concentrated blowdown stream for further treatment.

Feed Pretreatment

Chemical treatment for improved waste compatibility with membrane materials may be desirable.

Process Summary -- Electrodialysis

Process Description

Positive and negative ions are caused to move toward oppositely charged electrodes immersed in the solution. By putting alternate cationic and anionic membranes between the electrodes, the salts in solution are depleted in one output stream and concentrated in the other.

Development Status

Large-scale operations for production of potable water from sea water have been in use for many years. Newly developed membranes are being used in a continuous electrodialysis process to convert brackish water into boiler feedwater. The principles involved in electrodialysis have been known since about 1950, and applications, principally to water desalination, date to the early 1960's. Additional development would be needed for use on radioactive liquid waste.

Applicable Wastes

An aqueous waste stream with electrolyte concentrations to about 20 g/l is a candidate feed to this process. Very low level streams may be depleted of electrolytes to permit discharge to the environment.

Product Form

Clean water, concentrated solutions of electrolytes, and, in some cases, trace amounts of decomposition products such as H_2 , O_2 , or Cl_2 are process yields.

10.4.6.1 Background

Membrane separations are playing an ever increasing role in water and waste water treatment. Electrodialysis and reverse osmosis are presently used for desalting water on a large scale. Ultrafiltration is employed in a variety of water and waste treatment processes.

A membrane acts as a barrier to flow of molecular or ionic species. Osmosis is defined as the spontaneous transport of a solvent from a dilute solution to a concentrated solution across an ideal semipermeable membrane which impedes passage of solute but allows solvent flow. Solvent flow can be reduced by exerting pressure on the concentrated solution side of the membrane. At a certain pressure (the osmotic pressure), equilibrium is reached and the amount of solvent which passes in each direction is equal. The osmotic pressure is a property of the solution only, provided the membrane is truly semipermeable. If the pressure is increased above the osmotic pressure on the solution side of the membrane, the flow reverses. Pure solvent will then pass from the concentrated solution into the dilute, or pure solvent, side of the membrane. This phenomenon is the basis of reverse osmosis treatment of water and waste water.

Reverse osmosis is somewhat similar to filtration - both involve removing a liquid from a mixture by passing it through a device which retains the other components. However, there are at least three important differences. First, the osmotic pressure, which is very small in ordinary filtration, plays an important role in reverse osmosis. Second, filter cakes with low moisture are unfeasible in reverse osmosis because the solution osmotic pressure increases with the removal of solvent. Third, filters separate mixtures primarily on the basis of size, whereas the semipermeability of reverse osmosis membranes depends significantly upon other factors as well.

Membrane ultrafiltration, like reverse osmosis, depends upon a pressure driving force and a membrane that is permeable to some components in a liquid solution or mixture and impermeable to others. The two processes differ because ultrafiltration is not impeded by osmotic pressure and can sometimes be effected at pressure differences as low as 0.5 to 0.7 atmosphere. Ultrafiltration is usually applicable for separation of solutes above a molecular weight of 500, which have very small osmotic pressures at moderate concentrations.

Electrodialysis is a process in which positive and negative ions in solution are caused to move toward oppositely charged electrodes immersed in the solution. By alternately placing cationic and anionic membranes between the electrodes, the salts in solution are concentrated in one product stream and depleted in the other. Movement of the two product streams is counter-

current to each other and parallel to the membranes, while movement of the ions in solution is perpendicular to the membranes.

10.4.6.2 Product Characteristics

The products of each of the membrane separation processes are a purified aqueous stream and a stream which is concentrated in dissolved feed components. No chemical changes of the liquid waste constituents occur, except electro-dialysis can result in small amounts of decomposition products such as H_2 , O_2 , or Cl_2 .

10.4.6.3 Process Description

- Reverse Osmosis

Reverse osmosis consists of pressurizing (above the osmotic pressure) an aqueous solution and bringing it in contact with a semipermeable membrane. The product (or permeate) is the solution that passes through the membrane; its concentration of solutes is lower than that of the feed. The remaining feed solution is enriched in solutes and is called the blowdown. The membrane rejects phosphates, radioactive species, and other dissolved or suspended solids. The resultant permeate tends to be very low in radioactivity and dissolved solids. The concentrate will have its volume reduced sufficiently to be better suited for other treatment processes, such as evaporation. Additional reverse osmosis process information is presented in reference 10.

Several materials have been investigated for possible use as reverse osmosis membranes; cellulose acetate membranes are commonly used. The configuration of a reverse osmosis unit can vary, but depends largely upon providing adequate support for the membrane material. Both flat membranes supported by grids and small diameter tubular membranes have been used.

- Electrodialysis

In electrodialysis, the alternate compartments, separated by membranes, function as dilution and concentration compartments. The feed stream is directed through dilution compartments by manifolding to a multiplicity of dilution compartments. As this stream passes through each compartment, cations move through the cation membrane toward the cathode into an adjacent concentration compartment, but cannot pass through the anion membrane which forms the other side of that compartment. Anions move from the feed stream in a direction opposite to cation movement into an adjacent concentration compartment, and cannot then pass through the cation membrane forming the other side of that compartment.

Fluid flow channels between membranes are as narrow as possible to minimize electrical resistance; channel thicknesses are on the order of about 0.1 cm. Direct current flow between the submerged electrodes is provided at current densities to about 1200 amp/m². Additional process details are presented in references 11 - 13. Single pass or recirculation of dilution and/or concentration streams may be employed. Electrodialysis units having ion exchange materials incorporated in partitioning membranes may be operated in series to provide improved selectivity and/or overall stream decontamination.

10.4.6.4 Development Status and Objectives

- Reverse Osmosis

New reverse osmosis membranes have been developed which are not subject to hydrolysis as are the cellulose acetate membranes. The new membranes can withstand a wide range of pH and many oxidizing agents. Reverse osmosis has been used mainly on nonradioactive waste streams, such as in desalting brackish water, food processing, and experimentally in sewage treatment. In radioactive service, reverse osmosis membranes have been used for treatment of steam generator blowdown and, experimentally, on laundry wastes. However, additional development work would be required before systems can be designed for the treatment of radioactive wastes in the nuclear fuel cycle. Membranes would need to be tested on the various radioactive waste streams in order to determine solvent flux rates, flux rate declines, rejections of various radioactive contaminants, and membrane life in a radioactive environment. At the completion of this program, large-scale system studies could be started on the various waste streams so that final system designs could be developed.

- Electrodialysis

Current electrodialysis technology is in active use for large-scale desalination of brackish waters for use as boiler feedwater and for recovery of salt from sea water. Applicability to cleaning low-level nuclear wastes to permit water discharge or recycle appears promising, but would require in-service testing and evaluation as an alternate or supplement to reverse osmosis, ion exchange, and evaporative methods.

Development studies and demonstration of a practical system for electrodialysis of low-level nuclear waste streams are estimated to require up to five years. Areas of technology development include, but may not be limited to, the following:

Membrane materials development to provide high integrity mechanical support to ion exchange media while, at the same time, having adequate permeability to electrolyte ion transport and high resistance to radiation damage and to chemical attack by corrosive ions such as halides.

Selection of ion exchange materials which can be fixed in positions on supporting membranes and which provide high selectivity for ionic contaminants in aqueous waste streams and low transport for water ions.

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11.0 RECOVERY OF TRANSURANICS FROM NON-HIGH-LEVEL WASTES

11.0 RECOVERY OF TRANSURANICS FROM NON-HIGH-LEVEL WASTES

Recovery of transuranics for beneficial use from non-high-level waste and scrap materials has been practiced routinely at ERDA and commercial fuel cycle facilities. High recovery efficiencies are seldom obtained because of the diversity of waste forms and the refractory nature of plutonium dioxide, the most common form of plutonium in the wastes. Decontaminating wastes to low contamination levels for potential unrestricted release is usually not the goal of the recovery operation.

Of the three transuranic contaminants that may be present in non-high-level wastes, plutonium is by far the most prevalent. It is potentially present in recoverable quantities in nearly all fuel reprocessing, plutonium oxide preparation, and mixed-oxide fuel fabrication wastes. Americium formed in the reactor is discharged to the high-level waste stream during reprocessing. However, ^{241}Am formed by decay of ^{241}Pu is routinely recovered from aged-plutonium purification waste streams for use in preparation of neutron sources. Neptunium is also normally rejected to the high-level waste stream, but simple process modifications can be used to carry the neptunium to less radioactive waste streams for recovery if desired as a product. Methods for recovering transuranics from high-level liquid wastes are discussed in Section 16.0 of this report.

Non-high-level wastes that might be treated for transuranic recovery fall into five broad categories:

- surface-contaminated solids, including containment structures (e.g., glove boxes), process vessels and equipment, plastic bags, and drybox gloves
- plutonium-impregnated materials, generally porous and/or granular solids such as wipes, incinerator ashes, soils, insulation, and ion exchange resins
- HEPA (high-efficiency particulate air) filters
- organic solvents and lubricants
- aqueous solutions, derived in both main-line production and waste recovery operations

The processes developed and presently used to treat these wastes for transuranic recovery are discussed in the following sections, along with a description of nondestructive assay (NDA) techniques used for measurement of the transuranic content of the wastes before and after treatment. The recovery processes are performed in conjunction with decontamination, waste volume reduction, and scrap recovery operations and do not necessarily contribute significantly to the facility's waste disposal problems.

11.1 RECOVERY FROM SOLIDS

Plutonium in solid wastes is most often present as a refractory oxide, although it is also found in the form of sorbed or precipitated salts. Recovery operations involve one or more of the following steps:

- physical or chemical removal of plutonium from contaminated surfaces,
- conversion of wastes to forms amenable to leaching,
- chemical leaching or dissolution of plutonium from the solids.

The dissolution step is the most crucial of these operations since only dissolved, ionic actinides can be recovered and purified by conventional aqueous techniques. Dissolution of any high-fired actinide oxide is difficult because dissolution proceeds from dislocations or imperfections in the surface of the crystals, and high temperature treatment reduces the number of such imperfections. Oxides heated to less than 600°C are generally relatively easy to dissolve; oxides heated to temperatures between 600 and 1000°C require more stringent procedures; oxides fired at temperatures greater than 1000°C require extreme measures.⁽¹⁾

Nitric acid alone is not a good solvent for PuO_2 , but addition of fluoride ion at concentrations above 0.03M greatly increases the rate of dissolution.⁽²⁾ If cations that strongly complex fluoride (such as aluminum, zirconium, and molybdenum) are present, they must be removed or additional increments of fluoride added to dissolve PuO_2 completely. Salt-fusion techniques may be required to convert the most refractory compounds to soluble forms.

Most dissolution techniques for waste and scrap materials require highly corrosive chemicals, such as HF, not usually handled in the main-line processing section of the fuel cycle facility. Plastic equipment is frequently used in small-scale applications. Stainless-steel equipment can be used if aluminum nitrate is added to complex the fluoride.⁽²⁾ More flexibility is provided by using plastic-lined equipment. The Hanford Plutonium Reclamation Facility makes wide use of such equipment for handling reagents containing hydrofluoric, nitric, hydrochloric, and sulfuric acids.⁽³⁾ Kynar, a polyvinylidene fluoride plastic made by Pennwalt, has been particularly useful in this application.

Typical recovery operations applied to the various categories of wastes are described in the following sections.

11.1.1 Surface-Contaminated Materials

Loose dust in glove boxes is swept up with vacuum cleaners or brushes and deposited in cans for later recovery of the plutonium. Paper and cloth

wipes, sometimes moistened with water or nitric acid, are also used to clean surfaces. Drybox rubber gloves can usually be decontaminated satisfactorily by this technique if cleaned immediately after removal from service.⁽¹⁾ The wipes are burned and plutonium is recovered from the ashes.

A high pressure cleaning unit has been used at Mound Laboratory to clean in-line process equipment. This unit, consisting of a high pressure pump, a continuous dumping centrifuge, a recirculating pump, a liquid storage tank, and associated piping and controls mounted in two portable glove boxes, delivers high pressure (70 kg/cm^2 maximum) liquid to a spray nozzle. The cleaning solution is pumped through the continuous dumping centrifuge to a storage tank and recycled. The solids removed by the centrifuge are reclaimed by conventional recovery methods. This system was used to clean 60 linear meters of glove boxes containing process equipment contaminated with ^{238}Pu .

Similar methods, using both steam and water jets, have been used at both Hanford and Savannah River for decontaminating equipment.⁽⁴⁾ Jet techniques with water alone provide two important advantages: 1) they are effective aids in decontaminating equipment, and 2) they do not contribute chemical reagents or detergents to interfere with subsequent processing.

Small surface-contaminated items (e.g., rubber gloves, plastics, glass, and metals) are often transferred to a separate leaching tray or heated leaching vat for plutonium recovery. Depending on the application, nitric acid or a nitric-hydrofluoric acid mixture (typically 10M HNO_3 - 0.1M HF) may be used as the leachant. Optionally, rubber and plastic materials may be incinerated and the ashes treated for plutonium recovery.

Ultrasonic energy can be used to improve the efficiency of leaching procedures. Ultrasonic cleaning is based on the principle of cavitation, where contaminants are physically removed from the object's surface rather than by dissolution. Ultrasonic leaching has been used on a production basis at Mound Laboratory to clean metal, glass, and molded or extruded plastic objects. The equipment consists of three tanks about 0.4 m wide, 0.6 m long, and 0.4 m deep, with each containing an immersible piezo-electric transducer and 0.35M HNO_3 cleaning agent. The transducers are individually driven by 1000 W ultrasonic generators at a frequency of 25 kHz. The waste materials are cleaned ultrasonically in each of the three tanks for approximately 10 minute periods, followed by a rinse. After three to four runs, the less contaminated cleaning agent is moved to the next tank while the cleaning agent in the initial cleaning tank is filtered and stored for future reclamation of the plutonium. Occasionally, plastic waste has resisted ultrasonic cleaning.

Hot water ball milling has been used at Rocky Flats to recover plutonium from contaminated leaded drybox gloves and miscellaneous metallic wastes. Fifty leaded gloves and about 40 kg of metal wastes are used as separate routine loads, along with two pair of throw-away coveralls to provide a scrubbing action. Hot water is recirculated through the rotating ball mill over a 20 to 30 minute time cycle. The lead nitrate on the gloves, which could be pyrophoric, is removed during this operation. The spent slurry is pumped through a series of full flow filters, which are then incinerated to recover the plutonium. The treated gloves and metal are packaged as contaminated waste; the filtrate is processed, along with other waste liquids, into a discard sludge.

A cryogenic grinding process has been proposed at Cadarache Nuclear Study Center, France, for treating rubber gloves, plastic bags, and similar wastes for plutonium recovery.⁽⁵⁾ By this process, the flexible plastics are cooled to -70°C with liquid nitrogen or CO_2 to embrittle them for grinding. The ground material (less than 2 cm) is leached first with 0.1M citric acid to remove soluble plutonium, then treated with a detergent to remove the adherent PuO_2 . The detergent is recycled after centrifugation to remove the PuO_2 .

Studies by PNL in cooperation with ARHCO have shown that electro-polishing can be a rapid (less than 10 min.) and very effective technique for removing plutonium oxide contamination from relatively complex metal surfaces. The contaminated metal serves as the anode in a phosphoric-sulfuric acid electrolyte. Anodic dissolution of the contaminated surface releases the PuO_2 (without dissolving it) while the concurrent polishing of the surface minimizes recontamination. A simple water rinse after electropolishing is usually sufficient to remove the plutonium-containing electrolyte and leave a contamination-free surface. Initial studies used 40 liters of electrolyte to decontaminate samples with up to 1000 cm^2 of surface area. The process is readily amenable to scaleup. Plutonium recovery from the electrolyte has not yet been demonstrated.

An experimental program has been initiated at Argonne National Laboratory to investigate the feasibility of melt refining to remove plutonium contamination from steel.⁽⁶⁾ Melting with and without slags and the compatibility of slag-crucible combinations will be tested. Although plutonium recovery is not a primary objective of this work, recovery from slags should be possible if desired.

11.1.2 Plutonium-Impregnated Materials

Plutonium recovery from combustible, absorbent waste materials involves burning the waste to convert it to a more amenable form for leaching. Paper and cloth rags used to wipe up HNO_3 should be rinsed immediately with water

to avoid formation of potentially explosive nitrocellulose.⁽¹⁾ The ashes from the combustion process, typically containing 0.2 to 10 wt% plutonium, are ground, if necessary, and treated by one or more of the following procedures.

At LASL, ashes are leached with dilute HNO_3 to remove the more soluble components and rinsed with water to remove the nitric acid. The residue is then treated with gaseous HF at room temperature to convert the silica to volatile SiF_4 .⁽¹⁾ After leaching with $\text{HNO}_3\text{-Al}(\text{NO}_3)_3$ to remove any PuF_4 formed, the residue is dried and fused with six parts of a 10 to 1 $\text{K}_2\text{S}_2\text{O}_7\text{-NaF}$ mixture per part residue for two hours at 550°C . This forms a melt that, after cooling, can be dissolved in $10\text{M } \text{HNO}_3\text{-}0.3\text{M } \text{Al}(\text{NO}_3)_3$ to recover the remainder of the plutonium.

At Rocky Flats, plutonium is recovered from incinerator ashes by digestion in $\text{HNO}_3\text{-HF}$.⁽⁷⁾ For a given type of ash and a constant HNO_3 concentration, the dissolution rate increases with the fluoride ion concentration up to at least 0.4M . The pulverized ashes and acid dissolvent (typically $10\text{M } \text{HNO}_3\text{-}0.2\text{M } \text{CaF}_2$) are fed continuously into a series of air lift dissolvers heated with steam coils up to $90\text{-}100^\circ\text{C}$. The resulting solution is filtered, and aluminum ion is added to complex the excess fluoride. The solution is then sent to anion exchange for plutonium recovery. The residues may be further treated with gaseous HF at room temperature to remove silicon as SiF_4 . The fluorinated residue is then leached with nitric acid. A similar technique can be used for glove box sweepings, soil, and pulverized firebrick and fibrous insulation.⁽⁷⁾

In a process under development at Marcoule, France, concentrated HF is added to incinerator ashes at room temperature to dissolve the silica from the plutonium.⁽⁸⁾ The fluoride solution is discarded, and the plutonium containing residue is dissolved at elevated temperatures with $\text{HNO}_3\text{-HF}$, distilling off residual silicon as SiF_4 . Boiling with aluminum nitrate completes the dissolution. At least 95% plutonium recovery has been demonstrated.

Over 90% of the plutonium in milled incinerator ash has been recovered by leaching with a solution containing $10\text{M } \text{HCl}\text{-}0.5\text{M } \text{NH}_4\text{F}\text{-}0.1\text{M } \text{SnCl}_2$.⁽⁹⁾ A similar leaching procedure (one hour agitation at 90°C) has successfully decontaminated plutonium-contaminated Hanford soil.⁽¹⁰⁾

A peroxide fusion process has been proposed for recovering plutonium from incinerator ash and centrifuge sludge.⁽¹¹⁾ The ash is fused in single-use mild steel cans with a 1 to 1 mixture of sodium hydroxide and sodium peroxide at a salt-to-ash weight ratio of about 5 to 1. After one hour at $500\text{-}700^\circ\text{C}$, both the can and the cooled melt are dissolved in dilute HNO_3 . Laboratory tests demonstrated a plutonium recovery of over 95%. Gelatinous

solids, which could interfere with subsequent purification of the plutonium, were produced in some tests.

Two combustion processes under development, AI's molten salt combustion process and HEDL's acid digestion process, convert refractory plutonium oxide to a nitric acid soluble form. These processes are discussed in Section 9.0.

Ion exchange resins can be dissolved for plutonium recovery by charring them with hot sulfuric acid and adding concentrated nitric acid to complete the dissolution. Cation sulfonic acid resins, such as Dowex 50, can be dissolved at 80°C in 0.1M HNO_3 -6% H_2O_2 catalyzed with 10^{-3} M ferrous or ferric salts.⁽¹²⁾ Ion exchange resins and other organic semi-solids (greases) can also be incinerated for plutonium recovery.

11.1.3 Recovery from HEPA Filters

HEPA filters are used to trap airborne contaminated particles in process air streams, such as hood and glovebox exhausts and process exhaust plenums. Those used in PuO_2 preparation and mixed-oxide fuel fabrication facilities sometimes contain significant quantities of plutonium (greater than 20 g/filter) and may warrant treatment for plutonium recovery. These filters, which are typically 0.2 to 0.6 m square by 0.15 to 0.3 m deep, contain a honeycomb-like, pleated filtration surface of fiberglass, sometimes separated by a aluminum or asbestos spacers. The filters are enclosed by fire-retardant plywood, particle board, or metallic frames.

Various methods may be used to recover plutonium from HEPA filters. A simple but relatively ineffective method (perhaps less than 30% recovery) is tapping the filter to release the dust. A time consuming but more effective method, (up to 90% recovery) is cutting the filter apart and brushing the trapped plutonium from the filter surface with a small brush. At LASL, the filters are disassembled, and the filter media are leached once or twice with 10M HNO_3 -0.2M CaF_2 . The frame is wiped with a damp cloth and discarded to waste.

Rocky Flats is installing a filter shredder/incineration system to process plutonium-loaded HEPA filters. In the process, scheduled to start up in 1980, the finely-shredded filter material (metallic frames are removed before shredding) will be charged to a rotary kiln incinerator and burned at 700°C during a special campaign prior to rebricking maintenance. The incinerator ashes will be leached with HNO_3 -HF for plutonium recovery. An incineration-plutonium recovery system has also been used at Hanford by ARHCO.

11.2 RECOVERY FROM LIQUIDS

Recovery of plutonium from miscellaneous waste streams is dependent on plutonium being in an ionic form suitable for treatment by solvent extraction or ion exchange techniques. Methods for dissolving or solubilizing plutonium from solid wastes were described in the preceding sections. However, the resulting solutions, and other wastes that originate as liquids, may require additional treatment to remove complexing agents, unstable reagents, corrosive materials, and surface-active agents before further processing. In addition, some organic liquids (e.g., cleaning solvents and lubricants) may contain dissolved or suspended plutonium which must be removed prior to aqueous processing.

The choice of solvent extraction or ion exchange depends somewhat on the scale of operation. Small scale applications favor the simplicity of batch ion exchange; whereas, large scale applications favor the high capacities attainable with continuous solvent extraction equipment. Solvent extraction equipment also tolerates solids in the feed that would rapidly plug ion exchange beds.

Typical feed preparation methods and applications of both solvent extraction and ion exchange techniques are described in the following sections.

11.2.1 Feed Preparation

Typical methods used to prepare waste liquids for plutonium recovery operations include the following:

- Oxalate filtrates are treated by evaporation with 12M HNO_3 , room temperature oxidation with KMnO_4 , dichromate oxidation at 65°C , or ozone oxidation at 80°C to destroy the oxalate complexant.⁽⁷⁾
- Plutonium peroxide filtrates are treated by heating stepwise to 50°C and 90°C , oxidizing with KMnO_4 , or adding NaOH to destroy the peroxide. In the latter case, the plutonium hydroxide formed can be recovered by filtration and nitric acid dissolution.⁽⁷⁾
- Fluoride-containing solutions can be processed successfully by adding aluminum nitrate to complex the fluoride.⁽⁷⁾
- Plutonium can be recovered from miscellaneous analytical solutions by reducing the plutonium to Pu(III) with ascorbic acid (at 1M H^+) and precipitating plutonium oxalate with a two-fold excess of 1.5M oxalic acid. After filtration and drying, the precipitate is calcined at $350\text{--}400^\circ\text{C}$ to form a nitric acid-soluble oxide.⁽⁷⁾

- Organic liquids may be treated by filtration to remove particulate plutonium or incinerated along with other combustible wastes. Small amounts of volatile cleaning solvents, such as acetone, may be allowed to evaporate in air. Some organic liquids may be amenable to treatment with an appropriate aqueous reagent for plutonium removal.⁽¹⁾
- To avoid emulsification problems, waste solutions containing dissolved or colloidal silica may require a digestion treatment to coagulate the silica for removal before solvent extraction processing.⁽⁷⁾ Evaporation to dryness also effectively dehydrates the gelatinous silica so that it will not redisperse on redissolution of the plutonium in dilute nitric acid.

11.2.2 Solvent Extraction Techniques

Plutonium Recovery

Hanford's Plutonium Reclamation Facility (PRF) is the only major facility in the United States using solvent extraction to recover plutonium from scrap and waste materials. The solvent is tri-n-butyl phosphate (TBP), diluted to 20 vol% with CCl_4 . The present process is a derivative of the well-known Purex process and has evolved over the past 20 years from the TBP extraction technology developed and applied in the former Hanford Recuplex facility.^(13,14)

A simplified version of the reflux-type plutonium extraction flow-sheet currently used in the Hanford PRF is shown in Figure 11-1. Feed for this process is prepared by dissolving the miscellaneous plutonium scrap materials (primarily metallurgical scrap and PuO_2) in HNO_3 -HF media. Aluminum nitrate is added to the resulting solution to complex fluoride and to provide additional salting strength for plutonium extraction.

In the first column, over 99% of the Pu(IV) is extracted from the adjusted dissolver solution by the 20 vol% TBP solvent. Weakly extracted impurities are scrubbed from the solvent extract with nitric acid solution in the lower section of the same column. The plutonium is then stripped from the solvent in the second column by dilute nitric acid containing hydroxylamine nitrate reductant to reduce the bulk of the plutonium to inextractable Pu(III). After reoxidation, a large fraction of the plutonium product (70 to 90%) is returned to the first column as a reflux stream to increase the plutonium concentration in the product. A small amount of plutonium is held tightly as a dibutyl phosphate (DBP) complex in the spent solvent leaving the second column; it is removed in the third (CO) column by scrubbing with a small volume of a HNO_3 -HF solution. The spent scrubbing solution from the CO column is routed to the feed makeup tank; the solvent continues to the remaining columns which condition it for reuse.

The reflux feature of the PRF flowsheet is easily its most distinguishing characteristic. In addition to producing a concentrated plutonium product, the reflux flowsheet maintains a nearly constant product concentration in spite of large variations in plutonium concentration in the feed.

A modified partitioning-type flowsheet for use with feeds containing both plutonium and uranium has also been developed and operated in the PRF.⁽¹⁵⁾ The basic flow scheme is similar to that shown in Figure 11-1 except a solvent scrub stream is added to the top of the second (CC) column to re-extract uranium from the plutonium product stream. The uranium is rejected to the solvent wash system.

Most operating problems encountered in the PRF have stemmed from radiolytic and chemical degradation of TBP to form DBP, a solvent-favoring plutonium complexant. With the reflux flowsheet, radiolytic degradation is substantial because of the higher plutonium concentrations. Routine DBP removal by carbonate-washing the solvent is essential to prevent carryover of excess complexed plutonium (>0.3 g/l) to the fluoride-wash (CO) column where it can precipitate as PuF_4 . Such precipitation greatly complicates the process operation, and it was frequently encountered before the routine wash system was installed. The aqueous waste streams generated in the solvent washing system make up about one-fourth the total volume of liquid waste generated in PRF operations.

Recent laboratory studies to improve PRF performance by minimizing or eliminating the formation of DBP have focussed on two approaches: replace the CCl_4 diluent with a suitable aromatic reagent, and/or replace the TBP extractant with an equivalent secondary amine extractant.⁽¹⁶⁾

Radiolytic formation of DBP from TBP is highly dependent on the diluent.⁽¹⁷⁾ The present CCl_4 diluent, for example, significantly enhances the formation of DBP when compared with hydrocarbon diluents. Aromatic compounds, because of their resonant character, act as energy "sponges" and thus tend to protect the TBP from radiolytic attack. Of several compounds studied, trichlorobenzene appears most suitable for use in the PRF because of its radiation stability and its high density (essential for hydraulic performance in the present heavy-solvent system.)

Alpha radiolysis products of a secondary amine, such as Amberlite LA-2 (Rohm and Haas Co.), complex Pu(IV) much less strongly than does DBP. Moreover, plutonium retained by a highly-irradiated (100 W-hr/l) Amberlite LA-2 solution can be removed with HNO_3 solutions containing small concentrations of HF.⁽¹⁶⁾ A conceptual three-column reflux amine plutonium extraction flowsheet for use in the PRF has been devised and satisfactorily demonstrated in

multistage laboratory tests. Further development and plant-scale testing have been recommended.

Americium Recovery

Aqueous waste streams from the recovery and purification of plutonium can contain significant and varying amounts of ^{241}Am produced by beta decay of ^{241}Pu . As a trivalent ion, americium cannot be recovered by those solvent-extraction and anion-exchange methods designed primarily to recover plutonium from waste solutions; thus, a separate process must be provided if americium recovery is desired.

A solvent extraction process has been used for over five years in the Hanford PRF to recover ^{241}Am and residual plutonium values from the acid waste solution produced by the mainline PRF extraction process. This americium extraction scheme, which uses 30 vol% dibutylbutyl phosphonate (DBBP) in CCl_4 as the extractant, is the only plant scale solvent extraction process operated in the United States specifically for removal and recovery of americium from non-high-level wastes.

Feed for the DBBP americium extraction process is prepared by in-line neutralization (with NaOH) of the acidic CAW stream (Figure 11-1) to $\sim 0.1\text{M}$ HNO_3 . This high-nitrate, low-acid feed is essential because common organic phosphate esters, such as DBBP and TBP, do not extract trivalent actinides efficiently from acidic solutions.

The DBBP process uses three packed-pulse columns in series. Am(III) and Pu(IV) are co-extracted into the 30 vol% DBBP solvent in the first extraction column. In the second column, dilute HNO_3 is used to partition Am (III) from the more strongly extracted Pu(IV); and in the final column, a HNO_3 -HF solution is used to strip Pu(IV) and residual Am(III) from the solvent. Recovered plutonium is returned to the mainline PRF TBP process, and the recovered americium is concentrated and purified by an ion exchange procedure. Process flowsheets and details are described in Reference 18.

Typically, the DBBP process recovers greater than 99% of the soluble plutonium but only 60 to 80% of the soluble americium in the adjusted CAW solution. The poor americium recovery is ascribed to insufficient extraction stages and/or improper feed acidity adjustment.

Recent laboratory studies^(19,20) have been concerned with application of bidentate organophosphorus solvents to recovery of both americium and plutonium directly from the acidic CAW stream. Bidentate reagents, such as DHDEMP (dihexyl-N,N-diethylcarbonylmethylene phosphonate), have a high affinity for trivalent as well as tetra- and hexa- valent actinides from strong nitric acid solutions. Recent laboratory tests with actual CAW

solutions demonstrated that, under proper flowsheet conditions, a 30 to 40 vol% DHDECMP extractant can be used to reduce the concentration of both plutonium and americium to very low levels. Present favorable results indicate that further development and exploitation of bidentate extractants may provide the tool needed for easy and satisfactory removal of all soluble actinides from acidic solutions of transuranic wastes.

Neptunium Recovery

Neptunium is normally rejected to the high-level waste stream in fuel reprocessing. However, its chemistry is so similar to that of uranium and plutonium that it can be directed to either product stream in TBP fuel reprocessing. The most stable neptunium valence state in dilute nitric acid solutions is Np(V), which is inextractable in TBP. However, Np(V) is readily oxidized to the highly extractable Np(VI) valence by adding either sodium dichromate to the feed or catalytic amounts of nitrous acid to the solvent in the first extraction column. Common plutonium reductants, such as ferrous ion and hydroxylamine, will also reduce Np(V) to the extractable Np(IV) valence.

Several solvent extraction processes for recovering neptunium, based on its oxidation-reduction reactions, have been described by Benedict and Schulz.⁽²¹⁾ In the Hanford Purex Process, about 90% of the neptunium is co-extracted with uranium and plutonium in the first extraction column by using nitrous acid-catalyzed oxidation to Np(VI). In the plutonium partitioning column, the neptunium is reduced by the plutonium reductant to Np(IV), which follows the uranium stream. Finally, the neptunium is collected in the aqueous waste stream from the uranium purification cycle extraction column. The neptunium is recovered and purified from this waste stream by additional cycles of TBP solvent extraction.

Extraction processes for neptunium using hexone, trilauryl amine, and other solvents have also been described.⁽²¹⁾ Generally, any solvent extraction process applicable to uranium or plutonium recovery can be adapted to neptunium recovery using common and appropriate valence adjustment reagents.

11.2.3 Ion Exchange Techniques

Ion exchange processes are used widely in the nuclear industry to recover, purify, and concentrate uranium, neptunium, plutonium, americium, and curium from irradiated fuels, fuel fabrication scrap materials, and special irradiated target materials.⁽²²⁻²⁴⁾ Ion exchange has also been used in the recovery of uranium from ores,⁽²⁵⁾ the recovery and purification of certain fission products,⁽²⁴⁾ and the analytical-scale separation of various actinides and fission products from a wide variety of materials. The basic

theory of ion exchange and the principles and theory of the different modes in which ion exchange materials are used have been reviewed in detail.⁽²⁶⁾ The fundamental chemistry of ion exchange of transuranium elements has been recently reviewed.⁽²⁷⁾

Cation Exchange

Most organic cation exchange resins show their highest affinities for ions having the highest charge densities for the hydrated ions. This results in very high exchanger affinity for trivalent and tetravalent actinides (tetravalent neptunium and plutonium and trivalent plutonium, americium, and curium), lanthanides, and, to a lesser extent, trivalent aluminum and iron. Cation exchange resins are particularly useful for removing or recovering plutonium, americium, and curium from relatively low ionic strength waste solutions. As an example, Pu(III) distribution coefficients of 10^4 to 10^5 for a very low ionic strength plutonium-containing waste solution (combined contaminated steam condensate, wash water, etc.) have been obtained.⁽²⁸⁾

Cation exchange methods are only effective at relatively low ionic strengths since the distribution coefficient of a trivalent ion decreases as the third power of the monovalent ion concentration and as the $3/2$ power of divalent ion concentration. For this reason, cation exchange resins are efficiently eluted with 4 to 5N mineral acids. In addition to high ionic strength, complexing agents such as fluoride tend to interfere; therefore, it is better to absorb Pu(III) rather than the more easily complexed and hydrolyzed Pu(IV) ion.

Use of organic cation exchangers is thus a route to consider in recovery of transuranic elements from any relatively low ionic strength waste, particularly those low in highly charged ions and complexing agents. Such a method is particularly applicable to recovery of trivalent plutonium, americium, or curium from streams such as contaminated cooling water, washes, steam condensates, etc. Several applications of cation exchange are described below:

- Cation exchange has been used to recover trace concentrations of Np(IV) from uranium solutions containing 0.3M HNO_3 and 0.001M ferrous sulfamate.⁽²⁹⁾
- Cation exchange is currently used at Rocky Flats to recover americium and plutonium from the salt waste generated by fused salt (NaCl-KCl-MgCl_2) extraction of americium from molten plutonium metal.⁽³⁰⁾ The americium and plutonium are loaded from about 0.5M HCl containing about 4g Pu/l and 0.4g Am/l onto Dowex 50, X-8. The resin is then washed with water and eluted with 7.5M HNO_3 , the product being fed to anion exchange for plutonium removal.

- At Hanford, cation exchange is used in the PRF to concentrate the americium and plutonium in the dilute product stream from the DBBP extraction process
- Cation exchange chromatography is widely used for the purification and separation of americium and curium from each other and/or from fission-product lanthanide impurities after recovery from various process or waste streams (including high level wastes).⁽³¹⁻³⁴⁾
- It has been proposed that americium and curium be recovered directly from high-level power reactor fuels reprocessing wastes by cation exchange absorption and chromatographic elution.⁽³⁵⁾

The most likely application of cation exchange for transuranic recovery from non-high-level wastes in the LWR fuel cycle would be the recovery of ^{241}Am from wastes generated by the reprocessing of aged plutonium by either anion exchange or solvent extraction. These relatively high-acid, low-salt wastes can be thermally concentrated and/or denitrated to remove most of the nitric acid, followed by dilution to 0.1 to 0.5M HNO_3 and cation exchange absorption. Wastes such as dissolved incinerator ash or other rather high salt-content wastes would be less amenable to direct cation exchange recovery of americium because of the high metallic content, high ionic strength, and the possible presence of complexing agents and siliceous solids.

Anion Exchange

Absorption of metal ions by anion exchange resin occurs when the metal ion is capable of forming an anionic complex in the resin phase. Transuranium elements in several of their oxidation states absorb strongly into anion exchangers from solutions of several anionic complexants, including nitrate, chloride, thiocyanate, etc. Nitrate solutions are most commonly used in nuclear reprocessing applications.

Both Np(IV) and Pu(IV) absorb strongly and selectively from nitric acid (or nitrate salt) solutions in the range of about 4.5 to 10M nitrate, with maximum absorption in nitric acid being at about 7.5M.⁽³⁶⁾ Because of the very high selectivity, anion exchange for neptunium or plutonium is a very effective recovery method from almost any nitrate waste solution.

Anion exchange has been used to recover plutonium and neptunium from high-level fission product wastes,^(29,37-40) oxalate precipitation supernate wastes,⁽⁴¹⁾ peroxide precipitation supernate wastes,⁽²¹⁾ metal reduction residues,^(42,43) fuel fabrication scrap, dissolved incinerator ash,⁽²³⁾ and laboratory wastes, etc. Anion exchange has also been used widely in a variety of mainline process applications.^(21,23,29,30,37,44)

Although complexing agents lower distribution coefficients somewhat, most complexants have little effect in strongly acidic solutions because of their conversion to undissociated free acids. Fluoride does lower distribution coefficients, but this effect can be largely counteracted by the addition of aluminum nitrate. Large amounts of sulfate or phosphate are also detrimental. With oxalate supernate, increased acidity to 9M HNO_3 gives better resin loadings by repressing oxalate complexing.

Feed clarification may be necessary to avoid bed plugging if packed columns are used. Agitated beds have also been used with anion exchange to avoid solids removal.^(40, 43) Even though agitated bed efficiencies are considerably lower than packed bed efficiencies, the high anion exchange distribution coefficients have allowed satisfactory recoveries with two or three agitated beds in series. Peroxide supernates should be heated to destroy the peroxide thus avoiding resin attack and gassing. If Pu(VI) is present in liquids that will be fed to anion exchange, reduction with an appropriate reductant followed by heating to reoxidize Pu(III) is required.

11.3 NONDESTRUCTIVE ASSAY METHODS

Non-destructive assay (NDA) methods used in determining the transuranic content of radioactive wastes are based on one or more of the following transuranic attributes:

- radioactive decay
- spontaneous fission
- induced fission

None of the methods based on these properties entirely covers the range of application, and none is without specific interference. In practice, several methods may be used to confirm the analysis.

Recommended methods for low-density, plutonium-containing wastes, in order of preference, are passive gamma ray spectrometry, spontaneous fission, and stimulated (induced) fission.⁽⁴⁵⁾ Spontaneous fission and calorimetry, combined with gamma ray spectroscopy, are also recommended for high-density, high SNM-content materials. Most NDA waste applications screen packages or drums containing milligram to gram quantities of plutonium, but techniques are being developed and are in limited use for screening waste containing as low as 10 nCi of ^{239}Pu /gram of waste.⁽⁴⁶⁾

In the following sections, all of the NDA methods currently in use are described briefly, along with the mechanism that makes the analysis possible. Specific interferences are indicated.

11.3.1 Radioactive Decay

The methods by which radioactive decay can be used for NDA are shown in Figure 11-2. They include calorimetry, passive gamma and X-ray spectrometry, alpha counting and spectrometry, and portable alpha and gamma monitors.

FIGURE 11-2. NDA Applications Based on Radioactive Decay

Calorimetry

Calorimetry is the premier, nondestructive analytical method for nuclear fuel cycle materials because all modes of radioactive decay ultimately generate heat and heat can be measured very accurately. Because of the minute increments of heat, primarily from absorbed alpha decay products, the container to be measured must be small enough to be contained in the calorimeter chamber. It must also contain gram quantities of fissile material.

Calorimetry chambers are extremely well insulated boxes. They can be operated either singly with the heat measured directly, or in pairs with the heat measured differentially from a known heat source. Both forms are available commercially. Precisions and accuracies of $\pm 1\%$ (2σ) are readily obtained with long assay times.

Since heat alone is measured, the assay is no better than the user's knowledge of the specific activity and relative abundance of each isotopic component in the sample. For samples such as fuels and weapon fabrication scrap, fuel pins, etc., the isotopic content can be determined destructively

by mass spectrometry; then the abundance ratios can be applied to an entire batch of samples. Material without this pedigree can have it determined nondestructively by passive gamma spectrometry. The limiting factor for this method of analysis is the accuracy of the relative abundance of isotopes undergoing radioactive decay. The principal source of bias is the presence of unaccounted heat sources such as non-gamma emitting isotopes or chemical heat reactions.

Passive Gamma Spectrometry

Although calorimetry is the most accurate NDA method, passive gamma spectrometry is the most widely used. This method relies on the use of detectors to analyze the gamma emissions escaping the sample container. Gamma rays have good penetration properties, but they lose intensity as a function of energy, atomic number, the distance traversed between the emission source and the detector, and the density of the intervening media. The variable attenuation of the gamma rays by these mechanisms is the largest source of error in the gamma spectrometry NDA method.

A gamma spectrometry detector converts a gamma photon, sorbed within its active volume, to a voltage pulse proportional to the photon energy sorbed. If a photon is not fully sorbed in the detector, the output pulse will be smaller than the full energy pulse and thus be recorded as a lower energy continuum (Compton). All pulse outputs of the detector are analyzed in a pulse height analyzer and result in a spectrum of energy-versus-count rate. The activity of a photon emitter is proportional to the net peak area of the characteristic energy for that emitter. An emitter may have zero, one, or many energy peaks, but each peak will have a known proportionality to the radioactive disintegration rate (gammas per disintegration) of the emitter.

Detector performance is characterized by:

- its efficiency in totally absorbing a gamma photon of a specific energy (usually the 1332 keV peak of ^{60}Co)
- the resolution as measured by width of the resulting peak at half its height (FWHM: full width at half maximum)
- the ratio of the peak height to associated lower energy continuum (peak to Compton ratio).

Thallium-activated, sodium-iodide detectors [NaI(Tl)] were an early detector choice. They are available in very large sizes, providing high photon sorption efficiencies. This type of detector is referred to as a scintillator because the sorption of the gamma photon creates a scintillation of visible light which is converted to a voltage pulse by an optically coupled

multiplier phototube. Resolutions are typically 7%, or approximately 93 keV FWHM at the 1332 keV peak of ^{60}Co , with peak-to-Compton ratios of 2. For consistently packaged nuclear fuel cycle scrap and waste samples with little or no variation in isotopic composition, the NaI(Tl) detector is an excellent choice. Precisions of $\pm 5\%$ (2σ) are readily attained at one gram ^{239}Pu per m^3 with less than ten minute counting times. Much lower sensitivities can be obtained with increased counting times.⁽⁴⁶⁾ Plutonium-239 is used as a basis for comparison because it is the limiting isotope of interest with very low gamma-per-disintegration values.

Semiconductor detectors of lithium drifted germanium [Ge(Li)] and intrinsic germanium (IG) are a fairly recent development. The detectors are available with active volumes in both coaxial cylinder and planar shapes. Both types must be operated at liquid nitrogen temperatures and enclosed in a high vacuum cryostat. All have a dead layer of highly-sorbing, nondetecting germanium several hundred Angstroms thick on their operating faces. Typically, detectors are available with active volumes of 1 cm^3 to greater than 100 cm^3 . Resolutions are $<2.0\text{ keV FWHM}$ (1332 keV) and peak to Compton ratios of >35 to 1. The efficiencies measured as net-total sorption peak areas relative to photons received by the detector are equal to or are greater than those for scintillator detectors many times their size because of their greater photon cross-section and the vast improvements made in resolution.

Passive, gamma-spectrometric assay of samples with non-uniform isotopic or density contents should use semiconductor detectors because scintillators cannot resolve the necessary peaks. Attenuation corrections are required for the loss caused by sample and container sorption. For heterogeneous packaged wastes, the attenuation correction is usually obtained by measuring the attenuation of photons from an external source by the sample package. The external source is chosen to be close in energy to the peak being measured; i.e., the 356 keV peak of ^{133}Ba when the 413.7 keV peak of ^{239}Pu is the reference peak.

Because of self-absorption, the passive gamma assay methods will be biased low if the fissile content is in the form of large metal or oxide particles. Solutions and fine dusts dispersed on inert material are accurately assayed by these techniques.

Sensitivity is a function of counting time and the area of detector used on a given volume of sample. To enhance this relationship and to average the attenuation effects, samples are rotated, or rotated and oscillated, in front of the detector. Arrays of detectors are used to increase detector surface area. Collimation is used to isolate sections of packages and/or to reduce

radiation-center effects in rotated packages. All of these variations for passive gamma spectrometry are represented by systems in use, often with several variations within one facility.⁽⁴⁶⁾ All data acquisition system variations are commercially available or made from available components. Computer-assisted data reduction programs are available as an integral part of the commercially available systems, from domestic pulse height analyzer manufacturers, and from open literature.⁽⁴⁶⁻⁴⁸⁾

Precisions of ± 5 percent (2σ) are readily attained at one g ^{239}Pu per m^3 with less than ten minute counting times. Sensitivities of less than 10 nCi of ^{239}Pu per gram of sample have been achieved in large package samples by using arrays of semiconductor detectors.⁽⁴⁶⁾

The thin-window semiconductor detector is a variation of the planar detector used for X-ray and low-energy gamma analysis. These detectors are characterized by a very thin nondetector layer on the detector to facilitate maximum efficiency for low-energy photons and minimum detector depth for optimum high-energy interference. Passive isotopic analysis utilizes a thin-window germanium detector, which characteristically has a FWHM resolution of <0.600 keV at the 121.9 keV peak of ^{57}Co . Such resolutions are necessary to resolve peaks such as the 160.35 keV ^{240}Pu peak from the 161.45 keV ^{239}Pu peak.

Passive X-ray Spectrometry

When an atom radioactively decays, the daughter is formed with an excess of energy. This energy is discharged as X-rays characteristic of the daughter element. Thus, an alpha emitting plutonium isotope will generate uranium X-rays. Most of these X-rays have energies of approximately 17 keV (L series), with a much lower yield at approximately 98 keV (K series).⁽⁴⁹⁾ Because these low-energy photons are so readily sorbed, any detector proposing to utilize these emissions for assay should be in intimate contact with the source material. It therefore lends itself to in-line assay of low-level solutions. Either thin-window semiconductor detectors or thin scintillators may be used. This mode of assay is frequently used in destructive assay because of its excellent sensitivity in controlled conditions.

The FIDLER probe⁽⁵⁰⁾ contains a thin, large surface area scintillator detector (12 to 20 cm in diameter, 1.5 to 5 mm thick). Although primarily intended to monitor surface deposits of plutonium and americium, it has been used successfully to assay surface areas where the vertical distribution is known, i.e., fresh spills and fallout from stack discharges. It is used in LASL's Pancake counter to sort potentially contaminated, low density waste materials into TRU and non-TRU fractions for disposal. It has also been used for in vivo lung burden assay in conjunction with a phantom to determine sorption and scattering. The detector is thin to limit the interference from

higher energy emissions but has a large area to improve sensitivity to emissions within its capture range.

The MEGAS (Multiple Energy Gamma Assay System), developed by LASL, is a hybrid system capable of both X-ray and gamma ray detection.⁽⁵¹⁾ It uses a NaI(Tl) crystal with a thin beryllium window that allows X-ray transmission into the crystal. The detector is located 1.3 m from the centerline of a turntable and views the rotating package through a 25 mm wide by 100 mm high iron collimator. It is designed to monitor 0.06 m³ cartons of low density bulk wastes, generated in operating areas, for TRU contamination down to the 10 nCi/g level. Absorption of photons by the matrix material and self-shielding by the transuranics contribute to the measurement error, particularly for the low energy L X-rays. The hybrid system combines the high sensitivity (and relatively low accuracy) of X-ray detection at the 10 nCi/g level with the lower sensitivity, but improved accuracy, of gamma ray detection at higher activity levels.

Alpha Counting and Spectrometry

Radioactive alpha decay involves the emission of a charged helium nucleus from the parent atom. The alpha particle carries a high energy charge (2 to 8 MeV), which is characteristic of the emitting isotope. Because of their large relative size, alpha particles have very poor penetrating capabilities and a range of only about two centimeters in air. Therefore, the alpha emitting isotope must be present in a very thin layer so the emitted particle can reach a detector. For this reason, the only regularly used nondestructive assay utilizing alpha emission is air filter analysis.

Alpha counting usually takes place in a proportional counting chamber which operates on a voltage plateau set to discriminate against beta emissions. Proportional counters have a high efficiency for counting alpha emissions but no ability to differentiate between alpha energies of the parent isotope(s). This function is performed by another family of thin-window, planar semiconductor detectors. These detectors differ from X-ray oriented detectors by having an even thinner entrance window, as thin as a monomolecular layer of gold, and a very thin detector depth of about 100 μm . Usually, the detectors are made of silicon, and they operate at or slightly below room temperature. The sample is placed inside the vacuum chamber with the detector. Because of their small size, these detectors have poor counting geometries.* The detector provides a signal to a pulse height analyzer that identifies the parent alpha emitters and their relative activities. The results are then applied to the total alpha count data to provide for a quantitative assay of each alpha emitter. Commercial instrumentation and systems are available.

*Geometry is defined as a combination of the solid angle between the radiation source and the detector and the efficiency of the detector.

Alpha counting and spectrometry are extensively used for all levels of destructive assay of fissile materials because ultimately they have the greatest span of sensitivity. The fissile material is usually purified and electrodeposited on a disc for minimum resolution distortion.

Portable thin windowed ionization probes are available commercially and used to monitor alpha contamination.

11.3.2 Spontaneous Fission

The property of spontaneous fission can be used effectively in NDA applications for many transuranium elements, although not directly for fissile isotopes. The atoms with high specific activity for spontaneous fission are even atomic-weight isotopes while the fissile atoms are odd atomic-weight isotopes. (49)

Spontaneous fission (Figure 11-3) produces two fission product atoms, prompt gamma emissions from those fission products, radioactive decay characteristic of the fission product isotopes, and two or more coincident, prompt neutrons. The emissions related to the fission products are largely lost in the sample and are useless for assay purposes, but neutrons have very low

FIGURE 11-3. NDA Applications Based on Spontaneous Fission

capture cross-sections and are available as an assay signature outside the sample container. Because of the low capture cross section, neutron detectors have very poor counting geometries and must be set up in arrays. The most primitive passive neutron-counting systems maximize their efficiency by attempting to count every neutron they can capture. Very accurate assay systems have been built on this principle for the assay of metal and metal oxides.

Most spontaneous fission isotopes decay radioactively by alpha emission. When these isotopes are chemically or, to a lesser extent, physically associated with low atomic-number isotopes other than hydrogen and oxygen, an alpha-neutron reaction is highly probable. The low atomic-number isotope is transmuted to a radioactive isotope, and a neutron is emitted. The newly formed isotope decays with characteristic gamma emissions, providing a means of semiquantitatively determining the low atomic number composition of the sample. Conversely, large packages with a high hydrogenous content tend to absorb neutrons before they are available for detection.

The important consideration for passive neutron counting is that spontaneous fission produces two or more coincident neutrons. This is the reason that most passive neutron systems are divided into groups of detectors, and coincident detection of at least two neutrons is required to distinguish the multiple neutron-fission event from the single (α, n) reaction.

The two most commonly used neutron detectors are $^{10}\text{BF}_3$ and ^3He gas-filled proportional counters. Since the highest cross section for interaction is with thermal neutrons, the gas tubes must be surrounded by a neutron moderator. This moderator is a material with a high hydrogen content such as water, paraffin, or polyethylene which reduces the neutron energy to the thermal range by means of successive interaction. Usually, this layer is surrounded by a layer of boron or cadmium and another layer of moderator. Boron and cadmium have high capture cross-sections for thermal neutrons, and this double exterior layer reduces the background from external neutron sources. Obviously, these neutron detector systems can become massive. The gas-filled tubes are filled to pressures of one to ten atmospheres. They may be a few centimeters in diameter and up to a meter in length, and 3 or 4 tubes to over 100 may be present in a single system. The components are commercially available but only rarely is a stock system available because of variations in needs and applications.

The nuclear reactions that permit use of the $^{10}\text{BF}_3$ and ^3He tubes as detectors are as follows:

Both products are short ranged and record in the proportional counter chamber with high net efficiency. Both are relatively insensitive to external gamma emissions. Precisions attained are excellent but accuracy, except in production line applications, is poor.

Scintillators, also used as neutron detectors, utilize (n, γ), (n,p), (n,f) and (n, α) reactions within the scintillator material and detect the produced emission. A typical detector material is ^6LiI which, compared to gas filled tubes, has a very high efficiency for detecting thermal neutrons; but it has an even higher efficiency for gamma detection and interference.

The use of thin foils is another method of passive neutron detection but one incapable of coincidence differentiation. This is a form of neutron activation analysis where very large, thin foils (meter square) may be exposed to very low fluxes of neutrons, as from spontaneous fission in waste tanks. Typically, (n, γ) or (n,p) reactions occur during the course of an extended exposure period. The foil is then compacted or dissolved and sampled. A gamma energy analysis is performed, and the induced activity is used to calculate the starting neutron flux. The neutron flux is then related to the fissile content.

11.3.3 Induced Fission

Induced fission (Figure 11-4) produces the same array of emissions and products as radioactive decay and spontaneous fission; but because the fission is induced, several NDA benefits can be realized. First, the fissionable content is directly measured by fission. Secondly, the sensitivity is almost equally controlled by the fissile content of the sample and by the neutron or bremsstrahlung flux that is inducing the fission. Certainly, not least important is that the sample is available before and after the induced fission to provide a background measurement of interference regardless of the measurement mode. These methods include the only feasible NDA methods for high gamma background waste, scrap, and irradiated fuel.

Prompt Systems

Assay systems dependent on prompt products usually rely on the coincidence of high-energy gamma emissions and/or fast neutrons. Several systems have been developed that depend strongly on collimation of the incoming thermal neutrons and the exiting prompt gammas.⁽⁴⁶⁾ Because of this, samples are usually restricted to small sizes. As the collimation is reduced or eliminated, larger samples (up to boxes and drums) may be assayed. Fission-

FIGURE 11-4. NDA Applications Based on Induced Fission

induced events are characterized by a high multiplicity of prompt gamma and neutron events. Nonfission related events such as background are characterized by low multiplicity. Spontaneous fission is measurable as a low-level, fixed-rate background interference.

With bremsstrahlung-induced fission, incident energy can be varied above or below thresholds of reaction. This capability permits the active (induced) assay of both fissile and fertile contents in the same package.

The detectors used are the same as those mentioned previously. Indeed, with the activating beam shut-off, the detector system becomes a passive system for the measurement of background or fertile content. Precisions are good, particularly in samples containing multigram quantities of fissile material.

Delayed Systems

The most versatile appreciation of induced fission is found in delayed activity systems. The neutron flux may be pulsed, or the sample may be physically moved out of the fission producing flux. Many fuel rod scanners are built on the principle of passing the rod through an irradiation field and measuring characteristic delayed fission gammas downstream from the neutron source. Reversing the sample direction provides a background.

Small samples may be passively gamma or neutron assayed within a counting chamber. They are then irradiated in place for a short time and actively

analyzed in the same chamber. The sequence can be cycled for improved sensitivity and precision.

Delayed neutron measurement is particularly versatile because it can be used to assay fuel pins with nearly the same precision as gram-sized samples containing nanogram-per-gram fissile material. It can also be made insensitive to gamma activity. High gram-content samples can be irradiated by low-yield, isotopic neutron sources. Sensitivity is gained by increasing the neutron flux through the use of a subcritical assembly, a reactor, or even pulsing a reactor. The sample is rapidly transferred to a low-background, delayed-neutron counter where it is counted and cycled as necessary. As before, background can be ascertained in the same counting system prior to irradiation of the sample. The principle interferences are (n,dn) reactions from nonfission related sources, the most prevalent of which is oxygen with a 1.17 second delayed neutron half-life. Delay in counting for a few half-lives, however, greatly reduces its effect. Precisions of 2% at the higher levels and 10% (2σ) at the lower levels are attainable.⁽⁵²⁾

Variants of all of these applications are commercially available. Since implementation of these modes of assay can involve a large outlay of money and space, service assay for a fee can be arranged at many facilities or in mobile units.

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12.0 IMMOBILIZATION OF MISCELLANEOUS NON-HIGH-LEVEL WASTES

12.0 IMMOBILIZATION OF MISCELLANEOUS NON-HIGH-LEVEL WASTES

Virtually all nuclear fuel cycle operations generate liquid or solid wastes requiring additional treatment to immobilize them for improved safety in transportation and storage. These process residues include both primary and secondary wastes generated in the waste treatment operations described in the preceding sections of this report. Table 12-1 lists the sources and general characteristics of the wastes treated by the immobilization techniques discussed in this section. Immobilization techniques for high-level liquid wastes, chop-leach fuel bundle residues, and volatile radioisotopes are described elsewhere in this report. Immobilization, as used in this section, implies a treatment designed to reduce the mobility of as-generated wastes. In most cases, this is accomplished by incorporating the waste in a monolithic solid of low leachability.

12.1 IMMOBILIZATION TREATMENT ALTERNATIVES

Three possible options for treating as-generated process residues can apply:

- The waste requires no treatment other than packaging, and no solidification or immobilization treatment is imposed (e.g., failed equipment).
- The waste requires no treatment other than packaging; but for economy or improved safety, some immobilization or solidification treatment is imposed (e.g., ashes, dry salts, ion exchange resins, and similar dispersible solids).
- The waste requires immobilization treatment to meet Federal and state regulations for transportation and storage (e.g., wastes containing free liquids).

Immobilization technologies discussed in this section (Table 12-2) can be divided into two major groups: 1) those in common use in the U.S. and abroad, and 2) those being developed to provide improved product integrity and/or economy.

TABLE 12-1. Waste Characteristics

<u>Waste Forms</u>	<u>Waste Description</u>	<u>Source</u>	<u>Composition</u>
Liquids:	Radwaste evaporator concentrates	PWR BWR, PWR	Boric acid Sulfate & basic phosphate residues
	Intermediate Level Waste (ILW)	Reprocessing Plants	Sodium & mercuric nitrates, iodine, sodium carbonate & various other sodium salts

TABLE 12-1. Waste Characteristics (cont'd)

	Low Level Liquid Wastes (LLLW)	Reprocessing Plants & General	Sodium nitrate solutions containing a wide variety of other salts
	Neutralized scrap recovery wastes	Fab. Plants & Reprocessing	Sodium & ammonium nitrate solutions, may contain fluoride
	Resin regeneration liquids	General	Sodium nitrate, sulfate, or nitric acid solutions
	Organic solvents & Waste Oils	General	TBP, lubricants, cleaning solvents
	Neutralized lab liquids	General	Varied but mostly nitrates sulfates & chlorides
	Decontamination Soln's	General	Complexing agents in either acidic or basic solutions
	Laundry liquids	General	Detergents, bleaches & some complexing agents
Solids:	Spent resin (dewatered)	Reactors & General	Ion-exchange media
	Spent filters	LWR	Filter cartridge assemblies with high activity filter sludge
	Dewatered sludges	Reactors & General	Clay, zeolites, manganese dioxide, ferric & aluminum hydroxide, filter aids, powdered resins
	Incinerator Ash	Waste Treatment Facility	Various siliceous & clay materials with some metal salts & oxides
	Evaporator Salts	Waste Treatment Facility	Sodium nitrate & other common sodium salts
	Calcine	Waste Treatment Facility	Metal oxides

TABLE 12-2. Immobilization Alternatives

<u>Technologies in Use</u>	<u>Technologies under Development</u>
Absorbents	Aluminosilicate minerals (clay)
Salt matrix	Glass/ceramics
Urea-formaldehyde resins	Pelletization/compaction
Cement/concrete	Polyethylene and other organic polymers
Bitumen (asphalt)	Metal matrix

12.3

The technologies in use today are applied almost exclusively to liquids, sludges, ion exchange resins, and similar water-containing wastes. A comparison of these systems is presented in Table 12-3. At the present time, absorbents are used sparingly, usually for problem liquids such as organic solvents that cannot be immobilized conveniently by the other available techniques. The evaporation of aqueous solutions to salt cakes is a technique used primarily by ERDA reprocessing facilities for immobilizing aged, neutralized high level waste solutions. Urea-formaldehyde and portland cement systems are used extensively to solidify reactor wastes. Bitumen solidification systems are not used in the U.S. but are used in several foreign nuclear facilities.

The technologies under development are designed primarily to improve the leach resistance of the solidified products. Foremost in this field are the vitrification processes which yield glass products with leach rates of $5 \times 10^{-5} \text{ g}/(\text{cm}^2\text{-day})$ or less for more leachable components. Pelletization processes produce ceramic or cermet pellets which should have equally high leach resistance. The leach resistance of polyethylene products are comparable to those for bitumen products, while the leach resistances of the aluminosilicate mineral salt-fixation products are approximately comparable to those for cement products.

Comparisons of the leach rates for various solidified waste products are shown in Figures 12-1 and 12-2.⁽¹⁾ These figures also illustrate that the leach rates for rare-earth and actinide elements are several orders of magnitude lower than the leach rates for alkali and alkaline-earth elements. If only transuranic elements need to be considered, cement products may be as fully satisfactory as the more expensive glass products in assuring long-term confinement of radioactivity.

Development is continuing on the processes currently in use. In particular, modified cement and urea-formaldehyde mixes are being developed that provide better volumetric efficiencies and improved cesium leach resistance. These modifications are included in the following discussion of the immobilization treatment alternatives.

12.2 AVAILABLE IMMOBILIZATION TECHNOLOGIES

The immobilization technologies described in this section include absorbents, salt matrix, urea-formaldehyde resins, cement/concrete, and bitumen.

12.2.1 Absorbents

Absorbents have been widely used in the nuclear industry to immobilize liquids for transportation and burial. They are favored for oils, solvents,

TABLE 12-3. Comparison of Available Immobilization Technologies

Comparison Factor	Absorbent	Salt Cake	Urea-Formaldehyde	Portland Cement ^(a)	Bitumen
Shelf life of immobilizing agent	Long	NA ^(b)	Short (months)	Long	Long
Mix fluidity	Fair	NA	Good	Poor	Fair
Mixer cleanability	Good	NA	Good	Poor	Fair
Chemical tolerances					
Boric acid Sol'n	--	--	Good	Poor	Good
Na ₂ SO ₄ "	--	Good	Reduced efficiency	Fair	Good
NaNO ₃ "	--	Good	Fair	Good	Not recommended
Alkaline "	--	--	Reduced efficiency	Good	Good
Laundry det "	Good	--	Poor	Poor	Fair
Organic liquids	Good	NA	Poor	Poor	Fair
Ion exch resins	NA	NA	Good	Fair	Fair
Sludges	NA	NA	Good, may require pH adjustment	Good	Good, hazardous with MnO ₂ sludge
Volumetric Efficiency ^(c)	Low (0.3-0.5)	High (4-8)	Moderate (0.6-1.0)	Low (0.5)	High (>2)
Product Form	Moist granules or paste	Monolithic cake	Monolith	Monolith	Monolith
Product density, kg/m ³	400-1000	2000-2500	1000-1300	1500-2000	1000-1300
Water binding strength	Poor	Water evap during pre-preparations	Fair	Good	Water evap during pre-preparations
Residual free water	Occasionally	Occasionally	Occasionally	Seldom	Never
Mechanical strength	Nil	Low	Fair	Good	Good
Product stability	Poor	Fair	Fair (loses water and strength in open system)	Very Good	Good
Combustibility	Depends on liquid absorbed	No	Yes	No	Yes
Freeze/thaw resistance	NA	NA	Poor	Fair to good	Good
Leach resistance	Very low	Low	Moderate	Moderate to high	High

a Without additives

b NA = not applicable

c Ratio of the as-generated waste volume to the solidified waste volume

WASTE PRODUCTS

FIGURE 12-1. Comparison of Leach rates for Alkali and Alkaline-Earth Elements from Various Waste Products

WASTE PRODUCTS

FIGURE 12-2. Comparison of Leach Rates for Rare-Earth and Actinide Elements from Various Waste Products

and other organic and inorganic liquids that are difficult to solidify by other means. The practice is limited to radioactive liquids that qualify as "low specific activity" material (49 CFR 173.389) unless the disposable container is overpacked in a DOT-acceptable outer container. ⁽²⁾

Product Formulations and Properties

Typical granular or powdered absorbent materials used for liquid immobilization are listed below:

- vermiculite
- various clays
- diatomite (biological deposits of calcium silicate)
- calcium sulfate dessicants
- silica gel
- portland cement
- plaster of paris

Vermiculite, dehydrated clay granules, and diatomite absorbents have been routinely used for radioactive liquids, with vermiculite perhaps the most widely used. The ANSI recommended weight ratio of liquid-to-vermiculite is not more than 6 to 1. For #3 grade vermiculite at 80 kg/m³, the corresponding volumetric ratio is 1 to 2, although a 1 to 3 volumetric ratio provides greater assurance of no free liquids. Similar formulations are recommended for diatomites. ⁽²⁾

The absorbent method when properly applied will physically entrap the waste liquid such that no appreciable free liquid will leak out if the container is damaged. With most of the absorbents listed above, the liquids are physically entrapped and can be displaced readily by the addition of water. In comparison with other immobilization techniques described in this section, the absorbent product is readily dispersible and leachable. For these reasons, absorption processes may not meet future criteria for radioactive waste immobilization.

Preparation Methods

For vermiculite, the storage container is normally filled with the absorbent material; and a measured amount of waste, equivalent to about one-third to one-half of the container volume, is added. Channeling of liquids becomes more prominent as the container size increases; thus the liquid should always be added via internal dispersion pipes. For some absorbents such as diatomite, physically mixing the liquid with the absorbent may be necessary to assure wetting. At Rocky Flats, a mixer-extruder machine is used to incorporate organic liquids into diatomite.

The thick peanut-butter-like product is prepared by mixing 2.8 liters of liquid per kilogram of diatomite. Care must be taken with all absorbents to avoid supersaturation.

Status of Technology

The use of absorbents for organic liquids and nonacidic, low-level aqueous wastes is well established.

12.2.2 Salt Matrix

Two methods for incorporating radioactive wastes in salt matrices have been studied. The first method involves evaporating high-salt aqueous wastes to a sufficiently high concentration that the resulting crystalline slurry will solidify to a massive salt cake on cooling. The Hanford In-Tank Solidification process for solidifying aged high-level wastes is an example of this method.⁽³⁾ The second method involves casting a molten salt containing the waste material into a container to form a monolithic block of solid, anhydrous salt. AI's molten salt combustion process (described in Section 9.0) applies this method.⁽⁴⁾

Product Formulations and Properties

Virtually any neutral salt is a candidate for use as the salt matrix. The salt matrix itself may be waste material, or the waste solids may be incorporated into a salt matrix specially developed for the waste. Generally, the salt matrix should have a melting or liquefaction temperature well above any temperature anticipated in storage to minimize corrosion problems. Molten salts can be quite corrosive, and containment constructed of refractory materials is usually required. The solidified neutral salts, however, can be contained in mild steel or stainless steel containers with minimal corrosion.⁽⁵⁾ A small amount of residual moisture (10 to 20 wt%) is acceptable from a corrosion standpoint but may cause pressurization if the sealed waste container is subjected to heating or radiolysis.

Being a salt, the product is quite leachable, which makes long-term confinement difficult to assure but permits the option of future actinide recovery. Although salt cakes are not noted for their strength, their monolithic form should greatly reduce waste dispersibility if the container is accidentally ruptured.

Preparation Methods

Two evaporation methods have been used to prepare massive salt cakes from high salt aqueous wastes. In the first method, the water is evaporated from the wastes in situ by heating them in the storage container and applying an air purge to remove the evaporated moisture. For small containers, such as 55-gal (0.2 m³) drums, external heating is satisfactory.⁽⁶⁾

Larger vessels require an internal heating device such as a hot-air sparge, electric immersion heaters, or the like.

An external evaporation method is preferred for solidifying salt cakes in large vessels. The waste liquid is evaporated to a high salt concentration in an external evaporator before it is routed to final storage for cooling and crystallization. Liquid remaining after crystallization is returned, along with fresh feed, to the evaporator until the desired degree of fill is obtained. Residual moisture remaining on the surface at that time is removed by air-purging the vessel.⁽³⁾ Wiped film evaporators can be used to reduce the water content sufficiently (to 20% or less) so that the resulting free-flowing slurry will solidify completely on cooling.⁽⁷⁾

Fused-salt casting requires a separate melting vessel to which the dry salt ingredients are added. Small-scale applications, such as the melt-cast system used at Hanford for preparing radioactive cesium chloride capsules,⁽⁸⁾ can also be designed to evaporate aqueous salt wastes to dryness in the melter in a batch operation prior to melting. The molten salt can be transferred to the storage container by gravity through a freeze plug valve or by pressurization or vacuum transfer techniques.

Status of Technology

In-tank solidification, using external evaporators to remove the water, has been used for several years at Hanford to solidify aged high-level wastes from which most of the heat-emitting isotopes have been removed.^(3,9) The solidified salt cakes are stored in large, underground, mild steel tanks (up to 3800 m³) filled to a height of 5 to 7 meters with salt cakes, depending on the heat load. Approximately 140,000 m³ of salt cake will be accumulated by the completion of the program in the early 1980's.⁽¹⁰⁾ A typical composition range is 70 to 100 wt% NaNO₃, 2 to 10 wt% NaNO₂, 0 to 5 wt% NaOH, 0 to 5 wt% NaAlO₂, and 2 to 10 wt% Na₂CO₃. The salt cakes also contain small amounts of saturated terminal liquor, estimated at 5 to 10 wt%.

Recent pilot-scale studies⁽¹¹⁾ have shown that synthetic terminal liquor, a highly alkaline sodium-nitrate/nitrite solution, can be evaporated to as little as 25 wt% water at feed rates up to 60 l/hr in a wiped-film evaporator with 0.46 m² of heat transfer surface. Although the low water-content products were fluid when discharged, they solidified at room temperature with no visible free water. A similar performance has been demonstrated at the Savannah River Laboratory with synthetic Savannah River Plant and Hanford alkaline salt wastes.⁽⁷⁾ Feed rates for the SRL unit (0.92 m² heat transfer surface) were about 70 l/hr.

In-drum solidification by evaporation has been demonstrated for evaporator bottoms generated in the Wurgassen nuclear power station (KWW) of the Kraftwerk Union in Germany.⁽⁶⁾ The evaporator slurry, with a 15 to 20 wt% solids content, is added batchwise to an externally heated 0.2 m³ drum until a solid block has formed inside the drum. Moisture is carried away by purging air. The final product contains 10 to 20 wt% residual moisture, which is reported to be sufficiently low to preclude corrosion, fouling, or fermentation processes during storage.

Molten salt technology in support of ANL's pyrometallurgical processes for EBR-II fuel reprocessing, Hanford's Salt Cycle Process, and ORNL's molten salt reactor is well developed.^(12,13) The melt-casting technique for preparing radioactive cesium chloride capsules has been in use for about a year by ARHCO.⁽⁸⁾

Of more immediate application to waste disposal, Atomics International has prepared and cast 1000 to 1500 kg blocks of ash-containing salt as part of their molten salt combustion process development.⁽⁴⁾ The blocks, containing about 50 wt% Na₂CO₃, 10 wt%, Na₂SO₄, 20% NaCl, and 20% ash, are cast directly into a stainless steel cart, cooled to solidify (freezing point about 720°C), and dumped out. Several months of non-radioactive operation have been demonstrated without evidence of corrosion to the cart. Smaller drums of salt can be cast by a similar technique if desirable. Molten salt can also be used to encapsulate other wastes, such as cladding hulls or zeolites, during the casting process.

Major Development Objectives

The suitability of massive salt cakes as long-term storage media needs to be determined. Application of salt matrix techniques for immobilizing specific salts or salt solutions may require laboratory and pilot plant development. Future investigation could include optimum salt compositions, materials of construction, casting techniques, etc.

12.2.3 Urea-Formaldehyde Resins

Urea-formaldehyde (U-F) resins are widely used as molding compounds for thermosetting plastics, as adhesives, and as grouting materials to fix loose soil and seal rock surfaces. U-F adhesives were first investigated in 1971 for use in solidifying reactor radwastes by Protective Packaging, Inc. (a subsidiary of Nuclear Engineering Company, Inc.), which began marketing its Tigerlock system in 1972. Since then, a number of firms have developed and marketed similar systems that use commercially available U-F adhesives and grouts, such as Casco-Resin (Borden Chemical Company) and Cyanaloc chemical grouts (American Cyanamid Company).

U-F is a condensation product of urea and formaldehyde, which react together under neutral or alkaline conditions to yield monomethylol urea ($\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{OH}$) and dimethylol urea ($\text{CH}_2\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\text{OH}$), depending upon the ratio of reactants.⁽¹⁴⁾ For adhesive and grouting purposes, the resinous material is prepared in a water-soluble form as a highly viscous liquid (200 to 600 cP) of high resin content (typically 60 to 70 wt%) with a density of $1300 \pm 50 \text{ kg/m}^3$. During formation, the adhesive resin is partially polymerized by reacting under slightly acid conditions. The solution is then neutralized to pH 7-8, and excess water is removed by vacuum distillation. The products have limited stability of about six months, depending on the storage temperature. The liquid is completely miscible with water but immiscible with nonpolar solvents.

Although the resin is thermosetting, the hardening reaction is most often accomplished by adding an acid catalyst. The cross-linking polymerization reaction is slightly exothermic and is both temperature and pH dependent. Usually, a weak acid such as sodium bisulfate or phosphoric acid is used to produce a controlled set. The temperature and pH dependence for NaHSO_4 -catalyzed gelling of a typical resin (Cyanaloc 62) is shown in Figure 12-3.⁽¹⁵⁾ A pH of 1.5 ± 0.5 is normally used for radioactive waste

FIGURE 12-3. U-F Gel Times at Varying Catalyst Concentrations

solidification, with the weak acid catalysts usually added as concentrated solutions. To minimize the amount of catalyst required, dilute solutions of strong acids may be used to adjust the pH for highly buffered solutions, such as partially neutralized boric acid.

As a solidifying agent, the cross-linked U-F polymeric structure entraps the waste liquid, including water formed during the polymerization reaction. Because of the acid catalyst, the entrapped water is slightly acidic and mildly corrosive. When exposed to atmosphere, water evaporates from the mass leaving a light weight solid sometimes reduced in size. U-F solidified products are not considered flammable because of the water content.

Product Formulations and Properties

Aqueous waste solutions are mixed with U-F in the proportion of one to three volumes of waste liquid per volume of U-F. The catalyst, usually a saturated solution of sodium bisulfate, is added typically to about 2 to 3 vol% to initiate the polymerization-solidification reaction. The optimum amount of acid catalyst needed to achieve the desired pH of 1 to 2 must be determined for each waste. The use of weak acids avoids the premature gelling that can occur with an excess of strong acid.

The preferred formulations begin to gel within one to two minutes, and the waste is generally well solidified within 30 minutes. Curing to a reasonably hard, free-standing solid continues over a period of several hours, during which time small amounts of free, slightly acidic water are often released. Portland cement or other absorbents are often added to the waste container after the waste has gelled to absorb the residual water. The solid density depends on the waste content but is normally between 1000 and 1300 kg/m³.

U-F is also used to encapsulate solid waste materials such as filter sludge and ion exchange resins. The waste solid is usually slurried with a small amount of liquid waste before mixing with the U-F to improve both the handling properties and the volumetric efficiency of the solidification process. Typically, about one volume of U-F is used for each 4-to-6 volumes of slurry. Since the U-F and slurry water essentially fill the pore spaces between the solid particles, little or no volume increase is incurred.

Certain wastes, including soap solutions and concentrated sodium sulfate, are difficult to entrap in U-F. Good sodium sulfate products can be obtained by using fresh U-F, by diluting to less than 10 wt% Na₂SO₄ before adding the U-F, or by adding calcium chloride to precipitate excess sulfate. (16,17)

A number of materials can be added to the U-F formulation to improve its strength or leaching characteristics. Bleached paper pulp (α -cellulose) and wood flour are commonly used in U-F resin molding formulations to impart strength. Various clays, which are added to cement grouts to decrease the leachability of cesium,⁽¹⁸⁾ can also be added to U-F for the same purpose.

The properties of the solidified waste depend on the amount of liquid and/or solid incorporated by the U-F. Detailed information is very limited, but generally the product strength decreases and leachability increases as the ratio of liquid to U-F increases.⁽¹⁹⁾ A 2 to 1 liquid to U-F volume ratio is generally recommended as a compromise. In an open system, the solid readily loses liquid by evaporation at the surface. Some drying of the product does not affect the mechanical integrity of the block, but the solid may become friable if completely dehydrated.

Preparation Methods

Preparation methods for U-F radwaste solidification systems are similar to those using cement. Usually, appropriate quantities of U-F and neutralized waste (pH 5-8) are mixed together before a sufficient amount of catalyst is added to lower the pH to about 1.5. The waste and U-F can be batch-mixed in the storage container or premixed in a continuous system as shown in Figure 12-4. The catalyst in the latter case is added to the mixture as it

FIGURE 12-4. Urea-Formaldehyde Radwaste Solidification System
(United Nuclear Industries, Inc.)

enters the storage drum. The illustrated system uses a static in-line mixer to blend U-F with the waste. Flush water for the in-line mixer is automatically blended with U-F and solidified along with the waste in the storage drum.

Status of Technology

The use of urea-formaldehyde binder resin for immobilization of reactor radwaste and other radioactive liquid waste streams is well established and widely used in the U.S. (20,21,22)

Major Development Objectives

U-F solidification processes were developed originally as proprietary processes by private industry; thus detailed information on product characteristics and preparation techniques is somewhat limited. Development work is continuing at the vendor companies and primarily consists of applying U-F solidification techniques to new waste residues, improving present U-F applications, and testing new formulations of the U-F reagent for improved strength and leach resistance. A greater accumulation and publication of data on U-F products is needed to ensure its best use in the nuclear industry.

12.2.4 Cement/Concrete

For many years it has been common practice to incorporate radioactive wastes in cement or concrete, with or without additives. The two main reasons for using this procedure have been to simplify transport and storage and to reduce the possibility of release of radionuclides to the environment.

The chemical and physical properties of cement and concrete are well known, and its use for construction purposes extends over many decades. Cement is also readily available and comparatively inexpensive. However, knowledge of the effect of mixing cement with radioactive wastes is still limited, and experimental work is often necessary to optimize cement-waste formulations.

Although the term "cement" can be applied to many adhesive substances, in this section it is restricted to hydraulic cements. Such cements harden under water and consist primarily of a mixture of calcium silicates and calcium aluminates. The most common of these are the portland cements, although high alumina and pozzolanic cements are also used to solidify non-high-level wastes. (Pozzolans are siliceous and aluminous materials which will react with lime in the presence of water at ordinary temperatures to form cementitious compounds.) The density of portland cement is about 3100 kg/m^3 ; tapped density of the bulk powder is about 1500 kg/m^3 . Typical portland and high-alumina cement compositions are presented in Table 12-4. (23)

TABLE 12-4. Typical Cement Compositions

	Oxide Analysis, wt%			
	Portland Cements			Lumnite Cement (High Alumina)
	Type I ^(a)	Type II ^(b)	Type III ^(c)	
CaO	64	63	65	37
SiO ₂	21	22	20	9.6
Al ₂ O ₃	6.5	5	5.5	41
Fe ₂ O ₃	2.5	4	3	4.9
FeO	--	--	--	5.6
MgO	2.5	3	2.3	1.0
SO ₃	2.1	1.5	2.5	0.2

(a) Standard portland cement

(b) Sulfate resistant, less reactive and slower setting

(c) High early strength (ground to high fineness)

There is still not complete agreement as to the mechanism of setting (hardening) of cement. The first stage is reaction between water and the cement components, followed by partial solution of the hydrates formed on the surface of the solid particles. Crystallization of calcium hydro-silicate, hydroaluminate and hydroferrite occurs, and it is suggested that the interlacing of these crystals gives the strength to the hardened cement. (18)

Cement normally is used with an inert aggregate to form concrete, and the nature of the aggregate largely determines the strength of the concrete. Cement blocks prepared from waste concentrates and sludges will generally have less strength than conventional concrete. The strength is particularly dependent on the total salt content of the waste solution and of the cement block. A fairly narrow range exists in the desirable values for the ratio of basic and acidic oxides in the final product. If the ratio is reduced too much by the constituents of the waste, the strength of the cement block will decrease significantly. Poor mechanical strength can result in cracking and spalling of the cement, thus increasing the surface area available for possible leaching.

Product Formulations and Properties

The optimum proportions of cement and waste vary with the type of waste to be solidified or immobilized. Maximum waste contents for the solidified products are typically 75 wt% for solid waste materials or 33 wt% for aqueous solutions and slurries. Cements require a minimum proportion of water to obtain a workable mix. The minimum water/cement weight ratios are about 0.22

and 0.25 for high alumina and portland cements, respectively.^(24,25) Some waste solids (e.g., ferric and aluminum hydroxide sludges, filter sludges, zeolites and ion exchange resins) will absorb or retain large amounts of water. This must be supplied with the solid to prevent it from sequestering the required water from the cement and producing a dry, unworkable mix.

Excess water will result in a layer of free water on the surface of the solidified product. Absorbents such as vermiculite can be added to the cement to increase the amount of water that can be solidified. Without absorbents, the maximum water/portland cement weight ratio is about 0.5. With vermiculite, diatomaceous earth, or similar absorbents, the maximum water/cement weight ratio can be as high as 0.7 to 1.1.

Limited amounts of organic liquids can be incorporated in cement by adding a dispersing agent. Aqueous concentrates containing up to 15% dispersed organic liquid have been solidified at Kjeller, Norway.⁽¹⁸⁾ Small amounts of organic liquids absorbed on vermiculite can also be incorporated in cement.

Typical published waste/cement formulations are presented in Table 12-5. The original data, in several cases, were presented on a volumetric basis and were converted to a common weight ratio basis by making appropriate density assumptions. The data show that solutes in waste solutions and slurries can be incorporated in cement products at salt/cement weight ratios up to about 0.5, although the more typical ratios are about 0.15 to 0.3. Solidified product densities range from about 1500 to 2000 kg/m³, depending primarily on the water content.

Each waste must be considered individually because of the possible interaction between the waste constituents and the cement. One such interaction is the effect on the setting of the cement matrix. The set may be unaffected, accelerated, or retarded by the waste components. Acceleration of the set, which may occur with hydroxide sludge addition, can result in the cement setting in the processing equipment. Boric acid retards setting in portland cement; if sufficient boric acid is added, the set may be retarded such that the cement never hardens. The degree to which the waste interacts with the cement depends upon the amount of the interacting constituent and the manner in which it is added (i.e., solid salt addition as opposed to salt in solution, mixing mode, etc.)

Special additives can be used to improve the setting properties and/or the volumetric efficiency of the cementing process. Sodium silicate, added as a concentrated (Type N) solution at about 10% of the waste volume, has shown considerable promise for this purpose.^(16,17) Not only does sodium silicate provide a good set for boric acid solutions, but it also lowers the

TABLE 12-5. Typical Cement - Radwaste Formulations

Solutions and Slurries:

Waste Type	Weight Ratio, Waste Constituent/Cement		References
	Dry Waste Salt	Total Water	
25 wt% Na ₂ SO ₄	0.12	0.37	16
70 wt% NaNO ₃ slurry	0.52	0.22	24,25
30 wt% NaNO ₃ solution	0.15	0.35	24,25
Neutralized HNO ₃ -Al(NO ₃) ₃	0.37	0.37	26
20-25% water treatment sludge ^(a)	0.09-0.17	0.27-0.51	26
30-40% evaporator sludge	0.28-0.35	0.42-0.53	18
Conc. BWR reactor waste ^(b)	0.17	0.51	27
400 g/l evaporator concentrate	0.33 ^(c)	0.70	26

Solids and Wet Sludges:

Solids and Wet Sludges.

Waste Type	Weight Ratio, Waste Constituent/Cement				Wt% Water in Wet Sludge	References
	Dry Solid Basis		Wet Solid Basis			
	Solid	Water	Solid	Water		
Acid digestion process residue	0.12	0.37	--	--	--	28
Al ₂ O ₃ -ZrO ₂ calcine	2.4	0.25	--	--	--	24,25
Fly ash	0.33	0.30	--	--	--	24,25
Fe/Al hydroxide sludge	3.1	2.0	4.9	0.22	58	24,25
Diatomaceous earth	0.42	1.1	1.3	0.25	67	24,25
Linde AW-500 zeolite	1.21	1.0	2.0	0.23	39	24,25
Amberlite 200 cation resin	0.83	1.1	1.7	0.23	~50	24,25
BWR bead resins, recommended ^(d)	0.25	0.56	0.51	0.31	50	27
BWR bead resins, range ^(d)	0.25-1.0	0.45-1.3	--	--	50	27
BWR filter sludge, recommended ^(e)	0.26	1.19	0.51	0.94	50	27
BWR filter sludge, range ^(e)	0.04-0.28	0.48-1.3	--	--	50	27

(a) Miscellaneous flocculating and scavenging agents

(b) Assumed to be ~25% Na₂SO₄

(c) Plus 0.13 kg of vermiculite/kg cement

(d) Preneutralized with NaOH to prevent swelling and crumbling

(e) Cellulose fiber filter aid, powdered resins, etc.

volume-increase factor from about 2 with conventional cement formulations to about 1.4 when solidifying reactor waste concentrates. Typical formulations recommended by United Nuclear Industries, Inc. (UNI), the developer of the process (for which a patent is pending), are presented in Table 12-6. Densities of the products with sodium silicate additives are in the range of 1300-1500 kg/m³. The sodium silicate formulations are designed to minimize the waste product volumes and are not intended to produce high-strength products.

TABLE 12-6. Formulations for Solidifying Radwastes with Portland Cement - Sodium Silicate

Waste Type	Weight Ratio of Waste to Solidifying Agents		Volume Increase Factor	
	Dry Waste	Total Water ^(a)	With Silicate	Without Silicate
Bead resins (50 wt% water)	0.77	1.1	1.04	1.00
Powdered resin sludge (50 wt% water)	0.81	1.3	1.03	1.19
Diatomaceous earth (60 wt% water)	0.54	2.1	0.77	1.54
10 wt% boric acid	0.11	0.99	1.46	1.92 ^(b)
25 wt% Na ₂ SO ₄	0.46	1.4	1.33	1.92

(a) Excludes water added with sodium silicate solution.

(b) Free water is absorbed at this formulation, but the cement remains soft.

Cementitious grouts have been used for the disposal of intermediate level wastes in the Hydrofracture Facility at ORNL for about eight years.⁽²⁹⁾ The grout is made by combining the desired volume of waste solutions with a dry mixture consisting of the following components:

	wt%
Portland cement, Type I	38.5
Fly ash (a pozzolan-to improve strontium retention)	38.5
Attapulgate-150 (a drilling clay-to suspend the cement)	15.4
Grundite (an illite clay with a high affinity for cesium)	7.7

Also, small amounts of delta gluconolactone (to retard setting) and tributyl phosphate (to prevent foaming during mixing) are added. The final product contains about 40 wt% of the dry mix, 6 wt% neutralized salts, and 54 wt% water. The product density is about 1400 kg/m³, and the product volume is about 1.3 times the volume of waste incorporated. The compression strengths of about 14 to 20 kg/m³ are about 3 to 10 fold lower than obtained with conventional cement-waste products.⁽¹⁸⁾ Because of the mineral additives, fission product leach rates compare favorably with borosilicate glasses.

Cement is an open-cell structure because of the porosity that develops while the cement cures. As such, it is permeable to water and susceptible to radionuclide loss by leaching and exchange. Certain isotopes are more firmly fixed in the cement matrix than are others, and thus are less leachable. Strontium, rare earths, plutonium, and americium are tightly bound, whereas, cesium is not. Certain species of clay, such as bentonite and grundite, can be added to the formulation to improve cesium retention.⁽¹⁸⁾ Leach rates ranging from 2×10^{-9} to $0.1 \text{ g/cm}^2\text{-day}$, based on radioactive tracers, have been measured for cement. The rate depends on the tracer used, the waste type, and the cement-waste formulation.^(30,31)

Certain coating materials, such as bitumen, can be applied to cement to cover or fill the pores and thus lower the leach rate. More recently, soak techniques have been developed at Brookhaven National Laboratory to impregnate the pores with styrene monomer, which is then polymerized in situ by heating to 50 to 70°C.^(24,25) The result is a polymer-impregnated concrete (PIC) that is essentially impermeable with improved strength, durability, and resistance to chemical attack.

Styrene was chosen for PIC development because of its low viscosity, which enhances impregnation, and the excellent radiation stability of the polymer. Soak impregnation begins after the concrete has cured. Curing requires approximately 24 hours for high alumina, portland type III, or large castings of other cements. The monomer is introduced either through a port in the top of the mixing container or through the bottom of the mixing container under a hydrostatic head. Depending upon the formulation, soak impregnation requires 2 to 3 hours with resultant monomer loadings of 5 to 15 wt%. Benzoyl peroxide or AIBN [2, 2'-azobis-(2-methyl propionitrile)] at approximately 0.5 wt% in the monomer provides polymerization in several hours at 50 to 70°C. Catalyst content and process temperature can be varied to optimize the rate of polymerization. Product leachabilities for PIC are typically 100-fold lower than for similar conventional cement waste products while compressive strengths are from 3 to 10-fold higher. The product is nonflammable, but the polymer begins to decompose at $\sim 250^\circ\text{C}$.

The radiation stability of cement is excellent. No deterioration in strength or leachability occurs at an integrated dose of 10^9 rads (^{60}Co gamma rays) for cement products containing up to 30 wt% NaNO_3 .⁽²⁴⁾ Although the presence of water, nitrates, and other radiation-unstable compounds can create gaseous radiolysis products, this is not a serious problem because the gases produced are absorbed in the porous cement matrix.⁽¹⁸⁾

Preparation Methods

Preparation methods for incorporating radioactive wastes in cement can be divided into three broad categories: no-mix methods, in-drum mixers, and external mixers.

No-Mix Methods. Liquid waste is added to a preblended mixture of cement and a suitable, light weight absorbent; a typical formulation uses 1 part cement to 8-10 parts vermiculite by weight.^(18,25) The expanded vermiculite is porous and permits infiltration of dry cement into its structure. The material acts like a sponge, absorbing the liquid and thus presenting an enhanced surface for the cement to act upon. The recommended waste/cement weight ratio for this method is about 0.5,⁽²⁾ and the waste must be uniformly dispersed.

In-drum Mixers. In the simplest version of this technique, mixing weights (pebbles or half-bricks) are added to the drum along with the required amount of cement. A predetermined amount of waste slurry is then added, and the drum is capped and transferred to a tumbling or rolling station where the contents are thoroughly mixed. A schematic diagram of such a system is shown in Figure 12-5. In a second system, an external agitator is lowered into the drum to blend the waste and cement during or after filling. An in-drum mixer station designed for BWR's is shown in Figure 12-6.

FIGURE 12-5. Drum Tumbling Mixing Process for Incorporating Waste in Cement

External Mixers. Both continuous in-line mixers and conventional batch cement mixers can be used for blending wastes and cement prior to loading the storage drum. In-line blenders are preferred for their small holdup volume

FIGURE 12-6. In-Drum Mixer Station

and ease of cleaning. Various types of in-line mixers are used, including ribbon mixers, pug mills, and open-throat Moyno-type positive displacement pumps. Typically, a waste slurry, prepared with the desired amount of water and waste solids, and the cement are fed together at predetermined rates to the mixer, which discharges directly into the storage drum. Provision is made for flushing the mixer with water after loading is completed. If desired, the flush water can be diverted to a separate tank and used to prepare the waste slurry for the next batch of feed. A typical system, including UNI's sodium silicate modification, is shown in Figure 12-7.

Although the above technologies are generally used for solutions, slurries, and granular solids, cement can also be used to encapsulate larger solid wastes such as failed equipment, leached fuel hulls, and general trash. Improved volumetric efficiency can be obtained for compactable wastes such as trash by shredding and compacting them into wet cement. The latter technique is used at Aldermaston and Harwell, U. K.

Status of Technology

Cement solidification systems are widely used throughout the world to solidify or encapsulate virtually all types of

non-high-level wastes generated in fuel cycle operations. Several companies supply total radwaste solidification systems, including custom-designed systems, for liquids and sludges generated by reactors and other nuclear facilities. UNI's portland cement/sodium silicate radwaste system has been ordered

FIGURE 12-7. In-Line Mixing System for Portland Cement With Sodium Silicate Additive (United Nuclear Industries, Inc.)

by 5 utilities but is not yet in commercial use. Because of the complex chemistry involved in cement solidification, laboratory tests are recommended for each new waste requiring solidification.

Major Development Objects

Although cement technology is well developed, further improvements continue to be made in the areas of improved strength, lower leachabilities, higher volumetric efficiencies, and improved methods of preparation. Development efforts will continue in these areas to meet the competition of other solidification techniques.

Polymer impregnation technology for radioactive waste is still in the laboratory stage. Significant amounts of work yet remain to demonstrate and optimize polymer impregnation on large scale (>30 cm diameter) concrete castings. Design of processing equipment and process optimization for a particular waste could require six months to two years, depending upon the level of effort and any problems encountered with casting size or the waste to be incorporated.

12.2.5 Bitumen (Asphalt)

Asphalt and bitumen are synonymous terms used for a mixture of high-molecular-weight hydrocarbons found in natural beds but more commonly

obtained as a residue in petroleum or coal-tar refining. Bitumen has certain properties that are advantageous for immobilizing low- and intermediate-level radioactive wastes. It is chemically inert, insoluble in water, has good coating properties, and possesses a degree of plasticity and elasticity. These properties have led to several applications in foreign nuclear facilities, but the use of bitumen in the United States has been limited to laboratory and pilot plant development studies.^(18,26,32-44)

Several types of bitumen are available. They are obtained by:

- direct distillation of petroleum,
- air-injection oxidation of petroleum oils (blown bitumen),
- cracking of heavier fractions (cracked bitumen).

Direct-distillation bitumen is the most widely used. Blown bitumen is more radiation resistant but has a lower ignition temperature. Bitumen emulsions in water are available and may provide some advantage in the initial mixing of waste and bitumen. Being a natural product, bitumen can vary from batch to batch. Adverse effects are minimized by using named products that are produced in various grades, depending on such physical properties as softening point, flash point, ductility, hardness, etc.

The working temperature range for waste bituminization processes is 150 to 230°C, which is considerably lower than for any vitrification process. The elevated temperature is a disadvantage, however, when compared with cement or urea-formaldehyde solidification processes. The high temperature eliminates most of the water originally present in the waste and significantly reduces the waste volume to be stored. The resulting condensate, however, is an additional low-level liquid waste requiring treatment for disposal.

Product Formulations and Properties

Bituminization processes have been used to immobilize the solids content of a wide variety of wastes, including neutralized evaporator concentrates and sludges, ion exchange minerals and resins, incinerator ashes, sand, vermiculite, etc.⁽¹⁸⁾ In general, bitumen products with satisfactorily high mechanical strength and low leach rates may contain about 40 to 60 wt% solids. Up to 25 wt% tributyl phosphate has been incorporated into a marginally acceptable bitumen product by the addition of certain fillers such as fine clays, colloidal silica, and carbon black to a concentration of 37 to 40 wt%.⁽⁴³⁾ Although ion exchange resins have been incorporated into bitumen, they have a tendency for excessive frothing on mixing with hot bitumen; and nitrate-form anion resins in bitumen decompose during storage. Therefore, incineration of resins prior to incorporation into bitumen may be preferred.

Bitumen can also be used as a coating or sealing material for wastes. AERE, Harwell, U. K., has demonstrated incorporation of up to 50 vol% plastic waste in bitumen by allowing hot bitumen-sludge mixtures to flow onto the waste contained in the product storage drum.⁽¹⁸⁾ This technique can also be used to encapsulate other solid wastes.

The products are normally noncorrosive to mild steel. Bacterial attack on bitumen products appears insignificant although long-term tests are needed.⁽⁴⁵⁾ The thermal stability of bitumen products is good at ambient to moderate temperatures, fair at moderate temperatures (they soften), and poor at high temperatures (they ignite).⁽⁴⁶⁻⁵²⁾

Certain salts can have adverse effects on the properties of the product. The most widely studied are the nitrates and nitrites because of their wide usage and their potential as oxidants to increase the fire hazard. The ignition temperatures of bitumen samples containing 40 to 75 wt% sodium nitrate/nitrite salts were about 330°C for the nitrate salts and 275°C for the nitrite salts. The base bitumen alone did not spontaneously ignite at temperatures up to 450°C.⁽⁴³⁾ The bitumen burns more vigorously if appreciable quantities of oxidizing compounds (e.g., NaNO_3 , NaNO_2 , MnO_2) that decompose at the temperatures encountered during combustion are present.⁽⁴⁶⁻⁵²⁾

Sodium nitrate and other salts, notably ferric and aluminum compounds, can cause excessive hardening. Hardening caused by the iron and aluminum salts can be reduced by neutralizing the waste prior to bituminization. To avoid volatilization, boric acid must be neutralized before incorporating in bitumen; however, sufficient sodium hydroxide must be added to form the metaborate ($\text{Na/B} = 1$) rather than the tetraborate ($\text{Na/B} = 0.5$) to avoid hardening problems.⁽⁴³⁾ The sodium nitrate hardening effect is proportional to the time of heating at 230°C and can be minimized by using low-temperature bitumens or preparation methods with shorter residence times (e.g., screw extruders).

Bitumen products have leach rates, based on actinide tracers, of 10^{-3} to 10^{-7} g/cm²-day; leach rates based on alkali and alkaline earth tracers are up to 1000-fold greater. Cesium leach rates can be lowered by a factor of 2 to 10 by incorporating 2 wt% each Grundite (commercial name for a type of illite clay) and sodium metasilicate in the bitumen.⁽⁵³⁾ Addition of co-precipitants and neutralization to form hydroxides are also beneficial in reducing leach rates. Leach rates for salts increase almost linearly with crystal dimensions and are also affected by the amount of salts and residual water (normally less than 1% water). Storage temperatures should be kept below 60°C to avoid separation of salts and bitumen.⁽⁴³⁾

The radiation stability of bitumen products is adequate to about 10^9 rads but should be evaluated for each waste. Radiation damage is characterized by swelling (up to 70% volume increase at 10^9 rads for the less porous products) caused by the generation of gases such as hydrogen, methane, carbon dioxide, carbon monoxide, etc. To accommodate potential swelling, storage containers are not completely filled (typically only to 80-90%). The high flammability of some of the radiolytic gases may possibly be a detonation problem under some conceivable storage conditions.

Preparation Methods

Both batch and continuous units are used for solidification with bitumen. Batch units generally operate at temperatures of 220 to 230°C while continuous units operate at 160 to 180°C. In most of the processes, a low-melting wax or plastic such as polyethylene or polypropylene can be substituted for asphalt. (43,44)

A stirred-evaporator batch process for solidification of waste in bitumen, as depicted in Figure 12-8, has been developed at the Belgian Nuclear Center (CEN) at Mol, Belgium, (18,32-35) and at Harwell, U. K. (18,32,54) The

FIGURE 12-8. Stirred-Evaporator Batch Process for Incorporating Waste in Bitumen

Russians have described a similar process.⁽³²⁾ The facility at CEN has been in operation since 1964, while the British facility, commissioned in 1968, is not currently being used. In the CEN batch process, preheated bitumen is charged to the evaporator, and waste is metered into the stirred bitumen charge. Electric heat is provided through the vessel wall and by immersion heaters. A special agitator with adjustable blades is used for mixing and homogenizing the waste/bitumen mixtures. The average residence time of the bitumen charge in the evaporator is several hours. The off-gas is routed through a condenser and then through an electrostatic precipitator and an absolute filter. The long residence times and high surface temperatures used in this batch process cause hardening of the bitumen and distillation of light oils and tars, which make off-gas purification difficult.

A turbulent-film-evaporator continuous process for solidification of waste in bitumen, shown in Figure 12-9, has been developed on a pilot-plant scale at ORNL,^(44,53,55,56) in Japan,⁽⁵⁷⁾ and on an industrial scale in France.^(33,37,39) A commercial unit is operating at Saclay, France.⁽³⁹⁾ A cutaway drawing of the evaporator (LUWA Corporation) used in France (Marcoule and Saclay) is shown in Figure 12-10. It consists of a vertical tube with a heating (steam) jacket and an internal rotor that forms a thin

FIGURE 12-9. Turbulent-Film Evaporator Continuous Process for Incorporating Waste in Bitumen

FIGURE 12-10. Turbulent-Film Evaporator Used to Incorporate Waste in Bitumen

film of the bitumen/waste mixture on the heated surface. Preheated bitumen and waste are fed to the unit continuously and water is continuously evaporated. The steam is removed from the top of the unit, and waste/bitumen product is drained from the bottom. The average residence time in the evaporator of only a few minutes is a distinct advantage with thermally sensitive materials such as bitumen. This process is offered commercially by Saint-Gobain Techniques Nouvelles, which has sold a unit for a power reactor in Sweden.⁽³⁷⁾

A screw-extruder continuous process for solidification of waste in bitumen, as depicted in Figure 12-11, has been developed at Marcoule, France and Karlsruhe, Germany.^(33,38,41,42) A schematic diagram of the extruder (Werner and Pfleiderer Corporation) is shown in Figure 12-12. The extruder consists of two (or four) screws operating in a steel barrel that is divided into ten stages heated separately with steam. Preheated bitumen and waste are continuously pumped into the transmission end of the barrel. The screws mix and knead the waste/bitumen mixture in the barrel, circulate it in a thin film, and transport it forward. Water is continuously evaporated; the steam is removed through large pipes (steam domes) attached to the barrel and passed through oil filters and condensed. Carryover of radioactivity to the condensate is less than 0.1%.⁽⁴²⁾ The waste/bitumen product is discharged at the end of the screws into drums which are allowed to cool for 24 hours before

FIGURE 12-11. Screw-Extruder Continuous Process for Incorporating Waste in Bitumen

FIGURE 12-12. Twin-Screw Extruder for Incorporating Waste in Bitumen

capping and storing. Average residence time in the extruder is only a few minutes. This process is offered commercially by Saint-Gobain Techniques Nouvelles and by Werner and Pfleiderer Corporation. Two such units are operating at Marcoule, France, and two at Karlsruhe, Germany;⁽⁴²⁾ one is scheduled for operation at Eurochemic (Mol, Belgium) in late 1975.⁽⁴⁰⁾ Units are operational at a power plant in Argentina and in the Netherlands.⁽⁴²⁾

Status of Technology

Bituminization techniques and processes are well developed for many radioactive waste applications. Screw-extruders are available with water evaporation capacities of 4 to 210 kg/hr (solidified product rates of about 1 to 100 liters/hr).

Major Development Objectives

Bituminization is a relatively mature technology, and development objectives are essentially limited to refining existing techniques and evaluating the effects of specific waste compositions and radiation levels on product properties. No work is currently in progress in the United States.

12.3 IMMOBILIZATION TECHNOLOGIES REQUIRING DEVELOPMENT

Immobilization technologies described in this section include aluminosilicate mineral fixation, glass, pelletization, polyethylene, water-extensible polymers, and metal matrix concepts.

12.3.1 Aluminosilicate Mineral (Clay) Fixation

Aluminosilicate minerals can be used to immobilize radioactive wastes as glass formers,⁽¹⁰⁾ as ion exchange materials,⁽⁵⁸⁾ and as reagents for the incorporation of nuclear waste solutions inside crystalline aluminosilicate mineral lattices by hydrothermal processes.^(59,60) The latter technique, under development by ARHCO as the Aqueous Silicate Process, is the subject of this section.

The Aqueous Silicate Process has been developed specifically for immobilizing high salt wastes derived from earlier processing of Hanford HLLW. These wastes are typically salt cakes or highly concentrated salt solutions composed largely of sodium nitrate, sodium nitrite, sodium hydroxide, sodium aluminate, and sodium carbonate. The process involves a low temperature (30 to 100°C) reaction of the concentrated salt solution with a powdered clay, such as kaolin or bentonite, to form a cancrinite mineral containing the salt as part of the mineral structure.⁽⁶¹⁾ The reaction with kaolin can be represented by the following equation:

Results of early tests with synthetic waste have led to definition of three conceptual flowsheet alternatives shown in Figure 12-13.⁽⁶²⁾ The simplest, least expensive route, called the Rich Clay process, yields a product with a relatively high leach rate and low cohesion of the cancrinite particles. This product relies on excess clay to bind the particles together. A product formulation has been developed that contains 31 wt% cancrinite, 16 wt% kaolin, 17 wt% sodium salts (primarily sodium nitrate) and 36 wt% water. The total salt and water content, including that bound to the clay and cancrinite, is 60 wt% (39 wt% water). The initial mixing produces a soft, wet product with the approximate consistency of peanut butter which hardens on aging or heating to an adobe-like brick. Unreacted water and salts remain absorbed in the hardened product.

FIGURE 12-13. A Conceptual Flow Diagram for the Conversion of Radioactive Wastes to Aluminosilicate Minerals

The volumes of clay and waste solution are approximately additive; each gram of clay results in a volume increase of ~0.38 ml. The amount of clay necessary to form a solid product depends on the type of clay used and the composition of the waste solution. Minimum amounts of clay required for synthetic Hanford terminal liquors ranged from 0.7 to 1.3 g/ml. The use of calcined clays (clays heated to 700°C) increases the amount of waste that can be incorporated in the crystalline structure.⁽⁶³⁾ The calcined clay products have lower volume, greater hardness, and will not crumble when contacted with water. Reaction kinetics with waste solutions are also 5 to 30 times faster than obtained with uncalcined clays.

Leach rates are improved significantly when the Lean Clay process alternative is used. In this process stoichiometric amounts of clay are added so that there is no unreacted clay. A washing step is necessary to remove any unreacted salts that might be present in the cancrinite after reaction. These salts are then recycled and reacted with more caustic and clay. A binder, such as portland cement, lime, sodium silicate-curing agent, or an appropriate organic polymer, may be added to improve the mechanical strength of the product, which is otherwise inferior to the Rich Clay product.

In the Clay Calcination process alternative, a clay/salt-cake mixture is heated to 700 to 800°C, which converts it to the mineral-form nepheline according to the reaction:

This process makes a product with a lower volume and improved thermal and radiolytic stability. The theoretical upper limit for formation of pure nepheline from kaolin is 40 wt% NaNO₃ salt cake in the reaction mixture. By heating to 530-595°C, the cancrinite product of the other two process variations can also be converted to nepheline. On heating, zeolitic water is removed over the range 100 to 300°C, and trapped NaNO₃ and NaNO₂ begin to decompose at about 700°C. The melting point for the products is about 900 to 1200°C.

Leach rates for the products depend strongly on the processing mode used. Solid products prepared from actual Hanford terminal waste solution had extended bulk leach rates of about 10⁻³-10⁻² g/cm²-day for the Rich Clay process, 1 to 4 x 10⁻⁴ for the Lean Clay process (using a portland cement binder), and 2 to 6 x 10⁻⁴ for the Clay Calcination process, based on ¹³⁷Cs in the leachate.⁽⁶²⁾

Preparation Methods

The basic elements used in preparing the various clay reaction products are illustrated in Figure 12-13. At the heart of all processes is the requirement of a mechanical mixer capable of continuously mixing and conveying the nearly dry, granular or soft, peanut butter-like products. Equipment is commercially available that appears to be adaptable to this application.

Metering systems must be provided for the Rich Clay process for addition of the waste solution,, sodium hydroxide, and powdered clay. The product from the mixer can be discharged directly into the storage container for hardening. The container can be placed in a low temperature oven or furnace (75 to 100°C) to accelerate the hardening process. The use of calcined clays will greatly shorten the hardening reaction, which should be complete within about 1 or 2 hours at 100°C or about 10 hours at 75°C. Temperatures near or above 100°C tend to increase product void spaces and swelling.

Two methods have been proposed for preparing the nepheline bricks of the Clay Calcination process:⁽⁶²⁾ 1) the clay-salt mixture (30 to 40 wt% salt) is molded into bricks that air-dry before being fired at 700 to 900°C; 2) the loose mixture is fired, mixed with a binder, and formed into bricks. The latter method produces a denser product, free from the cracks formed in the premolded bricks because of gas release during firing.

Status of Technology

Development of the Rich Clay version of the Aqueous Silicate Process has progressed to the stage of preliminary pilot plant testing and conceptual engineering design activity. Most development work has been on a laboratory scale to establish the feasibility of the process. The characteristics of products formed with Hanford alkaline-salt waste solutions have been determined. Pilot plant studies demonstrated mixing clay with waste terminal liquor at processing rates up to about 5 kg of product per hour.

Approximately one to three years of additional engineering development work will be required to prepare the process for practical design. This time requirement will be governed by the need to develop or adapt mixing and conveying equipment for remote operation and maintenance.

12.3.2 Glass

The chemical durability of glass, plus its ability to contain a large number of disparate elements, has led to research and development work over the past 20 years on several different processes for the conversion of high-level waste to glass. This work has been described earlier in Section 6.0.

Much less development work has been done on the conversion of non-high-level radioactive wastes to glass, although certain principles of glass formulation have been developed that can be applied to vitrification of these wastes if such a product form is desired.

In many ways, the problems of glass making are simplified for non-high-level wastes by the absence of significant quantities of fission products. The reference high-level liquid waste composition used in current waste solidification studies contains 55 wt% fission products (on a non-volatile oxide basis); whereas, non-high-level liquid waste solids are principally sodium salts. Other solid, non-metallic waste residues, such as ashes and mineral ion exchangers, also are composed primarily of silicates and metal oxides commonly used in glass making.

Product Formulations and Properties

Glasses are composed of network formers and network modifiers. Silicon, boron, aluminum, and phosphorus are network formers because they bond to oxygen with high bond strengths to form an extended network. These elements, singly or in combination, are major constituents of all radioactive waste glasses or ceramics. Boron, for example, lowers the melting temperatures; aluminum and boron increase chemical stability (as measured by leach tests) and slow the rate of devitrification of glass; too much aluminum and boron make the viscosity of the melt too high. Borosilicate glasses are currently favored over phosphate glasses because of their greater stability and the much lower leach rates of the devitrified products.⁽⁶⁴⁾

Other elements used in glass formation, such as sodium, potassium, calcium, iron, and manganese, fit into interstices of the glass network and are called network modifiers. Each of these has a specific effect on the overall properties of the glass. The alkali-metal oxides lower the melting temperature of glass by decreasing the viscosity, but excessive amounts reduce chemical stability. Cesium is volatile at glass-forming temperature, but its volatility is effectively suppressed by oxides of boron, titanium, and molybdenum.⁽⁶⁵⁾ Calcium and magnesium oxides tend to improve chemical durability and/or to prevent crystallization. By proper formulation, a combination of waste constituents and additives can be found that yields a glass having the desired properties. Generally, no more than two parts-by-weight of glass-making additives are required to convert one part of radioactive waste, as oxide, to a good glass.

Two semi-empirical studies^(66,67) resulted in guidelines for formulation of acceptable glasses. The important atom ratios of glass components are:

<u>Designation</u>	<u>Atom Ratio</u>
A	$\frac{\text{Si}}{\text{Al}+\text{B}}$
B	$\frac{\text{oxygen}}{\text{network formers}}$
C	$\frac{\text{network formers}}{\text{network modifiers}}$
D	$\frac{\text{network modifiers}}{\text{oxygen}-2(\text{network formers})}$

When Ratio A is >1.5, leachability is low. Melting point of glass increases as A increases. With Ratio B between 2.2 and 2.4, glass formation is best and leachability is low. Excess oxygen is needed to balance the electronic charge of network modifiers. Density increases as A decreases and B increases. Ratio C should be ~2 for good glass formation. As C decreases, the glass network is disrupted and the tendency for glass formation decreases. Ratio D represents the ratio of network modifiers to excess oxygen not required for network formers to be four-coordinate. D should be as near as possible to 2.

A model developed at the Hahn-Meitner Institute⁽⁶⁸⁾ uses the following formula for determining optimum glass composition:

$$Y = 0.5 \text{ to } 1.0; \text{ m.p.} = 1100 \text{ to } 1200^\circ\text{C}$$

$$X = \sim 2 \text{ with } Y > 0.5$$

The suggested glass composition is 4 mol SiO_2 /2 mol B_2O_3 /1 mol Al_2O_3 /2 mol CaO /1 or 3 mol Na_2O plus 20 wt% waste.

An optimum glass mixture for incorporating iron-aluminum and iron-manganese hydroxide sludges was developed at the Savannah River Laboratory using the above guidelines.⁽⁶⁵⁾ Up to 45 wt% synthetic sludge was incorporated in a glass melting at 1150°C by using a glass additive mixture containing 52.5 wt% SiO_2 , 10 wt% B_2O_3 , 22.5 wt% Na_2O , 5 wt% CaO , and 10 wt% TiO_2 . Long-term leach rates, based on both cesium and strontium tracers (25°C), decreased from an initial $\sim 10^{-6} \text{ g}/(\text{cm}^2\text{-day})$ to $\sim 10^{-8} \text{ g}/(\text{cm}^2\text{-day})$. The laboratory work has been confirmed with actual SRP radioactive sludges.⁽⁶⁹⁾

Some intermediate-level liquid wastes are expected to contain substantial amounts of sodium nitrate or carbonate. In such instances, the sodium component can serve as an integral element of the glass compound.

This principle is employed in the "silicate melt" process being developed by ARHCO for possible use in immobilizing salt cakes obtained during the in-tank waste solidification program.⁽¹⁰⁾ Soda-lime, borosilicate and basalt formulations have been used to incorporate up to about 25 wt% Na_2O in the final glass, melted at 1100-1250°C. Addition of 10 wt% B_2O_3 to the basalt formulation lowered the melting point by 100 to 150°C and also decreased the volatility of cesium to 1% or less.⁽⁷⁰⁾ Typical 25°C leach rates, based on cesium tracer, decreased from an initial $3 \times 10^{-5} \text{g}/(\text{cm}^2\text{-day})$ to about $2 \times 10^{-6} \text{g}/(\text{cm}^2\text{-day})$ for the soda-lime formulation; prolonged leach rates with boron-containing basalt glasses were up to ten-fold lower. Glass densities were 2400 to 2800 kg/m^3 , with the higher densities obtained with the basalt formulations.

Basalt and borosilicate glass formulations have also been used to vitrify plutonium-contaminated soil,⁽¹⁰⁾ incinerator ashes,⁽⁷¹⁾ and a cesium-containing zeolite (Na-form chabazite).⁽⁶⁵⁾ Each of these wastes is composed largely of glass forming minerals (primarily silicon and aluminum compounds) and can be incorporated readily in glasses. The glass formulations for soil and ash residues contained typically about 45 to 50 wt% SiO_2 , along with 5 to 10 wt% Na_2O and 5 to 10 wt% B_2O_3 added as fluxes to reduce the melt temperature. Extended 25°C leach rates, based on plutonium, were in the range 10^{-8} - $10^{-7} \text{g}/(\text{cm}^2\text{-day})$. Up to 40 wt% ash residues were also incorporated successfully in a zinc borosilicate glass frit (~29 wt% ZnO) used extensively in high-level-waste glass formulations.⁽⁷²⁾ The glass formed from zeolite contained 24 wt% SiO_2 , 10 wt% Al_2O_3 , 24 wt% B_2O_3 , 19 wt% Na_2O , 12 wt% CaO , and 12 wt% TiO_2 ; accelerated leach rates were comparable to those obtained from glasses prepared with synthetic Savannah River Plant sludges. Additional work on the incorporation of incinerator ashes, vermiculite, and sludges in glasses is reported in Reference 73.

Although most elements can be incorporated into glasses as their oxides, a few elements are not compatible with standard glass formulations. The most important of these from the standpoint of non-high-level wastes are the halogens, sulfur, and mercury. Mercury, chlorine, and iodine volatilize completely during melting. Sulfur, as sulfate, has limited solubility; above about 1 wt% sulfate, a separate, water-soluble phase is formed. Sulfate can be volatilized as SO_2 by addition of a suitable reducing agent. Fluorine is also volatile, but can be retained in the melt to a large extent by the addition of calcium to form calcium fluoride. Ruthenium dioxide, if present, is not soluble and is encapsulated as particles. Certain oxidizing agents, such as nitrate and manganese dioxide, if present during melting, will convert an appreciable fraction of the ruthenium to volatile RuO_4 .

Preparation Methods

The technology developed over thousands of years of manufacturing commercial glass is useful but not directly transferrable to the making of radioactive waste glass. All steps must be made as simple as possible for remote, manipulator operation. Three steps are required to make glass objects: batching, melting, and shaping.

Batching of feed material for the glass melter is the most crucial step in the incorporation of radioactive wastes in glass. This step includes the selection of constituents and their physical form, and blending prior to melting. Since the overall constituents must be selected to produce an optimum glass from the waste being processed, the waste composition must be known within about 20 percent accuracy. For rapid dissolution of waste constituents into the melt, it is desirable that the waste solids be in finely divided form (particles less than 100 microns) unless encapsulation rather than dissolution is the objective.

A low-viscosity glass formulation is preferred to minimize blending requirements, and low-melting temperature formulations are advantageous in minimizing component volatilities and resultant off-gas cleanup requirements. The standard soda-lime glass (72 wt% SiO_2 , 15 wt% Na_2O , 10 wt% CaO-MgO , 2 wt% Al_2O_3 , 1 wt% misc.), which accounts for about 90% of all commercial glass tonnage made, is melted at 1475-1500°C. Formulations demonstrated for radioactive waste glasses melt at about 1000 to 1250°C. Holding the mixture at the melting temperature for two or three hours is usually sufficient to obtain a homogeneous melt.

The shaping step is kept very simple in making radioactive glass. The glass, prepared in equipment similar to that described earlier for vitrifying high-level waste, is poured into large steel cylinders. Alternatively, the glass may be prepared in situ in the steel storage container. Careful annealing is required to prevent cracking of the large blocks of glass as they cool.

Status of Technology

Several processes for vitrifying high-level waste are ready for practical design. Studies with non-high-level wastes have been restricted to laboratory-scale feasibility studies. In many cases, high-level waste and commercial glass-making technology should be transferrable to low-and intermediate-level liquid wastes with a relatively minor development effort (2 to 3 years). Encapsulation or incorporation of solid wastes in glass matrices is a longer range goal, requiring an estimated 4 to 6 years to practical design.

Major Development Objectives

Development objectives depend on the waste to be vitrified. General objectives include further definition and optimization of low-melting, low-viscosity glass formulations for specific wastes; development of off-gas treatment processes; development or adaptation of suitable melter designs and materials of construction; and development of hardware for melter remotability. For encapsulation, suitable casting or glass-coating methods are needed.

12.3.3 Pelletization/Compaction

Many waste solids, such as ashes and ion exchange minerals, are dispersible, have low densities, and are easily leached. For improved safety during storage and transport, these residues can be compacted or pelletized, either alone or with a binder.

A variety of compacting/pelletizing techniques are available and have been utilized in ERDA laboratories. Radioactive ceramic materials (PuO_2 , UO_2) have been formed into a variety of shapes and sizes by both cold-pressing and hot-pressing.

Ceramic pellets (1 to 6 cm diameter by 1 cm thick) of radioactive materials and of various nonradioactive oxides have been produced by vacuum hot-pressing.⁽⁷⁴⁻⁷⁶⁾ A current production program produces 3.8-cm diameter $^{238}\text{PuO}_2$ spheres with a density of 80 to 85% theoretical.⁽⁷⁷⁾ The 15 to 20% void volume permits the escape of helium produced by alpha decay and allows the sphere to maintain its original integrity. Studies on vacuum hot-pressing of inorganic hydrous-oxide ion-exchange minerals at Sandia Corporation (SLA) indicate that a wide variety of waste and waste/additive forms can be routinely hot-pressed. Technically, the hot-pressing technique is especially suitable for compacting waste residues or a waste residue/additive mix because it combines calcining, pressing and sintering into a single operation.

The various cold-pressing techniques offer a wide variety of capabilities. They permit the fabrication of large billets and the automated pressing of compacts/pellets. Several types of presses are available and have been utilized within ERDA. The technique for automated pressing is highly developed and is currently being utilized at Mound Laboratory to press alumina insulators and explosive pellets for detonators. cursory work at SLA on cold-pressing/sintering showed that the cold-pressed pellets were porous and leachable but that various additives improved the product. Successful development of this process to yield a completely suitable product is well within current technology.

Isostatic pressing is not as highly developed for processing radioactive materials as either of the two previously mentioned processes. However, isostatic pressing does offer the advantage of producing parts of more uniform density. The technique can be used to produce both small parts and rather large billets. Isostatic pressing as applied to high-level radioactive material has been limited by the difficulties in adapting this fluid-based technique to environments necessary for handling alpha radiation.

The injection/transfer molding of ceramic parts is relatively new. The technique has not been applied to radioactive materials and probably will never be suitable for processing pure radioactive materials. However, the process is especially suitable for use with materials not adversely affected by SiO_2 impurities. Developed at Mound Laboratory, it is used to fabricate Al_2O_3 insulators for detonators. Suitable formulation of compacts/pellets with waste residues are well within development capabilities. The injection/transfer molding fabrication technique offers several advantages: parts of various configurations can easily be produced and the process is adaptable to automation.

Product Formulations and Properties

The product formulation will consist of the various waste residues such as incineration ash, ion exchange minerals, etc. to which a ceramic matrix material may be added. Considerable development effort is needed to define both the composition of the additive and the amount of residue that may be incorporated into this matrix. It has been suggested that the utilization of a three-phase ceramic mixture could provide lattice "vaults" to disperse and hold both the fissile material and its fission products.⁽⁷⁸⁾

The final product will be a strong, nonleachable ceramic with the radionuclides dispersed and held in the ceramic lattice. The size of the product will depend on the compaction process chosen but could range from large billets down to small pellets.

Cermet composites can be prepared by hot-pressing a mixture of metal powder and waste residue. The advantage of the cermet is that the billet or pellet would have strength, thermal conductivity, and ductility similar to that of the metal phase. The pellet or billet could then be totally inerted by applying a metal coat through a chemical vapor disposition process.⁽⁷⁹⁾

Preparation Techniques

Preparation steps for the cold-pressing and hot-pressing pelletization/compaction options are shown in Figure 12-14. The steps for both processes are similar. The waste residues are blended, if desired, with a suitable ceramic or metal matrix material and the mixture pressed into a chosen configuration. The material formed by cold-pressing is sintered to an appropriate density; the hot-pressed material may be subjected to an oxidation step to remove adherent graphite if a graphite die is used.

FIGURE 12-14. Pelletization/Compaction Preparation Steps

The surface of the sintered products can be totally sealed (inertified) by coating with an appropriate ceramic, metal, or epoxy coat. The coating can be applied by one of the following processes:

- plasma spray
- castable alumina (spray or dip)
- chemical vapor deposition (CVD)
- epoxy dip (coat)

The epoxy coating can be applied to ceramic or metal coated products to improve containment integrity.

Status of Technology

The pelletizing/compacting technology suggested here is highly developed and widely used for nuclear fuel fabrication throughout ERDA and the ceramic industry. Much of the technology is currently used to compact/pelletize radioactive material. Engineering technology is still needed to adapt the equipment to the specialized environments of processing waste residues.

Major Development Objectives

The materials technology for incorporating waste residues into either a ceramic or metal matrix still needs considerable development, primarily the application of currently available crystal-chemistry and sintering technology to particular waste residues. A considerable screening process will be needed to optimize the product materials and their formation processes. Major development is needed in the following areas:

- The pressing of compacts/pellets by vacuum or inert gas hot-pressing requires development of reusable dies and automation. (The life of the present graphite die has been less than 20 pressings due to chemical and mechanical attack.) The operational parameters for forming composites with metals and ceramics need to be determined.
- The various cold pressing techniques require adaption of each system to the fabrication of compacts/pellets out of waste residues. Suitable operational parameters and binders used in fabrication must be determined.
- The parameters and atmospheres required for heat treating the fabricated compacts must be determined.
- The total inertification system, including coating techniques, must be evaluated.
- Engineering development and demonstration of the process or processes selected by the laboratory development studies will be required.

12.3.4 Other Immobilization Systems

Several additional systems for solidifying non-high-level wastes have been developed or proposed. Because of limited information on most of them, only highlight descriptions of the processes are presented.

Polyethylene

Both inorganic and organic waste materials have been satisfactorily incorporated in polyethylene.^(43,80) Most of the work has been performed by a batch process in laboratory equipment. Since the properties of polyethylene are similar to those of bitumen, similar (or identical) equipment can be used for both processes.

In the batch process, a suitable polyethylene was added to the agitated mixing vessel and heated up to 100 to 170°C to obtain a fluid melt. Liquid waste was then added at a rate proportional to the evaporative capacity of the vessel until the desired quantity of waste solids (typically about 40 wt%) was incorporated in the plastic. After all of the volatile liquids were evaporated, the product was drained to the mold or disposal container at ~180°C.⁽⁴³⁾ Leach rates of the products were comparable to those for bitumen products.

Incorporation of organic ion exchange resins was done similarly except that the resin was dried to minimize foaming before it was added to the molten polyethylene. Up to 80 wt% resin could be incorporated in the plastic, though increasing viscosity may limit the practical resin content to about 50 wt%. The compressive strength of the 50 wt% product was nearly 300 kg/cm². Generally, the strength and chemical resistance of the loaded plastic were comparable to that for the pure plastic.⁽⁸⁰⁾

Up to 40 wt% organic liquids, including tributyl phosphate, have also been incorporated into polyethylene.⁽⁴³⁾ The products retained the properties of the plastic matrix material.

The radiation resistance of polyethylene products equals or exceeds that of bitumen products. There was no visible effect at 10⁷ rads and only a slight discoloration at 10⁸ rads.⁽⁴³⁾

Burning tests showed that polyethylene containing 40 wt% solids derived from ORNL evaporator concentrate (primarily a basic sodium nitrate solution) lowered the spontaneous ignition temperatures from 550°C to 440°C. Burning was characterized by a steady yellow flame, in contrast with the vigorous burning obtained with bitumen products.⁽⁴³⁾ It was concluded that polyethylene was probably acceptable for use with oxidizing salts, but additional studies were recommended to assess the safety further.

Water-Extensible Polyesters

Simulated wastes typical of those generated in LWR's, including boric acid and sodium sulfate solutions, ion exchange resins, and filter sludges, have been incorporated in water-extensible polyester resins.⁽⁸¹⁾ The resins tested were Laminac EPX-289-4 (American Cyanamid Company) and PE-725 (Cargill Company). The polyesters as supplied contained promoters to decompose peroxides and initiate polymerization and gelling of the resin when organic peroxide catalysts were added.

In the laboratory emulsification procedure, the waste liquid or slurry was added to the polyester resin in a high-speed blender. The water-in-resin

emulsion formed was poured into suitable containers and solidified by addition of the catalyst, usually one percent by weight based on the resin. Generally, gel times increased with increasing water content. The uncatalyzed emulsions were quite stable and could be stored without phase separation. The result of the studies are summarized below.

- Aqueous solutions of Na_2SO_4 (10 to 24 wt%) incorporated at solution/resin ratios of 1:1 to 2.3:1 produced hard-set specimens.
- Aqueous solutions or slurries of boric acid (1 to 20 wt%) incorporated at solution/resin ratios of 2.3:1 yielded hard-set solid specimens.
- Up to 20 g of wet, drained bead resin could be incorporated in 50 g of preformed water-in-polyester emulsion (0.7:1).
- Retardation of polymerization occurred on attempts to emulsify a water-bead resin slurry directly with the polyester.
- Equal weights of wet bead resin and polyester resin could be mixed and catalyzed to form a soft gel that hardened after several hours. Powdered resins could be treated similarly.
- A 20 wt% slurry of "Solka Floc" filter aid was solidified with resin at a slurry/resin ratio of 2:1.

An average of 600 to 900 kg of waste solution or slurries (60-80% water) could be incorporated per cubic meter of solid. The solids were coherent, rigid and shock proof, with no apparent deterioration observed at ^{60}Co radiation doses up to 10^8 rad.

The feasibility of the process has been demonstrated, but further work is needed to optimize the process and to determine the cause of the polymerization retardation effect produced by ion exchange resins.

Metal Matrix

Waste residues can be incorporated in metal matrices by encapsulation methods described in Sections 6.0 and 12.3.3.

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13.0 VOLATILE RADIOISOTOPE RECOVERY AND OFF-GAS TREATMENT

13.0 VOLATILE RADIOISOTOPE RECOVERY AND OFF-GAS TREATMENT

Volatile wastes are released when fuel elements are chopped and dissolved during fuel reprocessing, or are generated in processes used to reduce the volume or combustibility of secondary wastes. Krypton-85, iodine-129, tritium, and carbon-14 are released during fuel preparation and dissolution; ruthenium, oxides of nitrogen, and particulates are released during solidification of by-product solutions, and hydrogen chloride and particulates are released during combustion of solid wastes containing chlorinated hydrocarbons.

Volatile radioisotopes and other off-gas wastes may either be released or recovered, depending on the potential environmental impact. The primary release technologies, dilution and dispersion from tall stacks, are now available. Recovery and treatment processes vary widely with the type of waste being handled. The more complex systems may involve combinations of steps, involving concentration, isolation, and immobilization.

Waste management systems for handling volatile radioisotopes pose a common problem. They tend to convert a low concentration (perhaps insignificant) waste with a high probability of escape ($P=1$) to a high concentration waste with a low probability of escape. Effective treatment technologies must therefore provide reliable physical or chemical systems for immobilization of volatile wastes after they are collected.

The technologies described in this section may not be required to meet existing standards for environmental protection. They are listed to provide an overview of the available and potential methods for gaseous waste management.

13.1 KRYPTON-85

Of the noble gases formed by nuclear fission (krypton and xenon), only krypton-85 (^{85}Kr) has a half-life sufficiently long to be present at the time of fuel reprocessing. Most of the ^{85}Kr in the fuel is released during shearing and dissolution, and is removed by the off-gas stream at low concentrations. (^{85}Kr is $\sim 6\%$ of all krypton isotopes present, and krypton is $\sim 0.003\%$ of the total off-gas composition.) The major activity of ^{85}Kr is beta radiation of 0.65 MeV energy, with a half-life of 10.73 years.

While the technology exists for dispersal of ^{85}Kr to the atmosphere,⁽¹⁾ methods have been proposed for its collection and storage to avoid long-term global build-up.⁽²⁻⁶⁾ Of these, collection of ^{85}Kr by cryogenic distillation and storage in pressurized cylinders are considered to be currently available technologies. Other methods which could be used at a commercial reprocessing plant, but which require further development include ^{85}Kr collection by liquid fluorocarbon absorption and storage by zeolite encapsulation. Additional collection and storage techniques have been considered,^(2,4,6) but their application to the process flow stream anticipated at a commercial facility ($\sim 12 \text{ mole s}^{-1}$ or $550 \text{ std. ft}^3 \text{ min}^{-1}$) is questionable.

Annual requirements of storing ^{85}Kr for the methods which are applicable to a typical commercial fuel reprocessing scale are presented in Table 1.^(7,8)

TABLE 1. Annual ^{85}Kr Storage Requirements for a 1500 Tonne/Yr Reprocessing Plant

Annual Production:

9.81 MCi of $6\% \text{ }^{85}\text{Kr}$ in Krypton

Storage Alternatives:

Pressurized Cylinders (50-l)

77 Cylinders @ 35 Atm (500 psig), 60°C wall temperature

24 Cylinders @ 137 Atm (2000 psig), 127°C wall temperature

Zeolite Encapsulation ($1.8 \times 10^{-3} \text{ mole Kr g}^{-1} \text{ zeolite}$ or $40 \text{ std. cm}^3 \text{ Kr g}^{-1} \text{ zeolite}$)

2,800 Kg Zeolite in 82 50-l containers

The annual production of ^{85}Kr from a 1500 tonne/yr reprocessing plant is assumed to be 9.81 MCi/yr.⁽⁹⁾ Pressurized cylinders⁽⁸⁾ (available technology) and zeolite encapsulation (requiring development) are compared in Table 1. Krypton is assumed to have a relatively pure composition; if impurities such as xenon are present, increased storage positions will be needed in the storage facility. A more detailed assessment of each of these storage techniques will follow in a later section of this report. (See 14.1)

13.1.1 Available Technologies

13.1.1.1 Release

This technical alternative is to release the krypton-85 resulting from fuel reprocessing to the atmospheric environment from a tall stack. Technology is available to design the stack and to assess the dispersal of the gas in the atmosphere.⁽¹⁾

Essentially all of the noble gases present in irradiated nuclear fuel are released during the headend dissolution of the fuel. The dissolution of most commercial nuclear fuels is accomplished in nitric acid. During dissolution, the fission product noble gases, krypton and xenon, are released along with unrecovered oxides of nitrogen, air, and water vapor. After treatment for nitric acid recovery and iodine removal, these off-gases pass through heaters (if necessary to avoid condensation), then prefilters, and finally high efficiency filters before release to the atmosphere from a tall stack. The volume of dissolver off-gas is usually mixed with a much greater volume of ventilation air in the stack before release.

Upon leaving the stack, the krypton-85 (the only remaining radioactive noble gas component) is further diluted to less than current regulatory requirements by diffusion processes which are reasonably well known, but dependent on meteorological conditions. Exposure to the public is primarily by immersion in the plume. The ground-level concentration reaches a maximum about 1000 meters from the stack for most wind categories, and continually drops in concentration beyond that point.

The general concentration of any gaseous component in a plume is dependent on the quantity released, distance from the stack, height of stack, and dispersion. Dispersion is dependent on wind category, velocity, nature (roughness) of the terrain, and other meteorological characteristics. Any dose to man is largely by immersion in the plume since krypton-85 is not incorporated in the food chain.

The distance from the stack to the boundary of the exclusion area is important, as well as the population density, in calculating dose to the public. Numerous reports have been published on estimating the concentration of airborne effluents under various meteorological conditions. (10-12)

The resulting doses from radioactive noble gas components have been very small. However, larger releases are anticipated in the expanding reprocessing industry, and local concentration of krypton-85 may become limiting. It has been estimated that eventually the world-wide level may rise to a limiting level.^(13,14)

Status of Availability

Although a development program is not needed, it is necessary to have meteorological data for the specific site where atmospheric dispersal is planned. In many cases, crude meteorological data are available, but several years of adequate data are needed to make a complete dispersal analysis.

13.1.1.2 Cryogenic Distillation

The cryogenic separation of the noble gases krypton and xenon (Xe) from the dissolver off-gas stream utilizes the different boiling points of the main components.^(2,4) At a pressure of one atmosphere, e.g., the following components and boiling points are: N_2 , $-196^{\circ}C$; Kr, $-157^{\circ}C$; and Xe, $-108^{\circ}C$. Figure 1 shows the process flow scheme to accomplish such a separation of krypton (containing 6% ^{85}Kr) and xenon.^(15,16) After various pre-treatment steps to remove potentially hazardous or troublesome components, krypton and xenon are separated from the off-gas stream by the recovery column, and are further separated from each other by the separation column. Further steps in Figure 1 depicting the compression of Kr and Xe into cylinders and the placing of ^{85}Kr in a shielded transfer cask are also applicable to other krypton removal processes such as the liquid fluorocarbon absorption method. The total off-gas flow rate in Figure 1 for a 1500 tonne/year reprocessing plant is $\sim 12 \text{ mole s}^{-1}$ ($\sim 550 \text{ std. ft}^3 \text{ min}^{-1}$).

A more detailed description of the individual process components shown in Figure 1 is given in the following. Although the purpose of the hold tank is to allow the fuel dissolution process to continue operation during a brief shut-down of the cryogenic separation equipment, the same objective could be met by providing redundant equipment for the krypton separation process. The relative economic merits of redundant equipment and hold tanks can be determined for the particular process rates.

NO_x must be removed to prevent solidification of NO_2 . Liquid scrubbing and solid bed adsorption have been used at the Idaho Chemical Processing Plant (ICPP),^(15,16) and additional removal technologies can be found elsewhere in this chapter (see section 13.4).

The O_2 removal step is necessary to minimize radiolytic ozone formation in the cryogenic distillation columns (an explosion hazard). The method used to remove oxygen is catalytic recombination with hydrogen to form water. (H_2 gas is added to the process stream over a palladium-platinum catalyst at $\sim 550^{\circ}C$.) While ozone formation in a cryogenic distillation system has been controlled by other means at the ICPP,^(15,16) they must be demonstrated on a plant scale before exclusion of the recombiner.

FIGURE 1. Process for the Collection of ^{85}Kr by Cryogenic Distillation

Removal of nitrous oxide (N_2O) and water is needed to prevent excessive freezing and plugging of the cryogenic equipment. The N_2O removal process involves a high temperature (370 to 600°C) catalytic step which decomposes N_2O to elemental nitrogen and oxygen. At the ICPP, rhodium metal coated on a substrate is used for N_2O removal and is regenerated at 870°C under a reducing stream of hydrogen gas.^(15,16) Water removal by the drier can be accomplished on an adsorber bed or a freezeout unit.

After the purified process gas is cooled in a regenerable precooler, it enters the recovery column. Krypton and xenon are stripped from the gas stream by a countercurrent flow of liquid nitrogen and are concentrated in the lower portion of the column. The reduced flow rate of concentrated Kr and Xe proceeds from the column bottom to the separation column, which operates in two stages. During the first stage, the separation column receives a continuous feed stream of bottom liquid from the recovery column. Krypton and xenon are collected continuously while light gases (mainly nitrogen and argon) are recycled to the hold tank. The second stage is operated periodically by shutting the feed stream to the separation column, and by fractionating the contents to

yield krypton ($\sim 75\%$ Kr, $\sim 25\%$ Xe) at the top and xenon ($\sim 99.9\%$ Xe, $\sim 0.1\%$ Kr) at the bottom of the column. Due to the presence of 6% ^{85}Kr in the krypton product, its compressor and cylinder are located in a shielded remote-handling cave. The filled cylinder is then placed in a shielded transfer cask for shipping to a storage facility.⁽¹⁷⁾ A source of the large quantities of liquid nitrogen (LN_2) required for the cryogenic portion of the system could be a small-scale liquid air separations plant if a commercial supplier is not available. All cryogenic equipment is located inside a sealed cold box, an insulated structure which could contain accidental process gas leaks. The process is operated remotely.

Status of Availability

All components of the process have been used extensively in liquid air plants of a much larger scale than that proposed for ^{85}Kr removal. A cryogenic distillation process has been operated intermittently at the ICPP to recover ^{85}Kr from fuel reprocessing off-gas for research and industrial applications.^(15,16) Although the ICPP unit was not designed to achieve the high ^{85}Kr recovery efficiencies necessary for environmental control, its operation has indicated such potential. Thus, the technology for ^{85}Kr recovery by cryogenic distillation is available for design of a demonstration system on a commercial fuel reprocessing scale.^(2,4)

Major Development Objectives

A total demonstration of the integrated process is required to establish the practical limits for ^{85}Kr recovery from commercial fuel reprocessing plants. Extended periods of continuous operation (up to one year or more) of the integrated system would establish the practical limits of reliability, catalyst lifetime, ozone control, operating cost, degree of equipment redundancy, and ^{85}Kr leak potential.

13.1.2 Technology Requiring Development

13.1.2.1 Liquid Fluorocarbon Absorption

While selective absorption by liquid fluorocarbons has been offered commercially for removing krypton from the off-gas of pressurized and boiling water reactors,^(18,19) the technology has not yet been demonstrated for removing krypton from the off-gas of a commercial reprocessing plant. The problem of krypton removal in this case is confounded by the presence of typical off-gas impurities such as nitrogen oxides (NO , NO_2 , N_2O), carbon dioxide, water, iodine, and methyl iodide. Several process solvents have been considered for the reprocessing application.⁽²⁰⁻²²⁾ Considering solvent capacities, separation factors, impurity tolerances, thermal

and radiation stability, and overall process safety and economic features, refrigerant-12 (dichlorodifluoromethane) demonstrated the most overall promise. Solubility data^(20,23) show that krypton is markedly more soluble in refrigerant-12 than nitrogen, oxygen, and argon. Additional results⁽²⁴⁻²⁶⁾ show that a fluorocarbon-based process designed for krypton removal not only can tolerate typical feed gas impurities but may be equally effective in removing the fission products, iodine, methyl iodide, and carbon-14 as carbon dioxide and chemical forms such as nitrogen oxides. At the present time, the selective absorption process is not known to pose any safety problems, but the long-term reliability of the process needs to be established.

FIGURE 2. Process for the Collection of ^{85}Kr by Liquid Fluorocarbon Absorption

Figure 2 is a schematic of the proposed fluorocarbon-based selective absorption process for removing krypton from the off-gas of an LWR fuel reprocessing plant. Three packed columns comprise the main working sections of the process. Each column is designed to exploit certain gas-liquid solubility differences that exist between the solvent and the various gas constituents that might be present. The main separation of the noble gases is accomplished in the absorber. The other two columns,

each fitted with a reboiler and an overhead condenser, comprise the intermediate and final stripper sections of the plant. The purpose of the first stripper is to remove the bulk of the co-absorbed carrier gas from the loaded solvent leaving the bottom of the absorber. The final stripper produces a highly concentrated krypton gas product suitable for long-term storage by removing the remaining dissolved gases from the solvent. The rest of the primary process equipment includes a gas compressor, solvent pump, gas and solvent heat exchangers, and several refrigeration compressors. The related support equipment items required for the reprocessing plant application include regenerable adsorption and chemical traps for solvent recovery and product purification and a distillation column for solvent purification.⁽²⁷⁾

Status of Availability

Pilot plant-scale development of the fluorocarbon process has been in progress at the Oak Ridge Gaseous Diffusion Plant (ORGDP) since 1968. Early effort, which was directed at reactor applications, demonstrated krypton removal efficiencies as high as 99.9 percent,⁽²⁸⁾ and work was initiated in 1972 to adapt the process to recover krypton from LMFBR fuel reprocessing plant off-gas.^(24,25) A pilot plant for the new program was built during FY 1973 and 1974 and put into operation in 1975.^(26,27) The pilot facility is approximately one-fifth the scale of the unit required for a 5 tonne per day (1500 tonne yr⁻¹) LMFBR fuel reprocessing plant and will provide an evaluation of process operability, reliability, and performance using simulated reprocessing plant off-gas. Of the series of seven pilot plant operating campaigns and three demonstration and application tests which have been planned, the first two campaigns are completed.

Major Development Objectives

Flowsheets incorporating a krypton recovery system using the fluorocarbon-absorption process have been developed for Allied-General Nuclear Services' Barnwell reprocessing plant⁽²⁹⁾ as well as for Nuclear Fuel Services' West Valley reprocessing plant.⁽³⁰⁾ While these two studies demonstrated the applicability of the selective absorption process to commercial fuel reprocessing plants, they pointed out the need for additional process development. Specifically, product purification options need to be explored; e.g., tests indicate that a relatively pure krypton product stream can be produced by passing the final stripper off-gas through a purification sub-system consisting of a desublimer and/or one or more adsorbent traps.⁽²⁷⁾ Long term impurity effects and process reliability also need to be established. Available data indicate that the fluorocarbon process can be used

to remove other fission products from the reprocessing plant off-gas. Tests have shown that a fluorocarbon process designed to remove 99.9 percent of the off-gas krypton can also be relied upon to remove at least that much of the off-gas carbon-14 if present as carbon dioxide. This potential capability of the basic process is important and needs to be better defined.

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13.2 IODINE-12913.2.1 Available Technologies13.2.1.1 Release

Gaseous-iodine species are released to the atmosphere from stack gases as elemental iodine and organic iodides. It is estimated that a 5 tonne per day reprocessing plant would generate 380 kg/yr of iodine-129.

Up to 90% of the iodine would be released without the use of iodine cleanup systems⁽¹⁾ and most of this would be deposited in the immediate plant environs.^(1,2)

13.2.1.2 Caustic Scrubbing

Caustic scrubbing has been used for the removal of iodine from off-gas streams. Caustic solutions in the range of 1 molar, with a reductant such as sodium thiosulfate added, effectively remove elemental iodine from pure air streams. The scrubbing system is ineffectual for organic iodine forms, which make up a significant fraction of the total iodine species in the off-gas of a typical nuclear fuel reprocessing plant. Application of a caustic scrubber on a dissolver off-gas stream where relatively large quantities of iodine are present could be expected to yield iodine retention factors on the order of 10. The application of caustic scrubbers to vessel off-gas streams often yield iodine retention factors of less than 2 due to the relatively small quantities of iodine present and the much higher fraction present as nonreactive species.

The caustic scrubbing media are typically employed in a packed tower through which the caustic solution is recirculated. Iodine containing caustic is bled from the system and fresh caustic is added to maintain caustic and carbonate concentrations within acceptable ranges. The caustic scrubbing media also remove CO₂ from the off-gas stream. If sodium hydroxide is used as the scrubbing medium, plugging problems are frequently encountered in the column packing due to the low solubility of sodium carbonate. This problem is reduced by the use of potassium hydroxide as the scrubbing medium. Waste volumes generated are usually determined by the carbonate buildup and thus are proportional to the volume of air treated. Typically, a scrubber handling 60 m³/min would produce 1800 m³/yr of waste solution containing 0.6 molar KOH and 0.2 molar K₂CO₃.

Status of Availability

Caustic scrubbing technology has been applied in numerous fuel-reprocessing systems, and is considered fully developed. The caustic scrubbing system has limited applicability for iodine removal in the

commercial fuel reprocessing industry because of the low iodine removal efficiency and the large volume of iodine-containing waste generated.

13.2.2 Technologies Requiring Development

13.2.2.1 Chemisorption by Silver-Loaded Adsorbents

In principle, gaseous-iodine species in process off-gas react with silver-exchanged or silver-impregnated adsorbents (e.g., zeolite, silica, alumina) to form chemisorbed-silver iodide. The advantages of this type of technology are: (a) it is simple, (b) the adsorbent is nonflammable, (c) high bed temperatures can be used, (d) the waste product is a dry solid easily handled and contained, (e) the chemisorbed iodide is highly insoluble, and (g) the adsorbent is highly efficient for the removal of both organic and inorganic iodides from gas streams. The disadvantages are the high cost of silver and the subsequent loss of a valuable resource by a once-used throw-away process. In Figure 1, the typical operating conditions and position of an iodine-adsorbent bed are illustrated. The off-gas from all sources of volatile iodine should pass through the adsorbent; otherwise, the overall iodine-decontamination factors (DF) in a reprocessing plant would be limited by the quantity of iodine that bypasses it.

FIGURE 1. Iodine-129 Waste Disposal Process for a 5 Tonne/Day Plant

The amount of waste generated from a 5 tonne/day reprocessing plant would be about 3.5 tonne/yr and occupy 3 M³ based on the following assumptions: (a) 380 kg/yr of iodine-129 is generated,⁽¹⁾ (b) 90% of the iodine in the processed fuel is released to the process off-gas,⁽²⁾ and (c) for DF's of 1000 or greater the loading capacity⁽³⁾ of the adsorbent is at least 100 mg iodine/g adsorbent.

The use of inorganic adsorbents for iodine removal is a relatively safe process in that corrosive liquids, high-pressure systems, and flammable materials are not involved. The adsorbent bed is maintained at some desired operational temperature (i.e., at least above the dew point of the gas stream) and the process off-gas is passed through it. When the bed is spent, it is removed and a new one substituted. Occupational exposure due to entrapped iodine-129 will be insignificant due to the low specific activity (1.63×10^{-4} Ci/g) and the type of radiation (β -emitter). Entrapped iodine-131 will rapidly die off. The waste could be placed in simple metal or plastic containers for interim storage.

Status of Availability

The use of silver-loaded adsorbents for iodine removal from air streams has been demonstrated. In laboratory tests,^(4,5,6) DF's of 10^2 to 10^5 for I₂ and CH₃I have been obtained using bed depths of 5 to 10 cm, face velocities of 15 to 30 m/min, and bed temperatures of 25 to 400°C. In plant slipstream tests,^(7,8) DF's greater than 10^3 have been obtained under similar operating conditions. Silver zeolite is being installed in the Barnwell Plant (BNFP) of AGNS as a backup for the primary iodine-removal system, which is a mercuric nitrate-nitric acid liquid scrubber.

Major Development Objectives

Although silver-exchanged zeolites (AgX) are developed for commercial application, the technology requires improvement. An experimental program⁽⁹⁾ is being conducted at the Idaho National Engineering Laboratory (INEL) to determine the loading capacity of AgX as a function of face velocity and bed depth. Other variables being tested are the effects of water vapor, oxides of nitrogen, and bed temperature.

Because silver is a valuable resource, a method to regenerate spent AgX would improve the economic feasibility of adsorbent technology. A dry method⁽¹⁰⁾ to regenerate and recycle spent AgX is being evaluated. In Figure 2, a conceptual design of this process is illustrated. Two

beds would be used, one bed for the adsorption cycle and the other for the desorption cycle. The desorbed iodine would be removed as gaseous HI with a pure stream of hydrogen at bed temperatures between 500 and 600°C. The HI would be chemisorbed by lead-exchanged zeolite (PbX) at a bed temperature of about 150°C. For a 5 tonne/day reprocessing plant, about 1.5 m³ of spent PbX would be generated per year. Because the re-cycle time is relatively fast compared to the loading period, smaller AgX inventories would be possible than indicated in Figure 1.

Design criteria for application to a reprocessing plant are expected by fiscal 1980.

FIGURE 2. Regeneration and Recycle of AgX for Iodine-129 Removal

13.2.2.2 Chemisorption by Metal-Loaded Adsorbents

The principle and advantages of this technology are the same as given for silver-loaded adsorbents. The more abundant and cheaper metals of interest are lead, cadmium, and those of the first-row transition series. The additional advantages would be the cheaper cost of the adsorbent and less concern about discarding used materials. The disadvantage is that the adsorbents tested to date have low efficiencies^(4,6) for organic iodides. However, they appear to have potential for elemental iodine removal.⁽³⁾

The safety factors and the environmental impact would be similar to those given for silver-loaded adsorbents.

Status of Availability

This technology is still being developed on the laboratory level. Time of readiness for practical design depends on the outcome of laboratory studies. Currently, no data on loading capacities of metal-exchanged zeolites (including silver) for elemental iodine have been reported. Cadmium-exchanged zeolite has been tested with methyl iodide, but its adsorption efficiency drops off rapidly after about 1% by weight loading⁽⁶⁾ is obtained. These results were considered too low to warrant further testing.

Major Development Objectives

The economic feasibility of iodine adsorbent technology would be greatly improved if a suitable metal-exchanged zeolite other than AgX could be developed. An experimental program⁽⁹⁾ is being conducted at the INEL to determine the iodine loading capacity of several metal-exchanged zeolites. If infeasible, the potential of PbX as a secondary adsorbent for use in regenerating spent AgX appears attractive (see the discussion on Chemisorption by Silver-Loaded Adsorbents). The development of PbX as a secondary adsorbent⁽¹⁰⁾ is in progress at the INEL.

13.2.2.3 Mercuric Nitrate-Nitric Acid Scrubbing

The mercuric nitrate-nitric acid scrubbing system originally developed used nitric acid concentrations in the range of 1 molar and mercuric nitrate concentrations in the range of 0.1 to 0.4 molar.⁽¹¹⁾ The scrubbing solution was normally recirculated through a packed-bed scrubber with the removal of scrubber solution to waste when mercury-to-iodine mole ratios dropped to four to ten. This system was effective in removing elemental iodine from off-gas streams, but was ineffective for organic species because of very slow reaction kinetics for organic iodides. The effectiveness is further reduced in actual plant applications by the bleed-off of iodine previously removed from the recirculating solution.

A significant improvement in organic iodide removal efficiency is obtained when the nitric acid concentration is increased to 8 to 12 molar at mercury concentrations in the 0.2 to 0.4 molar range.⁽¹²⁾ Bleed-off of previously removed iodine in a recirculating system, however, will probably limit the effective overall iodine retention factor to approximately 100. The iodine loading of waste streams is typically 1 mole of iodine for 4 moles of mercury; thus, the effluent stream from the mercury nitrate scrubber from

a 5 tonne/day fuel reprocessing plant might typically consist of 100 liters/day of 8 molar HNO_3 , 0.4 molar mercuric nitrate, containing 1300 g of iodine. This would amount to 30 m^3 liquid waste per year. Limited laboratory-scale development has been conducted to develop a process for concentrating the mercuric iodide as either solid mercuric iodate or sodium iodate with recycle of the mercury.⁽¹³⁾

Status of Availability

The mercuric nitrate-nitric acid scrub system employing recirculating solution through a packed tower, and direct storage or disposal of the solution has been used in government facilities and is being installed in the BNFP separations facility. Application of this process for removal of iodine from the off-gas of fuel reprocessing plants should be capable of removing iodine by factors of about 100. Refinements in the process related to recovery and recycle of the mercuric nitrate solution while converting the iodine waste to sodium iodate have been demonstrated to a limited degree in the laboratory.

Major Development Objectives

Further development of methods of reducing waste volumes produced by the mercuric nitrate-nitric acid scrubbing system and for recycle of the mercury would improve the overall applicability of the process.

13.2.2.4 Iodox Scrubbing

The Iodox scrubbing process (see Figure 3) for removing iodine species from a gas stream employs concentrated nitric acid in the 20 to 22 molar range as the liquid scrubbing medium in a bubble-cap tower. The process effectively removes all iodine species from either the dissolver or vessel off-gas stream and oxidizes them to a nonvolatile iodate form. Gas flow velocities in the range of 30 m/min in bubble cap columns of conventional design yield methyl iodide retention factors of 2 to 3 per plate, varying inversely with gas velocity.⁽¹⁴⁾ Retention factors for elemental iodine are normally about twice as high as for methyl iodide. Retention factors are not sensitive to liquid flow rate as long as the acid concentration is maintained above 20 molar and the solubility of removed HI_3O_8 (~ 1.4 g/liter in 20 molar nitric acid at 25°C) is not exceeded. The removed iodine in the liquid effluent from the bottom of the bubble-cap tower can be concentrated, by evaporation of the nitric acid, as HI_3O_8 all the way to the solid form for disposal. The nitric acid evaporated from the iodine waste is diluted somewhat by the moisture content of off-gas, and must be reconcentrated prior to recycle to the top of the iodine scrubbing column. This concentration

step can be achieved by use of an extractive distillation system using magnesium nitrate to break the azeotrope and permit production of hyperazeotropic acid by distillation⁽¹⁵⁾. Iodine waste volumes as low as 0.4 m³/yr from a 5 tonne/day fuel reprocessing plant are possible if HI₃O₈ is disposed of directly in metal canisters. This volume might be increased by factors of 2 to 10 if the iodate is converted to other forms, or cast in concrete for disposal.

FIGURE 3. Iodex Process Flowsheet for Iodine Removal

The concentrated nitric acid system is quite corrosive for ordinary stainless steel and most, if not all, of the Iodex system will have to be fabricated from corrosion-resistant materials such as zirconium or titanium.

Status of Availability

The scrubbing column technology has been thoroughly demonstrated on a laboratory and small engineering scale,⁽¹⁶⁾ and there appear to be no practical limits to the iodine retention factors attainable. Retention factors as high as 10⁶ have been realized. Iodine retention is adversely affected by high concentrations of NO_x in the inlet gas, and NO_x must either be removed to the few percent level or taken into account in the design of the system. The iodine waste concentration and

handling steps have been demonstrated to a limited degree on a laboratory scale. The acid concentration and recycle system has been in commercial use in nitric acid manufacturing plants for a number of years and can be considered demonstrated technology. At present, an engineering-scale system, including all parts of the Iodex process, namely, a scrubbing column, iodine waste concentration and solidification system, and an acid recovery and recycle system, is being operated to demonstrate system capability and operability. The Iodex process should be developed to the point of being ready for commercial application upon the completion of the engineering-scale system demonstration presently in progress.

Major Development Objectives

A demonstration of system capability and operability over extended periods of operation is required, and is planned for the present demonstration. Long-term corrosion effects on applicable materials of construction need to be confirmed.

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13.3 TRITIUM

13.3.1 Available Technology

13.3.1.1 Release

The release of tritium as produced in fuel reprocessing plants requires no change or development in present practice. 98% or more of the tritium produced in a nuclear reactor will be retained in the fuel elements.⁽¹⁾ The distribution of tritium releases during fuel reprocessing has not been well defined.^(2,3,4) Large variations have been observed or predicted for the variety of fuel types and reprocessing systems.⁽²⁾ The fuel reprocessing system for light-water reactors is typified by the Purex process. While no complete material balance for a reprocessing plant is available, a distribution has been estimated from the many references describing parts of the system.^(2,4,5,6,7,8,9,10)

A variable fraction of the tritium produced by fission will diffuse to the zirconium cladding and be bound there. This fraction may be of the order of 10-50%, depending upon the in-reactor time-temperature history of the fuel pin. Through the dissolving operation, about 1% will escape as HT, and the remainder will appear as HTO. If voloxidation or some other head-end step is not employed, then this HTO will follow the aqueous streams and be subject to discharge in either liquid or vapor form.

Release as vapor through a stack requires dispersal of the plume such that it is diluted before reaching populated areas. Because of the much smaller biological effect (ingestibility) of HT compared to HTO, and since HT is very slowly converted to HTO in the atmosphere, larger discharges of HT than HTO could be permitted^(3,4). The RCG for HT is higher by a factor of 200 than for HTO. Thus, small volumes of tritiated water could be electrolyzed to HT and released as gas.

Conversion of the HT in the dissolver off-gas stream to HTO could be accomplished by oxidation of the non-condensibles from a cryogenic system for krypton recovery. The release of such streams, either to the atmosphere or to surface waters, offers no advantage over current practice^(3,7).

13.3.2 Technologies Requiring Development

13.3.2.1 Voloxidation

Voloxidation is a proposed head-end process to promote the release of gaseous fission products from oxide fuels by further oxidation at an elevated temperature. In the process, sheared fuel is heated in air to 400-500°C. Oxidation converts the UO_2 to U_3O_8 , and the phase changes which occur result in the disintegration of the fuel pellets. The physical disintegration

and the change in crystal structure provides an easier escape path for the trapped or bound gaseous fission products. The process was visualized as a method of removal of tritium, iodine, krypton, and xenon from irradiated fuels prior to their dissolution for processing.

Goode⁽¹¹⁾ has summarized the studies to 1973. Although the process has only been partially successful with respect to iodine and noble gas removal, the tritium release appears to be complete. Thus, the potential exists for concentrating the fission product tritium in a small volume of water vapor which can be trapped and isolated. A conceptual flowsheet is shown in Figure 1.

FIGURE 1. Voloxidation Process

The dried fuel elements are first sheared into short sections, and then are fed into a continuous rotary kiln. The temperature is maintained at 450-500°C and air admitted at a rate sufficient to provide excess oxygen for the $\text{UO}_2 \rightarrow \text{U}_3\text{O}_8$ conversion. The Zircaloy hulls are washed and sent to disposal while the oxidized fuel passes to the dissolver; alternatively, the hulls may pass through the dissolver. The off-gas from the shear process passes through a catalytic oxidizer to convert any tritium to HTO and is then combined with the off-gas from the voloxidizer unit. Water is removed through the combined

use of a refrigeration molecular sieve cycle. Many variations of the water removal step are available. It is likely that hydrogen will be added ahead of the oxidizer or that excess water will be added at some point in the drying portion of the cycle to enhance the HTO removal. A possible addition point is shown in Figure 1.

The volume of water output has not been fixed, but would be less than 100 ℓ /day for a 5 MT/day plant, compared to the Purex plant total throughput of 10^5 ℓ /day.

The voloxidizer has been proposed as a rotary kiln about 1 m diameter and from 2-7 m in length.^(12,13,14) The minimum size may be limited by the heat evolution from the UO_2 oxidation, the time required to oxidize the encased pellets, and the necessity for good temperature control. A recent engineering design by Stearns-Rogers, Inc. recommended a minimum diameter of about 1 m and a length of about 50 m⁽¹⁵⁾ as the maximum probable length.

Cast 25-12 HH alloy or inconel, with a mild steel shell, has been suggested as a construction material. Mechanical abrasion and corrosion by the oxidizing gas are potential problems. Adequate seals must be provided at the kiln ends to prevent leakage. The kiln would be heated electrically, although the reaction is exothermic and heat must be removed from the reactor.

Oxidation of any H_2 or HT to H_2O and HTO would be accomplished by standard recombination catalysts, but may not be necessary if all the head-end shearing gases pass through the heated kiln. The AGNS survey⁽¹³⁾ suggests a Ni-Cr-Pd ribbon catalyst operating at 400-600°C.

The operating conditions of the voloxidizer unit are determined largely by the temperature constraints. Minor adjustments may be required for PuO_2 -containing fuels or due to differing irradiation histories. Tritium release begins at 100-150°C, but the peak concentrations occur at 450°C or higher.^(11, 16) A temperature range of 450-500°C has been suggested, and a residence time of about 4-6 hours may be required for LWR UO_2 fuel.

Higher temperatures have been employed but are generally not favored:

- a) the control of the very exothermic reaction becomes more difficult and,
- b) localized sintering may result, which may trap the fission product gases before they can diffuse out. The rate of oxidation has been found to increase with increasing oxygen content of the gas,⁽¹¹⁾ but for reasons of process control, i.e., slower reaction rate and greater heat removal, air is preferred. Higher temperatures, i.e., >480°C, result in a decrease in the oxidation rate of UO_2 .

Potential problem areas include the following:

- 1) A runaway reaction of UO_2 and O_2 due to insufficient heat removal
- 2) A rapid zirconium hull oxidation that could result if zirconium "fines" are present
- 3) Leakage of tritium and other fission product gases through kiln seals or through a breach of other parts of the system
- 4) Ruthenium and other fission products may be deposited throughout the off-gas system. If a counter-current air flow is employed in the voloxidizer, kiln reflux, which could aggravate the problem, may occur
- 5) The production of finely powdered U_3O_8 may increase the handling hazards and the dissolution control
- 6) Criticality control in the voloxidizer unit must be ensured
- 7) Potential thermal warping and failure of the kiln shell if the kiln drive fails while loaded with radioactive fuel
- 8) Dust control
- 9) Cleaning of voloxidizer

Status of Availability

Extensive laboratory data have been obtained under the LMFBR program on a variety of (U, Pu) O_2 unirradiated and irradiated fuels. Included are parametric studies involving temperature, time, tumbling rate, fuel preparation, and radiation history, including burnup and temperature. However, studies are mostly of a scoping nature; parametric studies have been limited by the availability of consistent fuel samples. Data were also obtained on the details of the reaction through X-ray crystallographic studies and thermal-gravimetric studies.⁽¹¹⁾

Engineering development has consisted of limited tests with unirradiated UO_2 in a rotary calciner. A pilot plant demonstration using irradiated LWR fuel is required. The AGNS study⁽¹³⁾ suggests that 4.5 years would be required from project initiation (at the reprocessing plant) to cold testing. A period of from five to seven years may be required before an operating unit could be "on line".

Major Development Objectives

The mechanism of release (or conversely the hold-up) of fission product gases is not completely understood, particularly when it is considered that only a portion of the iodine and noble gases are released. Further studies of the form in which these elements exist in the irradiated fuel and the reactions they undergo would be desirable.

Technological needs including design information include the following:

- Voloxidizer construction materials
- Development of seals for rotary unit
- Data for computation of size and operating conditions

- Information on Ru and Cs deposition and methods of removal
- Information on segment size required
- Further data on effects of fuel composition and irradiation history
- Determination of the amount of elemental hydrogen (tritium) and demonstration of recombination and water removal
- Construction and operational details to demonstrate heat dissipation from kiln

13.3.2.2 Pyrochemical Processing

Pyrochemical processing involves high-temperature, nonaqueous methods. The present description considers only the treatment of fuel prior to acid dissolution, i.e., head-end processing. As with voloxidation, head-end treatment involves two steps: (a) chopping and/or cladding removal and (b) treatment of the oxide fuel to effect release of volatile fission products.

Although considerable development work has been carried out involving various concepts, a complete process has not been demonstrated for LWR of individual processes that appear to have potential in a Purex head-end step.

Decladding by melting has been studied for stainless-steel clad fuels.⁽¹⁷⁾ In principle, it could be used for zirconium-clad fuels. However, the much higher melting temperature of zirconium, 1840°C vs approximately 1450°C, probably eliminates it as a practical scheme.

Alloying the cladding with another molten metal is an alternative. For stainless-steel clad fuels, zinc has been studied extensively. Zircaloy was also found to dissolve at 800°C;⁽¹⁸⁾ thus, zinc (or other molten metal) decladding of LWR fuels is possible. Tin has also been suggested.⁽¹⁹⁾

An alternative is to chop the fuel into small enough pieces that the oxide fuel is adequately exposed for the second step, release of volatile fission products.

Step two, in contrast to voloxidation where UO_2 is oxidized to U_3O_8 , will normally be a reduction step, and uranium and plutonium metals will be produced by reduction in the presence of a molten salt. A mixture of zinc, calcium, and magnesium or other reductant alloy and a salt such as $CaCl_2$ is heated with the oxide fuel at about 800-900°C. The principal reaction is $UO_2 + 2Ca \rightarrow 2CaO + U$. The salt is separated from the metal phase. After distilling off the magnesium and zinc for recycle, the U and Pu are sent to the acid dissolver for aqueous-solvent-extraction processing.

Problems have been found with metal distillation. An alternative procedure involves precipitation of the uranium and plutonium as the nitrates through addition of calcium nitride.^(20,21) The nitride is then fed to the acid dissolver for Purex feed preparation.

The reaction can be shown as:

Fission product tritium and the noble gases are both released during de-cladding and reduction steps and would be handled as in the voloxidation process. Evidence exists that iodine is largely contained in the salt phase. The significant volatility of other fission products may create severe problems. A simplified pyrochemical head-end is shown in Figure 2.

FIGURE 2. Pyrochemical Process

The process steps can be summarized as follows:

- Decladding
- Reduction with Zn-Mg-Ca alloy
- Composition adjustment. Sufficient CaCl_2 present to prevent CaO from separating. MgCl_2 added to react with excess Ca and to retain U in solution
- Evaporation of product solvent or precipitation of U, Pu product
- Recovery of zinc by evaporation (if zinc decladding employed)

For construction, refractory metals such as tungsten, molybdenum, and tantalum would be used along with ceramics and graphite. Material limitations would be applied to pumps and other transfer devices in addition to the reaction vessels.

Effluents would be fission product gases to storage operations, metal fuel to the dissolver, waste salt, and waste metal to recycle and waste storage. Excessive volatility of fission products such as Cs and other metals may complicate the fission product gas recovery. Aside from that, the principal change introduced by pyrochemical steps in the appearance of waste metal streams, zinc, magnesium, etc., and waste salt streams CaCl_2 , MgCl_2 , KCl, etc. The impact of these streams on total waste management will depend on the extent and ease of recycle. If zinc or other liquid metal decladding is employed, a large volume of waste zinc is produced.

The salt phase will contain, in addition to CaO produced by the reduction, considerable amounts of fission products, including iodine.⁽²²⁾ Recycle of the salt involves precipitation of a portion of the CaO in a minimum amount of salt.⁽¹⁸⁾

The advantages of the pyrometallurgical process are (a) potentially small volumes except for zinc decladding, (b) possible efficient removal of gaseous fission products and the trapping of iodine, (c) discharge of wastes as solids, (d) absence of neutron moderators, and (e) process flexibility.

Disadvantages include (a) difficulties with high-temperature processes involving corrosive metals, due largely to lack of industrial experience, (b) potential problems with excessive volatility of various metal fission products, and (c) large volumes of waste zinc and salt if recovery is not feasible.

Status of Availability

The technical feasibility has been demonstrated in the laboratory. Nearly all of the work has been carried out at Argonne National Laboratory (ANL), and has been directed towards LMFBR fuels, for which some special advantages can be shown. Further equipment development is required, and laboratory and pilot-plant testing of irradiated fuels is still to be done to determine the best combinations of the various schemes, develop equipment and further information on materials of construction, and to determine fission product behavior. Thus, although pyrochemical steps may be technically feasible, the process must be listed as not demonstrated.

Major Development Objectives

As discussed above, much of the information required is centered around the lack of technological data of pyrochemical operations. Individual flowsheet equipment items must be fabricated and exhaustively tested, and the total system evaluated from the point of view of operation and maintenance. The decladding process for LWR fuels has not been studied in depth.

Scientific data required include more information on equilibria and rates in both metal alloys and salts, especially with regard to fission products. The behavior of tritium is unknown, and although predictions can be made based on stabilities of various compounds, measurements must be made. One possible problem that has not been investigated is the partial reduction of the irradiated oxide by the dissolved cladding zirconium.

13.3.2.3 Isotopic Enrichment by HT/H₂O Catalytic Exchange

With the exception of tritium, all the radioisotopes produced in the operation of a light water reactor are amenable to some form of chemical or physical separation process for removal from the effluent water streams. The removal of tritium from these aqueous wastes, however, requires development of isotopic separation processes. Over 100 ideas have been considered for effecting the isotopic separation of tritium from water.^(23,27) Alternative methods have been discussed in a review by Ribnikar and Pupezin.⁽²³⁾ A number of technical and economic feasibility studies have been carried out on possible detritiation schemes-- mostly based on experience and data from heavy water (D₂O) separation processes.^(24,27)

Many of the basic separation methods for heavy water production processes are technically feasible for detritiating water. Detritiation, however, requires larger stripping and recovery factors than does heavy water production. To be capable of obtaining the needed high recovery, a feasible detritiation process will require a high isotopic separation factor.

The hydrogen-water chemical exchange process has the required high isotopic separation factor and is uniquely suited to a water feed. In addition, the technical feasibility of hydrogen isotopic enrichment through the exchange between hydrogen and water is established. The process has been employed to produce heavy water on a large scale.⁽²⁸⁾ The HT/H₂O catalytic exchange process was selected on the basis of high isotopic separation factors and technical feasibility to be the most likely process for development and demonstration of waste water detritiation.

Work is in progress at Mound Laboratory to develop an improved version of the basin process, and to demonstrate the separation of tritium for the particular concentrations and types of low-level aqueous waste (LLAW) obtained from light water reactors and fuel reprocessing plants. The process will also apply to the removal of tritium from heavy water (D₂O) used as the moderator and coolant in several research and all U. S. government production reactors.

The improved approach to HT/H₂O catalytic exchange is based on the use of antiwetting, hydrophobic catalysts, which permit the chemical exchange reactions between liquid water and gaseous hydrogen in direct contact, thus eliminating problems of catalyst deactivation and the complexity of reactor design normally associated with current catalytic exchange techniques^(29,30) involving gas-phase catalysis. Use of hydrophobic catalysts was first reported⁽³²⁾ in relation to studies directed toward an improved heavy water process. The catalyst consists of platinum on an alumina substrate with a coating of semipermeable, water-repellent material such as silicone or Teflon.

The highest isotopic separation factors for HT/H₂O exchange are obtained at low temperatures due to the nature of the chemical equilibrium, $\text{HT} + \text{H}_2\text{O} \rightleftharpoons \text{HTO} + \text{H}_2$, which is shifted to the right at lower temperatures: The equilibrium constant is about 6 at 25°C. The processes involving steam-hydrogen reactions in the vapor state require higher temperatures to prevent water condensation and are faced with the resulting lower isotopic separation factors.

The hydrophobic low-temperature mixed-phase system potentially has many advantages over the gas phase system, for example, higher isotopic separation factor, lower energy consumption, higher throughput rate, and simpler equipment.

There are two major alternative applications of the HT/H₂O catalytic exchange process to detritiation of LLAW. The first alternative is to apply the process to the total waste stream, and deplete the tritium to a degree that the resulting detritiated waste stream may be dispersed to the environment. This alternative has been referred to by Ribnikar and Pupezin⁽²³⁾ as the "stripping" scheme. The second alternative application would produce a similar enriched tritium stream, but the water is detritiated to a lesser degree and returned to the reactor (or plant), thus maintaining a desired steady tritium concentration in accord with applicable regulations for in-plant exposure of operating personnel. Ribnikar and Pupezin⁽²³⁾ have called this alternative the "recycling" scheme. A wide spectrum of options exist within either scheme when selecting a design basis for the detritiation system. For example, regulatory factors and in-plant parameters such as LLAW throughput quantity and tritium concentration levels could affect the size of the system and the necessary degree of separation and enrichment of the tritium.

A throughput required for removal of tritium from LLAW could vary over a wide range depending on the application. Likewise, the degree of separation and recovery required could vary considerably. For example, the internal flow of water in a PWR cooling water recycling detritiation application could be on the order of 10-50 liters/hr, with an overall separation factor requirement

of 100 to 1000. In comparison, application of the stripping scheme to the flow of LLAW from a fuel reprocessing plant could require a throughput of 500-2500 liters/hr with an overall separation requirement of 10^{11} to 10^{13} . Since the costs associated with detritiation of water increase with increased throughput and also increase with increased overall separation factor, the application of the stripping scheme (Figure 3) to the fuel reprocessing plant would be the least favorable from a cost viewpoint, as both throughput and separation requirement are a maximum for the fuel reprocessing LLAW stripping application.

FIGURE 3. Isotopic Enrichment by HT/ H_2O Catalytic Exchange

Status of Availability

A program aimed at creating a demonstration unit for detritiation of aqueous wastes using the HT/ H_2O catalytic exchange process is currently in progress at Mound Laboratory, and should be completed through the catalyst evaluation phase in 1976. If the catalyst evaluation tests are

successful, a multistage pilot detritiation system should be evaluated before proceeding to a field demonstration.

Basic design parameters for the catalytic detritiation process will likely be available in 1976, and conceptual design of a demonstration unit could then be started. Allowing three years for the detailed design of the demonstration plant plus equipment procurement, fabrication, and testing, a plant to demonstrate the HT/H₂O catalytic exchange detritiation process could be ready in about 5 years.

Major Development Objectives

Of primary importance to the success of the demonstration of this process will be the effect of traces of organic solvents, HNO₃, fission-product iodine, and metallic fission-product ions on the activity and life of the hydrophobic catalyst. Only data obtained in an actual demonstration test using LLAW from the PWR or fuel reprocessing plant will suffice to ultimately demonstrate the feasibility of the process.

13.3.2.4 Isotopic Enrichment by Laser Excitation

Molecular excitation by light has long been used by the chemist to initiate or affect chemical reactions. However, until the laser was available, such photocatalyzed reactions were practically all initiated by broadband radiation sources such as the sun or flashlamps. The laser now provides very high-intensity radiation with an extremely narrow frequency range. In many cases, this narrow frequency range allows the selective excitation of a particular type of molecule while leaving similar (but unlike) molecules in the same system unaffected. Thus, laser excitation may influence the rate of a particular reaction in a system, and make products which are not characteristic of thermal reactions. Goodman and Thiele⁽³³⁾ have shown theoretically that rate enhancement factors as high as 10⁵ may be possible in photocatalyzed reactions.

Since the HTO and H₂O molecules have different vibrational levels, it is possible to use laser radiation to selectively excite one isotopic species, thus permitting it to react preferentially. Extremely high separation factors are theoretically possible, thus leading to a concentrated tritium product for storage.

There are a number of ways in which optical excitation might be used to separate hydrogen isotopes. First, molecules containing tritium may be excited directly to unstable electronic states. Second, they may be excited to stable states whose potential action surfaces intersect with unstable electronic states allowing for free dissociation processes. This process is called predissociation. Third, molecules containing tritium and in the

ground electronic state may be vibrationally excited into sufficiently high levels to react readily and preferentially with other molecules to form products which are chemically separable from water. Fourth, a combination of vibrational excitation to effect selectivity and electronic excitation to effect dissociation might be useful. All of these processes have been considered.

If UV lasers were available, water could be dissociated directly with no energy loss to surrounding molecules. It is possible that HTO could be dissociated efficiently and selectively by this process, under the proper experimental conditions. What these conditions might be will depend on the electronic spectrum of HTO. The basic problem, however, is that no suitable lasers are currently available to execute this scheme. The second scheme, i.e., predissociation, would require higher frequency lasers than the first, and would be more inefficient.

The methods that appear most attractive with the present state-of-the-art then involve vibrational excitation of the HTO molecule. This may be accomplished in several ways: (1) with a detailed knowledge of the vibration/rotation transitions in the ground and excited states it would be possible to pick one or more frequencies which could pump the HTO molecule through several transitions to a reactive level; (2) excite the HTO molecule to a higher vibrational level and simultaneously supply energy by a second laser or flashlamp to selectively excite it on to an unstable electronic state; (3) supply sufficient power to the first vibrational transition that internal relaxation of the HTO water molecule will permit higher levels to be populated, leading to dissociation of the molecule.

All three appear possible. Lack of fundamental spectroscopic data prevents design of some of the experiments. However, calculations and measurements performed at Battelle Northwest⁽³⁴⁾ and Mound Laboratory⁽³⁵⁾ have continued to indicate the feasibility of the concept.

The conceptual process is illustrated in Figure 4. The effluents would be a water stream depleted in HTO, which can be recycled or discharged, and a low volume stream containing tritium in HT, water, or other compounds. The energy requirements include vaporization of the water and laser operation.

Status of Availability

The method is in the basic research stage.

Major Development Objectives

- Experimental testing of various excitation and separation schemes.
- Determine fundamental molecular data that are required for optimum design.

- Test the more promising methods on a scale large enough to make an economic evaluation.
- Approximately ten years would be required for development.

FIGURE 4. Conceptual System for Laser Isotopic Enrichment

13.3.2.5 Isotopic Enrichment by Reversible Electrolysis

The separation of tritium from tritiated waste water by electrolysis has been of interest because of the high value (10-15) of the separation factor for the electrochemical decomposition of H_2O and HTO . Water electrolysis by itself, however, is too expensive to be used, mainly due to high electricity costs. Reversible electrolysis has been proposed as an improvement over plain electrolysis, since in principle, the process can be staged without the production of hydrogen between stages. Thus, a multiple stage separation can be accomplished against the cell potential required for just one stage of plain electrolysis. (36)

Reversible electrolysis as originally proposed was never applied, possibly because of the high cost of the palladium membranes it requires. Recent research done by the Faculty of Technology, Belgrade University⁽³⁷⁾, has produced a workable electrode made of carbon and polyethylene, thus opening a possibility for a new tritium separation process based on this technology. Experiments with this electrode achieved a separation factor of about 8, half the possible value.

Status of Availability

The technology is at the laboratory stage of development.

Major Development Objectives

Since the bipolar carbon electrode has been shown to be effective for electrochemical separation of tritium from tritiated water, further work could be directed toward evaluating the economics of the process. If the economics appear favorable in comparison with other proposed waste water detritiation processes, a pilot plant electrochemical separation system, with several cells in series, should be built and used to evaluate the operating characteristics of the system, using typical reprocessing plant feed streams.

13.3.2.6 Recycle

The release of tritium from fuel reprocessing plants could be modified by recycle of all tritium-containing streams in the front end of the reprocessing system.^(3,4,5)

During the 1971 zirconium fuel processing campaign at the Idaho Chemical Processing Plant, several streams in the first-cycle uranium extraction system were sampled and analyzed for tritium. As indicated in Figure 5, all of the tritium is leaving the extraction system in the ICP and IAR streams. The ICP stream carries less than 0.1% of the incoming tritium. Therefore, the IAR stream is removing about 99.9% of the tritium from the system.

Further examination of the organic streams has shown that no detectable amount of tritium is present in nonlabile positions in the organic materials. A process barrier could be established at the first-cycle extraction system across which tritium will not be allowed to migrate. This would require the prevention of transfer of dissolved or entrained water and the complete avoidance of materials which complex water or compounds with labile hydrogen positions in the extraction system. Operation of a recycle system would provide, if successfully implemented, an enriched concentrate which could be more economically transported and stored than the total waste water stream.

FIGURE 5. Distribution of Tritium in the First-Cycle Extraction System at the ICPP

Recycle streams could be operated with or without isotopic separation. If practical, an isotopic separation process could also be used for a once-through treatment. The system could be operated in three different ways. These three systems are illustrated in Figures 6 through 9. In the first case, the total recycle stream is transported to storage for disposal at the time that the buildup of tritium has reached the maximum acceptable. In a process where the input rate is sufficiently low, the total recycle might occur over the operating lifetime of the facility (Figure 6). In such a case, eventual decommissioning might include making concrete with the water after it has been chemically purified, and leaving it on site for the tritium to decay.

FIGURE 6. Recycle and Batch Removal

In a recycle operation where the concentration will eventually build up (from a T/H ratio of 3.1×10^{-7}) to the maximum acceptable level, withdrawal for a bleedstream isotope separation or total removal will be necessary (Figures 6 and 7). Removal of a bleedstream and continual replacement with new feed is a special case of total replacement of the recycle volume. In either operation, enough tritium must be removed to be equal to or greater than the expected introduction rate. Steady withdrawal of a bleedstream, Figure 7, will allow more practical handling, whether removal is continuous or intermittent, than the total replacement of the process water. This bleedstream should be treated to remove all chemicals and radioactive isotopes with half-lives greater than a few years, so that when the tritium has decayed, the water, however stored, will be harmless.

The recycle system may be operated in a slightly different manner, as shown in Figure 8. In this system, isotope separation is used to remove sufficient tritium to equal the input rate. Here the requirements for the isotopic separations process are not as stringent as they would be for a process to produce a tritium-depleted stream acceptable for uncontrolled release. In this case, considerable latitude is available for alternative approaches to the tritium separation and the concentration ratio attained in the depleted (recycle) stream and the concentrated (disposal) stream. The isotopic separation system will be operated in a region out of the range of ordinary feed for the existing tritium and deuterium technology. However, the requirements

here are similar to those for ordinary enrichment, that is, high throughput and high concentration, without particular concern for the concentration in the tails. The tails are returned to the process. This removal process could also operate continuously or intermittently, but it is most probable that the isotopic separation process would perform most satisfactorily on a steady-state, i.e., continuous basis.

FIGURE 7. Recycle with Bleedstream Removal

The fourth option for removal of tritium from the stream is shown in Figure 9. Here the stream is treated on a continuing once-through basis to give a concentrate for storage and a tritium-depleted stream for release. Operating in this manner without recycle, a process with a very high throughput and a very high separation factor must be attained. In an LWR fuel reprocessing plant, the flow rate is approximately 20 liters liquid H₂O per minute with a T/H atom ratio of 2.8×10^{-8} . The required separation factor would be 10^{10} .

If the same plant operation requirements are handled by the system described in Figure 8, the advantages for recycle become quite apparent. In this recycle mode with the depleted stream returned to the process input, the process stream initially will have a concentration of approximately $T/H = 3.1 \times 10^{-7}$, with a flow rate of approximately 20 liters per minute. After

FIGURE 8. Recycle System for Tritium Control with Isotopic Separation for the Bleed Stream

FIGURE 9. Recycle System for Tritium Control with Isotopic Separation of the Entire Aqueous Inventory

recycling 300 times, the stream would be at a level of $T/H = 8.4 \times 10^{-5}$, and a bleed rate to remove 3,500 curies of tritium per day would be required. The tritium concentration in the recycle stream is approximately 300 curies per liter. Therefore, the process requirements are "complete removal" from about 12 liters per day or 10% from 120 liters per day, or the equivalent. The design requirements are listed below:

Tritium System Operational Requirements

Isotope ratio in feed $T/H = 8.4 \times 10^{-5}$

Curie Removal Rate - - - 3500 Ci/day

<u>T/H (Feed)</u>	<u>Feed Flow (ℓ/day)</u>	<u>T/H (Depleted Recycle)</u>	<u>Assumed Recycle Flow (ℓ/day)</u>	<u>Isotopic Separation Factor</u>
8.4×10^{-5}	12	2.6×10^{-6}	11	385
8.4×10^{-5}	120	7.6×10^{-5}	119	12

To use a minimum of energy, the isotopic separation process would operate with water feed rather than requiring conversion to hydrogen. However, the production of hydrogen by electrolysis would not be prohibitive for a small aqueous stream. Electrolysis is also a candidate for one stage in an isotope separation system. Electrolysis of water under proper conditions will concentrate approximately one-half of the tritium into less than 0.1% of the original volume. The released hydrogen, consisting of almost 100% of the original hydrogen, will contain one-half of the original tritium, for a net depletion of a factor of 2 in the process. The concentrate is enriched by about 500.

Handling of the withdrawn water will require equal precautions regardless of the tritium content because any spill of this concentration would be unacceptable. The cost of this handling and disposal will be proportional to the volume, and the cost of this handling can only be reduced by attaining the maximum recycle (i.e., maximum tritium buildup) tolerable.

These process requirements are less stringent than would be the case for a process to apply isotopic removal to a once-through stream or to any attempt to provide complete decontamination of the bleedstream to allow release. Successful application of this concept depends on the demonstration of a recycle capability for the front end of a fuel processing plant.

Status of Availability

The technology for recycle of tritium is not available. Conceptual studies have been made^(4,38) and a proposed development program described, but a major technical study would be required to evaluate the system. An integrated pilot-plant or plant-scale program would require five to six years for completion. Potential technical and occupational safety problems associated with high tritium concentrations could make the benefit-cost ratio unfavorable.

Major Development Objectives

The first phase of the proposed tritium management development program would provide the information required for:

- Definition of the distribution and type of tritium releases from chemical reprocessing of several types of fuel.
- Preliminary conceptual evaluation of a proposed reprocessing system which, by recycling tritium, would minimize releases to the environment.

The second phase would provide laboratory and pilot-plant data to:

- Predict the effects of fission product accumulation in the recycle streams.
- Determine and develop methods for the control of organic waste accumulation in recycle streams.
- Develop technology for preparation and addition of anhydrous nitric acid.
- Develop tritium containment technology, including air flow control and seals for cells.
- Evaluate and develop the technology for the separation of tritium from concentrated process streams.
- Develop the technology for chemical or physical "stabilization" of concentrated tritium (HTO).

The final phase would include hot demonstration of the developed recycle technologies in either an integrated hot pilot plant or in a modified reprocessing plant. Approximately six years would be required to complete the development program.

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13.4 OXIDES OF NITROGEN

13.4.1 Available Technologies

13.4.1.1 Release

The oxides of nitrogen (i.e., NO and NO₂ which are collectively designated NO_x) generated by nuclear fuel reprocessing plants are formed during the dissolution of fuel rods in nitric acid solutions and the calcination of aqueous waste containing nitrates. The ratio of NO to NO₂ depends on the oxygen content in the process off-gas, the concentration of the NO_x, and the residence time of the off-gas in the plant. A 5 tonne per day reprocessing plant, without an NO_x abatement system, would release via its stack gases about 500 tonne NO_x (as NO₂) per year from the calcination and fuel dissolution processes.

If only the fuel-dissolution step is considered along with a scrubbing system which removes 70% of the NO_x from the process off-gas, about 100 tonne NO_x (as NO₂) per year would be released.

13.4.1.2 Aqueous Scrubbing

The process off-gas containing oxides of nitrogen (NO_x) is passed through a scrubbing solution, and the NO_x is removed as a soluble compound. The solutions may be bases, acids, ammonia, amines, ammonium salts, or oxidizing reagents. Water without additives may also be used. In most cases, the reaction products are salts and acids containing the nitrate or nitrite anion. The aqueous wastes generated are either released to the environs or reprocessed and recycled.

Status of Availability

Aqueous scrubbing can be considered an available, but limited, technology. Abatement efficiencies above 70% are seldom obtained and large amounts of liquid wastes are generated. A water scrubber is planned for the Barnwell Reprocessing Plant, and an NO_x abatement efficiency of 70% is anticipated. As of 1975, only two out of 85 vendors in the United States which supply liquid scrub systems list commercial NO_x abatement systems.⁽¹⁾ Several laboratory and pilot plant studies have been conducted which yielded unsatisfactory results. The conclusions⁽²⁾ drawn by National Lead of Ohio in a pilot plant study were that: (a) the maximum removal efficiency with a caustic scrub was 64%, (b) the disposal of the waste solution was an unsolved problem, and (c) up to 90% abatement efficiency could be obtained with urea, but disposal and economic feasibility were questionable. An extensive laboratory study was performed by Esso R&E Co. and they concluded:⁽³⁾

(a) hydroxides of Ca, Mg, Zn, and Na are poor absorbers, (b) concentrated amines are good absorbers (i.e., 78% abatement efficiency), but exotic products are formed which couldn't be safely introduced into the environment, and (c) sulfite solutions are excellent NO_2 but poor NO absorbers. A pilot-plant study was conducted by Western Electric Indianapolis Works⁽⁴⁾ using caustic, chromic acid, and permanganate solutions. They were not able to exceed 67% efficiency under their test conditions and could not recommend wet scrubbing methods for NO_2 control at their plant. American Cyanamid Company⁽⁵⁾ conducted a vendor survey and concluded that scrubber manufacturers had little experience with NO_x abatement and that the size of the scrubbing unit required to achieve 90% efficiency was impractical. An ad hoc panel of the National Research Council⁽⁶⁾ on abatement of NO_x concluded that scrubber systems will not remove NO .

The aqueous waste generated by a reprocessing plant may eventually be calcined, thus evolving NO_x from the nitrates and nitrites. Therefore, scrubbing would be only an interim solution for NO_x abatement.

13.4.1.3 Non-Selective Gas-Phase Reduction

The NO_x in the process off-gas reacts with a reductant (H_2 , CO , CH_4 , propane, etc.) in the gas phase to produce N_2 and H_2O . Most or all of the O_2 in the gas stream must be consumed before the NO_x is reduced significantly. In air streams, a multistage burner must be used with heat exchangers or water injections to control temperature.

Status of Availability

A commercial NO_x Destructor is sold by John Zink.⁽⁷⁾ A unit has been installed and tested by Atlantic Richfield Hanford Co.⁽⁸⁾ and American Cyanamid.⁽⁵⁾ Both companies have reported that about 90% abatement of 1% NO_x in air streams can be achieved. However, the economic feasibility of this process needs further examination.

13.4.2 Technology Requiring Development

13.4.2.1 Catalytic Reduction by NH_3

Gaseous NH_3 is mixed with the process off-gas containing NO_x and passed through a heated catalyst such as (a) metal-impregnated alumina and silica, (b) metal-exchanged zeolite or, (c) hydrogen and sodium forms of zeolite. The reaction products are N_2 and H_2O and, in some cases, nitrous oxide (N_2O).

Status of Availability

Four chemical companies in Japan market this process.⁽⁹⁾ Gas flows up to 3×10^4 m³/min can be treated, and NO_x concentrations of 350 ppm or higher can be reduced to 10 ppm. Exxon Nuclear Company⁽¹⁰⁾ is using a hydrogen-mordenite catalyst and reducing 2 to 6% NO_x in process off-gas to 50 ppm. Laboratory studies^(11,12) have demonstrated 99+% efficiencies for this process using hydrogen mordenite as a catalyst for both NO and NO₂ in air streams. The fuel requirements are about 1.3 moles of NH₃ per mole of NO_x.

In Figure 1, a block diagram of an NO_x abatement system is illustrated. For a process off-gas flow of 140 m³/min, a bed geometry of 2.5 m diameter by 0.6 m depth and a bed temperature of about 400°C would be required. The NO_x abatement system should be positioned downstream of all potential NO_x sources and before all other gas clean-up systems that might be affected by NO_x.

FIGURE 1. NO_x Abatement Process for a 5 Tonne/Day Plant

Major Development Objectives

This technology is relatively new, and needs further pilot-plant and full-scale demonstration. A laboratory program should be conducted to develop a kinetic model which will quantitatively describe the catalyzed NO_x - NH_3 reaction. A pilot-plant program should be performed to verify the laboratory results, study the effects of scale-up, determine catalyst life, and obtain operational criteria for a full-scale conceptual design. Finally, the process should be proven by application in a reprocessing plant. The time required to conduct the laboratory and pilot-plant program would be about five years. Another five years might be required to install and test the system in a reprocessing plant.

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13.5 HYDROGEN CHLORIDE

13.5.1 Available Technology - None

13.5.2 Technologies Requiring Development

13.5.2.1 Aqueous Scrubbing

Process off-gas containing HCL is passed through caustic solutions or water. Soluble chloride salts or hydrochloric acid are formed. The waste solution is released to the environs or stored in containment vessels.

Status of Availability

The technology of removing HCL from gas streams by scrubbing is fully developed. About 28 vendors⁽¹⁾ list commercial scrubbers which remove HCL with efficiencies up to 99%. However, the applicability of this technology to off-gas cleanup of incinerators in the nuclear industry is questionable. The combustible materials contain small amounts of transuranics, along with the polyvinyl chloride (PVC) plastics which generate HCL. The liquid wastes generated would contain both corrosive chlorides and traces of transuranics and would have to be solidified. More liquid wastes might be generated than solid wastes consumed; the economic feasibility of the solidification step could be low.

Major Development Objectives

The corrosion resistance of process equipment used for scrubbing and the solidification of the aqueous wastes must be demonstrated in a prototype incineration plant. It must also be shown that transuranics will be concentrated and contained in the solidification step. About five years would be required to build the prototype plant and demonstrate the HCL abatement system.

13.5.2.2 Conversion to NaCl in the Burner

Gaseous HCL formed during combustion of the PVC is contacted with sodium carbonate in the solid or molten state at high temperatures and NaCl is formed in the fluidized bed.

Status of Availability

Pilot plant studies of a fluidized bed burner have been conducted by investigators at Rocky Flats.⁽²⁾ Although efficient removal of HCL can be obtained, only 25% of the sodium carbonate is converted to NaCl. In this process, the amount of wastes (by weight) is increased 240% over the PVC burned. Atomics International⁽³⁾ has studied the use of molten salt in the burner and has found that the HCL is efficiently converted to NaCl with a net reduction in waste compared to the weight of the PVC burned.

Major Development Objectives

The processes above should be demonstrated in a prototype plant over an extended period of operation. The major objectives are to demonstrate controlled burning and containment of radioactivity with a minimum of downtime. Therefore, the acceptance of either one of these methods would probably not be based on their HCl abatement capabilities.

13.5.2.3 Gas Phase Reaction With NH_3

Gaseous NH_3 is mixed with the gas stream containing the HCl at about 300°C . The gas is passed through a condensation and collection vessel at 150°C . An ammonium chloride mist forms and collects on the vessel wall. As the salt layer builds up, fragile crystals form which eventually break off and fall to the bottom for transport out of the vessel. Figure 1 illustrates the conceptual design for the process. The particles which are carried over are collected in the cyclone and backup filter.

FIGURE 1. Conceptual Process for HCl Abatement

Status of Availability

This method has been studied only on the laboratory level.⁽⁴⁾

Major Development Objectives

The success of the method hinges on proper condensation vessel design. The submicron particles of ammonium chloride initially formed, must plate-out with 100% efficiency in the condensation vessel. Otherwise, they will plate-out in the downstream ductwork and block the gas flow. Larger particles which break off from the vessel wall can be collected by the cyclone and filter without complications. About five years would be required to develop and demonstrate this process on a laboratory and pilot-plant scale.

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13.6 CARBON-14

Carbon-14 (^{14}C) is produced during the operation of nuclear power reactors as an activation product by the reaction between neutrons and the minor components nitrogen-14, carbon-13, and oxygen-17. In spent fuel elements the major source of ^{14}C is from approximately 25 ppm nitrogen originally present in the fuel. Estimates for the production of ^{14}C in the fuel from Light Water Reactors (LWR) vary from 750 to 2000 Ci/50 Gwe-yr.^(1,2)

Carbon-14 is also produced in the nuclear reactor in regions other than in the fuel^(3,4) and the recovery of ^{14}C from reactor off-gas may be much more difficult than from the dissolver off-gas at the reprocessing plant. The quantity of ^{14}C in reactor off-gas is similar to that in fuel. In some cases it may be possible to partially reduce production by reducing the ^{14}N content of the original fuel.

13.6.1 Available Technology

13.6.1.1 Release

To date, no effort has been made to remove ^{14}C from reactor or reprocessing plant effluents. The ^{14}C is released as $^{14}\text{CO}_2$ during the dissolution of spent fuel at the reprocessing plant; the estimated quantity is 750 to 2000 Ci/50 Gwe-yr. The dissolver off-gas contains mostly air with moderate concentrations of oxides of nitrogen and minor concentrations (1 to 1000 ppm) of rare gases, carbon dioxide, iodine, hydrogen and tritium. Essentially 100% of the $^{14}\text{CO}_2$ is released to the atmosphere. Of course, the $^{14}\text{CO}_2$ is mixed with natural $^{12}\text{CO}_2$ from the air which incidentally leaks into the dissolver system. The CO_2 concentration in air is approximately 0.03 vol%. The maximum concentration of $^{14}\text{CO}_2$ in the dissolver off-gas is approximately 250 ppm (0.025%).

Technology for the release of $^{14}\text{CO}_2$ from reprocessing plants (stacks) requires no change or development in current practice. Acid dissolution of fuel will ensure the evolution of essentially all of the ^{14}C to give a single source term. Dispersal technology references were given in the chapter on krypton-85 release.

13.6.2 Technologies Requiring Development

13.6.2.1 Caustic Scrubbing

The CO_2 in the dissolver off-gas is removed by reacting with caustic to produce a soluble carbonate. The block diagram in Figure 1 describes the process steps. The off-gas pump, which also serves to remove much of the acidic gases, such as NO , NO_2 , and CO_2 , uses a caustic solution for lubrication. However, to recover approximately 99% of the CO_2 , a second scrubber

is placed in series, and the scrubber liquids combined for subsequent recovery of $^{14}\text{CO}_2$. Nitrites are oxidized to minimize the generation of volatile oxides of nitrogen in the acidification step, where $^{14}\text{CO}_2$ is quantitatively removed from the scrubber liquid by the addition of dilute nitric acid accompanied by air sparging. The air- CO_2 gas stream is passed into a lime scrubber, which precipitates the CO_2 as CaCO_3 . The CaCO_3 is then filtered, dried, and packaged in metal containers for interim and/or long-term storage. Assuming 99% recovery of an average of 1000 Ci of $^{14}\text{CO}_2/\text{yr}$, the annual output of $\text{Ca}^{14}\text{CO}_3$ would be 1.6 kg; however, ten to one hundred times as much CaCO_3 from atmospheric CO_2 would probably be recovered with the ^{14}C species, which raises the annual CaCO_3 produced to 16 to 160 kg.

FIGURE 1. Caustic Scrubber Process for $^{14}\text{CO}_2$ Removal From Dissolver Off-Gas

The major waste stream is the CO₂-depleted scrubber solution from the acidification step, which will contain certain fission products that are known to be in the dissolver off-gas. The solution will be sent to intermediate-level waste storage.

Status of Availability

The technology of pumping dissolver off-gas has been developed at the Idaho Chemical Processing Plant (ICPP) in conjunction with the recovery of krypton-85 from dissolver off-gas.⁽⁵⁾ However, recovery of ¹⁴CO₂ from the caustic scrubber solution has not been demonstrated, although the chemistry is well-known. Similarly, the collection of ¹⁴CO₂ in lime water is unproven; alternative scrubber liquids are possible, since this operation is common in the chemical industry.

Major Development Objectives

Major development objectives are to produce a chemical flowsheet comparable to Figure 1, which will recover 99% of the ¹⁴CO₂ as CaCO₃, to test the chemical flowsheet in unit operations equipment for scale-up data, and to demonstrate the entire process in a pilot plant on actual dissolver off-gas. The process should include the packaging of radioactive CaCO₃.

13.6.2.2 Molecular Sieve Adsorption

Carbon dioxide in the dissolver off-gas is removed by adsorption on molecular sieve type 5A, as shown in Figure 2. CO₂ is kept in the gas phase during pumping by keeping the pump lubricant acidic. It may be necessary to use two pumps in series to adequately remove NO as well as NO₂. Nitrous oxide is removed by catalytic decomposition.⁽⁵⁾ The resultant gas is dried on molecular sieve 3A and collected on molecular sieve 5A; then the ¹⁴CO₂ is desorbed and recovered as solid CaCO₃ by scrubbing with a lime slurry, filtering, and drying. The CaCO₃ is packaged in metal containers for interim and/or long-term storage. As in the previous process, the annual yield of total CaCO₃ is 16 to 160 kg. The major waste from this process is the CO₂-depleted off-gas stream, which will be released to the environment or treated further for the removal of rare gases.

Status of Availability

Pumping of dissolver off-gas using an acid pump lubricant is not developed, although it is expected to be installed at the ICPP rare gas plant. The several molecular sieves have been used in removing moisture

and CO_2 from gases, but not for dissolver off-gas. Similarly, lime slurries have been used to scrub CO_2 from gases. All of these steps need application and demonstration on dissolver off-gas.

Major Development Objectives

Major development objectives are to prove the chemical flowsheet given in Figure 2 for 99% recovery of $^{14}\text{CO}_2$ as CaCO_3 , obtain unit operations data on the equipment, and demonstrate the flowsheet in a pilot plant on actual dissolver off-gas.

FIGURE 2. Molecular Sieve Adsorption Process for $^{14}\text{CO}_2$
Removal from Dissolver Off-Gas

13.6.2.3 Fluorocarbon Absorption

Carbon dioxide is readily soluble in fluorocarbons such as refrigerant-12, and can be recovered with high efficiencies. The CO_2 recovery can be performed during the recovery of krypton-85 by the same process. In Figure 3, an acid pump lubricant is used to avoid loss of CO_2 noted when alkaline

scrubber liquids are used. The drier could be a Lectrodryer or a bed of molecular sieve 3A. The absorber-stripper system using fluorocarbons is similar to the one described in the section on krypton-85 recovery.^(6,7) The separated CO_2 is recovered as CaCO_3 , as described in the previous two processes.

FIGURE 3. Fluorocarbon Absorption Process for $^{14}\text{C}\text{O}_2$
Removal From Dissolver Off-Gas

This process has no major radioactive waste streams. Spent fluorocarbon absorbent may occasionally need to be discarded, but it should not contain significant radioactivity.

Status of Availability

Fluorocarbon absorption of dissolver off-gas has been developed on pilot plant scale at Oak Ridge,^(6,7,8) but has not been demonstrated on actual dissolver off-gas. The process developed to date was specific for krypton-85, but should be applicable to CO_2 .

Major Development Objectives

Develop the system required for the recovery of CO₂ from an operating process used for the recovery of krypton from dissolver off-gas.

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13.7 RUTHENIUM-106

During high temperature solidification of waste raffinate from a fuel reprocessing facility, ruthenium is the single fission product which can volatilize and require removal from the off-gas system. The principal radioisotope of ruthenium present in 1-year cooled waste from the processing of fuel irradiated to 25,000 MWD/MTU is ^{106}Ru . It will be present at a concentration of 2.5×10^5 Ci/MTU and constitute approximately 3.7% of the total ruthenium present. ^{106}Ru decays by beta radiation (0.040 MeV), with a half-life of 1.0 yr.

In the reprocessing of waste from 5 MTU, 1.25×10^6 Ci of ^{106}Ru will be fed into the solidification facility. Volatile ruthenium may be considered soluble; particulate ruthenium from a high temperature solidification process is considered insoluble. However, it is possible that the gaseous form may be partially converted to an insoluble form.

The Final Safety Analysis Report⁽¹⁾ for the Barnwell Separations Facility lists the expected stack release for total ^{106}Ru as 4.6 mCi/day; this release should meet⁽²⁾ all standards and specifications promulgated by state and federal agencies.

Very little knowledge currently exists about volatile ruthenium generation during waste solidification. Laboratory data have been obtained for ruthenium volatilized during fluidized-bed calcination of simulated LWR commercial waste. When in-bed combustion is used, the volatility is $1.7 \times 10^{-3}\%$. This is probably as low as can be obtained with other high temperature processes.

13.7.1 Available Technology

13.7.1.1 Release

The quantities of ruthenium passing into process off-gases during waste solidification by the different types of processes are not known. The general impact of this on off-gas cleanup requirements is discussed in Section 13.7.2.2; similar considerations affect decisions regarding release of any generated gaseous ruthenium species.

Particulate removal from the off-gas by quench-tanks and venturi scrubbers will also remove a substantial amount of ruthenium. As discussed in Section 13.7.2.1, the DF of a recycling quench tank-scrubber system for volatilized ruthenium is approximately 20.

Status of Availability

Laboratory measurements were made on ruthenium volatilized during fluid-bed calcination of simulated LWR wastes. No studies have been made with actual waste, and no pilot-plant or demonstration plant studies have been made.

The quantities of ruthenium generated as gaseous species are of primary importance in calculating expected releases. Also, the effect of any off-gas components normally present on the volatilized ruthenium must be determined. Under conditions of high volatility, the effect of the ruthenium on the off-gas system should also be considered, for under certain conditions, ^(3,4) some of the volatilized ruthenium can plate out and cause potential plugging problems.

13.7.2 Technologies Requiring Development

13.7.2.1 Fluidized Bed Calcination

Nuclear fuel reprocessing wastes can be solidified by heating a fluidized bed by external means, e.g., a bundle of tubes inserted into the bed through which a heat transfer fluid is circulated. This mode was used for the waste calcining facility (WCF) during the first three operating campaigns at the Idaho National Engineering Laboratory (INEL). An alternative mode of heating, now in use, is to burn kerosene directly in the bed.

The mode of heating affects the quantity of gaseous ruthenium generated and passed into the off-gas system (type of waste also affects the quantity generated and its stability in the off-gas cleanup system). Recent studies at the INEL, using a simulated LWR commercial waste, show that, of the ruthenium fed into a fluidized-bed calciner, the quantity generated in the calciner as a gaseous ruthenium species during indirect heating varies with temperature from $6 \times 10^{-4}\%$ at 570°C to $3 \times 10^{-2}\%$ at 500°C , and 100% at temperatures below 375°C . When in-bed combustion (IBC) heating is used, the same volatility, $2 \times 10^{-3}\%$, is observed at 500°C and at 570°C . (This value is attained with indirect heating at 550°C .)

All aspects of fluid-bed calcination, except volatile ruthenium control, favor as low a temperature as possible for the calcination process. At temperatures significantly below 550°C , using indirect heating, the ruthenium volatility becomes intolerably high (exceeds $2 \times 10^{-3}\%$). Thus, in-bed combustion is the favored mode of operation; it will allow the lowest possible operating temperature. With indirect heating, an inadvertent drop in temperature would allow large quantities of ^{106}Ru to be generated. The IBC mode does require a minimum operating temperature near $475\text{--}500^{\circ}\text{C}$ to assure efficient burning of the kerosene.

Ruthenium from the calciner (particulate as well as gaseous forms) must be removed by the components of the off-gas cleanup system prior to reaching the stack. Removal of ruthenium as a particulate solid has essentially the same cleanup requirements as the other radionuclides. Components that can be considered for use to remove both particulate and gaseous ruthenium include cyclones, quench tanks, venturi scrubbers, adsorbers for ruthenium, and HEPA filters. Of these, the most effective in removing volatilized ruthenium is an adsorber. A number of adsorber materials was investigated in the laboratory.⁽⁵⁾ Of those studied, silica gel (Davidson Grade 40) was found to be the most suitable. It has a high DF for volatilized ruthenium (>1000), has a high capacity (exceeds 140 g Ru/ft^3), sorbs at a moderate temperature, is not attacked by the off-gas, and can be easily regenerated.

Operational data from the WCF, along with volatility measurements for the various types of waste calcined, have provided some information from which approximate values of DF's for ruthenium (particulate and volatilized) across the various off-gas components cyclone, quench tank-venturi scrubber, silica gel adsorber, and HEPA filter can be calculated. These approximate values are listed in Table 1. Also included is the DF across the calciner and cyclone for volatile ruthenium from LWR waste.

TABLE 1
Approximate DF's for Ruthenium Across Off-Gas Components

	<u>Calciner and Cyclone</u>	<u>Quench Tank and Scrubber</u>	<u>Silica Gel Adsorber</u>	<u>HEPA Filter</u>
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Particulate Ru	---	40	8	940
Volatilized Ru	5.9×10^4	20	1000	1

In the WCF, 30 to 40% of total solids produced are fines, and approximately 10% of the total solids produced leaves the cyclone, which has an overall efficiency of 75%. A state-of-the-art cyclone, as designed for the new waste calcining facility at INEL, would have an efficiency of some 99%. LWR waste will produce 25 to 30% fines; thus, only 0.3% of the total solids generated would exit the cyclone. The use of a condenser, which would provide a DF of 10 to 50 for volatilized ruthenium, is to be discouraged because of the problems associated with treatment and disposal of the condensate.

Based on laboratory measurements of ruthenium volatility and off-gas component DF's deduced from WCF operational data, a process flowsheet with ruthenium flowpath is given in Figure 1.

The silica gel can be regenerated by washing with hot water. The wash solution is small compared with the calcined wastes, and can be pumped to evaporators or feed tank and calcined.

BASES FOR FLOWSHEET

1. CALCINATION AT 500°C WITH IBC - Ru VOLATILITY $1.7 \times 10^{-3} \%$.
2. 0.3% OF TOTAL SOLIDS ENTER OFF-GAS STREAM.
3. AGNS WASTE; ONE YEAR COOLED; FROM 25,000 MWD/MTU FUEL.
4. CALCINATION RATE = WASTE FROM PROCESSING 5 MTU/DAY.
5. DF's FROM WCF OPERATING EXPERIENCE (TABLE 1).

FIGURE 1. Conceptual Process for Containment of Ruthenium During Fluid-Bed Calcination of Commercial Waste

Any ruthenium removed by the scrubber system will be recycled to the calciner by blending with the incoming waste feed. A material balance analysis shows that it will be accumulated with the product in solid. A steady-state concentration of ruthenium will be reached in the scrub solution, depending on the quantity fed to the calciner reaching the scrub system and the quantity of scrub solution recycled relative to feed volume.

Aside from ruthenium in the calcined solids, the only type of waste generated by the cleanup system is the filters used for removing particulates of all kinds, including ruthenium. The frequency of changing will be dictated by total fines reaching the filters, in conjunction with their loading capacities.

Status of Availability

Laboratory studies of ruthenium volatility during fluid-bed calcination of simulated wastes are near completion. No measurements have been made on actual LWR waste. Pilot-plant measurements using simulated waste will be carried out within a year. No operational demonstration with actual or simulated LWR wastes has been performed.

Major Development Objectives

Pilot-plant studies on simulated LWR waste should continue to the point that a selection of feed pretreatment steps can be made. The selected process should be tested in a hot laboratory facility or pilot plant with actual LWR waste; investigations must include ruthenium flow-path studies. Investigations might be made into chemical additives for the feed that will more completely contain the ruthenium in the calcine under various operating conditions.

In-depth studies of effectiveness of off-gas cleanup components for removing ruthenium should be made at the pilot-plant scale. Sufficient parametric data should be obtained to allow extrapolation to plant-scale equipment.

13.7.2.2 Other Solidification Processes

The treatment of off-gases which contain volatilized ruthenium from other types of waste solidification is essentially the same as described for the fluid-bed calcination process, Section 13.7.2.1. Any differences will be directly related to the quantity of ruthenium volatilized. Higher volatilities will require proportionally higher overall DF's and adsorber capacities.

Some processes may release such quantities of ruthenium that adequate off-gas cleanup will be impossible, or, at best, extremely difficult and expensive. For example, preliminary laboratory data indicate that 1% to 10% of the ruthenium may be volatilized during rotary-kiln calcination. This would impose overall DF and adsorber capacity requirements of 500 to 5000 times those needed for fluidized-bed calcination. For such a situation, careful consideration must also be given to the prevention of ruthenium plateout on pipe and component walls, which could lead to plugging. This must be done primarily by maintaining the wall temperatures between 150°C and 300°C.^(3,4)

An alternative to removing ruthenium from the off-gas is to use additives for holding ruthenium in the solid. For high pH (basic) systems at high temperatures, for example, formation of aluminosilicate in the melt immobilizes the ruthenium.⁽⁶⁾

Status of Availability

Little significant data are available on ruthenium behavior during solidification of LWR wastes by the different types of processes other than fluidized-bed calcination.

Major Development Objectives

For any process selected, the general development objectives outlined in Section 13.7.2.1 must be considered. In addition, substantial laboratory data, using cold simulated LWR waste, should initially be obtained for the flowpath of ruthenium during the process. Then, a preliminary evaluation could be made of the feasibility of the process or of additional developments that may be required for ruthenium control.

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13.8 PARTICULATE REMOVAL

13.8.1 Available Technologies

Fine particulates, those solid or liquid aerosols less than 3 μm in diameter, are a subject of major interest in nuclear operations because of the difficulty of removing them from ventilation air and from the exhaust and off-gas streams of a facility. Particles larger than 3 μm diam generally account for 96 to 97% of the mass of airborne particulates but are relatively easy to remove by well established methods. Particles smaller than this, however, account for 99.999-plus % of the number of particles present. Removal of these fines in nuclear facilities is normally accomplished either by deep beds of sand or fiberglass or by the more compact high-efficiency particulate air (HEPA) filters. Filtration is often preceded by pretreatment or prefiltration or both. Pretreatment includes the use of cyclones, settling chambers, wet collectors, fabric (i.e., shakeable bag) filters, electrostatic precipitators, and other air cleaning devices used in industrial and pollution abatement service. Pretreatment devices are sometimes used to remove heavy concentrations of dust, fume, or smoke released from certain operations before the off-gases are passed to other air or gas processing devices. Many pretreatment devices are ineffective for fine particles, and those that are effective, such as fabric filters and electrostatic precipitators, have operating cycles which can permit reentrainment of trapped material. Reentrainment is possible, for example, during the shaking cycle of a fabric (bag) filter or the rapping cycle of an electrostatic precipitator. Moreover, power outage in an "active" air cleaning device, such as a cyclone or electrostatic precipitator, would result in total loss of air cleaning function.^(1,2,3)

13.8.1.1 Prefilters

Prefiltration employs common ventilation-type air filters to collect larger particles and lint in order to extend the life of final filters downstream. Prefilters range from the 1- to 2-in.-thick fiberglass or metal mesh types often associated with residential and commercial air conditioners and furnaces to the extended media, dry type filters which may exhibit atmospheric "dust spot"* efficiencies as high as 90 to 95%.⁽⁴⁾ Most prefilters used in nuclear applications are modular units 60 cm^2 (24 x 24 in.) with an airflow capacity of 15,000, 30,000, or 60,000 liters/min. The prefilters are used singly or in multiples to build up the installed capacity required for the specific application.

Three types of modular prefilters are used, cleanable medium, replaceable medium, and throwaway. Cleanable medium types are seldom used in nuclear

* The dust spot test is a standard efficiency test for commercial filters. It compares the intensity of a stain on a filter paper before and after passing the gas stream through a filter.

applications because cleaning simply transfers a gaseous waste problem to a liquid waste problem. Also the low efficiency of cleanable medium filters is disadvantageous. Replaceable medium filters employ a permanent (but removable, not permanently installed) frame to hold the filtration medium, which may be a shaped knitted or woven bag or "sock" or simply a sheet of nonwoven fiberglass mat; a screen or wire assembly to support the medium may or may not be provided. Throwaway prefilters range from the nonwoven, fiberglass mat, low-efficiency panel or "furnace" filter to the high-efficiency (95% atmospheric dust spot), extended medium, dry-type filter. The "furnace" type filter is effective in collecting large particles and lint and is frequently used for roughing service to collect, but affords relatively little protection to the final HEPA filters (see below). The most used throwaway prefilters today are moderate (35% dust spot) to high-efficiency units consisting of a core of fiberglass medium pleated back and forth across aluminum or asbestos-paper separators, and enclosed in a rectangular metal, wood, or mineral board casing which extends the full depth of the core. Filters are simply discarded and replaced to rejuvenate the system when they become dust loaded.

Status of Availability

Prefilters of various designs and efficiencies are commercially available.

Major Development Objectives

The disposal of spent filters is an area which will require further attention. At present most modular prefilters are simply buried (after enclosure in drums or encasement in concrete in some cases) without modification of their geometry. Methods of economically compacting filters, in a manner that does not create new reentrainment or contamination problems, are needed. Methods of treatment of filters are included in Section 9.0.

13.8.1.2 Sand and Deep Bed Glass Fiber (DBGF) Filters

Alternatives to banks of modular prefilters in very large airflow capacity applications are the sand and DBGF filters. Sand filters have been used in a small number of ERDA facilities for radiochemical plant and building exhaust service since 1948.^(5,6) These consist of very large (several tens of square meters area by 2 to 3 m deep) beds of graded density sand and gravel contained in large concrete-walled underground pits. Advantages of sand filters include large dust holding capacity, low-maintenance requirements, inertness to chemical attack, excellent fire resistance and heat sink properties, and ability to withstand large pressure transients and shock loadings without damage or loss of function. Particle removal efficiencies approaching that of a HEPA filter (see below) are claimed, depending on bed depth and type of

sands employed. Drawbacks are high capital costs, large space requirements, high pressure drop, uncertainties in the selection and availability of suitable sands, and high cost of disposing of a spent unit (to date, disposal has been accomplished by sealing of the spent unit and building a new unit nearby). At some installations the sand filter is used as the final particulate collection device, although exhaust and process off-gas ducts leading to the sand filter are generally equipped with HEPA filters.

The DBGF filter has been used as an alternative to the more costly sand filter at a number of ERDA radiochemical installations. DBGF filters consist of deep beds of "fiberglass" insulation or "wool," contained in large (1 x 3 m surface dimensions up to 2 m deep) stainless steel boxes with perforated-plate screens top and bottom. Usually two or more beds are employed in series, with varying packing density of the wool from bed to bed. As many bed assemblies as are needed to meet system airflow requirements can be installed in parallel; the complete array is installed in an underground, concrete-walled pit. Like the sand filter, the DBGF filter has very large particle and dust holding capacity, low maintenance requirements, ability to withstand large pressure differentials, good design flexibility and, if operated properly, long life. Pressure drop, and therefore operating costs, is lower, and initial cost is less than for sand filters. Rejuvenation of a spent system can be accomplished by replacing the filter beds, reusing the same pit. On the other hand, the DBGF does not have the heat capacity or fire resistance of the sand filter, the chemical resistance of the sand filter, the capability to snub explosive overpressures or shock waves, or the self-repair characteristic of the sand filter. Only one fiber material has been found satisfactory to date; thus filtration efficiency can be varied only by varying the packing density of the wool or the airflow velocity through the beds. Efficiencies equivalent to a moderate-efficiency modular prefilter (i.e., 35 to 50% atmospheric dust spot efficiency) may be the best that can be practicably achieved.⁽⁷⁾ However, high-efficiency DBGF filters have been described.^(8,9)

Status of Availability

Both sand filters and DBGF filters have been used in a variety of nuclear industry applications. The components and design data are readily available.

Major Development Objectives

The reduction of capital costs and the disposal of spent filters are items which require further consideration.

13.8.1.3 HEPA Filters

Absolute, or final, filtration is nearly always effected by the high-efficiency particulate air or HEPA filter. By definition,⁽¹⁰⁾ this is a

throwaway extended-medium dry-type filter in a rigid frame, having minimum particle collection efficiency of 99.97% for 0.3- μ m particles when tested with monodisperse 0.3- μ m thermally-generated dioctyl phthalate (DOP) aerosol, and maximum clean-filter pressure drop of 2.54 cm water tested at rated airflow capacity. HEPA filters are available in wood or corrosion-resistant steel frames and generally have a core consisting of a continuous web of fiberglass paper pleated back and forth across corrugated aluminum or asbestos paper separators; one manufacturer makes a separatorless core. The best of the modular prefilters exhibit decontamination factors (DFs) of 6 to 7 for particles 0.3 μ m and smaller. By contrast, the HEPA filter must achieve a minimum DF of 3333 for particles in this range, and most of those being made today exhibit DFs of about 10,000 or better (efficiencies of 99.99% or higher). Because of this high efficiency, prefilters should be provided to protect the HEPA filters from large concentrations of large particles, dusts, smokes, and fumes. (The preceding sections of this discussion apply primarily to this function.) For plutonium, transuranic elements, and other applications requiring even higher decontamination factors, HEPA filters may be installed in series. If each stage is individually testable, decontamination factors of 9×10^6 and 3×10^{10} , respectively, for two and three stages of HEPA filters in series under normal operating conditions can be reasonably claimed; the actual decontamination value may be substantially higher.⁽¹¹⁾ Proper installation of HEPA filters is critical to the achievement of these high decontamination factors for submicrometer aerosols, and the recommendations of the Nuclear Air Cleaning Handbook (ERDA 76-21) should be closely followed.⁽¹²⁾

Status of Availability

The theory and technology of high-efficiency particulate collection are well established. Design, performance, and cost data are readily available. Rigorous standardized testing procedures have been established. HEPA filters are in wide use at present.

Major Development Objectives

As with prefilters, the disposal of spent filters is an area of concern. The treatment of HEPA filters is considered in Section 9.0. Methods of volume reduction for disposal in a manner that does not produce new contamination problems need development.

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14.0 IMMOBILIZATION OF VOLATILE RADIOISOTOPES

14.0 IMMOBILIZATION OF VOLATILE RADIOISOTOPES

The volatile radioisotopes which are separated, concentrated, or captured by the technologies described in Section 13 would be immobilized to assure reliable long-term storage.

Both the separation and concentration methods must be augmented by engineered storage or by physical or chemical fixation technologies. Many of the techniques for capture of volatile radioisotopes provide an adequate immobilization method. Only minor development of physical methods for containment and transportation of such fixed wastes would be necessary.

The degree of secondary containment required is a function of the primary storage technique. Engineered storage systems would require significant back-up technology; those methods using highly stable chemical or physical forms would require simpler secondary systems.

14.1 KRYPTON-85

14.1.1 Available Technology

14.1.1.1 Pressurized Cylinders

Existing technology limits storage of radioactive noble gases to pressurized gas cylinders.^(1,2) Whether such cylinder storage can be used for interim or long-term (~200 years) storage has yet to be determined. An engineered storage facility, such as is shown in Figure 1, consists of two parts, a remote handling transfer cave and a sealed storage area. Pressurized cylinders are transported to the cave in a shielded transfer cask⁽³⁾ using a straddle carrier, retrieved from the cask in the transfer cave, and transferred to a storage slot in the sealed storage area. Remote operation is accomplished using overhead cranes, mechanical manipulators, and viewing windows.

FIGURE 1. Pressurized Cylinder Storage Facility for ^{85}Kr

A leak-tight storage vault prevents accidental release of ^{85}Kr , should one of the cylinders develop a leak. The facility could be designed to store from 120 to 385 cylinders (equivalent to five years' supply at a 1500 tonne/year fuel reprocessing plant). The exact number depends on maximum allowable cylinder pressure and the degree of purity of krypton achieved by the separation process. In the event of failure of one or more cylinders, the released ^{85}Kr must be confined to the storage facility until it can be cycled through an adjoining krypton recovery facility. The design must provide for adequate cooling of the heat generated by ^{85}Kr decay.⁽²⁾

Status of Availability

The proposed design is similar to existing dry storage facilities of radioactive materials such as spent fuel assemblies. The technology is thus available to design a demonstration facility for ^{85}Kr storage in pressurized cylinders.

Major Development Objectives

A demonstration of a storage facility is required to establish reliability of the cooling system, krypton recycle procedure, and possible long-term effects of the decay product rubidium on the storage containers.

14.1.2 Technology Requiring Development

14.1.2.1 Zeolite Encapsulation

Zeolite materials are crystalline aluminosilicates which contain a regular array of pores of uniform size.⁽⁴⁾ For a given zeolite type, the pore dimensions are uniquely determined by the structure of the crystal.⁽⁴⁾ Figure 2 shows the structure of a group of sodalite zeolite

FIGURE 2. Representation of Sodalite Crystals Containing Krypton Atoms

cages, each containing one atom of krypton. Each sodalite cage consists of a truncated octahedron ($\sim 6.6 \text{ \AA}$ free diameter). Each six-ring face is shared with adjoining sodalite cages to make up the overall crystal structure. The krypton atom shown occupying each cage has a room-temperature gas-kinetic diameter of $\sim 3.5 \text{ \AA}$.

FIGURE 3. Calculated Release of Original ^{85}Kr Inventory from Sodalite as a Function of Time

The process by which krypton diffuses through such a pore structure is known as activated diffusion, since an activation energy is required for krypton atoms to pass through the $2.3 \text{ \AA}$ apertures.⁽⁴⁻⁶⁾ At high temperature and pressure (450°C ; 1000 atm),⁽⁵⁾ there is sufficient energy for krypton to diffuse into the crystalline cages, while at low temperatures ($<150^\circ\text{C}$) the encapsulated krypton does not have enough

energy to diffuse out at appreciable rates. Thus, krypton can be introduced into the cages at conditions corresponding to rapid diffusion and then trapped in sodalite at ambient external pressure, even though each krypton atom experiences a high effective "pressure" inside its cage.

Experimental encapsulation studies of argon and krypton in sodalite have been made.⁽⁵⁾ From these data, the release of original ^{85}Kr inventory (fractional net leakage of ^{85}Kr) can be predicted as a function of time at a storage temperature of 150°C . When the results are combined with a ^{85}Kr decay term, the curve shown in Figure 3 is obtained for two different sodalite samples. The resulting maximum net leakages of 0.3% to 0.01%, if attainable, represent safety factors (based on potential losses from a damaged storage vessel) of 200 to 6000 over pressurized tank storage. Since the rate of activated diffusion depends on temperature in an exponential manner, the rate of dissipation of ^{85}Kr radioactive decay heat during storage becomes critical. A heat-transfer model for a 23-cm diameter steel storage cylinder was used to estimate temperature profiles when filled with zeolite. At a krypton loading of 1.8×10^{-3} mole g^{-1} (40 standard $\text{cm}^3 \text{g}^{-1}$) of zeolite (equivalent to ~ 35 atm or ~ 500 psi storage of gas) and an ambient temperature (convective heat transfer) of 50°C , the calculated centerline temperature was 150°C ; the mean temperature was approximately 120°C . The predicted leakage rates at 150°C shown in Figure 3 can thus be considered conservative for such conditions.

A typical process flowsheet for encapsulating krypton in zeolite is shown in Figure 4. Activated zeolite (with interstitial water removed) is loaded into the pressure vessel and heated to the encapsulation temperature. Krypton containing ^{85}Kr is introduced and pressurized to the encapsulation pressure until the pores of the zeolite are filled. The temperature is then lowered, and the pressure of excess krypton is released back to the storage cylinder. The zeolite-encapsulated - ^{85}Kr is then removed and placed in the storage container for long-term storage in an engineered-storage facility.

In a 1500-tonne yr^{-1} reprocessing plant, $\sim 9.81 \text{ MCi yr}^{-1}$ of ^{85}Kr is produced. If 1.8×10^{-3} mole g^{-1} (40 std. $\text{cm}^3 \text{g}^{-1}$) of krypton (6% ^{85}Kr) is encapsulated in a zeolite such as sodalite, $\sim 2,800 \text{ kg yr}^{-1}$ is required. If 50,000 Ci of ^{85}Kr is to be encapsulated in one batch, a 20-x high-pressure vessel would be necessary. Such a scale of operation is within standard high-pressure industrial operation.

The encapsulation process, including solids transfer operations, must be remotely operated due to the high radiation field. In addition to mechanical shielding of the high pressure process equipment, capability for containing the large amount of radioactive krypton is required in

the event of failure of the pressurized system.

FIGURE 4. Process for High Pressure Encapsulation of ^{85}Kr in Zeolite

The storage of krypton-85 encapsulated in zeolite material could be in an engineered-storage facility, similar to one used for pressurized cylinders. A separate discussion of such a facility is presented earlier in this chapter (see 14.1.1.1).

Status of Availability

Experimental testing of this method is currently under way at the Idaho National Engineering Laboratory (INEL). Pilot-scale development could begin after approximately three years of experimental development and conceptual design criteria can be obtained in time for a 1980 design fuel reprocessing plant. The experimental studies are being conducted to test known materials such as sodalite, as well as new types of zeolites for storage characteristics. Optimization of encapsulation conditions is being studied and will be continued during pilot-plant-scale development. The pilot-plant design will

include scale-up of the pressure vessel, possibly to a plant-size prototype, and remote operation capability.

Major Development Objectives

Experimental-scale studies should determine the optimum conditions for encapsulation of ^{85}Kr in sodalite and in other available zeolites with promising structures. Basic studies of leakage rates at various temperatures will be used to predict leakage curves such as shown in Figure 3.

A process-scale encapsulation system may need to be designed. Technology exists for high pressure, remote operation, and remote handling capabilities, and these need to be combined into one operational system. Since relatively large amounts of ^{85}Kr will be present during the process-scale encapsulation, adequate cooling of radiation-generated heat is required during parts of the process-scale.

Long-term storage criteria need to be developed. Stored ^{85}Kr in zeolite will generate heat, which in turn must be dissipated so that the storage temperature does not exceed a value at which appreciable diffusion of ^{85}Kr out of the zeolite pores can occur ($\sim 150^\circ$ in Figure 3 for sodalite). Long-term radiation damage to the zeolite structure must be assessed and minimized. The effect of the ^{85}Kr decay product, rubidium, must also be determined. (A beneficial effect of rubidium might be to help plug up the pores in sodalite.)⁽⁸⁾ In any handling of zeolite-encapsulated- ^{85}Kr , dust formation must be prevented or contained.

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14.2 IODINE-129

The immobilization of ^{129}I from fuel reprocessing plants may be mandated by the extremely long half-life, 15.6×10^6 years. If future storage standards preclude the use of physical isolation (as a sufficient means), a solid matrix with a large loading capacity, low leachability, nonflammability, and simple handling characteristics will be desirable.

Investigators at the Oak Ridge National Laboratory have evaluated the use of cement for immobilizing iodine.⁽¹⁾ They found that 9 wt% iodine can be incorporated into the matrix in the form of barium iodate. This technology is especially designed to immobilize iodine which is collected by the Iodex process. About 3 m³ of cement per year would be required to immobilize the ^{129}I generated by a 5 tonne/day LMFBR reprocessing plant.

The use of silver- and lead-exchanged zeolites for recovery and storage of ^{129}I is now being studied at the Idaho National Engineering Laboratory (Section 13.2.2.1).^(2,3) Gas-phase iodine reacts with the metal ion in the adsorbent to form a chemisorbed iodide. The advantage of this technology is that collection and fixation of the iodine occur in the same process. It is expected that the chemisorbed iodides will have solubilities similar to the pure iodides. It is estimated that about 1.5 m³/yr of lead-exchanged zeolite would be required to collect the iodine generated by a 5 tonne/day reprocessing plant. Additional immobilization of the loaded zeolitic materials could be accomplished by the use of cements, glasses, or other simple bulk solidification methods.

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14.3 TRITIUM

14.3.1 Available Technology - None

14.3.2 Technologies Requiring Development

14.3.2.1 Chemical Storage

The number of hydrogen-containing compounds that may be utilized as solid storage media for tritium is substantial. These include hydrates, hydroxides, hydrides, organic solids, and adsorbents. In addition, materials which absorb hydrogen-containing compounds may also be considered. Important considerations for compound evaluation include the cost of raw materials, ease of preparation and its associated cost, tritium capacity, thermal, chemical and radiation stability of the product, the rate at which tritium is released as a result of leaching and exchange in various environments, mechanical properties and dispersibility of the product, and its compatibility with possible storage containers.

The factors which are important to the evaluation of tritium storage media are complex and interrelated and must be considered together in determining the economic and environmental consequences of a particular choice. It is unlikely that any one material will best satisfy all of these criteria. The particular waste application may strongly influence the choice of an optimum compound (or class of compounds). For example, the preparation cost of a tritium compound is of far greater importance for the fixation of a large volume of low-level tritiated waste than for a small volume of a high-level waste. Also, some materials may be superior for treating tritium in an elemental form while others are more applicable to aqueous tritiated wastes.

The heat generation of tritiated wastes are of little consequence due to the low energy associated with tritium decay (0.0181 MeV) producing 1.07×10^{-4} watts per curie of tritium. Similarly, the rate of ^3He production is also generally insignificant. However, container pressurization due to ^3He production and composite radiolysis should be considered for high level tritiated waste.

14.3.2.1.1 Hydrates

Few of the large number of hydrates (including hydroxides) deserve consideration. Most are soluble, many are expensive, and of those that are not soluble or only slightly soluble, many bind water poorly and exhibit high exchange rates. Among the low-cost compounds which deserve consideration are such compounds as silica gel, activated alumina, calcium sulfate, and molecular sieves. Hydrated silicates such as hydraulic cements and clays also exhibit desirable properties for tritium storage. Hydraulic cements

also have the advantage of producing monolithic solids, which are expected to exhibit lower tritium release rates than other hydrates in powdered or granular form.

Drying Agents

Of the commonly used commercial drying agents,⁽¹⁾ activated alumina, silica gel, calcium sulfate, and molecular sieves will be considered briefly. These agents are of value for the removal of water vapor from air or other gases because of the ability to absorb water rapidly. For long-term tritium storage, these materials would have to be containerized to prevent contact with water and water vapor which would result in tritium release. All of these drying agents are stable solids in water-loaded and anhydrous form. All are widely used for commercial applications, and their properties have been thoroughly studied.

Calcium sulfate forms a hemihydrate containing 6.2 wt% water, and up to this composition binds water strongly, giving a dew point of -62°C .⁽¹⁾ Higher water loadings can be obtained, but this water is not firmly held. It has the advantage of low cost, but its water capacity is low.

Silica gel has a high water capacity, being capable of adsorbing 40 wt % water. However, it binds water strongly, and exhibits low water vapor pressures only at low loadings.⁽¹⁾ The adsorption of water by activated alumina is similar, but the capacity is approximately 50% that of silica gel.⁽¹⁾

Molecular sieves exhibit high water capacities and flatter isotherms than silica gel. At 25°C , they have a higher water capacity than silica gel at all but the highest vapor pressures.⁽²⁾ Their capacities are typically 10-20%, based on dry weight. They are stable to regeneration by heating, liquid water, and many chemical environments. Molecular sieves retain their desiccant properties at temperatures higher than for other adsorbents.

Molecular sieve beds are used to remove tritiated water vapor from gas streams. Often they are used in conjunction with copper oxide or palladium catalysts which insure conversion of elemental tritium to the oxide.⁽³⁾ Silica gel beds have also been used. Molecular sieve and silica gel beds may be discarded when loaded, rather than regenerated.⁽⁴⁾

To reduce the rate of tritium release, such agents must be encapsulated or containerized to prevent air and water contact. The rates of tritium release from loaded silica gel, from molecular sieve encapsulated in polystyrene, and from polymer-impregnated concrete have been measured under water leaching conditions by a modification of the IAEA standard leach test.^(5,6,7) Fractional tritium releases of 10^{-3} - 10^{-4} per day are typical. The cost of HTO fixation by these methods is primarily a function of the formulation

and degree of water loading,⁽⁸⁾ with the cost of sorbant being the major factor.

The technology for the sorption of water vapor from a gaseous stream by a drying agent is well known and is described in the literature.^(1,3) Such a process can be either static or dynamic. The dynamic process has the widest application and consists simply of passing the gas stream to be treated over the drying agent bed. Gas flow rates and bed volumes would be optimized to provide the desired level of removal. In this application, the drying agent bed would generally not be regenerated, but rather treated as solid waste and disposed. This process may be used to reduce the tritium inventory in a closed system or with achievement of sufficient decontamination, the gas stream may be dispersed to the environment.

Drying agents may also be used for the adsorption of tritiated water in the liquid form by adding water to the drying agent or vice versa. The rate of heat liberation as a result of rapid adsorption by this technique may result in water vaporization, requiring containment.

Containment or encapsulation of the drying agent is required to minimize tritium release. Corrosion of the container in appropriate environments and also by water-loaded drying agents should be considered. The drying agent may also be encapsulated in concrete or polymer, forming a monolithic solid. Concrete, although a porous material, limits tritium release by an effective reduction of the available surface area. The process would consist simply of adding the drying agent to a hydraulic cement mix. The cement could also be coated or polymer-impregnated to further limit tritium release. (These processes are described more fully in the section on hydraulic cements.) The process to encapsulate a drying agent in polystyrene-styrene matrices is relatively simple.⁽⁶⁾ Monomer is poured over the drying agent, filling the voids between the individual particles and coating them. Catalyst or catalyst-promoter addition in the monomer allows a low temperature (50-70°C) or a room temperature monomer cure, respectively.

Status of Availability

The technology of the use of drying agents for tritiated water vapor removal from a gas stream or a liquid is available. Containerization or encapsulation of loaded drying agents in concrete and polymers are also available. Polymer impregnation of concrete containing drying agent as an aggregate requires further development, which is estimated to require one to two years, depending upon the level of effort. However, further work should be done to more fully evaluate the properties of these

materials relative to tritium storage, especially for high-level tritiated wastes. Applied to individual waste composite types, this evaluation would require three months to one year.

Major Development Objectives

Only polymer-impregnated concretes require significant development. Polymer impregnation of large-scale composites (> 15 cm in diameter) by soaking techniques requires optimization of concrete formulations and practical testing.

Hydraulic Cements

Portland cement is probably the cheapest material which will bind tritiated water strongly and have a moderately low exchange rate.⁽⁹⁾ The low rate of exchange is attributed to the monolithic nature of the solid rather than the actual rate of chemical exchange of the concrete. High alumina cement, although somewhat more expensive than Portland cement, could also be used. The water capacity of these cements is reasonably high; commercially available Portland cements can hydrate approximately 25 wt % water while high alumina cement combines with about 50 wt % water.⁽¹⁰⁾ Theoretical values are somewhat higher since they neglect non-hydrating impurities present in commercial cements. The chemistry of these cements is complex but reasonably well understood.^(10,11,12)

While concrete is a monolithic solid, it is quite porous. BET specific surface measurements of hydrated cements are typically about $200 \text{ m}^2/\text{g}$ dry weight.⁽¹³⁾ Thus, even though the solubility of cement hydrates is low,⁽¹⁴⁾ a gradual release of tritium is expected. Values for the leaching of tritium from cement paste blocks in an aqueous environment have been measured.^(6,7,15) Typically, the fractional release of tritium per day is the order of 1×10^{-2} for the first month. The rate of release decreases with time. This rate of tritium release can be decreased by the application of coatings to the cement block or by polymer impregnation.

Coatings of asphalt, beeswax, paraffin, enamel and grease have been used to decrease the tritium release for Portland type I cement paste blocks.⁽¹⁵⁾ Beeswax reduced the fractional release of tritium per day to $\sim 2 \times 10^{-4}$ over the first month. Samples that were asphalt-coated exhibited tritium fractional release rates of $\sim 2.5 \times 10^{-3}$ per day over the first month. Asphalt was also cast around cement blocks, resulting in coatings of up to one inch in thickness. By this method, the tritium fractional release rate per day was reduced to 3×10^{-4} for the first month of leaching. Such coatings are, however, subject to cracking, delamination, and spalling, which would result

in a sudden increase in the rate of tritium release equal to that for an uncoated concrete. Asphaltic coatings could be easily and cheaply applied to tritiated concrete.

Polymer impregnation procedures are under development.^(6,7,8,16) By this technique, the pores of the concrete are filled with a liquid monomer, which is then polymerized in situ, resulting in a composite that is essentially impermeable to water. Monomer loadings are typically 5 - 15% by weight. Aqueous leach rate testing has resulted in fractional tritium releases of the order of 10^{-4} per day for the first month of leaching. Polymer impregnation also results in a large increase in the strength and durability of the concrete, as well as its resistance to chemical attack.

The technology of hydraulic cement processing is well known.^(10,11,12) However, for application to tritiated waste disposal, consideration has to be given to reduction or elimination of low-level effluent from the process as a result of equipment maintenance, processing, and handling. It is possible to eliminate such an effluent during normal operation by proper selection and design of the process. Mixing can be achieved by drum tumbling, a gunite process, or by a rotating blade. Alternatively, tritiated water might be added to dry cement without mixing. This water addition could be made through a manifold system to promote homogeneity of the mix. Mixing and cement curing should be conducted in a closed system to prevent loss through water evaporation.

Hydrogeneous coatings may be applied to concrete blocks by several techniques such as dipping, painting, or casting around the block. The technique chosen should minimize handling to reduce the possibility of contamination. With proper process design, no effluent should be generated. Coating should be done in a closed system to prevent tritium release through evaporation. To minimize evaporation, coating materials should be selected to avoid high temperatures.

Polymer impregnation processes using styrene monomer are under development.^(6,7,8,16) Impregnation by a soak technique is desirable because of the simplicity of the process. Styrene monomer containing ~0.5 wt % benzoyl peroxide catalyst is introduced, either through the top of the cement casting container, or through the bottom under a hydrostatic head. For a 30 cm diameter casting, impregnation normally requires one to three hours. A clamshell drum heater is then placed around the concrete container, which is heated to 50-70°C for several hours for complete polymerization. This process should be carried out in a closed system to prevent tritium loss through evaporation.

Status of Availability

Technology for a cement process is available. Design efforts would be required to minimize or prevent tritium loss from such a system; such efforts are short term (less than 1 year).

Coating systems for concrete blocks are also available technology. Again, system design is important to minimize or eliminate tritium loss.

Polymer impregnation requires further development of six months to two years depending upon the level of effort.

Further work should be done to more fully evaluate the properties of these materials relative to tritium storage, especially for high-level tritiated waste.

Major Development Objectives

Concrete formulations need to be optimized for soak impregnation of large-scale (~15 cm diameter) concrete castings.

14.3.2.1.2 Organic Compounds

Many organic compounds with carbon-tritium bonds exhibit a slow rate of exchange of tritium for the hydrogen of water. Thus, exposure to the environment may occur without significant loss of tritium. Polymeric hydrocarbons are of particular interest, due to their low volatility, chemical stability, and hydrophobic nature. Polymeric materials under study for tritium fixation and storage include polyacetylene, bakelite analogs, polyacrylonitrile, and polystyrene. Based on process costs, polymeric materials appear best suited for high-level tritiated waste applications.

Polyacetylene

The cheapest and simplest approach⁽¹⁷⁾ to the preparation of polymeric materials from tritiated water is the reaction with calcium carbide to form an acetylene intermediate:

In this reaction, the tritium is partitioned equally between acetylene and calcium hydroxide. The calcium hydroxide can be calcined for recycle of tritiated water.

Polymerization of tritiated polyacetylene has been achieved both by ^{60}Co γ -irradiation and thermal catalysis over cupric oxide.^(6,8,18,19,20) Leach testing of ^{60}Co γ -polymerized polyacetylene showed a rapid 4% activity release, presumably due to surface contamination, with no further measurable

release over 28 days.⁽¹⁸⁾ This material was found to be thermally stable to 325°C, above which oxidative degradation was observed. A softening point was not observed, indicating the formation of cross-linked networks or cyclic structures. Polyacetylene was found to be insoluble in all solvents tested. A $G(H_2)$ value (number of molecules of hydrogen liberated per energy unit of exposure) of 0.15 molecules/100 eV was determined for polyacetylene on exposure to a radiolysis dose of 10^9 rads.

Hydraulic cement or polymers may be used to form a monolithic solid of the polyacetylene particles produced. This product would be expected to exhibit a lower rate of hydrogen release by leaching as a result of the reduction of effective surface in contact with the leachant.

The hydrogen from 0.68 grams of tritiated water can be incorporated into one gram of polyacetylene.

A process flow diagram for the fixation of tritium in tritiated water by conversion to polyacetylene is shown in Figure 1. Tritiated water is converted to tritiated acetylene and calcium hydroxide by reaction with calcium carbide. The tritiated calcium hydroxide is calcined with the water recovered and recycled. The calcium oxide resulting contains no activity. Tritiated acetylene is passed through a scrubber to remove entrained water before entering the polymerization reactor. Polymerization is either by ^{60}Co γ -irradiation or thermal catalysis over cupric oxide. Both methods have been studied in some detail.^(6,8,18) G values for acetylene conversion by ^{60}Co irradiation of 75-140 molecules per 100 eV were obtained. Thermal polymerization over cupric oxide begins at 200°C with a maximum rate at about 280°C. Higher temperatures promote byproduct formation. Unreacted acetylene is recycled through the reactor while by-products are burned, with combustion water recycled. The polyacetylene is washed prior to incorporation into monolithic form (concrete) or storage to remove tritiated by-products, which are burned, with the resulting water recycled.

Status of Availability

The technology for this process is available. However, additional study is required to identify favorable polymerization conditions to achieve practical catalyst life, and to develop procedures for the efficient recovery of catalyst from product polymer. Technology for calcium hydroxide calcination and recycle is available.

FIGURE 1. Tritium Fixation by the Polymerization of Tritiated Acetylene and Incorporation into Cement-Concrete

Bakelite Analog Polymers

Bakelite analog polymers formed by the reaction of tritiated acetaldehyde with phenol or resorcinol in the presence of aqueous NaOH have been studied for tritium fixation and storage.^(21,22) The tritiated acetaldehyde is produced by reacting normal acetylene or tritiated acetylene (as generated in equation (1)) with tritiated water in sulfuric acid solution of mercuric sulfate.

Resorcinol (or phenol) and tritiated acetaldehyde are mixed in the presence of aqueous NaOH to form the polymer.

These bakelite analog polymers are hard and brittle, and insoluble in water, acetone, ethanol, benzene, ether, and CCl_4 . Leach testing indicates that approximately 2% of the tritium is lost during rinsing, presumably due to unreacted tritiated acetaldehyde. No further loss was detected over a four to six week period. Thermal degradation of bakelite (phenol-formaldehyde) begins above 230°C .⁽²¹⁾ Phenol-formaldehyde radiolysis is reported to give G (total gas) = 0.08.⁽²³⁾ However, unfilled phenolics are fairly low in radiation resistance; they swell, become very brittle, and tend to crumble.⁽²⁴⁾

Status of Availability

Both acetaldehyde production from acetylene and polymerization (with formaldehyde) are established industrial processes. The polymerization reaction using resorcinol or phenol requires further development towards optimization, but basically is available technology. Technology for the calcination of tritiated calcium hydroxide for water recycle is available. Process modifications for control of radioactivity will need to be considered.

Polyacrylonitrile

Tritiated acetylene produced by the reaction of calcium carbide and tritiated water (Equation 1) can be converted to acrylonitrile by the copper-catalyzed addition of HCN (Equation 4). In the presence of a radical initiator such as potassium persulfate, polyacrylonitrile is formed (Equation 5).

In leach testing,⁽²¹⁾ tritiated polyacrylonitrile was found to lose ~5% of its activity during an initial rinse. This loss was presumed due to solvation in water of low molecular weight polymer by small quantities of the lauryl sulfate emulsifier used in the polymerization reaction. Subsequent leaching for four to six weeks resulted in no measurable additional tritium loss. Polyacrylonitrile is inert to many reagents, but is degraded by alkali and heat. It is flammable and undergoes thermal condensation above 200°C,⁽²⁵⁾ producing HCN, methacrylonitrile, ammonia, and nitrogen. Radiolysis of polyacrylonitrile results in G values of 0.39 and 0.1 molecules/100 eV for total gas and hydrogen evolution respectively.⁽²⁶⁾

The schematic for this process is shown in Figure 3. Tritiated acetylene is the intermediate for the process, and is produced by the reaction of calcium carbide with water. Conversion of tritiated acetylene to acrylonitrile occurs with HCN in the presence of a Nieuwland catalyst, which is regenerated and recycled. Effluents are condensed, and unreacted acetylene is recovered and recycled. The aqueous solution is purified by an extraction sequence and distilled to produce pure acrylonitrile. Organic by-products are burned, and the water produced is recycled. Polyacrylonitrile is prepared by emulsion polymerization in the presence of an initiator such as potassium persulfate. This process is more fully described in the literature.⁽²¹⁾

The hydrogen from 0.17 and 0.18 grams of tritiated water can be fixed in one gram of polymer, using resorcinol and phenol respectively. Figure 2 shows a flow diagram for tritium fixation in bakelite analog polymers. Tritiated water is reacted with calcium carbide to form tritiated acetylene and calcium hydroxide is calcined to remove tritiated water which is recycled through the reactor. The tritiated acetylene is scrubbed to remove water before acetylene hydration in a sulfuric acid solution of mercuric sulfate. Unreacted acetylene is recycled while by-products are burned and the resultant water also recycled. Purified acetaldehyde is then mixed with resorcinol (or phenol) in an aqueous NaOH solution to form the polymer. Volatilized acetaldehyde and water are recycled. The substitution of resorcinol for phenol was found to accelerate the reaction significantly.⁽²²⁾ A 1:1mole ratio of acetaldehyde:phenol is necessary to maintain the reaction at an acceptable rate.⁽²²⁾ The optional addition of formaldehyde is suggested to completely tie up the tritiated acetaldehyde. This process is more fully described in the literature.⁽²¹⁾

FIGURE 2. Bakelite Resin Process for Tritium Fixation

FIGURE 3. Process for Tritium Fixation in Polyacrylonitrile

FIGURE 4. Process for Tritiation of Polystyrene

Status of Availability

This process can be classified as available technology. However, for tritium fixation, purification of acrylonitrile is necessary. Purification techniques exist, but are complex and expensive. Because of the problems involved in this process, an extensive process evaluation is required.

Polystyrene

Tritium can be fixed by the catalytic hydrogenation of polystyrene over nickel-on-Kieselguhr, Raney nickel, or rhodium-on-alumina catalysts. This requires a gaseous hydrogen feed, which can be produced by electrolysis of an aqueous waste.

Tritiated polystyrene prepared using either Raney nickel or rhodium-on-alumina exhibited no measurable activity loss on rinsing or leaching for four to six weeks.⁽²¹⁾ The polymer is subject to depolymerization and thermal degradation above 280°C. Total gas production and hydrogen evolution G values for polystyrene radiolysis have been measured as 0.03 and 0.02 molecules per 100 eV respectively.⁽²⁶⁾

The amount of tritiated water that can be treated by this process varies with the degree of hydrogenation accomplished. A value of 0.5 grams of water treated per gram of polymer is the upper limit of tritium fixation by this process.⁽²¹⁾

Aqueous tritium is fixed in polystyrene by a hydrogenation process as shown in Figure 4. The hydrogen feed gas produced by electrolysis of tritiated water is introduced into a reactor containing polystyrene and catalyst. Nickel-on-Kieselguhr and Raney nickel catalysts require high temperatures and high pressures for hydrogenation, which makes tritium containment difficult. A rhodium-on-alumina catalyst which is known to promote hydrogenation of aromatic compounds at atmospheric pressure could possibly be used.⁽²¹⁾ Unreacted hydrogen is removed and recycled after hydrogenation. The catalyst is filtered off, regenerated, and recycled. Hydrogenated polystyrene is treated for solvent removal prior to storage. A more complete discussion of this process is found in the literature.⁽²¹⁾

Status of Availability

Hydrogenation of polystyrene at high temperatures and pressures is available technology. However, this presents problems in tritium control within such a process. Catalysts that allow atmospheric pressure and ambient temperature hydrogenation, such as rhodium-on-alumina,

require investigation. The effect of polymerization alternatives on the properties of the product need study. Comprehensive cost estimates should be made.

Major Development Objectives - All Organic Compounds

Tritium fixation by polymeric methods appears to be best suited for concentrated tritium waste on an economic basis. In the design and evaluation of these processes, the consequences of high-level tritiated waste must be more fully evaluated. These processes are, for the most part, modifications of current industrial methods. However, their development for tritium fixation requires consideration of containment, reaction rate, and effluents. Calculations suggest that radiation damage to the polymers will be minimal. However incasements should be made and, if shown necessary, available techniques to further minimize radiolysis could be employed.

14.3.2.1.3 Hydrides

Most metals form hydrides by direct combination with elemental hydrogen, and the metallic hydrides of Zr, Ti, Hf, Y, Nb, Ta, and U have been considered for tritium fixation and disposal application.^(16,18,19,27) A good candidate hydride must be stable towards reaction with water and air, and have a low dissociation pressure. These requirements leave Zr, Ti, Hf, and Y as possible materials. The relatively high costs of the metals may restrict their use to low-volume concentrated tritium wastes, and consideration may be further restricted to the more available zirconium and titanium. The metal hydrides are reasonably well characterized and techniques for their production (with hydrogen) have received much attention.^(18,19) Zirconium hydride in particular has received considerable study. The thermal and radiation stability is found to be dependent to some extent on the hydrogen content and upon the method of preparation. Resistance to oxidation is a function of particle size, but zirconium and titanium hydride powders appear to be stable below about 300°C and, in massive form, can be heated to higher temperature.⁽²⁷⁾ No quantitative work regarding the long-term storage of tritium in zirconium hydride has been reported.

Leach testing of tritiated zirconium hydride has been reported.⁽¹⁶⁾ Samples were leached in distilled water, saturated KCl and NaCl solutions, aqueous NaOH (pH = 11), and HCl (pH = 4) for over one year. The maximum fractional activity release over this period was 5×10^{-4} in the NaOH solution. This sample was pulverized by a stirring bar, and the increased surface area resulting was presumed to contribute significantly to the leach rate. Fractional releases in the other solutions ranged from 4×10^{-5} in distilled water to 2×10^{-4} in HCl for this period.

The amount of hydrogen that can be fixed and stored by this technique depends upon the hydrogen loading of the metal. ZrH_{1.4} contains 1.5 wt %

hydrogen, or equivalently, one gram of $\text{ZrH}_{1.4}$ represents 0.015 grams of hydrogen or 0.14 grams of tritiated water. The cost of zirconium is greatly dependent on its physical form and purity. Zirconium sponge in 1970 was quoted at \$5.50 - \$13.00 per pound.⁽²⁸⁾ Waste zircaloy cladding hulls may be available for tritium fixation.

Hydrides have been used for the temporary storage of concentrated tritium. The use of uranium beds for trapping tritium gas and storage as UH_3 is currently practiced.⁽²⁹⁾ The use of zirconium hydride for hydrogen and tritium storage has been studied. The hydride is made by heating outgassed zirconium in a hydrogen atmosphere at 500 - 900°C. High hydrogen-to-zirconium atomic ratios (>1.7) resulted at 900°C, but best results were obtained with $\text{ZrH}_{1.4}$ produced at 600°C. Increasing the pressure increases the rate of hydrogen uptake, but causes more damage to the product. Other hydride systems have been studied for hydrogen storage and regeneration for fuel applications.^(30,31)

Tritiated water can be treated by this process with a preliminary electrolysis operation. A simplified process is shown in Figure 5.

FIGURE 5. HT Fixation with Metal Hydrides

Status of Availability

The basic chemistry of the metal hydrides is well established. The technology has been established in other programs. They include: the development of metal hydrides for reactor moderators and development of hydrogen storage systems for hydrogen fuel utilization. The former included the Aircraft Nuclear Propulsion Program, the SNAP program, and some LMFBF reactors. These require hydrides which are stable at high temperatures, and the data obtained are pertinent to the present program.

The hydrogen storage fuel concept requires a hydride which can be cycled at a relatively low temperature, i.e., requires a high dissociation pressure. Thus, the hydrides considered are generally of insufficient stability. However, much of the technology developed is applicable.

Although the important steps have been demonstrated on a laboratory scale, the technology required to fix 50 kg H₂O/day as might be produced from a pre-dissolver head-end process of a reprocessing plant has not been evaluated. Process development and product testing and evaluation are both needed. A minimum of about four years would be required to answer the questions outlined in the next section and provide an engineering-scale demonstration.

Major Development Objectives

The basic chemistry and metallurgy of the metal hydrides are known, especially for zirconium, one of the most attractive candidates. However, a number of process chemistry questions arise. These questions concern purity of materials required, rates of hydriding achievable, and the effects of physical properties of the hydride.

Ignition temperatures of the hydrides as a function of composition and particle size need better definition. Tritium leach rates also require further study.

Many intermetallic compounds of Zr, Ti, etc., form hydrides. The reaction rates and the hydrogen capacity are high. Unfortunately, the hydrogen dissociation pressure is generally far too high for fixation applications. Further investigations seem worthwhile. The hydrides which exist in the intermetallics seem to bear little resemblance to those of the pure metals.⁽³⁴⁾

The relatively low hazard associated with tritium is due to the short biological half-life of HTO of a few days compared to its decay half-life, 12.3 years, and to the low energy of the β -radiation

emitted. However, the introduction of a metal tritide which is insoluble in aqueous systems and dispersible as a dust introduces a different class of problem. An evaluation of this form should be made.

Scale-up and demonstration of laboratory experiments are required. These include electrolysis of tritiated water, drying and, if necessary, further purification of the hydrogen, disposal of oxygen or purification for subsequent use, testing of high vacuum systems for degassing the metals, and testing of hydriding furnaces.

The transfer of the hydrided metal to containers for shipment or storage has not been considered. It may prove feasible to carry out the hydriding in the final container. Monitoring systems for T leakage, corrosion, and helium production represent rather simple problems, but have not been evaluated.

14.3.2.2 Engineered Storage

The storage of waste tritiated water in its unaltered form requires relatively simple technology. As a process, it would consist of piping the condensed tritiated water to corrosion-resistant storage tanks for controlled storage. The tanks would be sealed, monitored and, if necessary, provided with recombiners to oxidize back to water hydrogen that is produced by radiolysis. As a method, it has application either for interim storage until separation, reuse, or fixation can be achieved, or for long term storage, i.e., until significant radioactive decay results.

Two cases must be considered. The first assumes a head-end step in the reprocessing plant which results in the total tritium throughput, about 3,000 Ci/day for a 5 MT/day plant being concentrated in a small volume of water, <100 ℓ . The second case results if the tritium becomes diluted with process water in the extraction cycles of the reprocessing plant. The volume of water released per day would be of the order of 10^4 - 10^5 ℓ , depending on the degree of recycle in the plant. The application of isotopic enrichment would, of course, convert the second case to the first. However, it is clear that different storage problems can exist with the production of as little as 10^4 ℓ /yr as compared to 10^7 ℓ /yr. Table 1 lists pertinent data for the two cases. (4,32)

Extensive water recycle in the reprocessing plant along with control of the amount vented to the stacks would permit a considerable reduction of the volume for case 2. A study by the General Electric Co. (33) considered several flowsheet modifications.

In a fuel reprocessing plant incorporating recycle, the tritium level could be maintained by periodically replacing a portion of the water inventory. The excess would either be released to the atmosphere or sent to storage. At a release level of 126,000 Ci/yr, a 1500 MT/yr plant (at 510 Ci/MT) with a steady-state concentration of 2 Ci/l would require approximately 5.7×10^6 liters. Reduction of off-gas humidity would be required to maintain the release below 126,000 Ci/yr. If a portion of the recycle water could be periodically removed to inactive storage, the required inventory storage volume would be 3.2×10^5 liters.

High-pressure steel cylinders could be considered for the low-volume use, whereas for the larger volume, very large steel tanks, 10^7 l capacity, might be employed. Storage tanks designed for adequate lifetime, and provided with necessary temperature control and monitoring, are essentially the only equipment needed.

Above-ground storage tanks of 1.2×10^7 l were proposed for water storage from nuclearly stimulated gas wells.⁽³⁵⁾ The tanks were to be constructed of carbon steel and protected from freezing by insulation and tank heaters. A lifetime of 40 years was assumed. (10^{-3} Ci/l water requires 100 yrs to decay to the MPC of 3×10^{-3} μ Ci/ml.)

In the concentrated tritium case, more care must be taken in both transfer and storage operations. For the small volumes required, the use of high-pressure steel cylinders can be considered. A type IH gas cylinder, for example, could contain 18 kg of water and provide safe storage at elevated temperatures. The volume is adequate to contain the critical volume at the critical pressure of 218.3 atm.⁽³⁶⁾

Foster and Pence examined the use of high-pressure steel cylinders for the storage of fission product noble gas⁽³⁷⁾ and concluded that the method was practical. Admittedly, other problems are faced with respect to water storage. In particular, corrosion must be evaluated.

Monitoring in the case of concentrated HTO storage would include observing radiolytic production of hydrogen and oxygen. An equilibrium pressure will be reached, the H_2 and O_2 recombining to form water. However, the reverse reactions are very complex.⁽³⁸⁾ It is desirable to promote the recombination reaction, and thus lower the pressure by providing a catalyst in the gas phase.

The potential for leakage of tritiated water will likely dictate the need for continuous radiation monitoring. Fortunately, it is a relatively simple procedure to pump the contents to a second tank in case a leak is discovered. For

transferring highly concentrated HT0, double containment transfer lines may be used. Monitoring will include the vent system, and the air flow will be controlled both as to volume (flow rate) and water content (humidity). Refrigeration or molecular sieve traps can be employed, if necessary. These would also serve for secondary containment in the case of tank failure. The worst type of accident would probably be the sudden rupture of a tank containing highly concentrated HT0. Secondary containment would be a necessity here.

TABLE 1

TRITIATED WATER PRODUCED BY 5 MT/DAY
REPROCESSING PLANT

Source	Concentrated Tritium Waste	Diluted Tritium Waste
	Condensate from Head- End Process Such As Voloxidation	Condensate from Evaporators and Acid Fractionators
Volume/day	50 ℓ (a) (50 kg)	10 ⁵ ℓ (b) (10 ⁵ kg)
Ci T/ ℓ	60	3 x 10 ⁻²
Wt T/ ℓ	6 mg	3.0 μ g
H ₂ produced (c) by radiolysis	4 x 10 ⁻³ gms/day	4 x 10 ⁻³ gms/day

(a) Volume has not been determined. Probably less than 100 ℓ /day.

(b) Approximate volume indicated for AGNS Plant. (32)

(c) Assuming a G value of 1. (See ref. 4)

A small amount of HT formation can be tolerated. Considerably more HT than HT0 can be safely released to the atmosphere. Hydrogen monitoring could be carried out in closed systems to ensure that explosive mixtures of H₂ and O₂ were not formed.

Storage of water is a normal operation, and aside from the space required, has virtually no adverse effect on operations. The environmental impact is determined by the control of leakage and provisions for secondary control.

Tank storage may be an interim procedure, serving either until the water is reused or until separation or permanent fixation is decided upon. As mentioned above, it is not unrealistic to consider storage of diluted tritiated water until tritium decay will permit its discharge.

Status of Availability

Tank storage is technically feasible, and sufficient experience is available to apply this alternative storage method. Large-scale water storage is a common industrial practice. Storage of aqueous radioactive wastes has been practiced for 30 years. The application to the present problem, which involves storage of nearly pure water, would require little innovation. Adjustment of pH to control corrosion may be the only requirement.

Likewise, gas storage in high-pressure steel cylinders has a well established history. Some provision must be made for hydrogen-oxygen recombination. Corrosion evaluations may also be needed.

Major Development Objectives

Little technical development is required. Rather, evaluation of present water storage technology and the available materials is required. Some R&D will be required to determine the extent of radiolysis for the concentrated HT0 storage case (see Table 1), and to develop the best control system.

Storage for extended periods, e.g., 100 years or greater, may require reevaluation of data on corrosion and material fatigue.

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15.0 RETIRED FACILITIES (DECONTAMINATION AND DECOMMISSIONING)

15.0 RETIRED FACILITIES (DECONTAMINATION AND DECOMMISSIONING)

Upon retirement, facilities used and contaminated in the course of fuel cycle and waste treatment operations enter the fuel cycle waste stream and must be regarded as potentially a major waste form. For example, long-term operation of a 50-reactor complex could require the building and decommissioning of 1 or 2 reactors a year, a fuel reprocessing plant every 20 to 30 years, and a mixed oxide fuel fabrication plant every 5 to 10 years.* If all of these facilities were designed and built without regard to ultimate decommissioning and were dismantled upon retirement with today's technology, it would place a major burden on waste storage and burial facilities.**

Historically, the decommissioning of worn out or obsolete radioactive facilities has been accomplished in a variety of ways: laboratories, nuclear reactors, and fuel fabrication and reprocessing plants in some instances have simply been partially cleaned up and placed in layaway, under restricted access and continued surveillance; a power reactor (Hallam) has been entombed; some facilities have been decontaminated and converted to other uses; and some have been completely dismantled and their sites prepared for unconditional release. These same alternatives, identified as 1) Protective Storage, 2) Entombment, and 3) Removal of Radioactive Components and Dismantling are recognized in Regulatory Guide 1.86⁽¹⁾ as applicable to nuclear reactors. They are potentially applicable to all Light Water Reactor (LWR) fuel recycle and waste treatment facilities.

Extremely diverse technologies are required for decommissioning contaminated facilities. Most are available today, at least in primitive form. Technological requirements include procedures and techniques for:

- removal of surface contamination (fission products, transuranics, activated corrosion products) from reactor internals, reactor heat transport systems, fuel reprocessing plant piping systems and components, etc.

* The estimated decommissioning load for a 50-reactor (LWR) complex is based on the following assumptions:

- 50 ea 1000 MW(e) LWRs, each discharging 30 metric tons (MT) fuel per year, would be serviced by 5 mixed oxide (MOX) fuel fabrication plants of 300 MT/year capacity and 1 fuel reprocessing (FRP) plant of 1500 MT/year capacity.
- Service life of the plants is estimated at 20 to 30 years for the LWRs and FRPs, 30 to 50 years for the MOX.

Estimates of waste quantities are provided in Section 2.0.

** ERDA and NRC are emphasizing the need to plan for eventual decommissioning of nuclear facilities during design and construction. For example, Appendix 6301 of the ERDA Manual contains minimum design criteria for new plutonium facilities, and Reference 20 provides the results of an ERDA-sponsored study to develop recommended design considerations for new plutonium facilities which will help to minimize D&D costs.

- remote segmentation of highly radioactive equipment, including massive reactor pressure vessels and concrete shields, which contain large quantities of neutron activation products, and massive chemical process equipment such as evaporators, dissolvers, etc.
- decontamination of structural materials such as concrete surfaces, metal cell liners, and painted surfaces
- decontamination or packaging and storage or burial of contaminated soils
- measurement of contamination levels in decontaminated facilities and potentially contaminated wastes; estimation of transuranic (TRU) content of plutonium processing facilities; and assay of TRU content of waste containers
- packaging and storage or burial of waste materials.

This section reviews the available alternatives and their related technology for the decontamination and decommissioning (D&D) of the following categories of contaminated nuclear facilities:

- Light Water Reactors
- Spent Fuel Storage Basins
- Fuel Reprocessing Plants (FRPs)
- Mixed Oxide Fuel Fabrication (MOX) Plants
- Solid Waste Interim Storage Sites
- Burial Sites

15.1 ALTERNATIVE DECONTAMINATION AND DECOMMISSIONING (D&D) MODES

Three alternatives for decommissioning contaminated LWR fuel cycle facilities have been identified in Regulatory Guide 1.86⁽¹⁾ and characterized as follows:

15.1.1 Protective Storage (Identified in Reference 1 as "Mothballing")

The facility is prepared to be left in place safely for an extended period which might range from decades to two or three centuries. In general, it may be left intact except that all fuel assemblies, solid and liquid radioactive and nonradioactive process materials, and all packaged wastes are removed from the site. Radiation monitoring, environmental surveillance, and security procedures are established with the objective of ensuring that the health and safety of the public will not be endangered.

This mode may be adopted as a permanent measure for facilities which are not contaminated with long-lived radionuclides such as ^{14}C or the transuranics, providing control until the radioactivity has decayed and the facility can be

released for unrestricted use or disposal. Or it may be adopted as a temporary measure, to delay decontamination or dismantling operations until radiation levels have dropped off significantly through decay.

The protective storage mode has a number of potential advantages over other alternatives. Among these are: 1) a lower initial cost; 2) minimum potential hazard of exposing D&D workers to contamination or radiation; 3) minimum requirements to transport radioactive materials through the public domain to an approved storage or burial site; and 4) the option for reuse of the facility.

This mode also has a number of potential disadvantages, including: 1) residual radioactivity will be more susceptible to release to the environment than with other alternatives; 2) continued operation and maintenance of building ventilation systems and other services may be required; and 3) continued surveillance will be required for years to come, with the associated costs and the need for commitment by a long-lived agency to maintain control until the radioactivity has dropped to levels acceptable for release.

15.1.2 Entombment

After all fuel assemblies, process materials and wastes are removed, the remaining highly radioactive or contaminated components (e.g., the pressure vessel and internals of an LWR) are sealed within a high-integrity structure. The end product of conversion to a non-nuclear operation is a facility or site containing radioactivity which is safely isolated from man and the environment until it decays to innocuous levels. Unrestricted access to all uncontrolled parts of the facility is possible, with restrictions in those places relating only to excavation, drilling or otherwise breaching structures containing radioactivity. Warning signs are posted, and the necessary covenants endorsed on the relevant title, deeds and survey plans. Thus this condition provides radiological safety and alternative use of the site, but does not allow unrestricted future modification or development there. It should be noted that the Nuclear Regulatory Commission (NRC) will not accept the entombment mode for reactors without a possession license and an environmental monitoring program.

The entombment mode has the potential advantages that it will be less costly than dismantling, offers much better protection against release of contamination than protective storage, and will require little maintenance or surveillance effort. It has the potential disadvantages that 1) technology is not available to assure maintenance-free containment of TRUs in an entombed structure for the hundreds of thousands of years required, and 2) if future changes in conditions should necessitate removal of radioactivity from an entombed structure, this might be difficult and costly.

15.1.3 Removal of Radioactive Components and Dismantling

As a minimum, all radioactive components and materials which exceed the criteria for unrestricted release (see Section 15.4) are removed from the site. In addition, nonradioactive components may be removed, structures dismantled, and the site prepared for an alternative use. Once all the radioactivity is gone, all restrictions on use of the site are removed.

This mode may be applied immediately after facility retirement or following a period in protective storage long enough to allow decay of the short-lived radionuclides. Potential advantages include the opportunity for unconditional use of the site or cleaned-up facility, the elimination of any residual radiological hazard, and the elimination of long-term maintenance or surveillance requirements. Disadvantages include the high cost normally associated with dismantling radioactive facilities, the large volumes of contaminated wastes requiring transport and storage or burial, and the potential exposure of D&D workers to high radiation fields or radioactive contamination.

15.1.4 Considerations in Selecting a D&D Mode

The following guidance for decommissioning ERDA facilities which are exempt from licensing is provided in WASH-1202:⁽²⁾

1. At the time facility operations are shut down, steps are to be taken to minimize the probability that residual radioactivity or chemicals could become a hazard or nuisance to employees or to the public. Examples of such steps are the defueling of reactors; the removal of stored radioactive waste containers and contaminated mobile and portable equipment; decontamination where practical and painting of exterior surfaces to fix contamination in place; and physical securing of the facility against trespass. However, these immediate shutdown steps should not be allowed to preclude or impede later decontamination and decommissioning efforts. For example, power lines and cranes necessary for the disassembly and handling of heavy equipment should not be removed nor should contaminated areas be rendered inaccessible.
2. Where facilities are excess to the needs of the AEC due to programmatic changes rather than obsolescence, their conversion to beneficial nuclear use by others should be thoroughly explored. This transfer to others may be either "as is" or after decontamination by the AEC as negotiated. The receiving organization would have to be competent to operate the facility safely, including the surveillance and control of any residual radioactivity from the prior AEC period of operation.
3. When it is unlikely that an excess AEC facility can be converted to beneficial nuclear use by others, its conversion to beneficial nonnuclear use by others is to be evaluated.
4. A categorical recommendation cannot be made as to whether conversions to beneficial nonnuclear use by others should be with or without administrative restrictions upon that use. In each case, consideration must be given to the relative costs of decontamination; the advantages of an unconditional transfer;

the adequacy of the restrictions from a public safety standpoint, including the ease of enforcement; and the possible interference of the restrictions with further use of the facility.

5. Administrative restrictions on transfer of facilities to others should be limited to those imposed because of subsurface radioactivity. In decreasing order of desirability, these are:
 - a. Reservation of mineral rights to the AEC.
 - b. Reservation of groundwater rights to the AEC.
 - c. Restrictions on disposal of liquids into the ground.
 - d. Restrictions on excavations.

Restrictions imposed on above-grade activities would be more difficult to enforce and probably more objectionable to the user; thus, transfers of facilities dependent on such restrictions should not be considered. For example, it would not be satisfactory to transfer a building containing fixed radioactive contamination, relying upon an administrative restriction in the deed or lease to assure the imposition of satisfactory safety controls in the event future building repairs or renovations might disturb the contamination.

6. In the assignment of priorities for the decontamination and decommissioning of excess AEC facilities for possible beneficial use by others, favorable weighting should be given to:
 - a. Cases where there is a specific pending application for use by others, particularly one with a highly favorable economic impact on the area.
 - b. Cases where favorable qualities of the site make future applications likely, even though none are pending.
 - c. Cases where decontamination will permit the complete release of a site, or the release of a significant portion of a large site.
 - d. Cases where decontamination and decommissioning will be more difficult at a later time because people knowledgeable about the facility will no longer be available.
 - e. Cases where experience gained in decontamination and decommissioning will be valuable in planning such activities at similar facilities or valuable in the design of new facilities, including licensed facilities.
7. The transfer of excess contaminated AEC facilities "as is" for nonnuclear use, with the recipient assuming all responsibility for either immediate or eventual decontamination, is not considered advisable and should be pursued only in unusual cases. Such transfer would require that the recipient fully understand the kind and degree of residual contamination being transferred and be sufficiently knowledgeable and financially responsible so that the decontamination can be satisfactorily accomplished without likelihood of the property reverting to the AEC.
8. Facilities which are categorized as "standby" rather than "excess" are to be periodically reviewed to assure that there is still a realistic probability that they may still be needed. If the "standby" status cannot be reaffirmed they are to be reclassified as "excess" and included in the decontamination and decommissioning planning.

9. In cases where it is unlikely that an excess contaminated facility can be converted to any kind of beneficial use by others, decontamination activities should be concentrated on significant reductions in the needs for surveillance and maintenance of the facility.

Selection of the D&D mode for a specific commercial fuel cycle facility will depend on the answers to such questions as the following:

- What type of facility is it? With what is it contaminated? What are the radiation levels?
- Where is the facility located? (For example, a reactor awaiting decommissioning may be located at a power station where a series of reactors will be built during several decades or where an advanced reactor might be built.)
- Will protective storage provide adequate safety for the public and the environment? If so, is that the most economical route to take? (Protective storage carries the lowest initial cost, but the long-term expense of providing surveillance and maintaining necessary services may be substantial--particularly as the facility deteriorates.)
- Is there any incentive to delay the making of irrevocable decisions concerning the future of the facility? (Entombment might be an attractive mode today, but have to be reversed in the future if conditions or policies should change. Entombment is difficult and costly to reverse.)
- If protective storage is implemented, how is continued maintenance and surveillance to be assured for the decades or centuries required?
- To what use will the site or residual facilities be put following decontamination and decommissioning?
- To what level must the plant or site be decontaminated?
- Does the initial plant design incorporate systems that will enhance systems decontamination--that is, can all surfaces be contacted with decontaminants at the proper conditions and under proper controls?
- Will the D&D mode selected minimize the cost/benefit ratio when such items as total real estate committed to nuclear waste storage or burial (including retired facilities), potential exposure of workers and general public to radiation, and both short-term and long-term financial costs are considered?
- Are there current regulatory criteria that apply, and what are the storage or burial requirements for the wastes that will be generated?

15.2 APPLICATIONS TO LWR FUEL CYCLE AND WASTE MANAGEMENT FACILITIES

The technology required for decommissioning a given facility depends on the disposition mode and on the nature of the facility: the accessibility, radiation levels, size and weight of equipment to be decontaminated, segmented or treated in other ways; whether the facility handled primarily TRU or beta-gamma emitters; whether it has surface contamination only, removable by surface treatment, or induced radioactivity which cannot be so removed; whether or not the facility is designed for replacement of radioactive components by standard plant maintenance techniques; the nature of the facility structure, e.g., heavy shielding walls or relatively light walls, etc.

Section 15.2 has been included in this document to describe the significant features of the various types of facilities as they pertain to D&D; to review the implications of these features for D&D planning; and to summarize past D&D experience.

15.2.1 Light Water Reactors

The main nuclear steam components of an LWR include the reactor core and other reactor internals, the reactor pressure vessel, and the heat transport system. All are located within a containment shell designed to prevent release of radioactivity to the outside. LWRs are designed for replacement of the reactor fuel and either part or all of the reactor internals. The reactor vessel, usually low-carbon steel several inches thick and lined with stainless steel, weighs hundreds of tons and must be cut into segments for removal. The vessel and primary heat transport system are shielded with concrete which is many feet thick and frequently contains iron or iron ore for higher density.

15.2.1.1 Contamination Types and Levels

- Neutron activation products from the reactor core materials are expected to be distributed throughout the reactor core and the primary heat transport system. The potential also exists for contamination of these components by TRU and fission products. The contamination and radiation levels will depend on the extent to which the system is decontaminated at the time of retirement.
- Activation products are present in all reactor components exposed to appreciable neutron fluxes, such as the reactor internals, vessel and shield. Radiation levels inside the shield may be as high as many thousands of Roentgens per hour. A few years after shutdown, all the induced activities will have decayed away except ^{60}Co (a hard gamma emitter with a 5.3 year half-life), ^{63}Ni (a weak beta emitter with a 100-year half-life), ^{14}C (a weak beta emitter with a 5730 year half-life) and ^{55}Fe and ^{59}Ni (which decay by electron capture with half lives of 2.7 and 80,000 years, respectively).

- There is a potential for low to medium-level contamination in many areas of the reactor plant.

15.2.1.2 Implications for D&D

- Much of the fission product and TRU contamination in the reactor vessel and heat transport system can be removed at the time of reactor retirement by aggressive decontamination techniques. However, such decontamination would result in large quantities of contaminated and probably corrosive liquids requiring disposal.
- If the reactor is dismantled soon after retirement, the high radiation levels which will be encountered will necessitate remote operations and use of heavily-shielded casks for transport of D&D wastes to burial or storage sites. Furthermore, the high radiation levels will pose a significant potential hazard to D&D workers. A delay of 75 to 100 years between shutdown and dismantling would give time for the decay of the ^{55}Fe and ^{60}Co and reduce the radiation levels significantly, but would probably still necessitate the use of remote methods because of the residual ^{59}Ni .

15.2.1.3 Past Experience

Various alternatives have been used for decommissioning retired nuclear reactors:

- Protective Storage

Hanford Production Reactors. Eight reactors at Hanford, all of them water-cooled, graphite-moderated and uranium metal-fueled, were shut down, partially cleaned, and placed in indefinite protective storage. In some, the power to the reactor building was shut off, thus deactivating the ventilation system--with no apparent short-term adverse effect on external contamination control.

Enrico Fermi-1 Nuclear Power Plant.⁽³⁾ The Fermi reactor in Michigan, a fast breeder reactor power plant cooled by liquid sodium, was retired; all fuel elements, blanket elements, and sodium were removed and shipped offsite; all other contaminated or irradiated materials were shipped offsite or stored in onsite restricted areas; reactor building penetrations were secured; the primary and secondary sodium systems were sealed (after passivating residual sodium); and a surveillance plan was implemented. The amount of residual activity sealed up in the primary system was estimated as 5000 curies.

- Entombment

The Hallam Nuclear Power Facility, a 75 MWe sodium-cooled graphite-moderated power demonstration reactor near Hallam, Nebraska, was

decommissioned in 1969 under a plan which provided for salvaging as much of the plant as economically feasible.⁽⁴⁾ The highly radioactive components, containing (in 1969) about 200,000 curies of ^{55}Fe , 80,000 curies of ^{60}Co , 12,000 curies of ^{63}Ni and 6,000 curies of ^{151}Sm , were stored in the basement structures of the reactor building and were sealed and protected by concrete and coal tar epoxy material. Only the primary heat exchanger building (which is included in the sealed structure) and the former decontamination building (partly sealed) remain above ground. The sodium was shipped offsite for reuse, and the parts that had been in contact with sodium were carefully treated before disassembly by reacting the sodium with water vapor in nitrogen. Residual sodium contamination on the cut-off parts was removed later by steam-cleaning using a steam lance. In the sections not dismantled the resultant sodium hydroxide was dried at high temperature to a noncorrosive solid and left in place. The site is no longer used and needs minimal surveillance. The retirement cost is cited as slightly over 3.1 million dollars.⁽⁴⁾

Similar actions have been taken with the Carolinas Virginia Tube Reactor, which has been converted to a radioactive equipment store;⁽⁵⁾ with the BONUS Power Station, which has been converted to an exhibition center;⁽⁶⁾ with the Piqua Reactor, which has been converted to office and warehouse space;⁽⁷⁾ and with the Pathfinder Reactor, which has been converted to a fossil-fueled system,⁽⁸⁾ although in this latter case the reactor still requires further D&D effort.

- Decontamination or Dismantling

Elk River Reactor. The Elk River Reactor at Elk River, Minnesota, a 53 Mwt Boiling Water Reactor, was operated for 4 years, shut down in 1968, dismantled, and the reactor site returned to unrestricted use.^(9,10) The procedures included: removal of all piping, equipment and surplus structures external to the biological shield; removal of pressure vessel internals; segmenting and removal of the pressure vessel; removal of the biological shield; removal of the reactor building; and transport of all radioactive materials to authorized burial sites outside Minnesota. The total project cost was 6.1 million dollars. Physical operations took 2 years.

The calculated radioactivity inventory was 10,000 curies, of which 1,200 curies were in the pressure vessel and 8,700 curies were in the structural components inside the vessel. The most radioactive component was the core support plate, which read about 8,000 R/hr (contact). The inner thermal shield was a 2 1/2 cm thick cylinder, 205 cm in

diameter by 365 cm high, reading a maximum of 1,300 R/hr on contact. It was sectioned into 26 segments for burial.

EBR-I. The Experimental Breeder Reactor No. 1 at the Idaho Nuclear Engineering Laboratory (INEL) was decontaminated as far as practical.⁽¹¹⁾ Those portions which could not be made safe were dismantled and removed or sealed from public access; and the facility was opened to the public as a Registered National Historic Monument.

15.2.1.4 Current D&D Planning for Future Projects

Preparations are currently being made for the D&D of the following test reactors: the Materials Test Reactor (MTR) at INEL;⁽¹²⁾ the Sodium Reactor Experiment (SRE) at Atomics International;⁽¹³⁾ and the Heavy Water Components Test Reactor at Savannah River.⁽¹⁴⁾

15.2.2 Fuel Storage Basins

Spent fuel either at the reactor or awaiting reprocessing at the fuel reprocessing plant is stored in water-filled basins deep enough (about 14 m) to permit in-basin transfer of vertical fuel bundles. They are built of massive concrete walls and floor, usually lined with stainless steel, and equipped with devices for handling the fuel elements. The basin water is circulated through heat exchangers to prevent excessive water temperatures and through ion exchangers for purification.

15.2.2.1 Contamination Types and Levels

By the time of its retirement, the underwater sections of a spent fuel storage basin may be contaminated with TRUs and fission products from leaking fuel elements, and activation products from fuel elements and the primary heat transport loop. If so, the water treatment system and heat exchangers will also be contaminated.

15.2.2.2 Implications for D&D

If the basin liner has not leaked, it will be possible to treat only the liner and the water system as contaminated. Decontamination or removal of these components and the fuel handling machinery should then allow release or demolition of the concrete structure as uncontaminated.

15.2.3 Fuel Reprocessing Plants

The features of the typical FRP which are of major significance to D&D may be summarized as follows:

- Process operations (dissolution, solvent extraction, evaporation and ion exchange) are carried out in reinforced concrete cells. The concrete may be painted with acid-resistant paint or may be lined with

stainless steel plate. The Barnwell Nuclear Fuel Plant in South Carolina has stainless steel liners at the bottoms of the cells, painted concrete above.

- The typical FRP contains large amounts of varied and complex process equipment and process piping. Some of the piping, running between process cells, is embedded in concrete.
- The plant may be designed for either remote or contact maintenance of process equipment. The Barnwell plant will depend chiefly on contact maintenance, with provisions to reduce in-cell radiation levels by thorough spraying of cell walls and external equipment surfaces.
- Most of the process equipment can be removed through the tops of the cells, using overhead cranes. Some vessels will require segmentation before they can be removed.
- A tank farm is provided for storage of liquid radioactive wastes. The tank farm includes two types of large (multihundred thousand gallon) waste tanks: those equipped with cooling coils for removal of decay heat, and tanks with no cooling for intermediate and low-level radioactive wastes.
- The FRP of the future will have facilities for waste solidification operations.

15.2.3.1 Contamination Types and Levels

All process and waste treatment equipment becomes highly contaminated by deposition of fission products and TRUs on surfaces in contact with radioactive process solutions. Cell interiors will also be contaminated as a result of leakage of process solutions. Contamination will probably be found below concrete surfaces protected only by paint. Radiation levels will be high in some cells such as those used for head-end processing, much lower in cells used for final product cycles.

15.2.3.2 Implications for D&D

- With liquid radioactive waste treatment facilities readily available, the process equipment and cells can be flushed extensively with decontaminating solutions prior to retirement of the plant.
- The potential presence of TRUs may place constraints on entombment as an acceptable mode.
- The internal structure of the high-level radioactive waste storage tanks will make decontamination by flushing difficult. Dismantling may require special techniques which have not yet been demonstrated.

15.2.3.3 Past Experience

Although no commercial scale reprocessing plant has been decommissioned completely, pertinent information has been obtained at a number of sites. For example:

- Chemical separations plants and pilot plants at Hanford have been successfully decontaminated sufficiently that they could be re-equipped for other use or locked up and kept under limited surveillance.
- Experience has been gained at Oak Ridge National Laboratory (ORNL) in pilot plant programs, involving systems for the reprocessing of irradiated fuel, in which complete systems have been decontaminated, equipment disassembled, and the site prepared for direct installation of equipment for the next pilot plant run.⁽¹⁵⁾ Similar experience has been gained at Hanford and Savannah River.
- The Metal Recovery Plant at ORNL which operated for a 9-year period, employed all the unit operations common to reprocessing plants (irradiated fuel storage and handling, dissolution, solvent extraction, evaporation, ion exchange, and product polishing). Upon its shutdown in 1959, the facility was decontaminated with mineral acids and left in a standby condition. Since that time, there has been no detectable release of any of the residual radioactivity to the environs.⁽¹⁵⁾
- The small prototype reprocessing plant at the Fontenay-Aux-Roses Nuclear Research Centre, France, was totally dismantled.⁽¹⁶⁾ This operation took about 3 years and required 150,000 man-hours. The components removed were freed from loose contamination, baled and shipped off to Saclay for storage together with the contaminated soil and building rubble. Over 3000 tons of radioactive solid waste were produced.
- Five modules of the hot canyon in one of the chemical processing plants for irradiated fuel at the Savannah River Plant were successfully decontaminated for installation of a new process.⁽¹⁷⁾ The activities included: removal of the former processing equipment; remote decontamination of canyon walls and floor using the hot canyon crane; isolation of the five modules to be cleaned from the rest of the canyon; penetration of the 1 2/3-m thick wall for personnel entry; direct decontamination as required--e.g., chipping out contaminated concrete and concrete replacement and repainting. The work was completed in 1 year at a cost of about \$150,000.

15.2.3.4 D&D Studies: Fuel Reprocessing Plants

A recent LWR fuel cycle study⁽¹⁸⁾ conducted for the NRC proposes alternative plans for the D&D of a prototype chemical separations facility, based on the design of the Barnwell Nuclear Fuel Plant in South Carolina. Each of the D&D modes is discussed. The major activities proposed for the dismantling mode are outlined below to provide an idea of the technologies required.

- The process equipment and the interior surfaces of the process cells are thoroughly flushed with decontaminating solutions, which are then boiled down in the liquid waste concentrators and dumped to the tank farm.
- The process equipment in the Process Building cells is cut loose by contact maintenance techniques (men working from a shielded working cage inside the cell), segmented where necessary, and removed through access hatches in the tops of the cells.
- Concrete surfaces in the cells are decontaminated by removal of concrete layers, using explosives, a rock splitter, or a jack hammer.
- The stainless steel liners on the cell floors are sectioned with a plasma torch into pieces which fit a shipping container.
- Other equipment in the Process Building is removed and surfaces are decontaminated.
- The fuel storage basin is drained and decontaminated, the equipment removed, and the basin lines segmented and removed.
- Each waste tank is dismantled by working from a shielded cage suspended inside the tank. The tank internals are sprayed with decontaminating solution as they become accessible. Sections of tank internals are cut loose with a plasma torch and removed. The walls of the tank are partially decontaminated and segmented.
- Remaining equipment is decontaminated and removed.
- All contaminated equipment and waste materials are packaged and transported to storage or burial sites.
- A comprehensive radiation survey is made of the remaining structures to ensure that radioactivity levels meet the unrestricted use limits set by the authority having jurisdiction.
- The remaining structures are demolished and excavations filled, using normal demolition and construction techniques.

15.2.4 Mixed Oxide Fuel Fabrication Plants

The typical fuel fabrication plant is of relatively light construction, designed to assure containment of plutonium and uranium in solution, powder, and pellet form. It is not built for high radiation level work.* All phases of pellet fabrication are conducted in ventilated enclosures, with the contaminated air filtered by HEPA filters before discharge. Process facilities may include equipment for converting feed and waste solutions to solids, powder blenders, pellet presses and grinders, sintering furnaces and scrap recovery systems. This equipment is generally designed and installed to permit replacement by standard plant maintenance operations.

15.2.4.1 Contamination Types and Levels

The process cells and equipment and much of the process area ventilation system will be heavily contaminated with plutonium and uranium. Significant beta-gamma radiation levels are not anticipated, and the neutron flux from spontaneous fission or radiation-induced nuclear reactions is not expected to cause measurable activation of process equipment.

15.2.4.2 Implications for D&D

- Since plutonium and uranium are the only radionuclides present in significant amounts, remote decontamination and dismantling operations may not be necessary, and problems of personnel exposure to high radiation fields are not encountered. Precautions must be taken, however, against inhalation, ingestion or skin contamination.
- With a ^{239}Pu half-life of 25,000 years, there is no known technology for entombing a fuel fabrication plant and assuring integrity of the containment structure until the plutonium has decayed to innocuous levels (one-quarter million years or longer).
- If a proposed NRC ruling is adopted, contaminated wastes (equipment, structural materials, etc.) which exceed the TRU-waste dividing line will have to be packaged for retrievable storage and transported to an authorized repository.
- If MOX plants can be constructed so as to permit complete decontamination of any structural surfaces which may get contaminated, and obviate the treatment of plant structures (concrete walls, etc.) as contaminated waste, D&D waste volumes will be minimized.

* For example, a fuel fabrication plant designed by Westinghouse Electric⁽¹⁹⁾ confines the processing and storage of plutonium solutions and powders to a two-story canyon area capable of withstanding any credible natural disaster or internal accident. The canyon walls and ceiling are 45-cm thick reinforced concrete; the floor and internal partitions are 20 cm thick. High radiation shielding is typically about 170 cm in thickness.

15.2.4.3 Past Experience

Much experience has been gained in the United States with the protective storage, decontamination and dismantling of plutonium facilities, using techniques which could be applied to a MOX plant. Documented examples include the dismantling of Building 12 at Los Alamos, a plutonium-contaminated air filter facility which handled exhaust air from the main plutonium processing plant for many years;⁽²¹⁾ the demolition of the P-11 building at Hanford, a plutonium critical mass facility,⁽²²⁾ at a project cost of \$265,000; the D&D of facilities at Mound Laboratory which had been used for work with ^{210}Po , ^{226}Ra , ^{227}Ac , and ^{238}Pu ;⁽²³⁾ and the dismantling of a plutonium recovery facility at the Savannah River Plant.⁽²⁴⁾

15.2.4.4 D&D Studies: MOX Plants

A recent LWR fuel cycle study⁽²⁵⁾ conducted for NRC proposes plans for the D&D of a prototype mixed oxide fuel fabrication facility patterned after the proposed Westinghouse Electric plant.⁽¹⁹⁾ Each of the D&D modes is discussed. The major activities proposed for the dismantling mode are outlined below to provide an idea of the technologies required.

- All process equipment from the canyon area is transferred to the decontamination and repair cell to be sprayed with a fixing agent and packaged for storage.
- All canyon surfaces are decontaminated. The steel cell liners are sectioned using a portable plasma arc torch, and liner segments are packaged for storage. Concrete surfaces are decontaminated where necessary by removing a layer of the surface, using a rock splitter.
- Duct work is removed and packaged, using air-operated hacksaws.
- The canyon area is isolated from the rest of the facility to prevent recontamination.
- Other process areas of the building are decontaminated in the same manner as described above.
- The building is demolished using standard techniques.
- All cavities are backfilled, to return the site to approximately the condition that existed prior to construction of the facility.

15.2.5 Solid Waste Interim Storage Sites

The features of these sites (Sections 20.0 and 21.0) of most significance to D&D are that 1) they are to be designed for retrievability of waste containers; 2) although potentially diverse in construction, ranging from surface storage pads to caverns deep in the ground, they are not nearly so complex as reactors or fuel reprocessing plants; 3) leakage of a waste container may

contaminate soils, structures, handling equipment and other waste containers. Any of the D&D alternatives defined in Section 15.1 might be applied to this type of facility. The choice will depend on the extent of the contamination, the nature and value of the structure (if any) contaminated, the proposed future use of the site, and the associated limits on residual radioactivity (Section 15.4). If the area contaminated is small, cleanup for facility reuse could be simple and cost effective. If the contamination spread is extensive and has produced high radiation levels, the problem would be much more difficult and might call for a different D&D mode.

Whatever the mode selected, experience gained in other D&D activities provides useful guidance. The technology demonstrated in decommissioning plutonium and fuel reprocessing facilities, for example, will apply to the D&D of interim waste storage structures, including concrete storage pads and buildings.

15.2.6 Solid Waste Burial Sites

Solid waste burial sites (Section 23.2) are intended to provide for permanent storage of radioactive waste materials; hence the customary treatment of a burial site which has been filled to capacity should be some type of protective storage or entombment until the buried radioactivity has decayed to unrestricted release levels (Section 15.4). Two alternatives appear appropriate:

- Release of the site for controlled public use of the surface, such as paved parking or storage areas with necessary surface water control features engineered as part of the pavement design. Revenue from the public use of such areas could be applied towards surveillance and maintenance needs, thus reducing the public burden.
- Perpetual site control with restricted access. Care of a burial site may be required over an indefinite period to protect the public from entering inadvertently or deliberately and to prevent dangerous waste products from migrating from the site.

Application of either alternative will require several actions:

- Providing a protective cover for the site to minimize the potential for human or animal penetration of the radioactive zone or for the growth of radioactive vegetation.
- Routine monitoring of the environment to assure that the radionuclides are not migrating from the site.
- Establishing a plan and funding arrangements to assure that care is provided as long as it is needed. (Reference 26 gives the results of a study commissioned by the State of South Carolina to determine the

fees necessary for long-term care and the funding arrangements needed to protect the State if the licensee ceased operations before the planned decommissioning date. Reference 27 reports on an investigation by the Task Force on "Bonding and Perpetual Care of Nuclear Licensed Activities," the objective of which "was to assemble into a single document the guidance necessary for state officials to develop bonding and perpetual care programs." The report outlines the steps needed to be taken by the states, in order to meet their financial responsibilities once these responsibilities are known. The vehicles suggested for fiscal resources are the performance bond and the trust fund.)

It is possible, of course, that removal of radioactive materials from a burial site may be required because of migration of radionuclides from the site in sufficient quantity to cause an unacceptable radiation hazard to surrounding populations or because of inordinate costs for care.

15.3 D&D TECHNOLOGY

For the most part, the protective storage and entombment modes require the use of common decontamination, maintenance and demolition techniques, with occasional modification to cope with contamination control problems. Dismantling operations also depend on common maintenance and demolition techniques. The complexity and cost of dismantling a plant are greater for radioactive than nonradioactive facilities because of the requirements for tooling for remote operation to prevent overexposure of workers, precautions to assure control of radioactive dusts and aerosols, special measures for the packaging, shipping and storage or burial of radioactive wastes, and instrumentation to determine the proper disposition of potentially contaminated wastes or salvaged materials.

Decontamination and decommissioning procedures and techniques are reviewed in a number of recent publications: a discussion of the status (as of 1974) of D&D experience and technology by Bainbridge et al.;⁽²⁸⁾ a collection of papers discussing United States D&D policy, D&D experience, and plans for future projects;⁽²⁹⁾ annotated bibliographies;^(30,31) a review of D&D experience at nuclear facilities in the U.S. as it bears on design criteria for plutonium facilities;⁽²⁰⁾ and an extensive treatment, edited by Ayres, of methods for the decontamination of nuclear reactors and equipment.⁽³²⁾

Rather than attempt to describe the available D&D technology in detail, we have chosen to present in the following sections an overview of the types of operations performed and some of the tools used, leaving it to the references to provide the details.

15.3.1 Contamination Control

Control against spread of contamination may be provided by one or a combination of the following techniques: erection of a greenhouse or air-support structure over the work area; use of fresh-air suits for workers; use of chlorinated rubber water emulsion paint as a coating for equipment, cell liners, concrete walls, etc.; use of a local exhaust system for a given operation, discharging through a HEPA filter into the building ventilation system.

15.3.2 Decontamination of Nonporous Surfaces

Decontamination of reactor heat transport systems and of chemical processing plants and cells by flushing may be desirable. Various chemical cleaners have been used for internal flushing:⁽³²⁾ solvents and detergents to remove grease, dirt and organic solvents; acids, acid salts or alkalis to dissolve oxide films; complexing agents to solubilize certain ions; surfactants; oxidizing agents to dissolve certain types of films; and reducing agents for other desirable chemical effects. If there is no intent to reuse the facility or to salvage equipment, use of corrosive decontaminants which attack the surface of the equipment may be of aid in decontamination.

External steam-cleaning, flushing or high-pressure spraying of chemical process equipment and cells may also be used, especially if the facility has provision for collection and disposal of used cleansing liquids and if contact D&D operations are to be performed later.

Removal of surface contamination from walls, floors, ceilings, service piping, etc., may be needed. Sometimes this can be done by sand-blasting or spraying with liquid cleansing agents; sometimes application and removal of a strippable paint is helpful; often scrubbing by hand, with various types of cleansers, is required.

The problem of disposing of used liquid decontaminating agents often provides a strong deterrent to their use. If there is no onsite evaporation, calcination, or liquid waste storage facility, the contaminated flush solutions must be converted to solid in some way (e.g., incorporation in concrete) and packaged for handling as solid waste.

15.3.3 Decontamination of Concrete Surfaces

Although attempts are usually made to protect concrete surfaces from contamination by use of acid-resistant paints or stainless steel liners, the paint may wear off or the liner may leak. When contamination, particularly in liquids, contacts bare concrete, it is usually absorbed and standard decontamination techniques are inadequate. In such cases, either the concrete is removed to a depth sufficient to remove all contamination, or the entire concrete wall, floor or ceiling is treated as contaminated.

Surface layers of concrete have been removed with explosives,⁽⁹⁾ jack hammer and grit blaster. These three techniques have their limitations: explosives can be used only where the force of the explosion will not damage surrounding structures, breach the containment, or spread contamination in an uncontrolled fashion; using a jack hammer on walls or ceiling is difficult; and grit blasting is slow.

15.3.4 Removal of Contaminated Equipment, Cell Liners, and Ventilation Systems

Common maintenance equipment and procedures are available for removing much of the equipment in any of the three major classes of facility. Where necessary to cut equipment loose or to section it for handling and packaging, this has been done by remote or contact use of a plasma torch, an oxyacetylene torch, a power hacksaw, a portable milling cutter, or shaped explosive charges. Where the cutting is to be done remotely, special tooling and manipulators may need to be designed for the specific task.

Cell liners may need to be cut to produce sizes small enough for packaging. The plasma torch is a useful tool for this purpose.

Many of the components can be removed and packaged by standard maintenance techniques. Duct work can be cut by hacksaw, torch or sabre saw. Mechanical cutting is compatible with prior use of a spray paint on interior surfaces or filling the duct work with expand-in place polyurethane, to control contamination.

15.3.5 Volume Reduction of Waste Materials

Reduction in the volume of contaminated waste to be stored or buried may be achieved by evaporation and calcination of liquids (Section 10.0), incineration or pyrolysis of combustibles, mechanical compaction, cutting and packing, etc. (Section 9.0).

15.3.6 Needs for Improvements in D&D Technology

The above description of D&D experience and current technology may give the impression that decontamination or dismantling of a LWR fuel cycle facility is a simple and straightforward operation. That this is not the case is evidenced by the high costs of past D&D projects and by the magnitude of the cost estimates for potential projects in the future.* The costs of dismantling fuel cycle facilities will be higher than those for most non-nuclear plants for several reasons: 1) nuclear plants generally have massive structures, usually of reinforced concrete; 2) packaging, transporting and storing or burying radioactive wastes can be a major cost item, far more costly than hauling demolition wastes to the city dump; 3) the need for remote operations,

* A detailed estimate for dismantling the Barnwell FRP⁽¹⁸⁾ indicated a cost of about 20% of the construction cost. This is considered a minimum cost which is accurate to within a factor of two.

contamination control, and maintaining a radiological surveillance and protection system add significantly to the cost; and 4) the use of manpower is generally less efficient when working under radiation zone conditions. In assessing the costs of decommissioning a nuclear plant, however, it should be remembered that only the incremental costs incurred because it is nuclear should be considered part of the nuclear burden.

The high cost of D&D activities in the past may have also resulted in part from the fact that in general, decommissioning efforts have been performed using relatively routine decontamination and demolition procedures adapted on an ad hoc basis to the specific facility being decommissioned, or by adaptations of special techniques developed for ad hoc repairs to existing facilities rather than procedures specifically designed for D&D operations.

There appears to be considerable incentive for developing improved specialized D&D technology. Areas worthy of attention include:

1. Changes in plant design to facilitate eventual decommissioning (provide easier access to contaminated areas and surfaces, easier dismantling of large equipment and structures, etc.).
2. Development of decontamination techniques.
 - simple techniques for decontamination of slightly surface-contaminated metals (or those with minor induced activity) to permit recycle and reuse rather than burial or storage
 - techniques for decontaminating (removing thin layers) porous materials, e.g., concrete
 - treatment of decontaminating agents for reuse or disposal
3. Improved methods of size reduction of large equipment, glove boxes, cell liners, plant structures, etc.
 - various types of cutting tools for metals and concrete
 - explosive techniques
4. Development of remote operations
 - special devices for remote manipulation of tools
 - improved methods of viewing remote work areas
5. Improvement of waste packaging and storage or burial
 - more efficient or economic methods for the large volume of structural materials with low-level contamination that will result from dismantling and demolition
 - improved methods of packaging solid wastes to provide zero-release systems for burial and interim storage sites

6. Increased personnel protection in high-hazard areas
7. Improved equipment for the field measurement of alpha and beta-gamma emitters, to permit certification that a site, material or piece of equipment is not contaminated at a level greater than the unrestricted release limit.

15.4 REGULATIONS AND CRITERIA

The current status of official United States guidelines and criteria for the decommissioning of LWR fuel cycle facilities to provide acceptable contamination levels in decommissioned facilities is as follows:

15.4.1 Decommissioning Guidelines

- Regulatory Guide 1.86⁽¹⁾ provides for the termination of operating licenses for nuclear reactors.
- There is no similar guide for the decommissioning of fuel reprocessing plants or mixed oxide fuel fabrication plants. The code of Federal Regulations Title 10, Part 50, Appendix F, requires that "...a design objective for fuel reprocessing plants shall be to facilitate decontamination and removal of all significant radioactive wastes at the time the facility is permanently decommissioned."
- A standard sponsored by American National Standards Committee N46 has been drafted (but not yet approved), titled "Design Criteria for Decommissioning Nuclear Fuel Reprocessing Plants (N 300-1974)." This draft standard tacitly assumes that Hallam-type entombment will be the standard throughout the spent fuel reprocessing industry. It proposes criteria to be incorporated into the design of reprocessing plants to facilitate the future decommissioning of such plants, as well as criteria for the decommissioning operation.

15.4.2 Residual Contamination Criteria

Planning for D&D of a nuclear facility is dependent upon the maximum permitted levels of residual radioactive contamination. Regulatory Guide 1.86⁽¹⁾ prescribes (Table 15.1) acceptable surface contamination levels for the termination of operating licenses for nuclear reactors; these values may be reasonably extrapolated to surface contamination in other fuel cycle facilities, but do not provide guidance for situations wherein a mass is contaminated--such as soil or a porous concrete wall.

Universally accepted standards for maximum permitted levels of transuranic contamination in the environment do not exist as yet. Various limits, usually

TABLE 15.1. Acceptable Surface Contamination Levels

Nuclide ^(a)	Average ^(b,c)	Maximum ^(b,d)	Removable ^(b,c)
U-nat, ²³⁵ U, ²³⁸ U, and associated decay products	5,000 dis/min α-100 cm ²	15,000 dis/min α-100 cm ²	1,000 dis/min α-100 cm ²
Transuranics, ²²⁶ Ra, ²²⁸ Ra, ²³⁰ Th, ²²⁸ Th, ²³¹ Pa, ²²⁷ Ac, ¹²⁵ I, ¹²⁹ I	100 dis/min-100 cm ²	300 dis/min-100 cm ²	20 dis/min-100 cm ²
Th-nat, ²³² Th, ⁹⁰ Sr, ²²³ Ra, ²²⁴ Ra, ²³² U, ¹²⁶ I, ¹³¹ I, ¹³³ I	1,000 dis/min-100 cm ²	3,000 dis/min-100 cm ²	200 dis/min-100 cm ²
Beta-gamma emitters (nuclides with decay modes other than alpha emission or spontaneous fission) except ⁹⁰ Sr and others noted above	5,000 dis/min β,γ-100 cm ²	15,000 dis/min β,γ-100 cm ²	1,000 dis/min β,γ-100 cm ²

- Where surface contamination by both alpha- and beta-gamma-emitting nuclides exists, the limits established for alpha- and beta-gamma-emitting nuclides should apply independently.
- As used in this table, dis/min (disintegrations per minute) means the rate of emission by radioactive material as determined by correcting the counts per minute observed by an appropriate detector for back-ground, efficiency, and geometric factors associated with the instrumentation.
- Measurements of average contaminant should not be averaged over more than 1 m². For objects of less surface area, the average should be derived for each such object.
- The maximum contamination level applies to an area of not more than 100 cm².
- The amount of removable radioactive material per 100 cm² of surface area should be determined by wiping that area with dry filter or soft absorbent paper, applying moderate pressure, and assessing the amount of radioactive material on the wipe with an appropriate instrument of known efficiency. When removable contamination on objects of less surface area is determined, the pertinent levels should be reduced proportionally and the entire surface should be wiped.

based on the range of lower detectability for field survey instruments, have been recommended (and used) for the decontamination of soil containing plutonium. For example:*

- In the Palomares incident the Air Force established, in conjunction with the Spanish Government, these criteria:⁽³³⁾

<u>Contamination in the Top 1 cm</u>	<u>Action</u>
>4700 dis/min-g of dry earth	Top 10 cm removed and packaged for disposal in the U.S.
470 to 4700 dis/ min-g of dry earth	Area plowed to a depth of about 30 cm.

- In 1968 a proposal was published by Kathren recommending an interim permissible surface contamination level, due to plutonium oxide, that was equivalent to 10 dis/min-g earth.⁽³⁴⁾ This proposal was based on limitation of maximum permissible individual dose and not on limitation of overall general public exposure.
- The State of Colorado in January 1973, imposed an emergency interim standard for plutonium in the soil of 0.2 dis/min-g of dry soil. Sites exceeding this limit were not to be used for residential or business construction. This limit was later increased by a factor of 10, to 2 dis/min-g, which remains presently in force. Areas which exceed this limit must first be plowed or decontaminated by stripping before a building permit will be issued for a residential or a business structure.
- Healy has recommended the interim standard shown in Table 15.2 for plutonium in soils.⁽³⁵⁾
- Waite and Jenkins⁽³⁶⁾ have proposed a methodology for development of site release criteria which ties the allowable residual contamination level to the intended use of the site. They applied the methodology to the case of a plutonium facility and recommended the limits shown in Figure 15.1.

* For comparison, naturally occurring alpha-emitters (uranium and thorium series) will typically be present in concentrations of 1 to 10 dis/min per gram dry earth, although much higher concentrations can be found in ore-bearing areas.

TABLE 15.2. Recommended Interim Standards for Plutonium in Soils

	In <100 μm Particle Size Fraction			Total (a)		
	dis/ min-g	$\mu\text{Ci/g}$	$\mu\text{Ci/m}^2$	dis/ min-g	$\mu\text{Ci/g}$	$\mu\text{Ci/m}^3$
Top 0.1 cm (b)	500	2×10^{-4}	0.4	1,000	4×10^{-4}	0.8
Any 1-cm Layer	500	2×10^{-4}	4	10,000	4×10^{-4}	8

- a. With the provision that the fraction with particle sizes less than 100 μm is known not to exceed the limits given. If this is not known, the values for the <100 μm fraction should be applied to the total.
- b. For bare soil or areas with sparse vegetation. Where the area is reasonably well vegetated (greater than 50% of the area is covered with low vegetation) and a reasonable root mat exists to hold the soil, the concentration listed can be applied to a 0.5-cm layer, which would permit up to 2 $\mu\text{Ci/m}^2$ in this layer.

	SURFACE CONTAMINATION	ACTIVITY/MASS CONCENTRATION
UNRESTRICTED	220 dis/min-100 cm^2 fixed 220 dis/min- m^2 smearable	10 pCi/g
CONDITIONAL (NONSURVEILLANCE)	2,200 dis/min-100 cm^2 fixed 220 dis/min- m^2 smearable	100 pCi/g
CONDITIONAL (SURVEILLANCE)	22,000 dis/min-100 cm^2 fixed 220 dis/min- m^2 smearable	1 nCi/g
RESTRICTED	22,000 dis/min-100 cm^2 fixed 220 dis/min- m^2 smearable	>1 nCi/g

FIGURE 15.1. Disposition Criteria Matrix

15.5 COMMENTS ON MAJOR D&D ISSUES

The future contribution of nuclear facility D&D activities to the overall waste management problem may in general be characterized by the following:

1. Decommissioning will not lead to quantities of waste radionuclides which, in properties or magnitude, pose any new or major problems.
2. D&D could possibly lead to volumes (as distinct from curies) of radioactive waste posing new or major problems. Perhaps problems could arise, for instance, from a need to change the configuration of large objects to make transport easier; or transitory materials handling problems could be encountered if the waste from multiple large D&D projects should hit a repository all at once.
3. D&D could lead to a major increase in the number of different sites at which significant volumes and curies of radioactive wastes are stored or buried more or less indefinitely if entombment is accepted as a decommissioning mode.

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16.0 MODIFICATION AND USE OF SELECTED FUEL REPROCESSING WASTES

16.0 MODIFICATION AND USE OF SELECTED FUEL REPROCESSING WASTES

Technical alternatives for treating high-level waste described in this section are:

- potential beneficial applications of selected waste constituents
- technical considerations in waste fractionation recovery for selected fission products and actinides
- energy recovery utilizing the bulk solidified waste
- waste partitioning to remove the actinides and reduce the long-term risk.

Fractionation and partitioning are generally synonyms for recovering elements, or groups of elements, from a feed stream as purified fractions. For this section, however, fractionation refers to the recovery and purification of waste constituents for beneficial uses; partitioning refers to actinide recovery and purification for eventual elimination in order to reduce the long-term risk associated with isolating the high-level waste from the environment. The general features of these alternatives are described in Sections 16.1 through 16.3. Section 16.4 describes the partitioning alternative in greater detail.

16.1 POTENTIAL BENEFICIAL APPLICATIONS OF HIGH-LEVEL WASTE

There are a wide variety of uses for many of the fission product and heavy element isotopes found in spent LWR fuel elements.⁽¹⁾ Many proposals have been made for using various fission products, as well as the bulk solidified wastes for heat and radiation sources. The isotopes ^{90}Sr , ^{137}Cs , ^{244}Cm , and ^{147}Pm , for example, can all be used as heat sources.⁽²⁾

Technetium-99 can be used as a corrosion inhibitor, alloying agent, or semiconductor. Ruthenium-106 can be used as a heat source, while palladium and rhodium have value as chemical catalysts as well as other industrial uses. Cesium-137, a gamma source, could be used to sterilize food or sewage.^(3,4) Plutonium sources were used in the SNAP program to provide a highly reliable energy supply for the space probes to Mars, Jupiter, and beyond. In addition, there are many other beneficial uses for both the fission products and actinides present in spent fuels.

Many of these uses would consume only small amounts of the particular constituent produced annually by a growing nuclear economy; therefore, they are not important technical alternatives, since most of the constituent would remain in the waste. All conceivable needs for these materials could be met easily on a "campaign" basis and with relatively little impact on the nuclear economy or the fuel reprocessor.

Other potential uses would require virtually all the constituent produced annually, and their large-scale recovery would have a significant impact on the nuclear power industry, waste management, and, possibly, even the national economy. Ultimately, the decision to recover a constituent on a large scale should be based on a detailed risk-cost-benefit analysis that considers the risks of radiation exposure to man; this is in contrast to the economic value of the particular beneficial use of the constituent, as well as the additional costs to the fuel reprocessor and waste management. Such a balanced study has not been made.

Among the elements present in high-level waste, the following stand out as prime candidates for large-scale recovery:

- Palladium, rhodium, ruthenium, and technetium for mineral resources. The annual production of palladium by the nuclear power industry in 1992 should equal about one-half the total sales to the U.S. consuming industries in 1972. The annual production of rhodium in 1986 should exceed the total annual sales to all U.S. consuming industries in 1972. The annual production of ruthenium and technetium, as by-products of nuclear power generation, is expected to greatly exceed the U.S. demand. Because of their radioactivity, these products must either be aged prior to sale or, where this is infeasible, their use confined to those industrial applications where accountability can be rigorously maintained.
- Cesium, strontium, cerium, promethium, curium, and americium. These elements may be useful for heat or radiation sources in unusual applications or in remote areas. All the cesium produced could be used to irradiate and sterilize sludge. The demand for the remaining elements, largely military, can probably be met on a campaign basis. Because of their radioactivity and, in some instances, their chemical toxicity, the use of these materials must be tightly controlled.

It has been suggested that the fission products are valuable energy resources in themselves.⁽²⁾ The results of straightforward calculations shown in Figure 16.1-1, which were based on information obtained from References 5-7, indicate this assumption is incorrect if the constituents recovered are used simply for their heating value and in conventional circumstances. Actual operating experience at Hanford indicates that for each joule theoretically recoverable directly from strontium and cesium heating sources, approximately 17 J are consumed in chemical processing. A net energy loss is also associated with the recovery of the other fission products shown in Figure 16.1-1, although utilization of the bulk solidified waste (BSW) may result in a net energy gain. The recovery of uranium and plutonium results in a large energy gain.⁽⁶⁾

FIGURE 16.1-1. Estimated Energy Recoveries for Selected Fission Products

However, Figure 16.1-1 is not a representative energy balance statement for the fission products shown if they are put to unusual uses or utilized in remote areas for heating value. In particular, if a cesium radiation source is used to sterilize and recover sludge, there may actually be a net energy gain associated with its recovery and utilization when the heating value of the sludge is considered.

Similarly, if a strontium source is used for remote applications and is unattended as a heat source (e.g., in the Arctic regions), then the fuel savings for the maintenance and periodic refueling of a conventional energy source should be credited to the strontium energy balance. These secondary energy benefits from the recovery of particular fission products were not considered in Figure 16.1-1. When they are considered, a net energy recovery may be associated with some of the fission product recoveries; at best, the amount recovered will be small. Under no circumstances should the fission products be generally treated as energy resources comparable to uranium and plutonium.

More than 40 elements are in the high-level waste. The large-scale recovery of different combinations of these elements represents distinct technical alternatives with different processing and management requirements, and may result in various beneficial uses. The solidification and final storage of all waste now in existence do not significantly diminish the fuel reprocessor's ability to meet future demands for waste constituents in a growing nuclear economy, since large quantities of fresh waste will be generated annually. However, many uses are in competition with each other for the constituents; for example, the beneficial utilization of actinides is in competition with their immediate elimination to satisfy partitioning objectives.

16.1.1 Characterization of Various Technical Alternatives

Rather than enumerate all the alternatives, the qualitative characteristics associated with four distinct management and utilization directions are summarized below. The results define the broad trade-offs which occur between waste management and beneficial utilization or waste elimination.

1. Alternative: Solidify all existing and future high-level waste, place in final storage as soon as possible, and terminate any attempts at beneficial utilization or transmutation.
Results: Minimizes retrievable storage, waste dispersion and mobility, transportation requirements, and short-term safety risks. Simplifies waste management. Waste constituents are not made available. Long term, high-level waste radiotoxicity is not reduced.
2. Alternative: Partition and transmute actinides. Solidify all existing and future high-level waste residuals; place in final storage.
Results: Minimizes liquid waste inventories and long term, high-level waste radiotoxicity. Increases retrievable storage, waste dispersion transportation requirements, and short-term safety risks. Complicates waste management. Actinides are made available for beneficial uses.
3. Alternative: Begin limited solidification of some existing high-level waste based on its composition and most logical beneficial use. Part goes to final storage, part to beneficial uses. Continue the limited recovery of certain elements on a campaign basis as market demand is proven.
Results: Increases retrievable storage, waste dispersion and mobility, transportation requirements, and short-term safety risks. Complicates waste management. Waste constituents are made available.

4. Alternative: Neither solidify high-level waste nor place it in final storage. Expand recovery of all waste constituents for beneficial uses regardless of demand. Hold in retrievable storage. Partition and eliminate excess actinides from environment.

Results: Greatly increases retrievable storage, waste dispersion and mobility, transportation requirements, and short-term safety risks. Greatly complicates waste management. Excess waste constituents may be available. Minimizes long term, high-level waste radiotoxicity.

16.2 TECHNICAL CONSIDERATIONS IN WASTE FRACTIONATION

With these alternatives, elements or groups of elements in the high-level waste are recovered and purified. The purified, encapsulated products are used beneficially, or are prepared for transmutation or elimination by some other means, such as extraterrestrial disposal. The recovery and purification steps are envisioned as additions to an existing fuel re-processing plant designed for the economic recoveries of uranium and plutonium. Each recovery and purification sequence will involve at least four distinct steps:

1. crude product recovery
2. primary product purification
3. secondary product purification
4. product encapsulation and inspection.

Both fractionation and partitioning aggravate the short-term management problems, as compared to those existing when the waste is contained in one place. The recovery of selected waste constituents, such as cesium and strontium, does not significantly reduce the cost of managing the high-level waste residual.⁽⁸⁾ In addition, the terrestrial beneficial utilization of waste, regardless of its form, is a type of interim retrievable storage. It does not eliminate the waste from the environment, nor solve any waste management problems. An inventory must be maintained of all waste constituents utilized; eventually, all materials must be returned to a responsible authority for final storage or elimination.

The following characteristics appear to be most important with respect to the large-scale fractionation or partitioning of some or all of the waste constituents.

- Increased production of secondary wastes. Although the chemistry associated with the recovery of various elements is quite diverse,⁽⁹⁾ the secondary waste production from the recovery operations is highly correlated. The Hanford experience shown in Table 16.2-1 is typical

TABLE 16.2-1. Volume of Wastes Generated by Recovering 95% of the Cesium and 70% of the Strontium from 1 Liter of High-Level Waste

<u>Type of Waste Generated</u>	<u>Volume, Liters</u>
Secondary high-level aqueous waste, 8% solids	2.76
Low-level aqueous waste	0.10
Solid high-level waste (failed equipment)	0.04
Solid low-level waste (paper, misc. items)	<u>0.04</u>
Total waste	2.94

of what can be expected in terms of secondary waste volumes. These secondary wastes must be recycled or otherwise managed. Although a reduction in the high-level waste volume may be possible for some element recoveries, for many others this waste volume will be increased because of the addition of salting agents or other nonvolatile species during recovery. It is also expected that many chemical additives required for recovery will adversely affect any subsequent high-level waste solidification efforts.

- Increased transportation requirements. All elements isolated in fuel reprocessing must be transported to the beneficial utilization site and eventually returned. Many elements can only be transported safely with extensive shielding. For partitioning and transmutation, the actinides must be recycled between the fuel reprocessing plant and the transmutation reactor sites many times before they are eventually converted to fission products.
- Increased mobility of residual waste. A complete technical analysis of this problem is not available; however, many chemical additives will increase the leachability of any waste glass subsequently produced, and thereby increase the risks associated with final storage.
- Increased accountability requirements.

16.3 ENERGY RECOVERY FROM BULK SOLIDIFIED WASTE (BSW)

It has been suggested that the heat present in canisters of solidified high-level waste could be used to produce 177°C saturated steam.⁽¹⁰⁾ The steam plant would be located in some relatively secure area such as an army base. The plant cost could be minimized if temperature-safe elements are

formed by solidification of 4-year-old waste. The canisters would be utilized in the steam plant for 10 years and then sent to final storage.

This alternative is equivalent to retrievable storage of solidified waste for 10 years, followed by final storage of the canisters. Three characteristics result:

1. increase in canister transportation requirements
2. possible increase in canister damage due to the steam plant environment
3. increased accountability requirements.

16.4 PARTITIONING OF ACTINIDES FROM HIGH-LEVEL LIQUID WASTE

Present nuclear fuel reprocessing technology recovers about 99.5% of the uranium and plutonium in spent fuel. Most of the unrecovered uranium and plutonium, and essentially all of the other transuranium elements, are contained in the high-level waste.

These actinides have half-lives longer than all but a few of the fission products. After decay times of about 800 to 1000 years, the actinides contribute more than 90% of the waste radioactivity. A waste management alternative, with the objective of reducing potential long-term risks by reducing the amounts of actinides in wastes, is to process the high-level waste to remove the actinides. This concept is called partitioning.

This section describes alternative technologies for partitioning high-level waste. To be effective in reducing long-term risk, partitioning should be accompanied by an operation that eliminates the recovered actinides from existence on earth, or by a disposal method that is available and superior to other disposal alternatives because the actinides were separated. Elimination and disposal alternatives are described in Volume 4.

Studies of the feasibility of partitioning actinides from high-level waste resulting from current LWR fuel reprocessing technology have been carried out in the U.S. at Battelle Northwest Laboratories and at Oak Ridge National Laboratory,⁽¹¹⁻¹⁶⁾ and in Europe by EURATOM-Ispra.⁽¹⁷⁾ Partitioning of high-level waste generated at facilities owned by the Federal government has also been studied.⁽¹⁸⁻²⁰⁾ However, process development studies on partitioning have not yet progressed to the point where it is possible to determine cost-benefit tradeoffs. Laboratory-scale studies with synthetic wastes and conceptual material-balance flowsheets indicate that the chemistry required for the actinide separations (with the possible exception of plutonium) is theoretically feasible. Much additional development work would

be needed to select the best combination of chemical steps and to demonstrate feasibility in an integrated, high-radiation level pilot plant.

Technical feasibility studies⁽¹³⁻²²⁾ indicate that separations based on solvent extraction, ion exchange, and scavenging precipitation (or some combination of these methods) have the greatest potential in actinide partitioning. Many difficult problems will have to be solved before processes based on these methods can be developed. The most important of these appear to be:

- increasing plutonium recovery
- development of a satisfactory process for americium and curium removal
- devising methods for avoiding actinide losses to insoluble residues from fuel dissolution and to solids generated in subsequent processes
- adequate recycling of waste streams generated in partitioning.

These problems are largely interrelated. Also, the magnitude of the problems in relation to each other are dependent on the degree of the actinide removal sought; this, in turn, is an important factor in determining the choice of the separations method. Additional studies are needed to determine the degree of actinide removal and actinide product purity which will benefit waste management.

The most troublesome chemical problems in actinide partitioning are associated with the removal of plutonium, americium, and curium. The chief difficulty with plutonium lies in the need to maintain it in an extractable form at very low concentrations. The major difficulty in americium-curium processing is in effecting the removal of these elements without generating large quantities of radioactive chemical reagent wastes. In addition to the problem of plutonium inextractability from waste solutions, sufficient information has not been obtained relative to plutonium content and nature of the solids generated in spent fuel reprocessing. Much work is needed to define the scope of the solids problem and to develop methods for preventing plutonium losses to these solids. Material-balance flowsheet studies show that actinide partitioning will require extensive recycle. Demonstration that this recycle can be accomplished will require conclusive proof that none of the steps involved will lead to a buildup of impurities which could cause process failure. There is only a very limited amount of experience concerning the operation of a radiochemical plant which utilizes extensive recycle of the waste streams.

The optimum processing sequence for partitioning of the individual actinides has not been established. One of the more recent studies indicates it may be desirable to accomplish partitioning by a combination of modified Purex processing in the reprocessing plant and secondary (or adjunct) processing of the high-level waste (Figures 16.4-1, -2).⁽¹⁴⁾ According to this concept, removal of uranium, neptunium, and most of the plutonium is accomplished by adding an extra extraction cycle in the Purex process. The high-level wastes are then stored for several years to reduce the radiation damage to process reagents, solvents, and ion exchange resins in the subsequent processing. In the next step, any remaining inextractable plutonium and the plutonium daughter from curium decay would be removed. The americium, curium, and remaining transuranic elements would be isolated following final removal of the plutonium. Insoluble residues from fuel dissolution or solids generated in the processing would be separated in feed clarification steps and treated, where necessary, to reclaim the actinide values.

FIGURE 16.4-1. Conceptual Processing Sequence for the Removal of Actinides

FIGURE 16.4-2. Conceptual Flowsheet for Solvent Extraction Processing of Irradiated LWR Fuel, with Waste Fractionation and Recycle of Heavy Metal and Nitric Acid Values

The separations methods discussed in this section are confined to those involving separations from aqueous solutions containing nitric acid and metal nitrates. Separations based on other systems, such as chloride salts, pose serious corrosion problems; in addition, they show no clear superiority over the nitrate system now in use.

16.4.1 Solvent Extraction

Technical feasibility studies have not yet shown that a simple solvent extraction flowsheet can be developed for partitioning all of the actinides. Results to date indicate that a multistep solvent extraction process based on more than one solvent has the greatest probable chance of success. Also, solvent extraction has many possibilities in partitioning when used in combination with other methods, such as ion exchange. Solvent extraction processes are potentially applicable to the following separations in waste partitioning:

- removal of uranium, neptunium, and plutonium

- separation of the americium, curium, higher transuranic elements, and the lanthanide elements from the other fission products
- separation of americium, curium, and higher transuranic elements from the chemically similar lanthanide fission products.

16.4.1.1. Uranium, Neptunium, and Plutonium Partitioning

Tributyl phosphate (TBP), which is used in the Purex process, has been demonstrated on a plant scale for the separation of uranium, neptunium, and plutonium from the other fission products. Uranium,^(12,21) neptunium,⁽²²⁾ and plutonium⁽²¹⁾ recoveries of up to 99.9, 90 to 95, and 99.8%, respectively, have been demonstrated in processes which employ TBP as the extractant. Many other solvents have the same potential capability, but none of these solvents has yet replaced TBP in large-scale applications where high-radiation levels are involved.^(11,14,23) Therefore, TBP is the leading solvent candidate for partitioning uranium, neptunium, and plutonium from wastes.

Modifying the Purex process to include the separation of americium-curium and higher transuranic elements from all fission products does not appear feasible. However, modifications may be possible which permit its use as a process step in americium-curium separations. Studies at Savannah River Laboratory have shown that TBP extraction from solutions heavily salted with metal nitrates and of low acidity can be used to separate the trivalent actinide and lanthanide elements from the light lanthanide and other fission product elements.⁽²⁴⁾ About 95 to 99% of the americium-curium is recovered by this process. Recycle of a significant fraction of the metal nitrate salts would have to be developed to adapt this process for use as a step in waste partitioning.

A number of solvents other than TBP have been reported that are capable of extracting uranium, neptunium, plutonium, and americium-curium along with the lanthanide fission products. However, satisfactory methods are yet to be developed that permit selective stripping of the solvents in which separations of the actinides from each other and from the lanthanide fission products are accomplished. Solvents having the greatest potential in this respect are the bidentate organophosphorous compounds^(18,20) and di(2-ethylhexyl)phosphoric acid.^(11,14)

16.4.1.2. Americium-Curium Partitioning

Solvents having the greatest potential in partitioning americium and curium are tributylphosphate,⁽²⁴⁾ di(2-ethylhexyl)phosphoric acid,⁽²⁵⁻²⁸⁾ bidentate organophosphorous compounds,⁽¹⁸⁻²⁰⁾ and dibutylbutyl phosphonate.⁽²⁹⁾

Additional research and development will be required to develop processes based on these solvents that are satisfactory for waste partitioning. Because of the nearly identical chemical properties of the trivalent actinide and lanthanide elements, solvent extraction separations depend on selective stripping of the actinide elements after coextraction of the trivalent element mixture. Aqueous solutions of organic complexing agents (partially neutralized with sodium or ammonium hydroxides) at low acidities are employed for stripping.

The selective stripping methods depend on first separating the trivalent element mixture from other troublesome fission products such as zirconium and noble metals. The Talspeak process, which uses di(2-ethylhexyl)phosphoric acid, is the most extensively studied of the processes that employ this selective stripping (or preferential extraction) concept.⁽²⁵⁻²⁷⁾ However, di(2-ethylhexyl)phosphoric acid has not been shown to be a suitable solvent for preparing a satisfactory actinide-lanthanide feed solution for the process. Recent studies indicate the bidentate organophosphorous compounds may be the leading candidate solvents for preparation of suitable feed solutions of the trivalent actinide mixture.⁽¹⁸⁻²⁰⁾ These compounds require neither chemical additions nor low acidity to effect the separations.

16.4.2 Ion Exchange

Cation exchange processes may be viable methods for partitioning americium-curium from high-level waste if certain problems regarding recycle of process waste streams and satisfactory disposal of spent resin can be solved.^(11,14,16,28) Evaluation of the ion exchange literature indicates that potential methods based on anion exchange resins exist for plutonium and neptunium separations.⁽¹¹⁾ However, these anion exchange methods have not been applied to high-level waste partitioning.

16.4.2.1. Plutonium and Neptunium Removal

Anion exchange is an alternative to solvent extraction of these elements by TBP in secondary processing of the high-level waste. Although TBP extraction may, perhaps, be superior in facilitating recycle of process waste streams, inextractability problems with plutonium may be less severe in ion exchange separations. Separations results and absorption coefficient data reported in the literature indicate that high plutonium recoveries are attainable from nitric acid solutions. Research and development work is needed to establish the advantages and disadvantages of anion exchange processes for the partitioning of high-level waste.

16.4.2.2. Americium-Curium Removal

Laboratory-scale studies with simulated wastes have indicated that americium-curium can be partitioned by the use of two ion exchange steps;^(14,16) the potential recovery capability of the process appears to be 99.9%, or greater. First, the lanthanides, actinides, and some of the other fission products are sorbed on a cation exchange resin column and selectively eluted with nitric acid. The actinides and lanthanides are then separated by cation exchange chromatography on a second column.⁽³⁰⁻³²⁾ The cation exchange chromatographic method utilizes aqueous solutions of organic complexing agents (partially neutralized with sodium or ammonium hydroxide) to effect the actinide-lanthanide separation. Conceptual flow-sheet studies indicate that the problems remaining to be solved with this ion exchange process are the development of:^(14,16,28)

- satisfactory processes for converting the actinide-bearing ion exchange resin wastes to forms acceptable for waste disposal
- methods for treating or recycling the waste streams generated in the chromatographic separation.

16.4.3 Precipitation

Although solids handling in remote operations is generally to be avoided, precipitation methods may be advantageous in waste partitioning when used in conjunction with ion exchange or solvent extraction. Methods for obtaining a crude concentration of plutonium, americium, curium, and lanthanide fission products from high-level waste by oxalate precipitation are under investigation at EURATOM-Ispra.⁽¹⁷⁾ The actinides would be separated from the lanthanides in subsequent ion exchange or solvent extraction steps. A decontamination factor of about 10^3 is obtained for plutonium, americium, and curium in laboratory studies with the use of tracer levels of these elements in simulated high-level waste. At ORNL, a study is being made of oxalate precipitation coupled with ion exchange as a possible method to isolate a moderately pure concentrate of the lanthanides and trivalent actinides.⁽¹⁶⁾ About 95% of the lanthanides and trivalent actinides are removed by one precipitation stage, and the quantity remaining unprecipitated is removed on a cation exchange column. Tracer-level studies show that greater than 99.9% overall recovery of americium-curium is achieved. Essentially complete removal of americium-curium has also been demonstrated using multiple stages of oxalate precipitation in which lanthanide carrier elements are added.⁽¹⁶⁾ Further work on oxalate precipitation is required to adequately evaluate the solids handling problem and to determine the effects of radiation on the stability of these precipitates.

16.4.4 Current Status

The net benefits, technical feasibility, and costs of partitioning actinides from high-level waste are yet to be established. Assuming that partitioning is feasible and that the net benefits justify its use, about 15 years will be required to develop and demonstrate a satisfactory partitioning process in an integrated, high-level radiation pilot plant.

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