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CHEMICAL ENGINEERING DIVISION

FUEL CYCLE PROGRAMS PROGRESS REPORT

January—September 1977

by

M. J. Steindler, Milton Ader, R. E. Barletta, G. J. Bernstein,
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A. A. Ziegler, D. S. Webster, and Leslie Burris



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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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ABSTRACT

Fuel-cycle studies reported for this period include pyrochemical separation of plutonium and americium oxides from contaminated materials of construction such as steel. When slag and actinide-contaminated metal in the same process vessel are heated until liquified, the actinides are partitioned to a high degree into the slags. Also, studies of advanced solvent extraction techniques are focussed on the development of centrifugal contactors for use in Purex processes. A miniature contactor is to be used for performance studies applicable to larger units. In other work, literature on the process chemistry of zirconium and ruthenium has been reviewed to aid in improving the process when short-residence-time contactors are used. In addition, a review of information on the dispersion of reagents and products during accidents in fuel reprocessing facilities has been initiated to develop systematic data useful in identifying source terms.

A review and evaluation of the encapsulation of high-level waste in a metal matrix is continuing. The data will be used to identify the state of the art and the importance of selected features of this process. In other work, criteria for the handling of hulls are being developed on the basis of past work on the pyrophoricity of zirconium alloys and related criteria from several sources. These suggested criteria will be assembled with the necessary technical rationalization into a package for review by interested parties. Other work consists of a brief program to explore the disposal of noble gas fission products by deep-well injection and laboratory-scale experiments to study the migratory characteristics of nuclear waste confined in geologic formations.

SUMMARY

Development of Advanced Solvent Extraction Techniques

Parallel programs are under way to develop advanced solvent extraction techniques for Purex reprocessing of LWR and FBR fuels.

The LWR program for developing advanced methods of separating uranium and plutonium from fission products is being carried out in cooperation with

Savannah River Laboratory and comprises (1) the development of a full-scale centrifugal contactor and miniature annular centrifugal contactors, (2) the investigation of the kinetics of ruthenium and zirconium extraction with the objective of improving decontamination from these fission products in short-residence contactors, and (3) the investigation of plutonium reduction kinetics.

A single-stage miniature contactor has been built and has been used for studying contactor performance, as well as extraction kinetics, at mixing times as low as 1 s. Tests under various conditions of rotor speeds and throughputs have demonstrated throughputs as high as 160 mL/min at rotor speeds between 6000 and 9000 rpm. Nitric acid-uranyl nitrate solutions were extracted into 30% tri-n-butyl phosphate in n-dodecane with efficiencies exceeding 96%.

An eight-stage miniature annular centrifugal contactor has been built. Preliminary tests have demonstrated excellent mechanical performance at rotor speeds up to 7000 rpm and good hydraulic performance at a throughput of 80 mL/min and 5000 rpm.

Studies of zirconium extraction in a single-stage miniature contactor show that in ~ 4 s of contacting, extraction is about 60% of that in 5 min and about 50% of that in 1 h.

A literature review has been conducted to evaluate various reducing agents for the reduction of Pu(IV) to Pu(III) for the partition of plutonium and uranium in short-residence contactors. Several quinones show promise for this application.

The FBR program includes the development of a critically safe annular centrifugal contactor sized to process 0.5 Mg/d of fuel. Fabrication of this contactor is nearing completion. An existing contactor test facility is being modified to permit installation of the unit for mechanical and hydraulic performance testing.

The program also includes work on solvent damage by radiolysis and hydrolysis (not studied during the report period) and techniques for improving solvent cleanup methods. The use of organic acid complexing agents to scrub the metal complexes of dibutyl phosphate (HDBP) out of 30% tributyl phosphate (TBP)/70% n-dodecane (nDD) has been investigated. Formic acid was found to be ineffective in breaking either the Zr(IV)- or Pu(IV)-HDBP complexes and washing the metal ion out of the organic phase. Both 1M citric acid and 1M tartaric acid were found to be very effective, removing more than 95% of zirconium and plutonium out of the organic phase after a one-minute contact of equal volumes of aqueous and organic phases. Preliminary experiments with a single-stage miniature centrifugal contactor indicated that within short residence times of ~ 4 s, tartaric acid will probably remove most of the zirconium from an organic phase containing HDBP in 30% TBP.

Environmental Effects

The purpose of this program is to develop a systematic and coherent body of knowledge as a basis for realistic source terms for accidents in fuel reprocessing plants.

The generation of source terms consists of three phases: the formation of aerosols, dusts, and mists by accident events; modifications of airborne material during its transport within a facility to an air-cleaning system; and modifications of the material by the air-cleaning system. Principal attention to date has been given to explosive events.

Literature related to nuclear and nonnuclear explosions is being examined. In tests in the open air, mass concentrations of solid airborne material of several hundreds of grams per cubic meter have been observed in the first several seconds, decreasing to 50 mg per cubic meter after 1 h. Particle sizes tend to be distributed log normally after about twenty minutes with geometric standard deviations ranging from 2.0 to 2.8. Mass median diameters range from 30 to 2 μm depending on how much time has elapsed since the event.

Explosive experiments conducted with rock suggest that the resulting particle sizes can be described by a log-log model. Such a model has been used to describe distributions obtained in various comminution operations.

Blast effects and pressure transients are being examined to obtain a better understanding of the physical integrity of HEPA filters under accident conditions.

Salvage of Alpha-Contaminated Metals

Nuclear operations involving work with transuranic (TRU) elements generate large quantities of contaminated waste. Because of the contaminants, the waste is subjected to special treatment, as specified in existing or proposed regulations. Metals constitute a large fraction of the volume of such waste and can not be burned or otherwise treated as can combustible material. Furthermore, detection of very low levels of contamination in convoluted metallic forms is not feasible.

The purpose of the present study is to demonstrate a method of cleaning contaminated metals and transforming them into a readily assayed form. Both purposes aim at more efficient disposal or even recycle of the metals. Melt-slugging (melt-refining) techniques were evaluated as a decontamination and consolidation step for metals contaminated with oxides of plutonium and americium. Experiments were performed in which mild steel, stainless steel, and nickel that were contaminated with oxides of plutonium and americium were melted in the presence of silicate slags of various compositions.

The metal products were low in contamination; the plutonium and americium strongly fractionated to slag, some of which adhered to the metal ingots and in defects within ingots. Sonic imaging was found to be a promising technique for detecting internal defects in the ingots.

Partition coefficients (plutonium in slag/plutonium in steel) were measured to be 7×10^6 with borosilicate slag and 3×10^6 for calcium, magnesium silicate slag. Decontamination by this technique of metals containing as much as 14,000 ppm plutonium appears to be as efficient as for metals with plutonium levels of 400 ppm.

Staged extraction (that is, remelting of processed metal with clean slag) results in further decontamination of the metal. The second extraction is accomplished effectively by either resistance-furnace melting or electric-arc melting.

These experimental results indicate that melt-refining is an effective decontamination method for several metals (mild steel, stainless steel, nickel, and mild steel containing a minor amount of copper) over a range of slag compositions and process conditions.

Also described are conceptual designs of two plants that would use a melt-refining process to convert highly contaminated metals to homogeneous and compact forms containing very low concentrations of plutonium and americium.

Metal Matrix Encapsulation of High-Level Waste

Metal matrix encapsulation of solidified high-level waste forms is being evaluated as a waste management alternative. Laboratory-scale experiments have been initiated to generate data required to further establish the feasibility of encapsulation concepts. Metal matrix composites of simulated waste forms (Al_2O_3 , glass beads, and sintered pellets of calcine with additives produced at ANL by cold pressing, and at PNL by disc pelletizer) dispersed in metallic lead or an aluminum alloy have been fabricated with casting techniques. Differential thermal analysis (DTA) spectra from ~ 50 to 900°C showed no large exothermic reactions in mixtures of calcine, metal matrix powders, and/or additives.

A series of experiments has been initiated to identify the chemical interactions, or reactions, between dispersed waste forms and matrix metals over a range of conditions that simulates fabrication, handling, storage, transportation, and terminal storage. The extent and rate of chemical reactions are being examined by (1) optical and scanning electron microscopy, (2) energy-dispersive X-ray analysis, and (3) ion microprobe techniques. Preliminary results with a molten aluminum alloy indicate that the reaction rate should be rather low at storage temperatures.

A new procedure based on neutron activation of simulated solid waste forms has been used to study their aqueous leaching characteristics. The induced radioactivity in the leachant, as well as in the solid matrix, was determined by γ -ray analysis. Radiochemical separations combined with B^- counting techniques were used to increase the sensitivity of the leachant analyses. Results of leach rate determinations for two simulated waste forms and for the potential metal matrix, lead, are given.

Establishment of Tentative Criteria for Hull Treatment

The primary objective of this work is to develop a set of criteria to ensure that hull wastes are managed without undue risk to either operating personnel or the public. The final product of this work will be a set of guidelines useful to persons involved in the development or regulations, and also to those involved in (1) the design of buildings and equipment, (2) operational procedures and conditions, (3) maintenance procedures, and (4) packaging and transport to a Federal storage site.

A basis for criteria development is the set of existing regulations, directed generally to the handling of radioactivity or reactive metals, which can be adapted to hulls handling. Therefore, regulations were selected from the Code of Federal Regulations which although not specifically addressed to hulls handling were considered to be applicable to it. For comparison with these regulations, a list of statements by organizations proposing to reprocess nuclear fuels was assembled describing intended hull treatment operations. Similarly, regulations on transportation were selected from the Code of Federal Regulations which though not specifically aimed at hulls handling are considered applicable to the type of wastes that hulls represent.

One proposed method of reducing the volume of hull waste is separation of zirconium from transuranic elements by volatilization of $ZrCl_4$. (Considerable savings in packaging, interim storage, shipping, and burial costs of hulls might be realized if the volume that must be stored in a Federal repository can be reduced.) The conversion to $ZrCl_4$, followed by the conversion of $ZrCl_4$ to ZrO_2 by pyrohydrolysis, would also eliminate the pyrophoric hazard of handling Zircaloy.

The chemical feasibility of the $ZrCl_4$ -volatilization concept was tested on a laboratory scale at ANL. Each experiment consisted of passing either HCl or Cl_2 over a small fragment of UO_2 - PuO_2 -fissia* and some combination of Zircaloy-2 tubing, high-purity arc-melted zirconium, 304 stainless steel rod, or Inconel 718 rod. The volatile products were passed through an air-cooled condenser. After each experiment, the condenser was rinsed, and the rinsings were analyzed to determine the amount of plutonium in the condensate.

The results indicate that HCl is a satisfactory chlorinating agent. Of the major constituents in hull waste only the zirconium was volatilized by reaction with HCl at $\sim 400^\circ C$; also, the zirconium in Zircaloy was readily separated from TRU oxides. Despite the exaggerated $(U, Pu, Fs)O_2$ /Zircaloy ratio employed, less than 0.05 nCi of plutonium accompanied the 1- to 2-g quantities of volatilized zirconium. Chlorine is a less satisfactory chlorinating agent. Upon reaction of hull waste with chlorine, separation from plutonium was less favorable: 2-20 nCi of plutonium accompanied the 1- to 2-g quantities of volatilized zirconium.

Experiments were carried out in which irradiated Zircaloy tubing was reacted with HCl or Cl_2 , mainly to determine the behavior of radioactive fission elements. With HCl, virtually no radioactive fission products volatilized with the zirconium except 1% of the antimony and 2% of the cesium; with Cl_2 , a considerably larger fraction of fission products was volatilized.

Deep-Well Disposal of Noble Gases

An evaluation of the feasibility of disposing of fission product noble gases released in fuel reprocessing by subsurface injection has been carried out. The evaluation covers four concepts: (1) disposal in abandoned oil or gas wells, (2) underground disposal as a gas, (3) disposal between shale layers

* Fissia denotes a mixture of fission elements.

as bubbles entrapped in grout (hydrofracturing), and (4) storage as a solution in a deep well. Because of the diversity of disciplines needed to properly make this assessment, a consulting firm, Dames & Moore, with experience in chemistry, geology, geological engineering, nuclear science, and engineering economics was retained as a subcontractor on this project. Some of their qualitative conclusions are presented here.

Support for the Environmental Impact Study of Waste Management

A contribution to ERDA's Generic Environmental Impact Statement on management of commercial nuclear wastes was completed. This contribution was the quantitative description of expected waste characteristics. Data was obtained from calculations, estimates, published information, and also from ORIGEN Code computations by Battelle (PNL). The waste types were characterized in terms of their radioactivities, volumes, densities, and chemical identities. The Impact Statement is expected to be issued before the end of calendar year 1977.

Transport Properties of Nuclear Wastes in Geologic Media

The confinement of nuclear waste in geologic formations is being considered as a method of permanently disposing of the waste. Laboratory experiments are being performed with nuclides of cesium, plutonium, neptunium, and americium to examine the migratory characteristics in rock of long-lived radionuclides that could be mobilized by groundwaters infiltrating a nuclear waste repository and the surrounding geologic body. Apparatus operation, and results for ANL column infiltration experiments, static absorption experiments, and batch partitioning experiments are described in this report.

Column infiltration experiments were performed with cesium-135 in columns of shale aggregate and chalk aggregate and with plutonium, americium, and neptunium in columns of solid limestone, and solid sandstone. In the column infiltration experiments with shale and chalk, the peak concentrations of cesium were seen to move with low velocity, which is consistent with strong partitioning of the nuclide onto rocks. However, cesium activity was also seen in a long tail extending from the cesium peak in the direction of water flow. The relative migration rates of this cesium were up to three orders of magnitude higher than those for the primary peaks.

Nuclide activity downstream from the peak activity was also seen for plutonium, americium, and neptunium in solid rock columns of limestone and sandstone. Thus, dispersion of the relative migration rates of these elements in the common rocks studied is large, and the behavior of these elements cannot be accurately described by models that predict a single migration rate based on simple absorption properties and local chemical equilibration. For similar reasons, partition coefficients measured in batch experiments are not adequate to characterize the migration of these nuclides in geologic media.

The experimental data indicate that the amount of activity traveling with a higher velocity than the migration rate of the peak concentration may be large enough to present a potential radiological hazard and thus may be of concern in safety assessments of nuclear-waste repositories.

Static absorption experiments were done with rock tablets from a variety of different formations to determine the absorption of plutonium and americium nuclides, both singly and in combination.

The results of the static absorption experiments indicate that plutonium and americium are strongly absorbed from solution by the common rocks studied. Thus, their migration relative to groundwater flow would be retarded.

However, the reaction rates of nuclides in solutions and rocks vary considerably for different rock-nuclide systems. Therefore, for a solution containing several nuclides and moving through rock, conditions of local equilibration may exist for some nuclides and not others. Thus, models of nuclide migration need to consider the reaction rates of the individual nuclides. Plutonium and americium were found to be strongly absorbed by tablets of oxide composition. Relative migration rates for plutonium and americium by fluid flow, based on the static absorption experiment data, are considerably lower than the velocity of the infiltrating water.

In experiments not described in this report, tablets of rocks were allowed to dry between absorption and desorption tests, and it was found that in general plutonium and americium were not then desorbed from sample tablets. This is consistent with an observation reported by other workers that once plutonium has dried on a rock surface, it becomes fixed and will not desorb into a solution.

In batch partitioning experiments with particulate basalt in which the material was prevented from drying between absorption and desorption steps, it was found that plutonium and americium were desorbed from rock and repartitioned between rock and solution to an extent comparable to that occurring during adsorption. Thus, the adsorption process appears to be reversible in the absence of a complicating step such as drying of the rock material.

In batch partitioning experiments, partitioning of americium and plutonium was measured in relation to the particle size of the basalt but was not found to correlate with either the calculated fracture surface or the measured surface area of the material. Partitioning may be a bulk rather than a surface phenomenon; the penetration depth of the solution may be comparable to the particle radius of 30-40-mesh material.

I. DEVELOPMENT OF ADVANCED SOLVENT EXTRACTION TECHNIQUES

A. Development for the Reprocessing of LWR Fuel

1. Introduction

A program is under way to develop advanced solvent extraction techniques for Purex reprocessing of light water reactor (LWR) fuel. This program is being carried out in cooperation with the Savannah River Laboratory (SRL). Specific features of the program are: (1) design, construction, and testing of a large annular centrifugal contactor having a capacity of about 10 Mg/d of LWR fuel; (2) design, construction, and testing of a single-stage miniature annular centrifugal contactor; (3) design, construction, and testing of an eight-stage miniature centrifugal contactor based on the annular mixing concept; (4) a study of the chemistry and kinetics of solvent extraction of ruthenium and zirconium for the purpose of developing flow sheets capable of enhanced decontamination based upon differential extraction kinetics in short-residence contactors; and (5) investigation of plutonium reduction kinetics to achieve improved uranium-plutonium partition in short-residence or other types of contactors.

2. Development of a 10 Mg/day Contactor (G. J. Bernstein, R. A. Leonard, A. A. Ziegler)

The previous report in this series (ANL-77-36) showed the general configuration and dimensions of a large annular centrifugal contactor capable of processing LWR fuel at the rate of 10 Mg/d. This unit has a rotor 25 cm in diameter and 42-cm long (36-cm separating section and 6-cm weir section). The rotor will be driven at about 1750 rpm by a 5-hp (3.7-kW) commercial precision motorized spindle which has already been purchased. However, detailed design of the contactor is being deferred while a 0.5 Mg/d unit of similar design (see Section B.2) is being built and tested. It is anticipated that successful operation of the smaller unit will provide a valid basis for the design and construction of the large unit.

3. Development of a Single-Stage Mini-Centrifugal Contactor (G. J. Bernstein, R. A. Leonard, A. A. Ziegler, D. Goetch*)

A single-stage miniature annular centrifugal contactor has been built and is being used for experimental work. Objectives of these experiments are to evaluate operating characteristics of the eight-stage miniature contactor (see Section A.4 below) and to investigate possible improvements in future multistage miniature contactors. In addition, the single-stage unit has served as an experimental tool for studies of the kinetics of extraction of ruthenium and zirconium (see Section A.5 below).

A single-stage 2-cm-ID[†] centrifugal contactor with annular mixing is being operated over a wide range of conditions. Our purposes are: (1) to identify a satisfactory operating range for the eight-stage 2-cm-ID centrifugal

* Summer undergraduate research participant.

† Dimensions for centrifugal contactors are IDs of the rotors.

contactors now under construction; (2) to minimize testing required on a larger 0.5 Mg/d contactor now built and a planned 10 Mg/d contactor; (3) to guide any changes required for these larger units; (4) to test promising new designs; and (5) to ensure that process flow sheets tested on the 2-cm-ID contactor banks can be scaled up to the larger contactors.

Figure 1 is a photograph of the 2-cm-ID contactor installed in the test apparatus. A diagram of the contactor internals is shown in Fig. 2. Some variations in rotor and housing have been used to test effects of specific changes. In operation, two phases, (1) 30% tributyl phosphate (TBP) in n-dodecane (nDD) and (2) nitric acid (0.04 and 3.0M), are fed through side inlet ports and are mixed in the annular region. The mixture flows into the rotor through its bottom orifice, and the phases are separated under centrifugal force. Appropriate weirs direct the separated phases out of the rotor into collecting rings. Figure 2 shows the radial vanes in the casing that serve to direct the mixture to the orifice at the center of the rotor bottom. Excellent performance was also obtained when a disk was mounted on the radial vanes, permitting the mixture to flow under the disk and up through a center

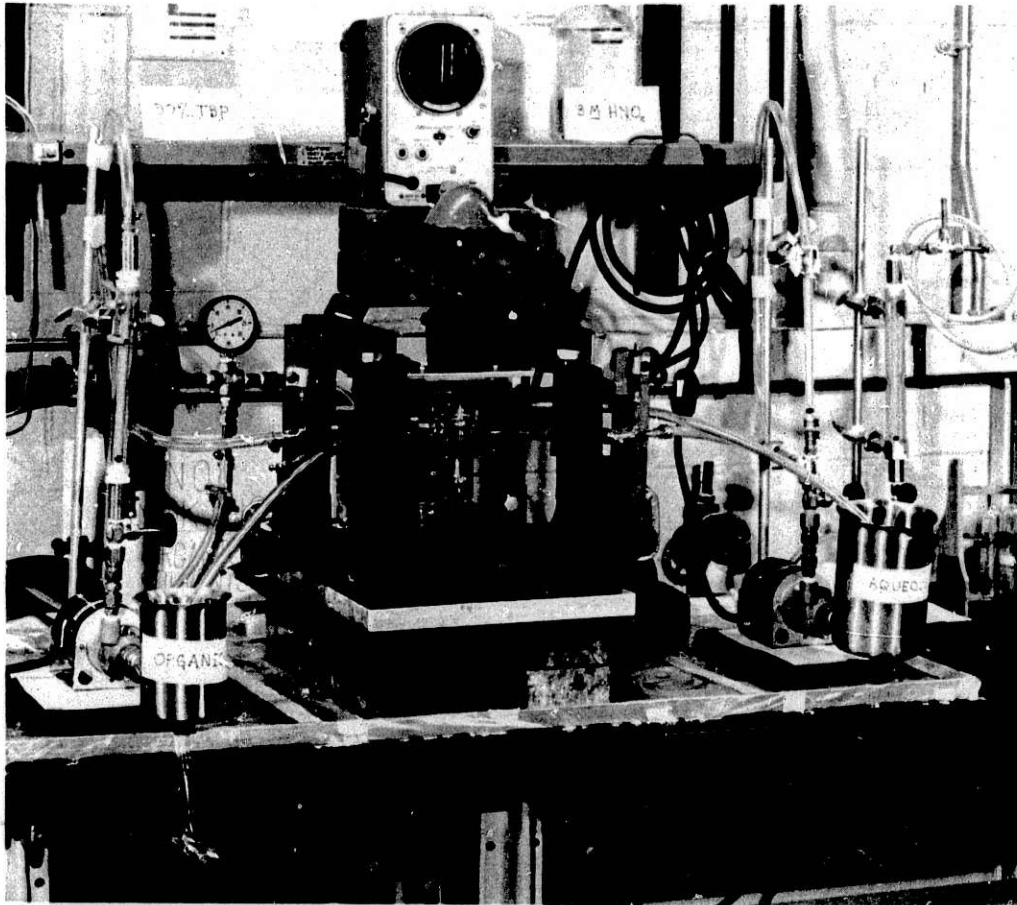


Fig. 1. Overall View of 2-cm-ID Centrifugal Contactor Test Apparatus.
ANL Neg. No. 308-77-375

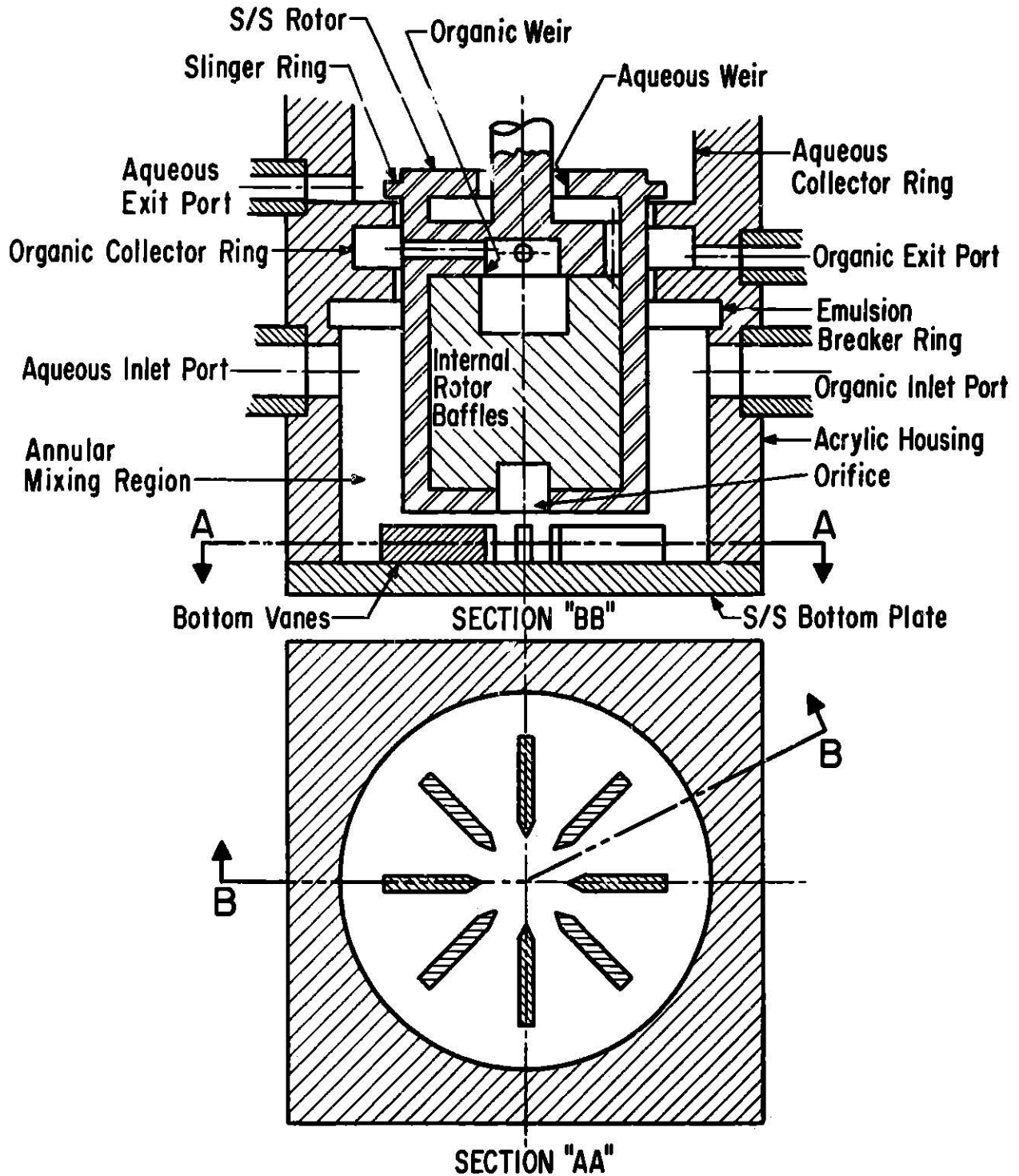


Fig. 2. Cross Section of a Centrifugal Contactor

opening into the rotor orifice. Figure 3 is a photograph of the operating contactor showing the liquids mixing in the annular region, the air gap above this emulsion, liquid in the emulsion breaker ring at the top of the annulus, and the organic-phase collector ring. The aqueous-phase collector ring, which is above the organic-phase collector ring, is obscured in the photograph.

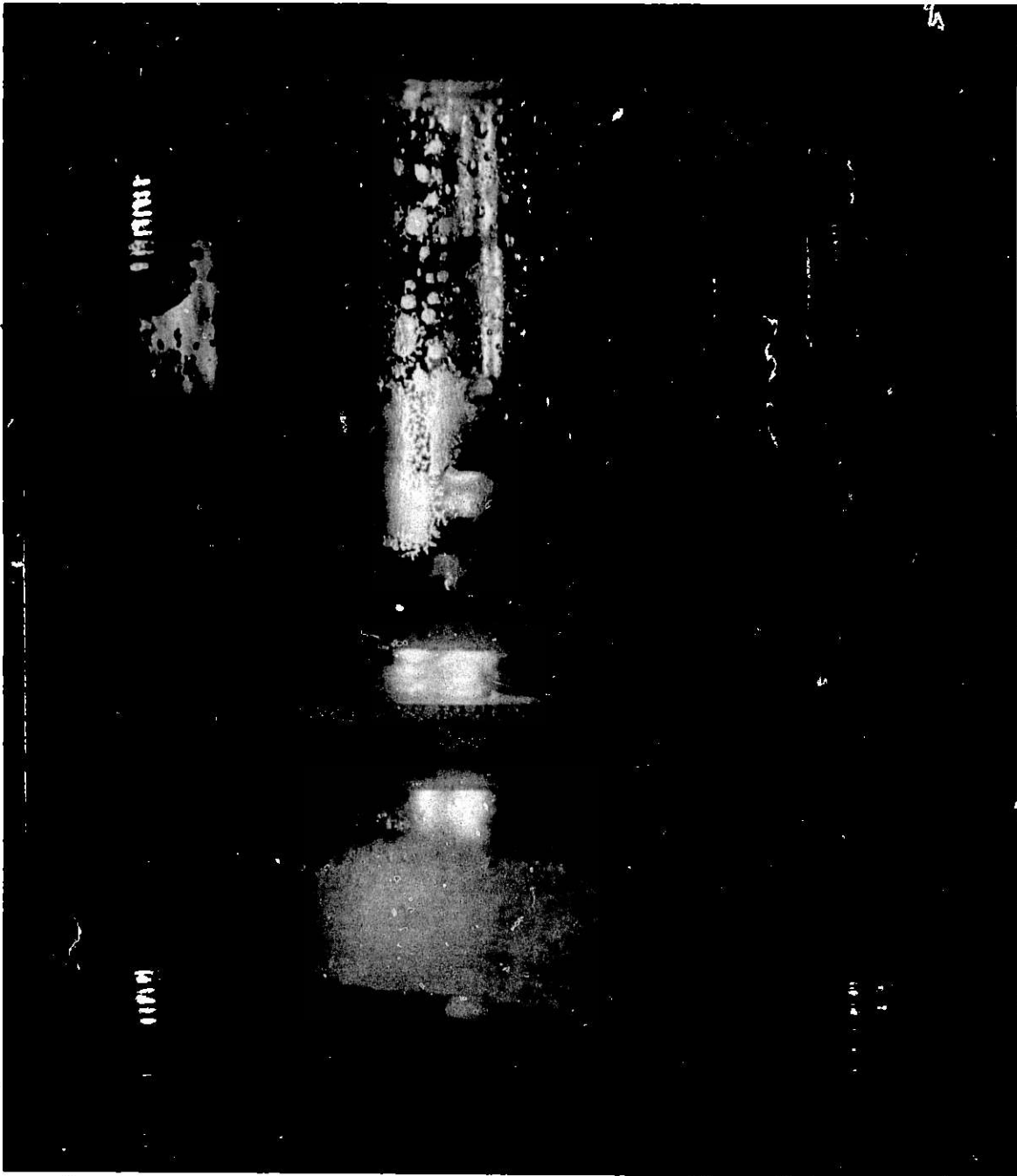


Fig. 3. Operation of a 2-cm-ID Centrifugal Contactor.
Total flow rate = 40 mL/min. Rotor speed =
6000 rpm. ANL Neg. No. 308-77-403

An extensive series of tests was carried out to investigate the performance of the contactor over a broad range of rotor speeds, flow rates, and aqueous-to-organic flow ratios. Most of the tests were made with 0.04M HNO₃ or 3M HNO₃ as the aqueous phase and 30% tributyl phosphate (TBP) in n-dodecane (nDD) as the organic phase. In general, rotor speeds above 4000 rpm were needed to obtain throughputs (total of both phases) of 80 mL/min or better. When the vane assembly (shown in Fig. 2) was used, the maximum throughput was 110 mL/min at 8000-9000 rpm. When the disk covering the vanes was added, the maximum throughput was 160 mL/min at 6000-9000 rpm.

Only those throughputs were considered at which neither effluent stream showed more than 1% contamination by the other stream. In general, the organic stream was the first to show excessive contamination. This appeared to be due to surging of the mixture from the annulus up into the organic-phase collector. When the bottom disk was employed, such surging was reduced, which may account for the higher throughput with the disk in place.

It was also noted that semisolid impurities in the test streams tended to accumulate in the rotor and to reduce total throughput by as much as 30%. This effect had not been noted several years ago when a much larger contactor was tested and may be due to the very small passages in the miniature rotor being sensitive to semisolid impurities. Process solutions will be cleaned by filtration or centrifugation before being used in the eight-stage contactor.

Other variations in operating conditions had little effect on the hydraulic performance of the contactor. These changes included (1) the use of alternative organic phases such as dialkyl phosphoric acid and quaternary ammonium salts in diethylbenzene, (2) small changes in the inside diameter of the housing, and (3) changes in the gap between the rotor and the housing base. Decreasing the size of the rotor orifice reduced the throughput when the bottom vanes alone were used but had little effect when the disk was present.

Efficiencies of extraction of 3M HNO₃ and 0.011M uranyl nitrate into 30% TBP in nDD were measured at various throughputs and rotor speeds. Extraction efficiencies were found to be above 96% at residence times in the annular mixing region as low as 2 s. The tests were performed with the bottom vanes and will be repeated with the bottom disk in place.

4. Development of an Eight-Stage Mini-Contactor (G. J. Bernstein, R. A. Leonard, A. A. Ziegler)

An eight-stage miniature centrifugal contactor has been built for use as a multistage counter-current extractor for laboratory-scale studies of solvent extraction systems. Figure 4 shows an overall view of the eight-stage assembly. The individual stages are very similar in form to the single-stage unit described in Section A.3. The main differences are that in the eight-stage contactor, inner dams are used on the effluent stream collector rings and the rotor is slightly longer. These changes were incorporated in the eight-stage unit to reduce the possibility that the organic-phase discharge stream might be contaminated by aqueous phase leaking down from the aqueous-phase collector ring or by mixed phases rising too high in the annulus.

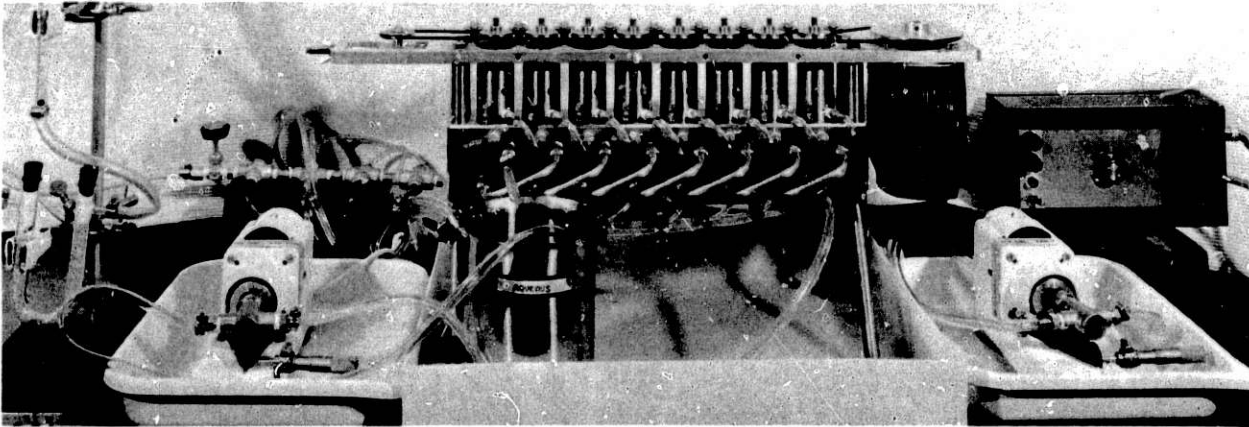


Fig. 4. Eight-Stage Miniature Centrifugal Contactor.
ANL Neg. No. 308-77-598

Figure 5 shows the individual components of a single stage. Shown in order from top to bottom are the drive pulley, high-speed spindle, spacer ring, coupling, rotor, and radial vane plug. All of these items except the radial vane plug fit into a sleeve which is pressed into the contactor block. The aqueous-phase and organic-phase collector rings are machined into the lower portion of the sleeve. The plug is pressed into the bottom of the contactor block.

As shown in Fig. 4, all of the rotors are driven by a common belt from a single variable-speed motor. Mechanical tests without liquid throughput have shown that the unit operates smoothly at speeds above 7000 rpm. In a preliminary throughput test, flows of 40 mL/min of each phase have been handled at 5000 rpm with no measurable contamination of either output stream.

A sampling system is being designed that will permit samples of each phase to be taken from each stage.

5. Extraction of Ruthenium and Zirconium in the Centrifugal Contactors in the Purex Process (A. A. Siczek)

a. Introduction

Our objective is to develop improved flow sheets for reprocessing uranium fuel in centrifugal contactors. With these contactors, decontamination of uranium and plutonium from fission products may be improved by utilizing the differences in the kinetics of extraction of actinides and fission products into the organic phase. In a centrifugal contactor, the phase contact time is only ~ 3 - 10 s per stage--fifty-fold reduction from the ~ 5 min contact time in pulse columns. An extraction time of 2-5 s is sufficient for the mass transfer of uranium, plutonium, and nitric acid since their extraction rates are essentially diffusion-controlled [PUSHLENKOV, BERGEONNEAU]. The rate-controlling processes in the extraction of zirconium and ruthenium are slower since they involve the formation of solvates, conversion among different chemical species,

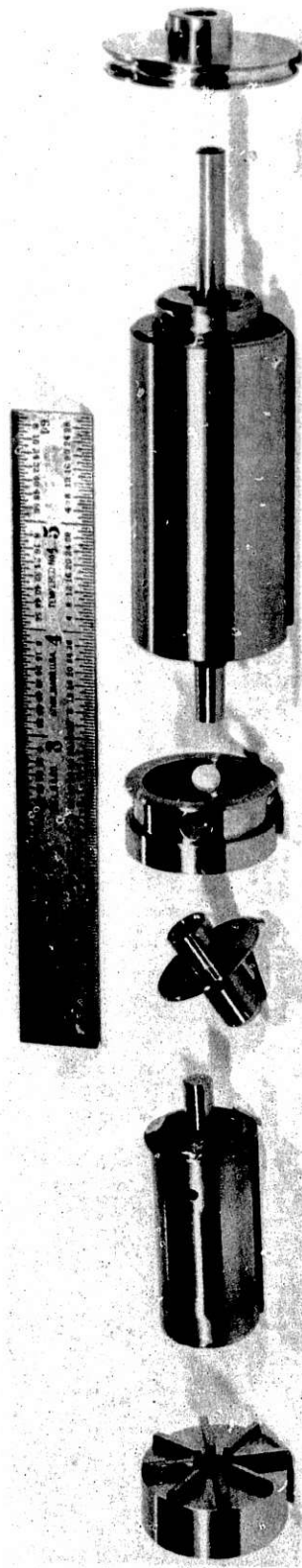


Fig. 5. Exploded View of Components of a Single Stage of the Eight-Stage Miniature Contactor. ANL Neg. No. 308-77-595

and the formation of complexes.* These processes are much slower than diffusion across a phase boundary, and the equilibrium state may not be reached for several minutes or more [BROWN, YAGODIN]. The difference in effective extraction rates can provide a basis for improved separation of uranium and plutonium from these fission products.

However, a short contact time also affects the efficiency with which these fission products are removed in the scrub section of the first extraction bank. Quite a few species of zirconium and ruthenium are present in the organic phase whose removal is controlled by conversion rates from extractable to inextractable species (half-times approximately 1/2 h to 3 h). Thus, longer scrubbing time can be expected to yield improved decontamination [ORTH-1971, NAYLOR]. Since residence time in the scrubbing section of the centrifugal contactors is anticipated to be less than 10 s, these elements will probably not be scrubbed out completely. Nevertheless, if short-residence-time contactors are used for plutonium partition and uranium stripping, the total contact time in these operations may be short enough that little zirconium, niobium, and ruthenium is transferred into the aqueous phase. The total contamination of plutonium or uranium may still be reduced, and the bulk of fission products should remain in the organic phase to be washed out in the solvent cleaning cycle.

b. Kinetics of Extraction

A study has been initiated of the kinetics of the extraction and reextraction of ruthenium and zirconium in a single-stage annular centrifugal contactor. The experiments were done with nonradioactive Ru and Zr as well as tracer solutions of ^{95}Zr - ^{95}Nb . The results of the zirconium experiments are reported in Tables 1 and 2. The analyses, chemical[†] and of gamma activity,[‡] were performed by the Analytical Chemistry Group; gamma activity was resolved to distinguish between zirconium and niobium.

Experimental Procedure. The solution of zirconium nitrate was prepared by dissolving $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ in water and nitric acid to give a final concentration of $\sim 0.01M$ of zirconium in $\sim 3M$ nitric acid. Ruthenium nitrate solution was obtained from Research Organic/Inorganic and diluted to

* Ruthenium exists in nitric acid solutions in the form of various nitrato and nitro or mixed nitrato-nitro complexes of trivalent ruthenium nitrosyls (RuNO^{3+}) which have extractabilities that differ very significantly. The equilibrium among them is established slowly ($t_{1/2} = 10$ to 60 min for nitrato ligands and $t_{1/2} = 1$ to 30 days for nitro groups at 20°C) [BROWN]. Zirconium complexes in the nitric acid medium undergo hydrolysis and/or polymerization to produce polymers of very different extractabilities. The formation and interconversion among them is also slow [YAGODIN].

[†] Analyses by K. J. Jensen and F. L. Williams.

[‡] Analyses by E. T. Kucera.

Table 1. Distribution Coefficients of Zirconium Extracted by 30% TBP/n-dodecane from 0.01M Zirconium Nitrate Solution^a in 3M HNO₃ at Ambient Temperature (32°C). Final concentration of nitric acid in the aqueous phase was 2.3M.

Approx. Contact Time, rpm	$D_{Zr}^a, \frac{[Zr]_{org}}{[Zr]_{aq}}$
1.5 s (9000)	0.055
3.8 s (3000)	0.047
3.8 s (9000)	0.045
7.2 s (9000)	0.045
3 min	0.052
5 min	0.062
1 h	0.082

^aNo significant differences in D_{Zr} were found between freshly prepared solution of zirconium nitrate and solution aged for 10 days.

Table 2. Distribution Coefficients^a of Zirconium and Niobium Extracted into or from 30% TBP/n-dodecane at Room Temperature (20°C)

Contact Time	D_{Zr}	D_{Nb}	D_{Zr+Nb}
<u>Extraction from 3M HNO₃</u>			
45 s	0.098	0.039	0.051
5 min	0.136	0.028	0.049
<u>Scrubbing into 3M HNO₃</u>			
45 s	1.63	3.066	2.21
5 min	0.93	0.81	0.86
<u>Stripping into 0.1M HNO₃</u>			
45 s	1.57	4.53	2.64
5 min	0.817	1.38	1.087

^aDistribution coefficient, D_n , is

$$\frac{\gamma \text{ counts min}^{-1} (\text{ml organic})^{-1}}{\gamma \text{ counts min}^{-1} (\text{ml aqueous})^{-1}}$$

The analysis of gamma activity was performed by the Analytical Chemistry Group. Counting statistics of <1.5%.

0.01M Ru in 3M nitric acid. These solutions were contacted individually with 30% TBP/n-dodecane in the centrifugal contactor. Additionally, the organic and aqueous phases coming out of the centrifugal contactor were equilibrated for 3-5 min and 1 h by vigorous shaking.

Zirconium tracer solution was prepared from 0.1 ml of ^{95}Zr - ^{95}Nb (2.15 Nb to 1 Zr) in the form of oxalates and 0.03 ml of 0.1M zirconium nitrate carrier. The solution was heated for 1 h with 0.5 ml of 16M HNO_3 to destroy oxalates and mix the isotopes of zirconium. No niobium carrier was added. One milliliter of zirconium tracer solution of final concentration 10^{-3}M Zr in 3M HNO_3 was stirred in the vortex stirrer with 5 ml 30% TBP/70% n-dodecane for (a) 45 s and (b) 5 min. The organic phase obtained in case (b) was stirred with (1) 3M HNO_3 and (2) 0.1M HNO_3 . On all cases, 1 ml of organic solvent was contacted with 5 ml of nitric acid solution.

Zirconium. The distribution coefficients of zirconium, D_{Zr} , between 30 vol % TBP/n-dodecane and zirconium nitrate solution are essentially constant within initial 8 s of extraction time (Table 1), and represent about 60% of the zirconium equilibrium concentration. About 80% equilibrium is achieved in 5 min. This may be compared with the Savannah River Group observation that 90% is extracted in 15 s and 95% in 5 min [ORTH-1971]; according to the Russian Group, 50% of equilibrium is achieved in 1 s and 90% in 6 s [PUSHLENKOV]. Since the interfacial area and the mixing efficiency are not well defined, the differences in the reported values are not surprising. Our actual value of $D_{\text{Zr}} \approx 0.05$ is in good agreement with data of others [ORTH-1971].

Preliminary conclusions based on Tables 1 and 2 are that the amount of zirconium extracted in the short-residence-time contactor in 1-8 s is reduced by about 40% compared with that extracted in 5 min and by about a factor of two compared with that extracted in 1 h. The experiments with the tracer solution of ^{95}Zr - ^{95}Nb also showed that 35% less zirconium is extracted in 45 s than in 5 min. Over the same range of contact times, niobium extraction is almost unchanged.

Scrubbing effectiveness of zirconium was found to be reduced by 10-20% in the series of experiments in the centrifugal contactor (following tabulation) and the tracer studies (Table 2).

<u>Contact Time</u>	<u>D_{Zr}</u> *
1.5 s	0.38
4.0 s	0.40
5 min	0.36

* The two series of experiments, one with tracer amounts and one with gross amounts of zirconium, do not give comparable values of distribution coefficients. Tracer zirconium was probably in a form of monomer and thus more extractable since it was formed from oxalates. No precautions were taken to prevent polymerization of carrier zirconium or gross zirconium.

Ruthenium. A study of kinetics of ruthenium extraction has just been initiated. Preliminary tests indicate that in 5-s contact time, 70% of ruthenium is extracted as compared to the amount extracted in 5-min contact time. The kinetic effect in back extraction of ruthenium has been found to be ~15%.

The Russian group [PUSHLENKOV] found the following:

<u>Contact Time</u>	<u>D_{Ru}</u>
9 s	0.043
22 s	0.043
30 min	0.06

That is, about 70% of the quantity of ruthenium extracted in 30 min was extracted in 22 s.

Further experiments known to be required are planned.

6. Kinetics of Plutonium Reduction in the Purex Process (A. A. Siczek)

The literature on the kinetics of the reduction of Pu(IV) to Pu(III) has been reviewed in order to determine the compatibility of proposed reductants with short-residence-time contactors. Since the total contact time is usually of the order of 5 to 15 s per stage, the kinetics of reduction become critical for efficient uranium-plutonium partition in the Purex solvent extraction process. Evaluated were reductants that introduce no undesirable materials into the process and hence into the waste. The results of the literature review are presented briefly.

a. Ferrous Sulfamate and Ferrous Nitrate

Until recently, ferrous sulfamate or ferrous nitrate was used as a reductant for Pu(IV). Use of ferrous sulfamate has the advantage of very rapid reduction of Pu(IV) to Pu(III), even in moderately strong acid, but the disadvantage that a metal impurity is introduced into the plutonium stream [CLEVELAND, WALSER]. Also a several-fold excess of either compound is required to ensure complete reduction; this increases the waste volume. The sulfate ion (generated from sulfamate) would contribute to stainless steel corrosion and to plutonium losses (since plutonium forms complexes with the sulfate). Although ferrous nitrate does not introduce some problems associated with the use of sulfamate [HORNBER-1969], its use still results in iron contamination of the system. Ferrous nitrate cannot be considered to be a significant improvement over ferrous sulfamate.

b. Uranium(IV)-Hydrazine System

The possible use of tetravalent uranium as a reagent for reducing plutonium(IV) to the trivalent state was considered by Rydberg [RYDBERG] and Newton [NEWTON-1959]. Uranium(IV) is thermodynamically a stronger reductant than iron(II), but reduction is slower [NEWTON-1964]. When tetravalent uranium is used to reduce Pu(IV), the rate of reaction is more acidity-dependent

than is the rate of reduction by ferrous ion. Kinetic studies have shown that the rate for U(IV) is proportional to $1/[H^+]^n$, where n is reported to be approximately 2 [HORNER-1969, RYDBERG, MARCHENKO]; for ferrous ion, the reaction rate varies with $[H^+]^{-1}$.

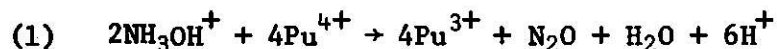
The use of uranium(IV) as a reductant has an advantage of not introducing additional impurities into the Purex system, but the uranium(IV) has the disadvantage of being susceptible to oxidation by side reactions, which can occur in the organic phase [SALOMON, SCHLEA-1963A, SLADE]. It can only act as an effective reducing agent in the presence of hydrazine or other stabilizers which destroy nitrite [STREETON]. The use of hydrazine is also required to prevent eventual reoxidation of the plutonium by HNO_2 present in the solution.*

In the absence of stabilizers, U(IV) fails to reduce Pu(IV) completely since nitrous acid (or N_2O_4) rapidly oxidizes the Pu(III) formed [DUKES-1960, NEWTON-1967]. The uranium(IV) nitrite is consumed in threefold excess of its stoichiometric requirements [SCHLEA-1963A], because of the side reactions. The unreacted uranium(IV) and the uranium(VI) are extracted into the organic phase and follow the original uranium stream, leaving plutonium in the aqueous phase. There are also disadvantages in introducing uranous ion in a step in which plutonium is being separated from uranium. One would expect the U(IV) to be recycled, but at the start it would be necessary to use uranium from another source and so the problem of controlling isotopic composition might arise.

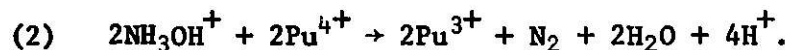
In preliminary studies on the use of U(IV) as a process reductant, Baxter and Naylor [BAXTER] found that 5-15 min contact time is required to reach equilibrium in a single stage (a miniature mixer-settler) at 2-3.8M HNO_3 . Thus U(IV) cannot be used in short residence contactors.

c. Hydroxylamine as Plutonium(IV) Reductant

Barney studied the reduction of plutonium(IV) to plutonium(III) with a large excess of hydroxylamine in nitric acid solution. This multistep reaction is very complex, and its rate is very dependent on acid concentration [BARNEY-1971, 1975]:



or



Hydroxylamine for plutonium reduction in the Purex process has the following advantages over other reductants: it contains no metallic cations that would contaminate the plutonium stream, and it decomposes entirely (in boiling HNO_3)

* At concentrations of nitric acid above 0.5M, the oxidation of Pu(III) by nitrous acid proceeds almost irreversibly; in dilute nitric acid solutions, however, Pu(IV) is reduced by nitrous acid, although at low rate. Nitrous acid can be used as a reductant in uranium-plutonium separation [BATHELLIER, KOLTUNOV-1975].

to water and gases, leaving no salt and thus reducing waste storage problems. Hydroxylamine can be used in the form of the nitrate, since sulfate ions are undesirable [MCKIBBEN, RICHARDSON, PATIGNY]. Reaction with hydroxylamine nitrate (HAN) gives complete and rapid reduction of tetravalent plutonium. Since the reduction rate by HAN decreases sharply with increasing acidities (at 0.3M HNO₃ the reaction is 99% complete in three minutes, whereas at 0.94M HNO₃ more than 10 h would be required [MCKIBBEN]), a catalyst should be used to extend the utility of HAN reductions into higher acidity. Another possibility is that adjustment of the parameters of the process would increase the reaction rate.

Factors favoring high partition performance have been found to be [RICHARDSON, PATIGNY]:

- (1) low acidity
- (2) low nitrate ion concentration
- (3) high temperature
- (4) high plutonium and uranium solvent saturation
- (5) the presence of hydrazine
- (6) longer aqueous phase residence times.

Also, the relative flow ratio of organic to aqueous phase is important, since it determines the separation factors.

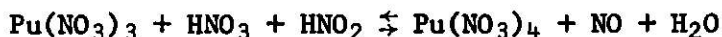
The presence of hydrazine (or some other reagent) with the hydroxylamine is essential for efficient reduction; hydrazine destroys nitrous acid.* However, hydrazine in excessive amount acts as a salting agent and opposes the transfer of plutonium to the aqueous phase and thus prevents reduction.

The following reactions can occur:

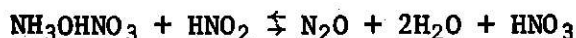
- (1) reduction of tetravalent plutonium



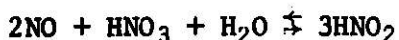
- (2) reoxidation of trivalent plutonium



- (3) destruction of hydroxylamine by nitrous acid [too slow to provide adequate protection against reoxidation (reaction 2)]



- (4) formation of nitrous acid



* Hydroxylamine reacts with HNO₂ also, but the reaction is too slow. The relative rate constants for hydrazine and hydroxylamine reactions with nitrous acid at 50°C are 2860 and 50M⁻² s⁻¹, respectively [KOLTUNOV-1974, 1966, BARNEY-1971B].

and lead to an autocatalytic oxidation cycle with extensive destruction of the reducing agent, accompanied by an increase of acidity and thus, an inefficient process.

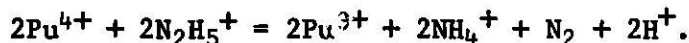
The experimental work at La Hague [PATIGNY] has shown that there is a limiting value of the quantity

$$\left[\frac{\text{HNO}_3, \text{NH}_3\text{OH}}{\text{Pu}} \right]$$

beyond which the process becomes inefficient. The value depends on the type of apparatus, contact of the surface with air, and whether there is recycling of the phases, which leads to solvent degradation. In mixer-settlers, the limiting value has been found to be 2.5 to 3.

d. Hydrazine-Hydroazoic Acid

Hydrazine, whose presence is required to prevent reoxidation of Pu(III) by nitrous acid, also serves as a reductant for Pu(IV), although at a lower rate than hydroxylamine [KOLTUNOV-1974, 1966]:



A disadvantage of using hydrazine as a nitrite suppressor is that a by-product (hydroazoic acid, HN_3) forms. Since this is explosive and can detonate if given a chance to accumulate, it should be destroyed or converted to metallic azides. It is readily extractable by TBP, but can be washed out from the TBP, *e.g.*, by sodium carbonate. The amount formed depends on the nature of the reductant used and on the solvent acidity [DUKES-1962] and is equivalent to 6-12% of the initial amount of hydrazine [SCHLEA-1963A]. Thus, in a dilute solution of hydrazine (less than 0.2M N_2H_4), hydroazoic acid should not be accumulated up to explosive limits of hydroazoic acid in aqueous solutions, *i.e.*, 17% [SCHLEA-1963A]*

e. Electrolytic Reduction

A possible way (other than chemical methods) of adjusting plutonium valence to facilitate stripping is electrolytic reduction [FINLAYSON, WAIN, LATIMER, SCHMIDT, KRUMPELT-1971, SCHMIEDER]. This method, however, may not be very suitable for short-time contactors since acceptable plutonium reduction would require a longer residence time; it has been found difficult to achieve an adequate reaction rate in the Argonne group studies [KRUMPELT-1973].

f. Complexing Agents for Pu(IV)

The use of complexing agents can help in stripping plutonium from the solvent. Many anions form very stable complexes with Pu(IV) which can be broken down under suitable conditions to permit subsequent re-extraction of plutonium. Among these are formic, acetic, oxalic, and hydroxamic acids [CAO, GERMAIN-1974, 1976].

* Dukes and Wallace give a value of 0.05M as a conservatively safe HN_3 concentration [DUKES-1962].

The complexing action of formic acid in conjunction with the reducing properties of hydroxylamine can be used for the stripping of plutonium from organic solutions containing plutonium and uranium. Formic acid complexes plutonium, but not U(VI), and the distribution coefficient of plutonium between aqueous and organic phases decreases with increasing concentration of the formate ion. Formic acid will be especially efficient at the last stages where the Pu(IV) concentration and reduction rate are low and the HCOOH/Pu ratio is high. Also, since formic acid is a weak acid, the acidity will not increase as much as in the case of nitrate ion, and kinetics of the reduction will not be influenced so unfavorably. The formic acid-nitric acid solutions of plutonium can be boiled in a later stage to destroy formic acid and hydroxylamine and increase the plutonium concentration. The use of hydroxylamine formate has been proposed by Germain and Bathellier and has been successfully tested* on a laboratory scale [GERMAIN-1974, 1976].

g. Discussion

Although ferrous ion has been successfully tested as a reducing agent for short-residence-time contactors [PUSHLENKOV, SCHLEA-1963B], we are not considering ferrous sulfamate or ferrous nitrate as possible candidates for the reduction of plutonium(VI) in centrifugal contactors since the radioactivity-contaminated iron would contribute excessively to the volume of high-level waste.

The difficulty with using uranium(IV) as a reductant for plutonium(IV) is that the oxidation rate can vary significantly, depending on the operating conditions, which may be hard to control. The concentration of nitrite in the nitrate solution, foreign cations, radiation, contact with oxygen in the air, and storage time all play important roles and may significantly decrease the efficiency of the reduction process. The required 5-15 minutes to reach an equilibrium [BAXTER] (about 2-4 minutes per stage, [OCHSENFELD-1970]) will disqualify this reductant for our purpose unless methods can be found to increase the contact time of ~ 10 s per stage in short-residence contactors. Also, there are problems with making uranium(IV) nitrate solution and storing it, since uranium(IV) is not stable in nitric acid [VAN GEEL].

An attractive choice for reducing plutonium is hydroxylamine nitrate, HAN (or formate), stabilized by hydrazine. This reagent does not add to the waste problem, although some treatment of radioactive gas must be made in disposing of it. Hydroxylamine gives complete and rapid reduction of plutonium(IV) at low nitric acid concentrations. The reaction rate is extremely dependent on acid concentration, and is approximately proportional to $[\text{HNO}_3]^{-4}$. If it is desired to use a higher nitric acid concentration, a catalyst might be used to extend the utility of hydroxylamine nitrate into higher acidity. Iron catalyzes the reaction, especially in the latter stages. Copper has also been tried as a catalyst and found to be twice as effective as iron [RICHARDSON]. However, as has been shown by Barney [BARNEY-1971C], the effect of a catalyst is less significant than the effect of changing other variables of the process such as temperature, acidity, or hydroxylamine concentration. The effect of HAN concentration is smaller than the effect of acid concentration since the rate is proportional to $[\text{HAN}]^2$. Temperature has a large effect on the rate; roughly,

*The Oak Ridge group found that the presence of formic or acetic acid did not improve plutonium stripping enough to be of interest [HORNER-1977].

the rate increases by a factor of five with each 10-degree (Celsius) increase in temperature. This is an unusually high temperature dependence.

Hydrazine-stabilized hydroxylamine nitrate (HAN-H) mixture has been used rather successfully by Richardson and Swanson [RICHARDSON] and by French experimenters [GERMAIN-1977] to partition plutonium from uranium. The plutonium and uranium content of the solvent feed was close to that obtained from fast breeder reactor fuel (Pu/U = 0.12 in the U.S. studies). When the process was operated at 50°C, plutonium losses were smaller than $4 \times 10^{-4}\%$. The residence time of the aqueous phase (0.3M HNO₃) in the mixing zone (centrifugal contactors) was estimated to be about 30 s per stage in a 12-stage contactor. The French group obtained good plutonium stripping results in a 45-stage bank that had a 2-s residence time per stage. They found that the half-time for the reduction of Pu⁴⁺ to Pu³⁺ (two phase) when HAN-H is used is of the order of a few seconds [GERMAIN-1977].

Hydroxylamine formate should be tried as a substitute for hydroxylamine nitrate in case of low acidity and low plutonium concentration. Since the solvent is to be recycled, one may expect dibutyl phosphate complexes of plutonium [Pu(NO₃)₄·2DBP] to be formed. These are very strongly complexed and hydroxylamine nitrate does not strip plutonium efficiently from DBP, but formic acid does so* [GERMAIN-1974, 1976]. This is another advantage of using the hydroxylamine formate-hydrazine system.

Although the application of an electrolytic method to the Purex process is very attractive as a clean technique, it is difficult to achieve an adequate reaction rate and this procedure will not be selected.

Some other reducing agents have been proposed, such as substituted hydrazines (*e.g.*, phenylhydrazine), aminophenols, polyamines [COUSINOU], but no kinetic data are available which would allow evaluation of their compatibility with short-time contactors. Another reducing agent known to be an extremely effective reductant of plutonium(IV) is hydroquinone, but its product quinone is highly undesirable [HORNER-1977, KOLTUNOV-1975]. Presently, the Italian group is working to develop an "instantaneous" reducing agent for Pu⁴⁺. They work with organic-soluble hydroquinones [GROSSI] and find that the best practical application is di-tert-pentyl hydroquinone (DTPQH₂), which is readily available in the reduced form, soluble in TBP (and other organic solvents) but not in the aqueous phase, and very stable. The kinetics of reduction and capacity of DTPQH₂ are better than for ferric ions. Reduction is virtually instantaneous. An alternative choice is 2,3 dichloro-1, 4 naphthoquinone if the redox potential of DTPQH₂ appears to be inadequate. The oxidized forms of the proposed reducing agents are soluble in the organic phase so that there is the possibility of regeneration for additional cycles. The reduction rate is independent of the plutonium concentration and is only affected by the ratio of hydroquinone to plutonium; it is little affected by uranium and HNO₃ concentrations. The presence of impurities may reduce reduction rates due to complexes forming. Hydroquinones should be considered for stripping plutonium when the process is carried out in centrifugal contactors.

* Hydrofluoric acid will also strip Pu from DBP quantitatively and nitric acid will prevent PuF₄ precipitation [BRUNS].

B. Developments for Reprocessing of FBR Fuel

1. Introduction

A program has been undertaken to develop improved solvent extraction techniques for use in Purex reprocessing of fast breeder reactor FBR fuel in a 0.5 Mg/day pilot plant. The work is being carried out in cooperation with the overall Oak Ridge National Laboratory program for FBR fuel reprocessing. The objectives of the ANL work are (1) development of an annular centrifugal contactor and (2) general chemical studies in support of contactor development (reported in Section A.6). The studies include investigation of (1) the extraction kinetics for uranium, plutonium, and fission products applicable to high-plutonium, high-fission product Purex systems and (2) the kinetics of plutonium reduction as they affect uranium-plutonium partition in short-residence contactors. Solvent washing techniques designed to avoid the formation of interfacial crud will also be examined. The accomplishments relative to contactor development and solvent cleanup are reported below.

2. Development of 0.5 Mg/day Centrifugal Contactor (G. J. Bernstein)

An annular centrifugal contactor sized to process about 0.5 Mg/day of FBR fuel is being built. This unit has a rotor 9 cm in diameter and about 27-cm long, which makes it critically safe for all concentrations of plutonium solutions. The rotor will be coupled directly to a 1-hp (0.75-kW) commercial precision motorized spindle which will operate at about 1750 rpm. The rotor design incorporates an air-controlled weir with the air being supplied through a rotary air seal mounted on top of the hollow shaft of the motorized spindle.

Fabrication of the contactor is nearing completion. Figure 6 shows the contactor casing. The two lower pipes on the side of the casing are the inlet lines to the mixing annulus for aqueous and organic streams. The two upper pipes are the outlet lines for these streams after they have been separated in the rotor. Figure 7 shows the rotor with the internal vanes visible through the orifice in the bottom of the rotor. The phases, which are mixed in the annulus between the rotor and the casing, enter the rotor through the orifice and are accelerated to rotor speed by the four radial vanes. As the mixture flows up through the spinning rotor, the phases are separated under centrifugal force, with the heavy phase moving toward the periphery of the rotor and the light phase moving toward the axis.

At the top of the rotor, the separated phases are directed to appropriate discharge ports by a set of weirs. In the lower portion of Fig. 8 can be seen the "hollow cross" through which the light phase flows to the lower set of discharge ports. The heavy phase flows upward through the peripheral slots between the arms of the cross and then through a series of circular weirs to the upper set of discharge ports. The upper portion of Fig. 8 shows the heavy-phase weirs and the inlet for the weir-control air which enters through the hollow shaft.

An existing contactor test facility is being modified to permit installation of the contactor. A mounting plate and support bracket are being fabricated to support the casing along with the combined motorized spindle and

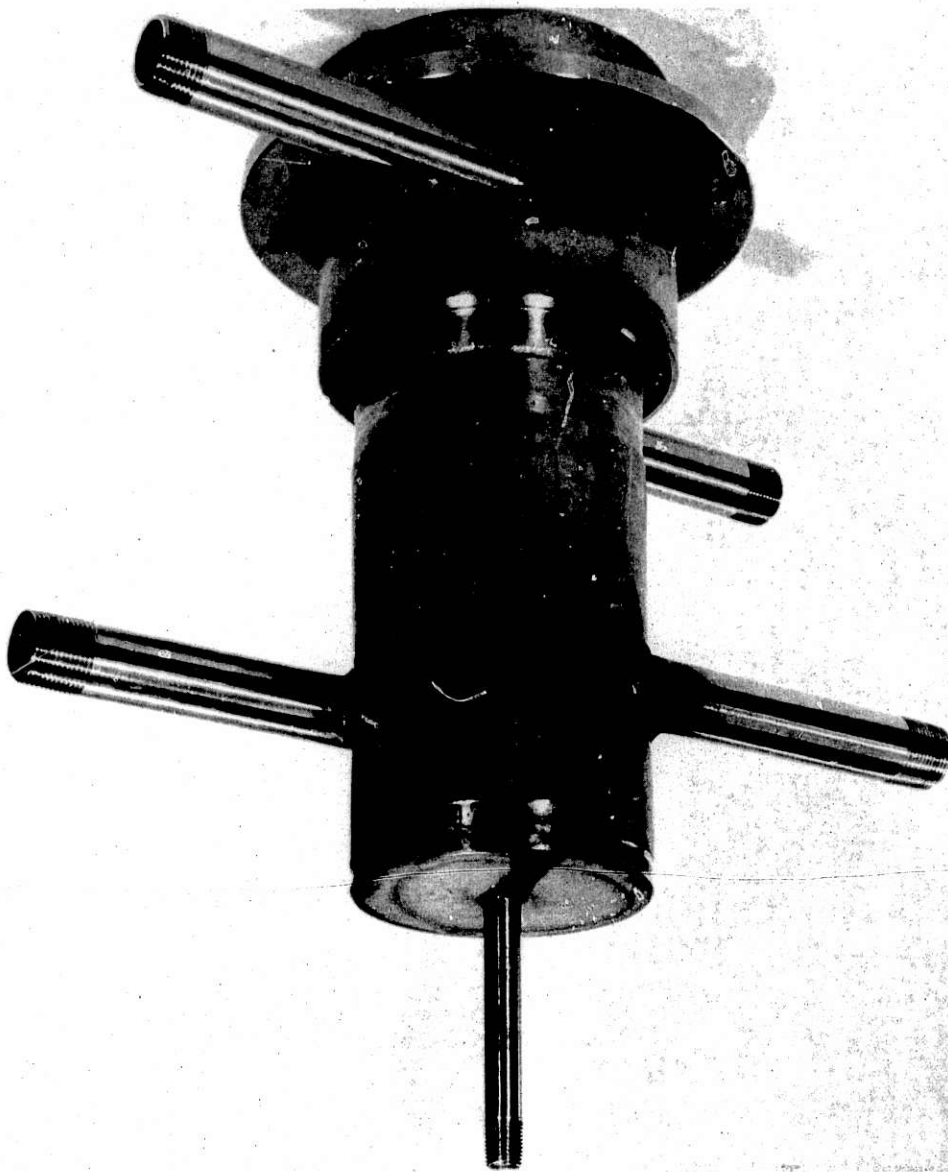


Fig. 6. Housing for 0.5 Mg/d Centrifugal Contactor.
ANL Neg. No. 308-77-605

rotor. Although the mounting assembly is not designed for remote handling, it will be possible to evaluate the adaptability of this design to remote handling.

The preceding report in this series (ANL-77-36) noted that tests were planned on an existing annular contactor to be modified to have an extended housing. Such an extension could serve to increase the volume and residence time in the mixing zone while retaining the critically safe diameter of the housing. Increased residence time may be desirable for enhancing the extent of desirable reactions whose kinetics are too slow for short residence contactors. In addition, the stages with extended casings would each have the

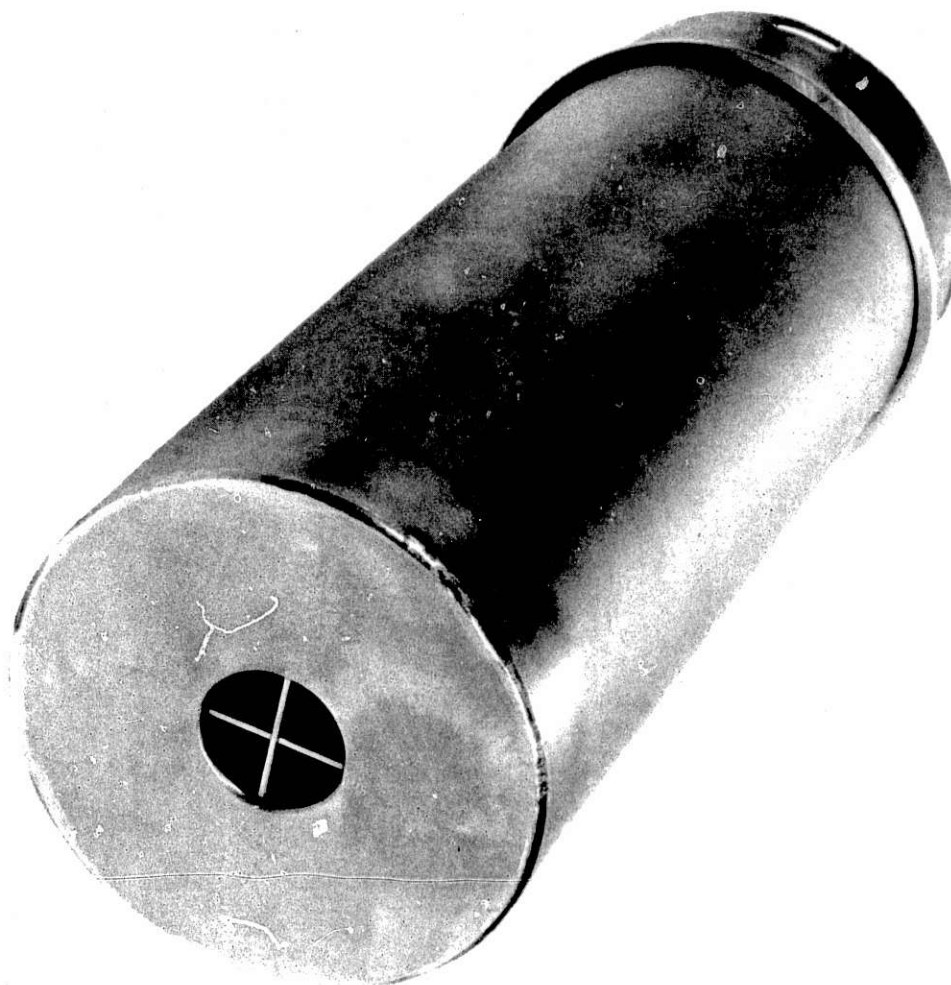


Fig. 7. Rotor for 0.5 Mg/d Centrifugal Contactor.
ANL Neg. No. 308-77-594

same type of rotor and motorized spindle assembly as the standard stages. During the past period, an extended plastic casing was attached to the existing contactor as shown in Fig. 9.

Tests were performed with dilute nitric acid and 30% tributylphosphate in n-dodecane flowing through the unit. Observation of the extended mixing zone showed vigorous mixing throughout the zone at a rotor speed of 1800 rpm. Present plans do not include incorporating the extended casing feature in a stainless steel housing. However, the design will be available should it prove necessary for improving plutonium reduction reactions or for increasing the extent of fission product scrubbing.

3. Solvent Cleanup (B. B. Saunders)

The decomposition of tri-n-butyl phosphate (TBP)/n-dodecane (n-DD) used in the Purex process (which causes problems such as clogging of contactors, retention of fission products in the solvent, reduced decontamination factors, and plutonium losses) occurs by both radiolysis and acid hydrolysis. The



Fig. 8. Upper Zone of 0.5 Mg/d Centrifugal Contactor Showing Weirs. ANL Neg. No. 308-77-593

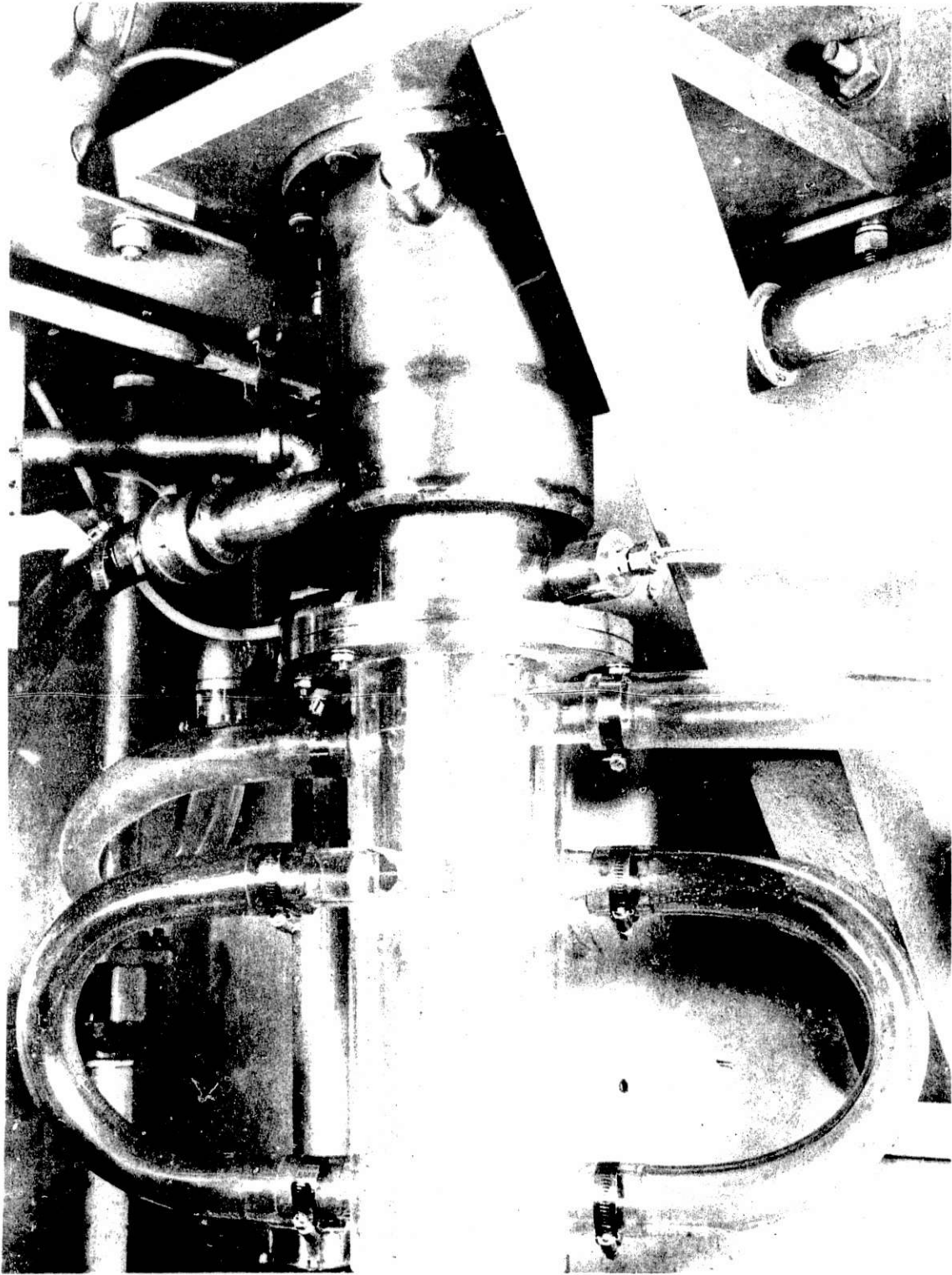


Fig. 9. Annular Centrifugal Contactor with
Extended Housing. ANL Neg. No. 308-77-399

major decomposition products of TBP are di-n-butyl phosphate (HDBP) and mono-n-butyl phosphate (H₂MBP). Also, some radiolytic decomposition of the hydrocarbon diluent occurs, but the identity and amount of the products are not well known. The postulated products of the TBP and diluent include long-chain hydroxamic acids, nitroparaffins [BLAKE, LANE], long-chain alkyl butyl phosphates [HORNER-1976], and alkyl phosphates containing carbonyl groups [STIEGLITZ]. The predominant decomposition product in the 30% TBP/70% n-DU mixture will be HDBP (~70%), and the major organic solvent damage occurs in the first cycle extraction section where both the radiation dose and the acid concentration are highest.

All of the above decomposition products form complexes with metal ions present in the system [UO_2^{+2} , Pu(IV), Zr(IV), and Nb(V)]. These complexes are soluble in the organic phase or form precipitates and oils at the interface of the aqueous and organic phases [BRESCHET, OCHSENBERG-1977]. The concentration of the metal ions in the process is high enough to completely complex all of the HDBP. It is expected that the complexes with Pu(IV) and Zr(IV) will be stronger than those with U(VI).

a. Solvent Cleanup Methods and Results

There have been many laboratory methods reported in the literature for removing the degradation products and purifying the solvent. These include stream distillation [SICILIO], complexing agents [BLAKE, LANE], alkali scrubs [ORTH-1963], and sorption [SCHULZ]. The method actually used by the reprocessing plants and still proposed for future plants is scrubbing with sodium carbonate (5% solution) or sodium hydroxide (0.1%). Alkali scrubs have been shown to be ineffective in removing the decomposition products in the laboratory [NOWAK], and the presence of alkali metals may hinder the solidification of the processing wastes. Accordingly, a more desirable method would exclude alkali wastes and would improve solvent purification.

Since the major decomposition products are complexed to the metal ions, a reasonable approach is to scrub the organic phase with aqueous solutions of non-alkali complexing agents which would not be very soluble in the organic layer and would form metal complexes which are water-soluble. Once the metal ions are removed from the organic phase, the HDBP, which is water-soluble, would be washed out into the aqueous phase. When complexing agents were used at another site [BLAKE] to scrub the organic solvent, resulting solvent quality was described only qualitatively.

Three organic acids were tried, formic acid (HCOOH), citric acid ($CH_2(COOH)-CH(OH)(COOH)-CH_2(COOH)$), and d-tartaric acid ($COOH-CHOH-CHOH-COOH$). Formic acid, which has been reported to strip Pu(IV) from 30% TBP by breaking the strong Pu-HDBP complexes [GERMAIN-1974, 1976], seems a reasonable choice for a complexing scrub solution since the chemistries of zirconium and plutonium, Zr(IV) and Pu(IV), are often similar. Citric acid forms complexes with Pu(IV) and Zr(IV) which are not extractable into 30% TBP solutions [KOLARIK, ZAITSEV]. Tartaric acid would likewise be expected to form non-extractable complexes with Zr(IV) and Pu(IV).

Three types of experiments were performed at ANL to determine the ability of these complexing agents to remove metal complexes of HDBP from organic solutions: (1) radioactive tracer ⁹⁵Zr solutions, (2) radioactive

tracer ^{239}Pu solutions and (3) cold Zr solutions. The radioactive tracer work was performed in test tubes and that with cold zirconium in the minicontactor.

For the experiments with tracer ^{95}Zr , an aqueous solution of zirconium was prepared as follows: 0.100 mL of ^{95}Zr in 0.5% oxalic acid and 3M HNO_3 , 0.030 mL of 0.1M $\text{Zr}(\text{NO}_3)_4$ in 2M HNO_3 , and 0.5 mL concentrated HNO_3 (16M) were heated with a heat lamp for 1 to 4 h. The solution was then diluted with 2.5 mL of H_2O to final concentrations of 3M HNO_3 , 10^{-3}M Zr(IV), and $2 \times 10^{-3}\text{M}$ oxalic acid. This procedure was necessary to ensure that the zirconium was in an extractable form. Solutions heated for 1 h gave the same distribution into the organic phase in the Zr tracer experiments as those which had been heated for 4 h. The tracer solution was an equilibrium mixture of ^{95}Zr - ^{95}Nb (2.15 Nb to 1 Zr).

One milliliter of the aqueous (3M HNO_3) zirconium was stirred on a vortex stirrer for 1 min with 5 mL of 30% TBP/70% dodecane/ $4.2 \times 10^{-3}\text{M}$ HDBP. A 4-min stirring time used in later experiments increased the distribution coefficient from 0.2 to 0.7. In one experiment, 3M HNO_3 was saturated with HDBP by stirring with three successive portions of organic phase before zirconium addition to ensure that the nitric acid solution did not scrub the HDBP out of the organic layer.

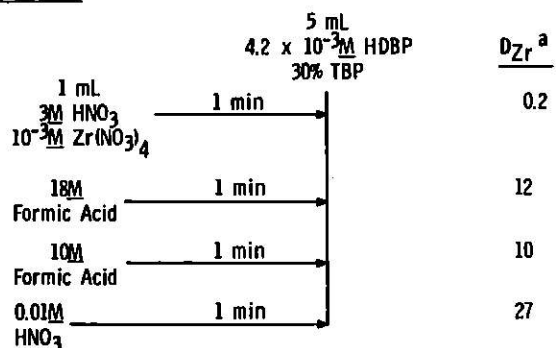
Zr(IV)-loaded solvent containing $4.2 \times 10^{-3}\text{M}$ HDBP in 30% TBP/nDD was scrubbed with aqueous solutions of 10M, 18M, and 24M formic acid; 1M citric acid; and 1M tartaric acid. The results are shown in Fig. 10. It is evident from these experiments that citric acid and tartaric acid were able but formic acid was unable to strip zirconium from its HDBP complexes. Concentrated formic acid removed the activity from the top layer of three layers (Fig. 10), but investigation of the middle layer showed that it consisted of TBP completely dissolved in concentrated formic acid. The middle layer was subsequently washed with a more dilute formic acid solution, the TBP separated into a separate organic phase, and the bulk of the activity remained in the organic phase, indicating that the zirconium had not been stripped.

To prepare the plutonium-loaded organic phase for the ^{239}Pu tracer experiments, 5 mL of 30% TBP/70% n-DD/ $3.8 \times 10^{-3}\text{M}$ HDBP was contacted with 1 mL of $3 \times 10^{-11}\text{M}$ $^{239}\text{Pu}(\text{NO}_3)_4$ in 3M HNO_3 for 2 min. As shown in Fig. 11, the plutonium-containing organic phase was first washed with 0.01M HNO_3 ; then one portion was washed with 6M formic acid and another portion with 1M citric acid. In direct contrast to reported results [GERMAIN], formic acid was not effective in stripping the Pu(IV) from its HDBP complexes, but citric acid was.

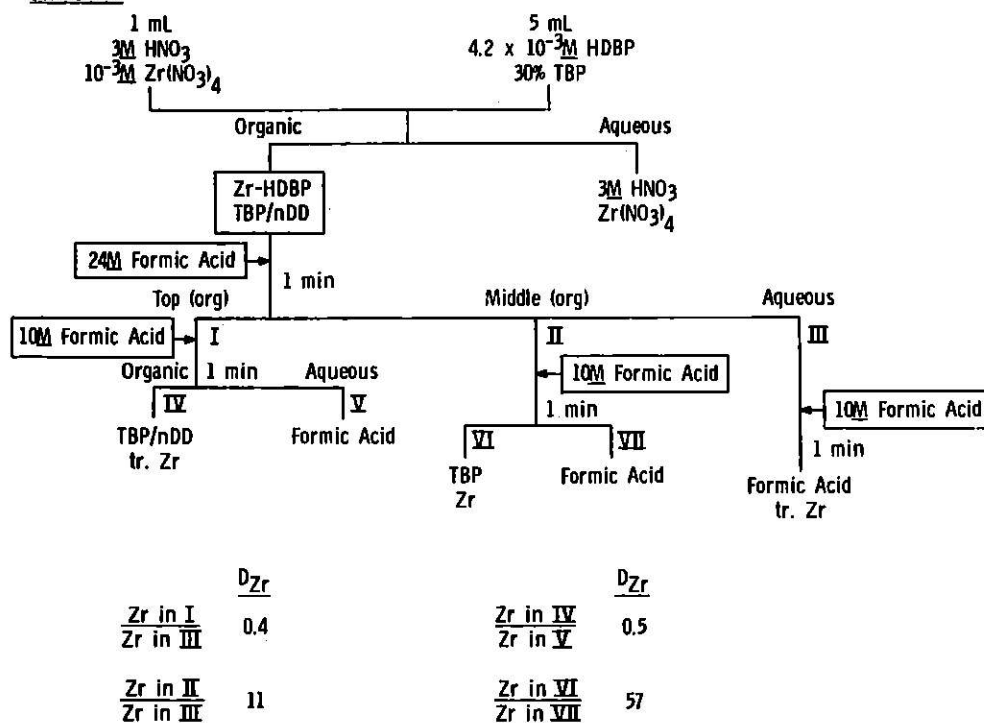
These tracer experiments* each had a 1-min contact time of the HDBP-containing organic solvent and the complexing scrub. The use of a centrifugal contactor would require completion of the reaction in times shorter than one minute. Preliminary experiments were performed in a single-stage mini-centrifugal contactor to determine whether or not zirconium and its HDBP complexes could be removed from the organic layer in short contacting times. A solution of 30% TBP which had been contacted many times with nitric acid and thus was believed to contain some HDBP was used because no HDBP was available at the time of the nonradioactive experiment.

* Special thanks go to Phil Horwitz and George Mason for their helpful discussions and for allowing the use of their laboratories in the Chemistry Division for these tracer studies.

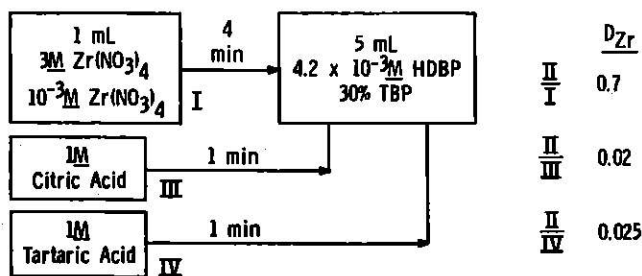
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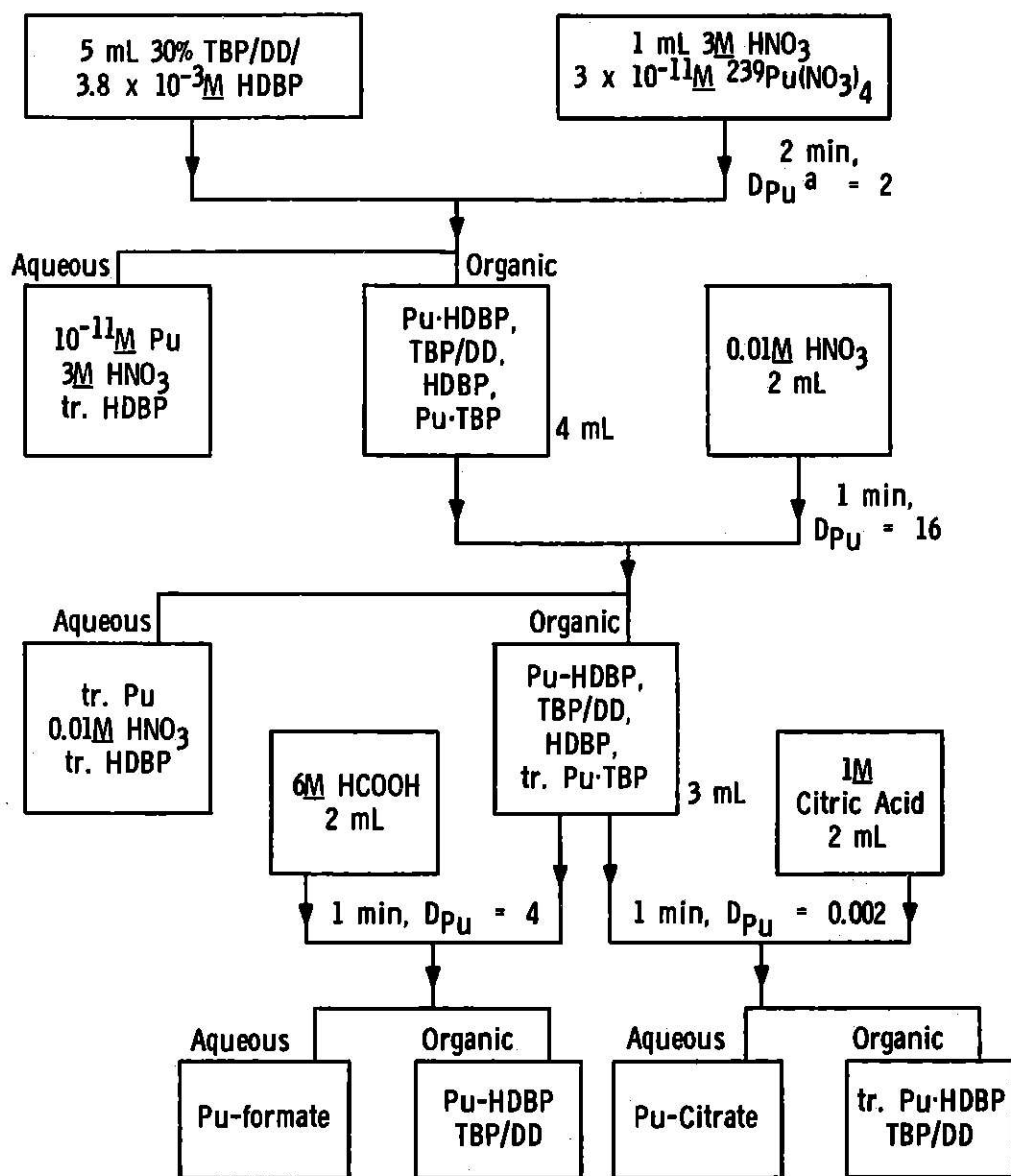


Series B-8



$${}^a D_{Zr} = \frac{[Zr]_{org}}{[Zr]_{aq}}$$

Fig. 10. Distribution Coefficients and Conditions in Zr(IV) Scrubbing Experiments. Some streams are assigned Roman numerals.



$$^a D_{Pu} = \frac{[Pu]_{org}}{[Pu]_{aq}}$$

Fig. 11. Stripping of Plutonium from HDBP Complexes in 30% TBP Solutions

A zirconium-laden TBP solution was used that had been prepared by stirring 500 mL of 30% TBP/70% nDD with an equal volume of 0.1M Zr(NO₃)₄ in 3M HNO₃ for 1 h on a magnetic stirrer at room temperature. The organic phase was separated in a separatory funnel, and a white precipitate that had formed at the interface of the two phases was discarded.

In the contactor, the zirconium-laden solvent was washed with 1M d-tartaric acid, 2.5 wt % sodium carbonate, or distilled water. Approximately

equal flow rates of 20 mL/min for the two phases provided a 1:1 volume ratio. The contactor conditions were: ~ 4 s residence time in the mixing zone, 40 mL/min total flow, and 9000 rpm rotational speed.

The zirconium analyses were performed by Florence Williams [WILLIAMS] and Kenneth Jensen of the Analytical Chemistry Group, who used a procedure which extracts the zirconium from an aqueous solution into a HDBP solution in toluene. The zirconium is then detected by the addition of 1-(2-pyridylazo)-2-naphthol, which forms an orange-red complex with the zirconium.

Tartaric acid (1M) aqueous phase was able to remove 93-99% of the zirconium. A sodium carbonate (2.5 wt % Na_2CO_3) aqueous phase and distilled water were also able to remove the Zr(IV) but less effectively (88 and 81%, respectively). This experiment will be repeated at the condition that zirconium is known to be bonded to the HDBP.

A preliminary flow sheet for the solvent washing step which uses the results of the radioactive tracer experiments is presented below (Fig. 12). This may be compared with the flow sheet expected for solvent washing using a 1-2% sodium carbonate wash in a turbo-mixer, Fig. 13. The data from the preliminary minicontactor test were not used. It is assumed that a high-burnup fuel is used and that the solvent is subjected to approximately 10-min contact with the feed. After stripping of plutonium and uranium with 0.01M HNO_3 , but before the solvent washing step, the solvent contains these impurities: $3 \times 10^{-3}\text{M}$ HNO_3 , $2 \times 10^{-6}\text{M}$ UO_2^{2+} , $5 \times 10^{-5}\text{M}$ Pu(III, IV, VI), $5 \times 10^{-5}\text{M}$ $^{95}\text{Zr}/^{95}\text{Nb}$, and 10^{-5}M Ru. It also contains $5 \times 10^{-4}\text{M}$ HDBP, $5 \times 10^{-5}\text{M}$ H_2MBP , and 10^{-6}M hydroxamic acids, which are expected to be complexed with these metals. These concentrations are approximate upper limits. In addition, we have assumed that citric acid and tartaric acid behave similarly to formic acid, and that their distribution coefficients between TBP/dodecane and nitric acid will be independent of the concentration of HNO_3 and equal to about 0.5 [GERMAIN-1974, 1976].

Our proposed method of cleaning the organic phase is based on complex formation with plutonium and the fission products. The types of complexing agents considered are citric acid and tartaric acid. Factors that are important to this procedure are the following: (a) the stabilities of the DBP complexes relative to the formation stabilities of the additive complexes; (b) relative solubilities and, hence, extractabilities of the additive complexes in water and in 30% TBP/70% dodecane; (c) solubility and extractability of the complexing additive in water and 30% TBP/70% dodecane; (d) kinetics of complex formation with the additive; and (e) the net effect of (a), (b), and (d), the distribution coefficients of each component, (*i.e.*, D_{Zr} , D_{Nb} , D_{Ru} , and D_{HNO_3}) in the time period of contact or washing. Since little of these data are available from the literature, these are areas we will study.

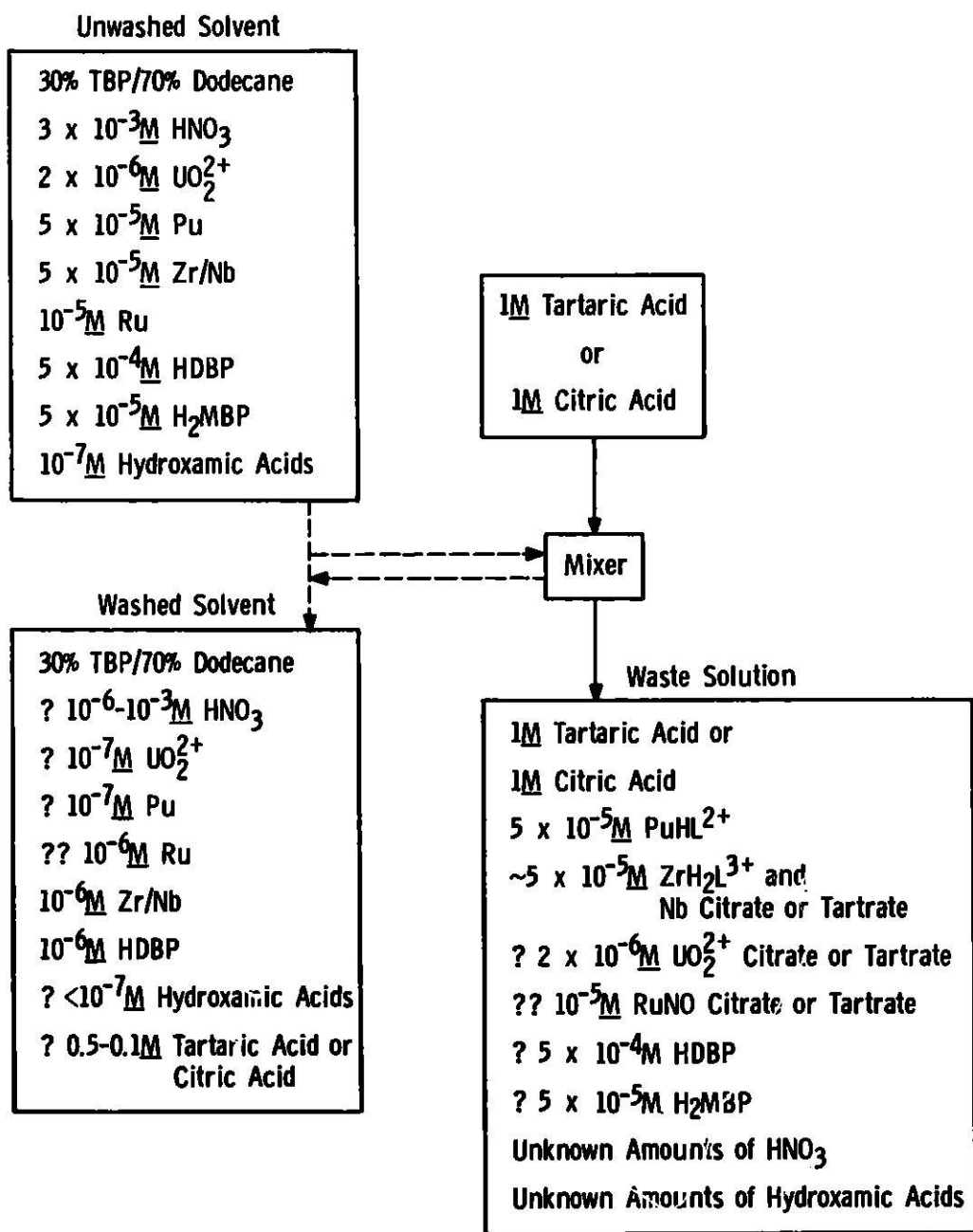


Fig. 12. Chemical Flow Sheet for Complexants Scrubbing. (H_3L = Citric acid or tartaric acid. "?" indicates a "best guess" value. In the mixer it has been assumed that there is one contact of equal volumes of aqueous and organic solvent and that the contact time is 1 min to 30 min.)

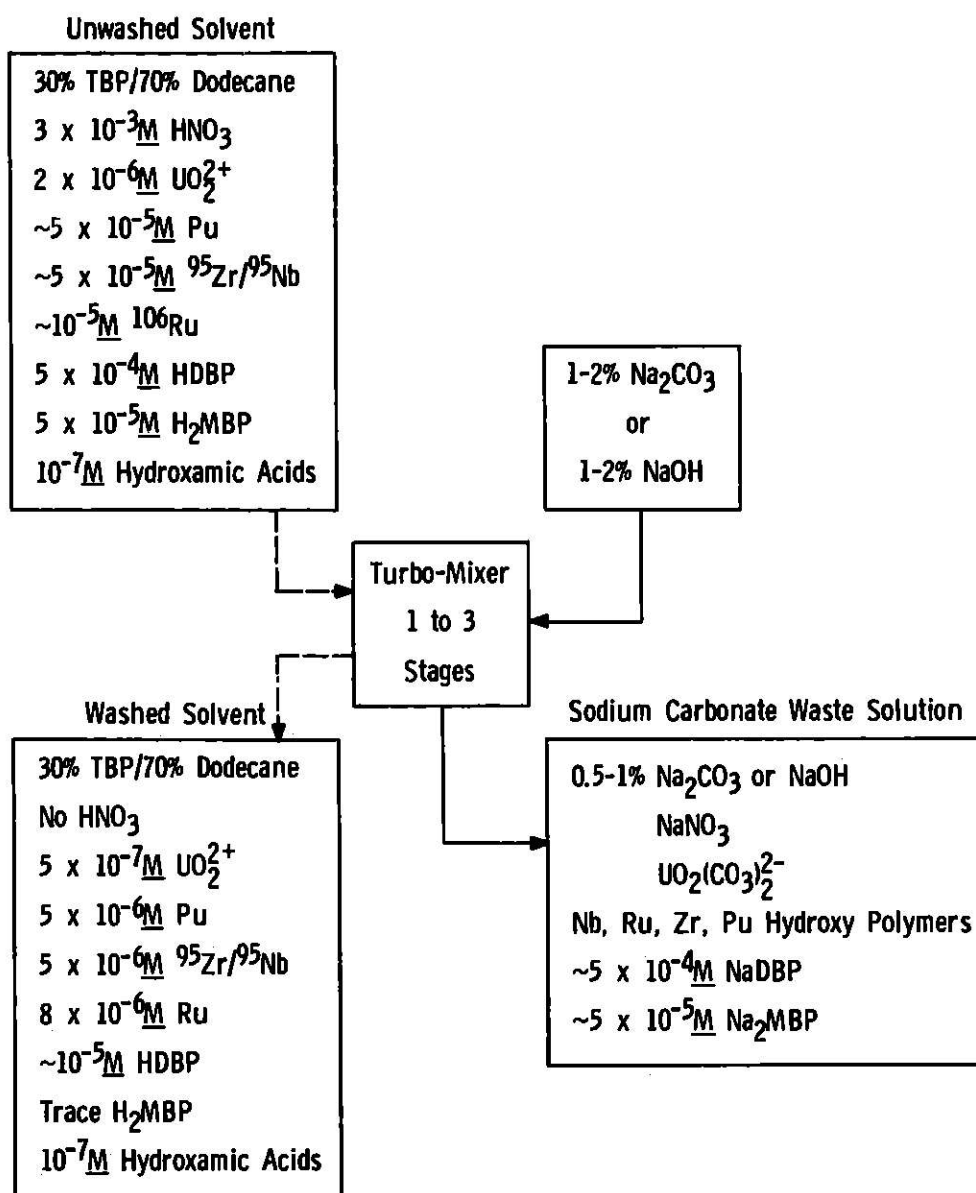


Fig. 13. Chemical Flow Sheet for an Alkaline Wash

II. ENVIRONMENTAL EFFECTS (W. B. Seefeldt and W. J. Mecham)

A. Introduction

An objective of this work is to provide a compilation of information to aid in the prediction of accident consequences in LWR fuel reprocessing facilities. The scope encompasses (1) definition of source terms from hypothetical accidents in reprocessing plants in terms of the physical and chemical properties of materials released to the first stage of air cleaning, (2) the modification of the properties of airborne materials undergoing transport to the first stage of an air-cleaning system, (3) quantitative estimation of the penetration of radionuclides through various stages of air cleaning, and (4) definition of the corresponding properties of the products of accidents as they are released to the environment at the stack or similar boundary of the plant. Operations in a processing plant are concerned mostly with liquids, and the dispersion of liquids is of principal concern for this study. Nevertheless, solids are not to be ignored, and information in the literature pertaining to solids is also being examined.

Work continued during the report period on obtaining information germane to the characteristics of material that has become airborne as a result of an explosive event. The information desired includes mass concentration, particle size distribution, and chemical form. Since no experimental work has been performed that would aid in the prediction of accident consequences for fuel reprocessing plants, work in other fields was examined to obtain information that may be useful.

An extensive literature review was conducted in many areas of technology including nuclear-related testing, blasting and quarrying operations, and coal mining. Although interest in experimental work on explosions is extensive, little of that interest is focused on information desired for this work.

B. Nuclear-Related Explosive Tests

Numerous nuclear-related tests have been conducted, including some of nuclear origin and some of high-explosive origin. Though the objectives have varied widely, the dust clouds generated by the events have been studied on many of them. Our interest centers on time periods ranging from several seconds after an event to about one hour after the event. This time period corresponds to the time period when airborne material would be expected to be present in a fuel reprocessing plant after an event and an air cleaning system would be challenged. Most studies of dust clouds cover periods beyond this time range of interest.

Reasonably typical of the results are those reported by Gudiksen [GUDI KSEN] for Project Schooner, a nuclear test (31,000 Mg TNT equivalent) conducted as part of the Plowshare program. The samples of greatest interest were those obtained by aircraft and parachutes within the first 1 1/2 h following the event. Airborne materials probably consisted of tuffaceous material since the explosive was detonated in such rock. Particle size measurements were performed by optical microscopy. The particle size distributions were found to closely approximate log-normal. The characteristics of the

distributions and mass concentrations at three different times after the event are shown in Table 3.

Table 3. Characteristics of Airborne Material from Project Schooner

Time after Event, min	Particle Size Distribution		Maximum Mass Concentration Observed, mg/m ³
	Mass Mean Diameter, μm	Geometric Standard Deviation	
12	30	2.8	240
40	20	2.8	100
70	17.5	2.6	50

This kind of data should be useful in making estimates for our purposes except for several difficulties. First, the magnitude of the event is many times larger than that which would be expected in a reprocessing facility. In addition, the explosion was unconfined; in a plant, the proximity of cell walls and barriers would have a pronounced influence on the propagation of shock waves and the manner in which materials would become airborne. The third difference is in the nature of the materials becoming airborne in a plant in contrast to a nuclear explosion; the materials would principally differ in density.

Samples were taken of clouds relatively soon after two other nuclear tests, Cabriole and Buggy, the yields of both being considerably less than that of Schooner. Cohen [COHEN-1968] describes the results from Cabriole (which had a yield of 2600 Mg) for samples taken with cascade impactors 23 and 26 min after the event. The medium at the site of the explosion was hard, dense, dry volcanic rock. Quantities in impactor stages were determined by gross beta counting, which is directly translatable to mass if the beta activity is uniformly distributed in the debris. However, fractionation of activity in different sizes of debris particles is well known; such fractionation was observed in this test by gamma spectroscopy performed on material in individual stages of the impactor. Cohen states that the size distributions from the samples taken soon after the event appear to be bimodal and that the large-particle mode disappeared in about two hours. If the quantities of material larger than 25.3 μm are ignored (42 and 29%, respectively, are >25.3 μm for the 23- and 26-min samples), the distributions are approximately log normal, and the means are 2.6 and 2.4 μm . It would be expected that the ranges of particle sizes for the two samples would also be similar, but they were not--geometric standard deviations were 2.8 and 2.0 for the 23- and 26-min samples.

Size distributions for particles larger than 25.3 μm were not reported. Mass concentrations also were not given.

The yield for Project Buggy [COHEN-1970] was 1100 Mg. Again, the distributions were obtained by gross beta counts of material collected on the individual stages of the impactor. Nearly 88% of the activity was associated with particles larger than 25.3 μm . When the large-particle fraction was ignored, the

distribution was approximately log-normal, having a mean of 4.5 μm and a geometric standard deviation of about 2.5. Mass concentrations of the airborne material were not given.

Several efforts have been made to determine particle mass concentrations in airborne material in the several seconds immediately following an explosive event. Freeman [FREEMAN] described the development of instrumentation for measuring dust parameters that included dust cloud density histories. Freeman further described its application to Project Middle Gust. This was a nonnuclear event in which a 100-Mg sphere of TNT was exploded. Maximum mass concentrations, which ranged from 700 to 1100 g/m^3 , occurred within 1 s of the detonation. A very rapid decrease in concentration with time (several seconds) is indicated, which would be expected if particle sizes were large. Size distribution measurements were not made.

Comparable information was obtained by Banister and Emrich [BANISTER] who used high explosives and a cruder technique. Greased stakes and specially designed collector plates intercepted the blast-induced debris, and dust densities were estimated to range from 300 to 2400 g/m^3 .

The distribution of large solid airborne particles can be inferred from the particle size analyses of materials deposited within a short distance of an event. As a part of project Stagecoach, Miller [MILLER] reported that at a distance of 105 m from the event, the mean particle size (by weight) was 2200 μm and at 335 m it was 170 μm . The range of size distributions (as expressed by the geometric standard deviation) was extremely wide at the close-in location ($\sigma_g = 11$) and narrowed rapidly at more distant locations ($\sigma_g = 2$). Whether this kind of information would be useful in constructing the time history of airborne material is not clear at this time.

C. Experience with Coal and Rocks

The U.S. Bureau of Mines is interested in the dispersal of coal debris (induced by a primary explosion) since the dispersed debris could in turn lead to secondary explosions. Initial studies were made under steady state conditions in a wind tunnel in which were placed coal dusts compacted to various degrees [SINGER-1972]. Voluminous data on mass concentration of dispersed material, E , for free-flowing Pittsburgh seam coal (particle size range of 100 to 150 μm) was subjected to regression analyses, resulting in the following relationship:

$$E(\text{g}/\text{m}^3) = 31.2 U_L^{1.1} \rho_B^{5.9}$$

where U_L = air velocity at mid-height of the compacted coal, m/s
 ρ_B = bulk density of the compacted coal, g/cm^3 .

The relationship yields about 10 and 90 g/m^3 for air velocities of 5 and 40 m/s, respectively ($\rho_B = 0.604 \text{ g}/\text{cm}^3$).

In later tests [SINGER-1976], dispersal of coal and rock debris was induced by explosions at one end of a shock tube. Measurements of debris uptake were made, together with instantaneous velocities. The scatter of the data was broad for both coal and rock, with little apparent relationship between air velocity and solids dispersal. Calculated airborne mass concentrations of coal-rock mixtures ranged from 4 to 30 g/m^3 for measured air velocities of

9 to 65 m/s. Comparable numbers for rock only were 10 to 60 g/m³ for air velocities of 11 to 70 m/s.

Data obtained to date indicate that airborne material concentrations up to several hundred grams per cubic meter can be obtained. The modification of such airborne materials by mechanisms such as settling, sedimentation, and agglomeration is yet to be examined.

Hamilton [HAMILTON] found that the breakage products of a variety of coals and coal measure rocks could be expressed in the form

$$\frac{dF_N}{dD} = \alpha D^{-\beta}$$

where D is the particle size, dF_N is the number of particles in the size range from D to $D + dD$, and α and β are constants. For coal and rock, the values of β are about 2.25 and 3, respectively. This relationship was found to be reasonably valid in the size range, 1 to 100 μm , for dust-producing operations such as rotary and percussive drilling, coal cutting, and shatter.

Grimshaw [GRIMSHAW] studied particle size distributions resulting from detonations produced by placing explosives in stone blocks. In his studies, Grimshaw placed stemmed charges of high explosives in axial holes fabricated in cylindrical stone blocks 45 cm in diameter and 75-cm long. Dust that was made airborne was extracted by an air current and retained on a filter. Other debris was confined and collected in a large rubber-lined steel confinement cylinder. Grimshaw concluded that the distributions are of the form proposed by Hamilton [HAMILTON]. The distribution proposed by Hamilton is basically a log-log distribution, the characteristics of which are quite dissimilar to the frequently observed log normal distribution. Grimshaw's conclusions indicate that the use of larger quantities of explosives does result in a shift of distributions to smaller sizes, but that the distribution still follows the Hamilton model. This data is to be examined further.

D. Experience with Dispersion of Liquids

The dispersion of liquids into air is a subject of interest to those concerned with chemical warfare agents. Gerber [GERBER], wishing to determine the range of propelled liquids, developed a reusable, vertical, high-explosive projector to simulate the dispersion of chemical agents in a confined space. The projected droplets were sampled by an array of interception/impaction devices (horizontally oriented) located above the projector. A nonvolatile tracer added to the liquid allowed subsequent quantitative assessment of the material deposited on the interception/impaction devices. The datum of interest was the percentage of liquid that penetrated a series of horizontal planes above the projector. The energy of the explosive charge was not stated.

Eleven liquids, including hot and cold water, were used in the testing program. The fraction of liquid not reaching height Z above the projector was found to exhibit a two-parameter Weibull type distribution as follows:

$$F(Z) = 1 - \exp \left[- \left(\frac{Z}{N} \right)^\beta \right]$$

where $F(Z)$ = fraction not reaching height Z (ft)
 N, β = constants

For cold water, values of N and β were 12.3 and 3.28. Though data in this form is not of direct interest to us, it should be possible to calculate a particle size distribution from the information presented.

Similar information may be available in the classified literature, which has not been studied.

E. Pressure Transients and Filter Integrity

An important part of this work is to determine how airborne material characteristics are modified by the air-cleaning system of a reprocessing plant. Understanding of the design and operation of an air-cleaning system is fundamental to analysis. Germane to this subject is the ability of an air cleaning system to withstand accident stresses such as might be caused by an accidental explosion inside a plant.

In a search for possible bases for modelling the effects of explosions on the dispersion and confinement of radioactive materials, the literature on blast effects was reviewed.

Much of the technical literature on blast characterization is specifically related to the effects of nuclear weapons, rather than explosions of chemical origin. A blast wave from a moderate amount of TNT, for example, would be of much shorter duration than a massive nuclear explosion, and this would affect reflection and propagation. The rate of detonation or deflagration in chemical explosions also is widely variable. Information is being examined on (a) scaling laws of blast parameters, (b) propagation of blast effects in open air and in ducts of various configurations, and (c) air-blast-resistant and protective designs.

A visit was made to Los Alamos Scientific Laboratory (LASL) to discuss a program directed towards the effects of pressure transients on the behavior of HEPA filter systems. The transients of principal current concern at LASL are those induced by tornadoes. However, transients resulting from plant accidents are of interest for future studies. Comprehensive models of air flows through hypothetical plant ventilation systems under tornado conditions have been established with a view of ascertaining perturbations to normal pressure differentials and flows. Flows as large as $\sim 700 \text{ m}^3/\text{min}$ (25000 cfm) with pressure pulses up to 20 kPa (3 psi) have been predicted.

In an experimental program explained during our visit, HEPA filters are being subjected, for sustained periods, to pressure differentials high enough to make filters fail. An important question not yet addressed is the filtration efficiency under these off-normal conditions.

III. SALVAGE OF ALPHA-CONTAMINATED METALS (M. G. Seitz and T. J. Gerding)

A. Introduction

Of the large amount of plutonium-contaminated waste generated in defense-related industries and in reactor development programs, some is metal which cannot be burned or otherwise treated with combustible material. The purpose of this study is to demonstrate a method of cleaning contaminated metals for economic disposal or even recycling.

In the experimental effort, melting in the presence of slags of metals contaminated with oxides of plutonium and americium (*i.e.*, melt refining) was evaluated as a decontamination step. This technique can be used on a large scale to clean metals, as well as to convert them into homogeneous forms for assay and handling.

B. Experimental Techniques

In a typical experiment, a massive metal sample, plutonium oxide, and slag were loaded into an alumina crucible. A plutonium concentration of 400 ppm was used in most experiments because it is considered within the range of most contaminated scrap material. The metals used in these experiments were a cold-rolled mild steel,* 304 stainless steel, nickel-200, mild steel containing a minor amount of copper, and mild steel and stainless steel containing a minor amount of brass. The plutonium oxide contained 83.81 wt % plutonium and 0.528 wt % ^{241}Am . The slags were borosilicate glasses, industrial slags from steel-making processes, and fused mixtures of metal oxides. Both resistance furnace and electric arc-melting techniques were used for melt refining.

Before being loaded into the furnace, the plutonium oxide was placed in a cavity of the metal sample and was retained in the cavity with a metal plug (1) to restrict the accessibility of slag to the plutonium prior to melting and (2) to simulate contamination in cracks or embedded on wear surfaces of the metals. In the experiments with mild steel, the effects on metal product purity of varying the amount of slag and its composition were studied.

Most melting experiments were conducted in a tungsten-mesh resistance furnace (Brew, Model 1064-C) that was capable of providing temperatures up to 1800°C as well as any desired atmosphere. The furnace was loaded either with one large crucible (100-mL capacity) containing about 200 g of metal or with three small crucibles (each of 5-mL capacity) containing about 10 g of metal each. In most experiments, the melts were held at temperature for 1 h.

After melting and solidification in the resistance furnace, the crucibles were removed from the furnace. They were often cracked, probably having cracked during cooling due to differential thermal contraction of the crucible, metal, and slag. The metal and slag were removed from the crucible for analyses or for reprocessing. The metal ingots had shiny surfaces, varying from smooth to pitted; generally fragments of slag adhered to them.

* Steel analysis: Fe, >99%; C, 0.08-0.23%; P, 0.24%; Si, 0.03%; Mg, <0.001%.

Other experimental approaches were taken to determine whether (1) arc melting was useful in decontaminating metals and (2) whether staged extraction (*i.e.*, successive melt-refining steps) produced a cleaner metal product.

Analyses of massive samples (~10 g) of metals and of slags to determine the average plutonium concentrations were accomplished by aqueous dissolution and radiochemical counting.* Two additional methods were used to identify the sites where plutonium was associated with the metals and slags: An autoradiographic technique, sensitive to alpha particles, was used to reveal the microscopic distribution of plutonium and americium in the metals and slags. The second method was a fission-track analysis technique that is highly sensitive to plutonium.

Borosilicate slags, as well as metals, were analyzed by neutron activation. In this procedure, the glass samples were placed in individual assemblies to minimize neutron shielding effects on other samples caused by boron in the glass. Small silvers of glass were used in the analyses to reduce self-heating and self-shielding effects.

C. Experimental Results

Conditions for plutonium-extraction experiments performed in the melt-refining program during the past nine months are listed in Table 4.

1. Distribution of Plutonium and Americium in Metal Matrix and Slag

Samples of the slags from melt-refining experiments were analyzed for plutonium and americium. Analyses of slags for some current experiments and earlier experiments (ANL-77-36) are reported in Table 5. Each total quantity of plutonium in a slag was calculated from the measured concentration by assuming that there was no weight loss or weight gain of the slag (*e.g.*, by dissolution of the crucible material) during melt refining. Plutonium in the slag is also expressed as a percentage of the initial amount added to the metal in Table 5.

Because most of the plutonium was removed from the metal during refining and because crucibles that were analyzed were found to not be reservoirs for plutonium, it was expected that most of the plutonium used in the experiments would be found in the slags, and that the total plutonium content in the slag would be near 100%. However, the values for total plutonium in the slag ranged from <1% to 220%, suggesting an error either in the analyses or in the assumptions used to calculate total plutonium.

The alpha radiograph of the sectioned ingot from experiment 121-3 revealed that most of the plutonium was associated with slag on the lower surface of the ingot. Proportionately little plutonium was associated with the slag on the top surface of the ingot, where the sample for radiochemical analysis was obtained. Thus, inhomogeneity of plutonium in the slag accounts for the low plutonium concentrations found by radiochemical analysis. The analyses and

* Analyses for plutonium and americium by aqueous dissolution and radiochemical counting were done by E. T. Kucera and E. A. Huff of the Analytical Chemistry Group.

Table 4. Conditions for Melt-Refining Contaminated Metals.
Cover gas of helium at 5.3×10^4 Pa and a temperature
of $\sim 1500^\circ\text{C}$ was used during melting.

Expt. No.	Metal Weight, g	Metal	Plutonium Weight, mg	Initial Metal Contamination, ppm Pu	Slag ^a Weight, g	Slag/Steel Weight Ratio	Time at Temp., h
126 ^b		Mild Steel		0.01			0.016
129	204.4	Mild Steel					
	9.4	Copper	84.5	407	20.23	0.10	1.0
130-1	201.3	Mild Steel	84.5	412	20.03	0.10	1.0
130-2	204.2	Mild Steel	88.4	439	20.22	0.10	1.0
133 ^c	40.4	Mild Steel			4.16	0.10	1.0
135	204.1	Mild Steel,					
	9.51	Copper	86.1	403	20.00	0.09	1.0
137	102.5	Mild Steel,					
	85.1	304 Stainless	79.5	424	10.08	0.11	1.0
139	108.0	Mild Steel,					
	87.0	304 Stainless	84.0	431	20.10	0.10	1.0
141	84.2	Mild Steel,					
	83.3	304 Stainless,					
	16.6	Brass	85.3	462	20.21	0.11	1.0
143	89.8	Mild Steel,					
	85.8	304 Stainless,					
	17.0	Brass	86.5	449	20.14	0.10	1.0
145	200.2	Nickel 200	104.4	521	20.09	0.10	1.0

^aThe slag was borosilicate glass having a nominal composition of 81.0% SiO₂, 13.0% B₂O₃, 4.0% Na₂O, 2.0% Al₂O₃, and 0.5% K₂O by weight.

^bExperiment 126 was performed with unweighed samples of mild steel (contaminated with plutonium and slag), which were melted in an electric-arc furnace.

^cIn experiment 133, the metal consisted of steel turnings produced by trimming ingots from experiments 130-1 and 130-2.

Table 5. Transuranic Content of Slags from Melt-Refining Experiments^a by Aqueous Dissolution and Radiochemical Counting

Expt.	Slag	Actinide Concentration		Total Pu in Slag, mg	Percent of Initial Pu In Slag
		Pu, mg/g	Am, ppm		
73	CaSiO ₃	4.7	27.3	48	52
76	CaSiO ₃	2.7	24.4	61	74
78	CaSiO ₃	2.1	15.8	86	105
80	B ₂ O ₃ Glass	4.1	26.0	83	95
82	B ₂ O ₃ Glass	2.0	17.6	78	88
101	CaMgSi ₂ O ₆	4.8	41.6	96	115
105	Hearth Slag	1.5	13.2	31	37
107	Ca-Al silicate	1.9	16.9	38	46
109	B ₂ O ₃ Glass	9.3	71.4	187	220
111	B ₂ O ₃ Glass	0.83	6.7	33	38
113	B ₂ O ₃ Glass	0.1	0.7	2	-- ^b
115	B ₂ O ₃ Glass	2.3	19.0	46	78
117	B ₂ O ₃ Glass	2.9	27.1	59	72
119	B ₂ O ₃ Glass	3.0	27.2	60	71
121-1	B ₂ O ₃ Glass	1.0	8.1	1	24
121-2	B ₂ O ₃ Glass	2.4	18.6	3	3
121-3	B ₂ O ₃ Glass	1.1	10.0	1	0.8 ^c
124-1	CaMgSi ₂ O ₆	2.5	19.1	6	71
124-2	CaMgSi ₂ O ₆	27	200	52	56
124-3	CaMgSi ₂ O ₆	37	330	73	39
129	B ₂ O ₃ Glass	6.5	48.4	131	155
130-1	B ₂ O ₃ Glass	7.4	55.8	148	145
130-2	B ₂ O ₃ Glass	6.6	47.8	133	125

^aThe experimental conditions for expts. 73-124c and metal ingot analyses for expts. 73-115 (except expt. 105) were reported in ANL-77-36.

^bInitial plutonium concentration not accurately known.

^cAutoradiographic analysis of this slag indicates that there was inhomogeneity of plutonium in the slag phase.

the assumption of homogeneity will be investigated by alpha-radiographic techniques for other slags showing the greatest departures from the expected plutonium contents.

Analyses of metal samples (from ingots) and slag samples for TRU content by radiographs indicated that the alpha activity was predominantly on the surface of the ingots and associated with adhering slag material. Samples of all metals showed this effect. There was also plutonium in the interior of some ingots, associated with large defects that were visible on cut surfaces. The metal matrix had a low plutonium concentration in comparison to the slags. Plutonium levels in metal matrix samples are given in Table 6.

Table 6. Plutonium in Metal Matrix Samples^a by Alpha Radiography

Expt.	Sample	Concentration of Plutonium, ppm
121-1	Diametral section along axis	0.0006
121-2	Diametral section along axis	0.0059
121-3	Diametral section along axis	0.018
124-1	Diametral section along axis	0.0035
124-2	Diametral section along axis	0.015
126	Diametral section along axis	0.0006-0.0017
129	Mid-top cross section ^b	0.060

^aThe weights of plutonium charged (along with ~12 g of mild steel in each experiment) were 5.0, 99.7, 164, 7.8, and 93 mg in experiments 121-1, 121-2, 121-3, 124-1, and 124-2, respectively. Experiments 121 and 124 were performed with borosilicate slag and diopsidic slag, respectively.

^bA mid-top sample was taken between the top and middle samples, as shown schematically in ANL-77-36.

2. Effect of Plutonium Concentration on Its Distribution in Metal Matrix and Slag

Experiments 121 and 124 were devised to determine the effect of increased plutonium contamination (ANL-77-36, p. 11) on the extraction process. This was done by simultaneously processing three contaminated metal samples in the furnace. The metal samples were smaller than used when only one sample was processed (10 g vs. 200 g) and were spiked with various amounts of plutonium. In these experiments, the weight of slag and the size of the crucible were reduced so that the slag to steel weight ratio and the geometry were approximately the same as when the larger sample size was used.

The analyses of plutonium in the metal matrix for experiments 121 and 124 are plotted in Fig. 14. against the concentrations of plutonium determined in the slag phases. The results indicate a continuing and high partitioning of plutonium to the slag phase, even with very high plutonium levels initially in

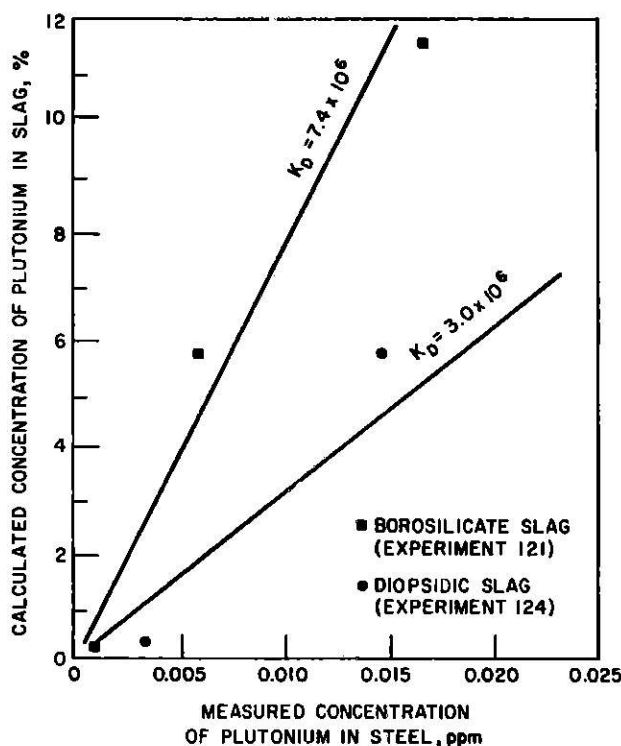


Fig. 14.

Plutonium Concentration in Slag *vs.* Plutonium Concentration in Metal Matrix. Analysis by alpha radiography. The concentration of plutonium in the matrix was calculated assuming no weight change of the slag occurred during melting and solidification.

the metals. The partitioning coefficient, K_D , obtained for borosilicate glass (7.4×10^6) is higher than that obtained for a slag of diopsidic composition, calcium, magnesium silicate (3×10^6), where the partitioning coefficient is the ratio of the plutonium concentration in the slag to the plutonium concentration in the metal after melting and solidification.

3. Arc-Melting of Metal-Borosilicate Glass

In experiment 126, a metal sample containing about 0.004 ppm plutonium was arc-melted with borosilicate glass in an atmosphere of flowing argon. The metal and slag were maintained in contact in a molten state (at $\sim 1500^\circ\text{C}$) for 1 min. After cooling, the metal sample was spherical, with two solidified slag nodules on the top surface of the ingot. From Table 6, it is seen that the arc melting was effective in removing some plutonium from the steel. Preliminary observations indicate that the plutonium remaining with the steel is uniformly distributed throughout the matrix rather than being clustered (as occurs in samples produced using the resistance furnace). This may be due to the rapid melting and solidification that occurs when the arc-melter is used, preventing plutonium in the melt from consolidating as it would upon slow cooling. The metal from this experiment will be examined in more detail, using neutron activation techniques, to establish the exact distribution of the plutonium.

4. Effect of Copper on Distribution of Plutonium in Metal Matrix and Slag

Experiments 129 and 135 were performed using mild steel with a small amount of copper. The plutonium concentrations in the metal matrices are higher than in metals from experiments with mild steel alone. After

similar treatments, 0.060 ppm plutonium remains in the copper-containing mild steel in comparison to about 0.0001-0.004 ppm in steel alone.

5. Locale of Plutonium and Americium in Metal Matrix

Analytical work was performed to establish the relative importance of the two locales of TRU-element contamination in processed metals. These are (1) slag adhering to the metal ingots and (2) slag in defects in the ingots. In these experiments, the surface of the ingots was removed and then the remaining metal was analyzed. Only TRU-element contamination at metal defects within the ingot was determined--not TRU elements associated with slag at the surface of the ingot.

Two metal ingots were produced by processing contaminated metal with borosilicate glass in the conventional manner. The conditions for experiments 130-1 and 130-2 are listed in Table 4. After processing, large pieces of slag were separated from each ingot, and a thin surface layer was removed from the entire ingot, using a metal lathe. One ingot (from Exp. 130-2) was cut into five pieces, and the top, middle, and bottom sections were analyzed by chemical dissolution and radiochemical counting. A top section was cut from the second ingot (from Exp. 130-1) and the large remaining section was radiochemically analyzed without further sectioning. The analyses are given in Table 7.

In addition, the top sections of both ingots were analyzed by alpha-track radiography; these analyses are also given in Table 7.

Table 7. Analyses of Sections of Metal Ingots from which Surface Layer Had Been Removed

Sample Number	Section	Sample Weight, g	Plutonium, ppm	Americium, ppm	Plutonium by Alpha-track Radiography, ppm
130-1-I	Top	----	----	----	0.0003 ^a
130-1-II	Middle and Bottom	151.1	0.0015	<0.0006 ^b	----
130-2-I	Top	30.9	0.00009	<0.0006	0.0001
130-2-II	Middle	75.2	0.00007	<0.0006	----
130-2-III	Bottom	17.2	0.00007	<0.0006	----

^aAreas of the metal matrix without visible defects were analyzed by radiography.

^bNo activity from americium was detected by gamma counting.

The analyses of plutonium by radiochemical counting are very low and comparable to the analyses by alpha-track radiography (Table 7). This indicates that defects were not a source of large amounts of plutonium in

these metal ingots. Slag that adhered to the surface of the metal ingots may have been the major source of plutonium in the processed metal ingots. The slag was effectively removed by trimming the surface of the ingot, reducing the plutonium levels of the ingots to nearly those found in the matrix of the metal.

No activity of americium was detected by gamma counting, and if americium was the source of the low alpha activities detected by the radiography, the americium concentration would still be very low ($\lesssim 0.000008$ ppm). Thus, americium is also believed to have been effectively removed from the metal by melt refining and trimming.

The lower section of ingot 130-1 and the middle section of ingot 130-2 given in Table 7 are significantly larger (151 and 75 g, respectively) than samples that were previously analyzed (~ 15 g). The low TRU content of these samples indicates that samples whose size is close to the size of the metal charge of the furnace can be obtained that are free of large amounts of contamination.

6. Determination of Plutonium Concentration and Distribution by Neutron Activation Analysis

Neutron-activation analyses of materials containing very low concentrations of plutonium were conducted to determine plutonium concentrations and distributions more precisely than was possible using alpha radiographs. The samples were examined for cross contamination, which could occur during sample preparation, and only analyses of samples with low cross contamination are reported. Descriptions of the experiments for which materials were analyzed are given along with the analyses in Table 8.

The plutonium-contaminated metal used in experiment 113 was from two earlier experiments and contained 0.2 ppm plutonium before melt refining as determined by dissolution and radiochemical counting. The very low concentration of plutonium in the metal after the second extraction (Table 8) indicates that repeated or "staged" extraction is a useful process step for producing metal having a very low plutonium concentration. This conclusion was also suggested by analyses in the preceding report in this series (ANL-77-36) showing a relatively high plutonium concentration in the slag from experiment 113.

An additional conclusion reached from analyses for experiment 115 in Table 8 is that plutonium from the slag may enter the metal, presumably to establish a chemical potential balance between the metal and slag. This suggests that the clusters of plutonium in the metal are not particles of slag dispersed in the metal, but rather precipitates of plutonium (and perhaps other oxides) that form during cooling of the metal ingot.

The metal from arc-melting (experiment 126) cooled much more rapidly than did the metal in the resistance furnace. Plutonium clusters were absent from the metal that was arc-melted, possibly due to time not being available for the precipitates to accrete during cooling. The slag used in the arc-melting experiment has considerably higher plutonium concentrations than the metal. This indicates that arc-melting with a slag covering may constitute an effective decontamination process.

Table 8. Experiments and Analyses of Experimental Products by Neutron Activation

Expt.	Description of Experiment	Sample	Plutonium, ^a ppm	Comment
113	Second stage of extraction; both extractions performed using borosilicate glass	Metal sample, top of ingot, center to edge	0.0001	Plutonium in metal matrix is clustered. The second extraction effectively lowered the plutonium content of the metal.
115	Back extraction, plutonium was added in the slag (borosilicate) which was melted with uncontaminated metal	Metal sample, top of ingot, center to edge	0.0005	Plutonium in metal matrix is clustered.
		Metal sample, top of ingot	0.0004	Plutonium entered the metal from the slag.
126	Low Pu-bearing metal (0.010 ppm) refined with borosilicate slag by arc melting (melting time of 1 minute)	Metal, cross section of ingot	0.00004	Background of 0.00003 ppm was subtracted. The few fission tracks indicate that the plutonium in the metal is not clustered.
		Borosilicate slag, adjacent to metal	0.090	Concentration of plutonium in the slag adjacent to the metal was high, diminishing at a distance from the metal.
		Slag furthest from metal	~0.00003	
		Average of slag	0.0098	

^aActivation done with a neutron dose of 6.7×10^{19} n/m².

The existence of a concentration gradient of plutonium in the slag from experiment 126 suggests that the slag is not agitated during arc-melting. The plutonium concentration in the slag increased in the vicinity of the metal (which is the source of the plutonium), possibly as a result of atomic diffusion in the slag during processing. The plutonium concentration at a depth of 2.0×10^{-2} cm in the slag is 50% higher than at the surface. If it is assumed that the metal is a continuous source of plutonium for the slag and that diffusion occurred in the one-minute duration of the melting experiment, a diffusion coefficient of 7×10^{-6} cm²/s is suggested for plutonium in molten

slag, applying Fick's law of diffusion (CRANK-1975). In the absence of stirring or mixing, the amount of slag that interacts with molten metal in a given time is limited by this diffusion rate.

D. Locating Defects in the Metal Ingots

High concentrations of plutonium are often associated with defects in processed metal ingots. Although defects are not abundant, they are a major source of the plutonium associated with processed metal. Consequently, methods of quickly scanning ingots in a nondestructive manner to locate this type of defect were examined. Metals found to contain such defects could be treated appropriately.

Ultrasonic probing was found to be the most promising technique [YUHAS]. An ultrasonic imaging system (shown in Fig. 15) may be devised using a single piezoelectric transducer, an ultrasonic driver, and an oscilloscope. The transducer is shock excited with a voltage spike, and the generated sound pulse is transmitted to the ingot. The difference in the acoustic impedance (mass density \times sound velocity) caused by a defect gives rise to an echo which can be picked up by the same transducer, amplified, and viewed on the oscilloscope. For voids in metals, the impedance discontinuity is essentially infinite, giving high sensitivity of ultrasound in defect detection. The position of the defect can be determined from the time of flight of the pulse and echo.

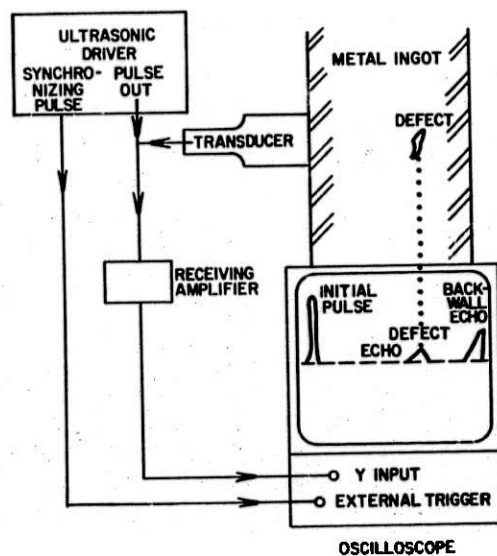


Fig. 15.

Schematic of Ultrasonic Imaging System for Detecting and Locating Defects in Metal Ingots

The sensitivity of ultrasonic imaging is directly related to the ultrasonic frequency and the nature of the defect being imaged. The smallest defect that can be detected is related to the frequency employed and is not limited by transducer size (as is resolution). For frequencies in the range, 2 to 20 Mhz, voids in metals about the size of the sonic wavelength or larger can be detected (approximately 0.3 to 0.03 cm for compression waves and half this for shear waves over the stated frequency range). This sensitivity is more than

sufficient to detect significant defects that arise in the metal ingots. Yee and Couchman summarized ultrasonic examination principles and methods [YEE].

E. Conceptual Design of Pyrorefining Plant For Decontamination of TRU-Contaminated Metals

1. Introduction

The laboratory-scale experimental program revealed that melt-refining has the potential to effectively decontaminate TRU-contaminated ferrous and nickel metals for low-level disposal or possibly recycling. A conceptual design of a refining plant (to use laboratory-tested melt-slagging techniques) is being formulated to assist planning for an operating plant. The conceptual design is based on a significant scale-up of laboratory operations. The design incorporates some operating procedures which appear advantageous on the basis of experience gained from the experimental program but have not yet been tested.

2. Metal and Glass Product

The process is designed to produce a consolidated metal (1) with no activity on loose particles and (2) with a concentration of TRU elements whose combined activity is less than 10 nCi/g of metal. Under a proposed Federal regulation [FEDREG-1974B], such low-activity material may be disposed of in commercial burial facilities and need not be stored in a retrievable fashion. The primary waste stream from the process is designed to contain the TRU elements in as concentrated a form as possible in a glass matrix. Further concentration of the TRU elements in the waste or their possible recovery, allowing reuse of the slags, may be possible, but no provisions have been made to incorporate a slag cleanup step in the processing scheme.

3. Process Capacity

Processing facilities of two sizes (a pilot plant and a larger-sized facility) have been considered. Both facilities are designed for batch operation, and the sizes of the furnace and crucible principally determine the capacity of the facility. In the pilot plant, the furnace and crucible are designed for a maximum capacity of 40 kg of metal and 4 kg of slag. In the larger sized facility, charges of up to 150 kg metal and 15 kg of slag can be handled in the furnace and crucible. The two facilities are larger by factors of 200 and 750, respectively, than previous laboratory facilities. The two facilities have many features in common, and essentially they are dissimilar only in scale of operation (which determines portability, type of support facilities, etc.), not in their processes. Therefore, the following discussion applies to both sizes of facility.

4. Input Materials for Processing

For design criteria, metals (predominantly steels) containing about 400 ppm TRU contamination are considered to be typical of the contaminated materials to be processed in a plant. In the experimental program, it was found that even inclusion of up to 5 wt % copper in steel had no detrimental effect on processing; until additional experimentation is done, this behavior may be considered to hold for other common metals also so that a ferrous and nickel metal containing less than 5% of other metals would be suitable for the

refining process. In the experimental program, it was found that the melt-refining process is not sensitive to the composition of the slag. Therefore, a small amount of glass (*e.g.*, bottles, beakers) could be incorporated into silicate slags without reducing the effectiveness of the process. The amount of other nonmetallic components that could be tolerated in the metal being processed would depend on which materials they were. Generally, however, the proportion of materials that do not form slag (such as combustibles) should be kept low--possibly less than 2% of the weight of the metal. A ventilation system for the furnace is provided in the design to accommodate a small amount of fuming from combustible material.

5. Process Steps

a. Sorting

In the conceptual design, TRU-contaminated metal wastes are handled in a sorting area, where ferrous and nickel metals are separated from other materials. The "other materials" may constitute part of the shipping containers (*e.g.*, plastic) or be parts of the disposed-of items (*e.g.*, Bakelite terminal boards, copper motor armatures, etc.).

b. Size Reduction

In size reduction, the sizes of metal waste objects are reduced so that the waste can be handled in the loading and batching operation of the melt-refining process.

c. Melting

After sorting and sizing operations, the metal waste is ready for refining and is loaded, along with 10% by weight slag, into the crucible. During melting, additional metal and slag are loaded up to 60% of the crucible capacity.

The metal and slag are maintained molten for one hour. The solution is stirred for 45 min and allowed to settle for 15 min. Prior to pouring of the metal, a sample of the slag is obtained for analysis of the plutonium concentration of the slag.

d. Pouring and Casting

The molten metal is tapped from a bottom hole in the crucible. A sample of the molten metal is intercepted in a ladle before the metal reaches the mold. The metal sample is cast in disc shape for radiochemical analysis and, if necessary, subsequent archival storage. The total amount of steel that may be tapped from a crucible is restricted by the necessity of preventing slag from draining with the metal. Two ingots are poured from one heat. After the metal ingots cool, they are surveyed for surface alpha activity. An ingot is then imaged by ultrasonic techniques to verify that there are no voids or slag inclusions in the ingot. Any metal ingots suspected of containing TRU contamination in excess of 10 nCi/g metal may be recycled. The slag is reused or stored, depending on its plutonium content.

In Table 9, the conceptual process steps for a melt-refining facility are summarized.

Table 9. Conceptual Process Steps for a Melt-Refining Plant

Conceptual Process Step	Design Specification
Sorting	Ferrous metals containing nickel and chromium with less than 5% other metals and less than 2% combustible materials
Size Reduction	Size reduction of scrap allows the scrap to be loaded into a furnace crucible
Crucible Loading	Metal-slag mixture in the ratio, 10:1 by weight. Load the crucible to 60% of maximum capacity
Melting and Slagging	Molten system maintained for 45 min with stirring and 15 min settling
Slag Sampling	A slag sample is ladled from the top of the crucible for analyses.
Metal Casting and Sampling	Bottom-tap to obtain two ingots without slag admixture. A sample of molten metal is taken with a ladle at the bottom tap.
Ingot Analyses	Measure the alpha activity of ingot surface and the alpha activity of the metal sample. If the activity is greater than $10nCi/g$, recycle the ingot.
Slag analyses	Pour slag if its plutonium concentration exceeds 0.1%. Introduce additional slag into the crucible if the plutonium concentration of the slag exceeds 1%.

6. Other Considerations

The design data for the pilot plant and large-scale facility are given in Table 10. Although the plants are for basically the same operations, their difference in size allows plant construction design to differ. The pilot plant is envisioned to be built in modules that would be transportable. They would operate for as long as necessary to process the metal scrap at a site and then be transported to another location where processing would again commence.

Table 10. Design Data for the Pilot Plant
and the Large-Scale Plant

Equipment or Design Feature	Pilot Plant	Large-Scale Plant
Transfer Containers	5-gal drums	55-gal drums
Size Reduction	15-cm max dimension	25-cm max dimension
Furnace	Induction	Electric-Arc
Crucible Size	20-cm ID 25-cm height	33-cm ID 35-cm height
Metal Charge	40 kg	150 kg
Slag Charge	4 kg	15 kg
Plant Portability	Portable, three trailer units	Stationary

The larger plant would be built as a stationary facility. Metal waste would have to be transported to the facility, and the processed materials would be transported for permanent storage. This facility would have the advantage over the portable unit of being able to run continuously with permanent support capabilities (work force, utilities, etc.).

In Table 11, the design outputs of the two plants are considered. The furnace utilization factors (crucible loading and metal tapping efficiencies)

Table 11. Design Output for the Pilot Plant and
Large-Scale Melt-Refining Plant

Factor	Pilot Plant	Large-Scale Plant
<u>Furnace Utilization</u>		
Crucible loading efficiency	60%	60%
Metal tapping efficiency	80%	80%
<u>Batch Time Requirements, min</u>		
Loading and Melting	30	90
Stirring	45	45
Settling	15	15
Tapping and Slagging	<u>30</u> 2h	<u>60</u> 3 1/2 h
Batches in an 8-h period	4	2
Output in an 8-h period	76 kg	144 kg

were estimated, consistent with process requirements. The crucible loading efficiency is limited by the amount of time permitted for loading, and the amount of metal that can be tapped from the crucible is limited by the requirement that no slag may be removed with the metal. Batch time requirements were estimated which allow for more time being required to load and melt the charge and to remove the metal and slag in the large furnace. Although the large plant can handle nearly four times as much material per batch, the output of the large plant is only twice that of the pilot plant.

F. Conclusions

The experiments performed on steels and the analyses obtained during this period indicate that plutonium fractionates very strongly into the silicate liquid, in preference to the steel liquid. This behavior was reported previously (in the preceding quarterly report, ANL-77-36) and indicates that pyrorefining with a silicate slag is a useful process for decontaminating metals. In work reported during this period, it was found that a 35-fold increase in the contamination level of steel did not alter the effectiveness of the process.

The analyses indicate that staged extraction, that is, recycling of processed steel through the melt-refining process, reduces the plutonium level of the product metal below that obtained with a single extraction. The second extraction is effective with either resistance furnace melting or arc-melting of the metal. When the arc melter was used, the extent of decontamination was less than with the resistance furnace. (The run time with the arc melter, 1 min, was much shorter than in the experiments using the resistance furnace, 1 h.)

Perhaps more importantly, the arc melter produced homogeneous plutonium distribution in metal on a very fine scale, an effect not seen with the resistance furnace. Therefore, an arc melter may remove dispersed plutonium particles (seen in resistance-melted metal as track clusters) from the metal.

A small amount of copper in mild steel was seen to interfere with the removal of plutonium. This suggests that sorting of metals prior to melt refining would be an important step.

The properties of ultrasonic imaging systems were found to be useful in locating defects nondestructively in metal ingots. An imaging system is suggested for a large-scale pyrorefining process to monitor the quality of ingots and to locate defects, allowing their removal from processed metals.

A conceptual process, representing the initial design of two processing plants, has been completed for single-stage processing of contaminated metal to produce a metal product containing less than 10 nCi/g plutonium. Two plant sizes are described. The smaller plant may be made portable; the larger one would be stationary.

IV. METAL MATRIX ENCAPSULATION OF HIGH-LEVEL WASTE

(L. J. Jardine, R. E. Barletta, K. F. Flynn, R. H. Pelto,
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A. Introduction

The major objective of this task is to identify any additional net attributes gained by encapsulating solidified radioactive high-level waste (HLW) forms in a metal matrix, as compared to glass vitrification. This task is divided into two separate efforts: (1) an evaluation of concepts and (2) a series of laboratory-scale investigations. Existing data are being used to compare metal encapsulation concepts with already-developed HLW solidification alternatives (*e.g.*, calcination and glassification).

A series of laboratory-scale investigations has been begun, specifically aimed at generating data required to further assess probable or unresolved problem areas. These efforts are expected to yield sufficient background material for metal encapsulation concepts so that informed decisions can be made by others regarding either the need or effort required for practical demonstrations of the encapsulation concepts evaluated here. Any remaining problem areas that could throw doubt on the feasibility of the concept will be explicitly identified so that they may be quickly examined if metal encapsulation of high-level-waste forms is selected as an alternative waste management option meriting further demonstration.

The evaluation portion of this task has included the preparation of a report [JARDINE] which (1) reviews the literature pertaining to metal encapsulation and (2) presents a thermal analysis of the decay heat which identifies conditions under which metal matrix encapsulation may be more advantageous than either calcine or glass monolith waste forms. Metallic lead and an aluminum alloy were evaluated as reference-case matrix metals. Some evaluation is given in that report of a conceptual metal-encapsulation process flow sheet for a 5 MTHM[‡]/day reprocessing plant and of problem areas likely to require further examination for the demonstration of technical feasibility.

As stated above, data are being collected in the laboratory to further assess the metal encapsulation concept. Major experimental areas include (1) studies of chemical reactions between simulated high-level-waste forms and metals or alloys that can serve as matrices and (2) determination of the effects of metal encapsulation upon the leach rates of high-level waste form/matrix metal composites under conditions representing a spectrum of potential storage environments.

A number of reactions between (1) the many individual constituents of solidified waste forms and (2) the matrix metals are possible thermodynamically. Changes brought about by reactions could affect any or all of the following:

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‡ MTHM = metric tons (Mg) of heavy metal (U + Pu).

thermal conductivity, mechanical strength, leachability, and volatility. However, since the exact chemical forms or phases of the constituents in high-level-waste forms are not known, calculations would provide insufficient information to complete the evaluation in the absence of experiments. Also, the kinetics of such reactions might be quite slow; another possibility is that self-protecting reaction product barriers may be produced which would limit the extent of any proposed reaction. Thus, there is a need to examine the chemical reactions that actually take place in systems of simulated high-level waste forms encapsulated in metals. This would allow estimation of the effects, if any, of such reactions upon the attributes of solid waste forms for normal and accident scenarios involving fabrication, interim storage, transportation, and terminal storage.

Leach rate data for metal-encapsulated composites will be required to allow predictions of radionuclide releases for (1) long-term terminal storage scenarios and (2) the more probable scenarios involving (a) a premature canister breach (*i.e.*, during interim storage at the reprocessing plant, during transportation from the reprocessor to terminal storage, or during handling at either facility) and (b) simultaneous contact with a leachant (*e.g.*, water). Leach rate data for conditions that simulate a range of potential storage or accident environments of composites would be the most informative. However, it may be impossible either to define or to reproduce such conditions in the laboratory at present. Hence, experimental determination of leach rates for various reference parameters of temperature, pH, and leachant chemical composition is an alternative approach for generating data usable in future waste management scenario models that predict radionuclide source terms.

B. Experiments on Reactions of High-Level Waste Constituents with Matrix Materials

1. Preparation of Metal-Encapsulated Synthetic Waste

Casting in air of laboratory-scale, typically ~3-cm-OD × 10-cm-long, ingots of metallic lead, an aluminum alloy, or to a lesser extent a copper alloy as the encapsulating metal, has been examined as a method of fabricating waste composites. In these experiments, beads (1-5 mm) of Al₂O₃ were used as a stand-in for agglomerated calcine or sintered waste forms. Beads were pre-loaded into baskets of stainless steel mesh and lowered into crucibles or molds containing previously melted metals. Each basket was centrally located in the crucible so that upon metal solidification it was completely encased in a metal sheath. The baskets served to retain the Al₂O₃ beads within the liquid metals during solidification. After solidification, the composite had a protective layer of matrix metal free of any dispersed waste (as previously described in ANL-77-36). Standard resistance furnace and induction heating techniques were employed.

Composites were prepared by lowering baskets containing ~9-12 mesh Al₂O₃ beads into containers of liquid lead at 400°C. Stainless steel beakers were normally used as molds or containers. Sectioning revealed that this technique generally produced a composite which was well penetrated by lead except at the extreme top portion of beads in the retainer basket. At the zone of poor penetration, volumes of air appeared to be collected and/or trapped. The Al₂O₃ beads in this zone were not surrounded by continuous metal and were

primarily retained within the composite only by the wire mesh and the outer continuous layer of lead. One experiment with a ~25-cm hydrostatic head of excess lead produced a uniform composite that was fully penetrated. These experiments lead to the conclusion that vacuum/pressure casting techniques may be required to avoid nonuniform composites. Such examinations are now in progress.

Aluminum composites of dispersed Al_2O_3 beads were also cast in air, using a mesh basket as described above. Castings were made at the temperature range of 600-900°C with temperature equilibration times of several hours. Graphite or alumina were the crucible materials. Acceptable composites were made at ~750°C with a commercially obtained aluminum (*i.e.*, Alcan #46020)-12.5 wt % silicon alloy. Some castings were done with pure aluminum and yielded poor composites, probably due to the reduced flow characteristics compared with aluminum-silicon alloy. Pure aluminum was not considered further as a matrix metal with this technique.

Good penetration of the aluminum alloy in the basket of beads was generally observed except near the uppermost portion of the retainer basket where penetration was poor as in the lead castings. Improved penetration was sought by mechanical vibration of the crucible support and/or direct vibration of the basket of Al_2O_3 beads (the latter was clearly the more effective technique). However, the volume of composite for which metal penetration was poor was only reduced--the zone of no penetration was not eliminated. If Al_2O_3 beads are representative of a solidified waste form, it is concluded that production of a uniform composite will probably require the use of vacuum/pressure casting techniques with the aluminum alloy.

Before a solidified waste produced from a fluid bed or a spray calciner can be encapsulated by casting techniques, agglomeration is probably required [BERRETH]. Pelletization of calcine using a hydraulic press and dies is one agglomeration method; an alternative is the disc pelletizer under development at INEL and PNL. Some examination has been made by Samsel and Berreth [SAMSEL-1977] of both hot pressing and cold pressing of mixtures of fluid-bed calcine containing some stabilizing additives. Additives (*i.e.*, INEL flux [SAMSEL-1977]) were developed to achieve better leach resistance and mechanical strength (or friability) than that of pellets containing calcine alone. Mixtures of INEL fluid-bed calcine and PNL spray calcine product identified as PW-7a with various additives (*e.g.*, SiO_2 , PNL glass frit, INEL flux [SAMSEL-1977]) were cold-pressed at $7 \cdot 10^4$ kPa into 1-cm-diameter pellets of varying heights (or thicknesses) with 10^5 N laboratory press. Water (0-5 wt %) was used as a binder. Most pellets had sufficient green strength for transfer without crumbling to a sintering furnace. Sintering of such pellets at ~900°C for several hours generally decreased the friability. Further characterization of the sintered pellets is under way.

It is tentatively concluded that conventional press and dye pelletizing of premixed dry or wet powders of calcine containing stabilizing additives is another method of agglomeration. Suitable automatic commercial pelletizers apparently can be obtained easily if required. However, further effort is probably required to develop appropriate additives which stabilize the solidified waste form against high leach rates or low strengths after a sintering process.

2. Chemical Interactions of Metal-Encapsulated HLW Forms

a. Introduction

Metal encapsulation of high-level-waste (HLW) forms in metallic lead or aluminum alloys is being evaluated as a waste management alternative to the well-developed glassification concepts. The nature and extent of reactions at the interfaces of the metal and solidified HLW form could have consequences affecting the long-term stability, mechanical strength, and leachability of the encapsulated waste form. Chemical reactions may also be an important facet of the wetting of HLW oxides by molten matrix metal during fabrication [LIVEY].

It is possible to estimate the thermodynamic stability of the individual fission product oxides and other oxides present in solidified HLW forms in relation to their reduction by the metals (*e.g.*, Pb, Al-Si) used for matrix encapsulation. Table 12 gives the results for most of these oxides at 500, 700, and 1000 K. A positive sign of a given free energy of reaction in this table implies that the encapsulating metal is stable with respect to the waste oxide considered. Solidified HLW forms encapsulated in aluminum or in alloys of Al-Si should be more reactive with these metals than with lead. This is indicated in Table 12 by the fraction of negative free energies of reaction of oxides with aluminum or silicon being larger than that for lead. However, calculations of this type are probably of limited value since solidified HLW forms encapsulated in a metal matrix cannot be treated as a binary system. Thus, one might expect that the actual stability of oxides present in solidified HLW forms (in relation to reduction by the encapsulating metal) will be much different from those indicated by the free energies of reaction given in Table 12.

b. Procedure, Results, and Discussion

Since it is not possible to predict, *a priori*, the stability of this multicomponent system of HLW oxide and encapsulating metal, an experimental program has been initiated to investigate the descriptive chemistry and kinetics of reactions which occur at the interfaces of the dispersed waste phase and the metal phase. Initial experiments were directed toward two goals: (1) the preparation of composites containing simulated solidified HLW dispersed in metal and (2) the identification and implementation of analytical techniques to determine the nature and extent of reactions occurring within composites.

Composites were prepared by casting techniques, using two substitutes for solidified HLW: Al₂O₃ (√3-mm dia) and sintered waste form (SWF) beads (√4-mm dia). The SWF (PW-7a) beads were obtained from PNL and contained a mixture of 85 wt % simulated agglomerated spray calcine (PW-7a) and 15 wt % glass frit which mixture had been sintered for 1 h at 1000°C. All castings were done in air and at ambient pressures, using either lead (m.p. 327°C) or an aluminum-12 wt % silicon alloy (m.p. 577°C) as the metal matrix material. The casting temperature was √400°C for the lead castings and √750°C for those containing the aluminum alloy. Figure 16 shows typical specimens obtained after sectioning and polishing with standard techniques.

Table 12. Free Energy (kcal/mol of reaction product oxide) for the Reaction^a of Oxides Contained in Solidified High-Level Waste Forms with Matrix Metals at 600, 700, and 1000 K

Waste Oxide	Pb Metal Matrix						Al-Si Metal Matrix		Al-Si Metal Matrix	
	PbO ^b		PbO ₂ ^b		Pb ₃ O ₄ ^b		Al ₂ O ₃ ^b		SiO ₂ ^b	
	600 K	700 K	600 K	700 K	600 K	700 K	600 K	1000 K	600 K	1000 K
Rb ₂ O	20.6	19.55	78.4	76.0	114.5	110.0	-179.8	-193.2	-66.8	-78.7
SrO	88.5	88.95	214.9	214.8	387.5	387.6	25.0	27.0	69.8	68.1
Y ₂ O ₃	99.3	99.2	235.7	235.3	429.2	428.7	56.2	56.8	90.6	88.0
ZrO ₂	79.1	79.3	195.3	195.4	348.3	348.8	-4.5	-1.2	50.2	49.3
MoO ₃	10.1	10.5	57.3	57.9	72.4	73.9	-211.4	-204.3	-87.8	-86.1
Tc ₂ O ₇	---	---	---	---	---	---	---	-289.1	---	-127.6
RuO ₂	-22.2	-21.7	-7.1	-6.5	-56.5	-55.0	-308.1	-301.2	-152.3	-150.7
Rh ₂ O ₃	-27.4	-26.8	-17.6	-18.7	-77.5	-75.3	-323.8	-316.2	-162.8	-160.7
PdO	-27.2	-26.8	-17.2	-16.6	-76.7	-75.2	-323.2	-316.5	-162.4	-160.9
Ag ₂ O	-40.4	-38.95	-33.6	-27.0	-109.5	-96.0	-347.8	-302.1	-178.8	-151.3
CdO	10.1	10.0	57.4	56.8	72.5	71.6	-211.3	-212.1	-87.8	-91.3
TeO ₂	-12.1	-11.7	13.1	13.6	-16.1	-14.8	-277.8	-274.5	-132.1	-127.9
Co ₂ O	15.1	13.6	67.4	64.0	92.5	86.0	-196.3	-212.7	-77.8	-91.7
BaO	81.5	81.7	200.2	200.2	358.1	358.4	2.9	8.1	55.1	55.5
La ₂ O ₃	87.6	87.3	212.4	211.4	382.6	352.6	21.3	17.2	67.3	61.6
CeO ₂	78.0	78.1	193.3	193.1	344.2	344.2	-7.51	-5.4	48.1	46.5
Pr ₆ O ₁₁	73.9	74.1	184.9	185.2	327.6	328.3	-20.0	-16.2	39.8	39.3
Nd ₂ O ₃	92.7	92.9	222.5	222.7	402.8	403.4	36.4	40.0	77.4	76.8
Pm ₂ O ₃	---	---	---	---	---	---	---	13.2	---	73.3
Sm ₂ O ₃	92.4	92.9	222.1	222.7	401.8	403.3	35.7	40.8	76.9	73.3

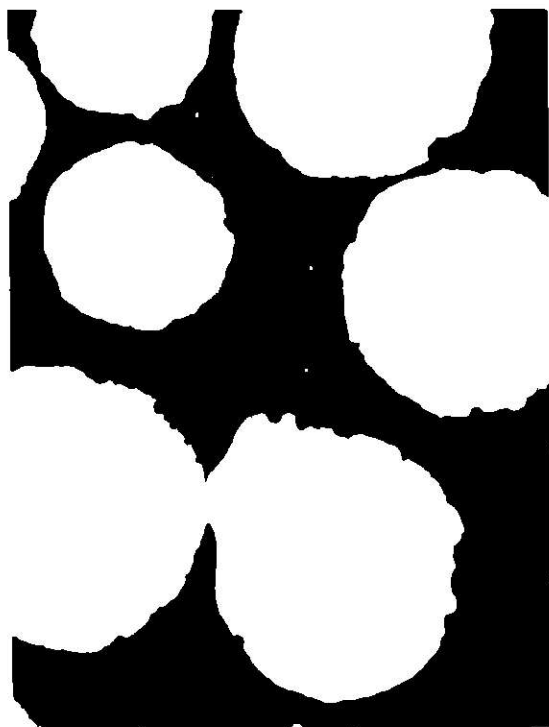
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Table 12. (contd)

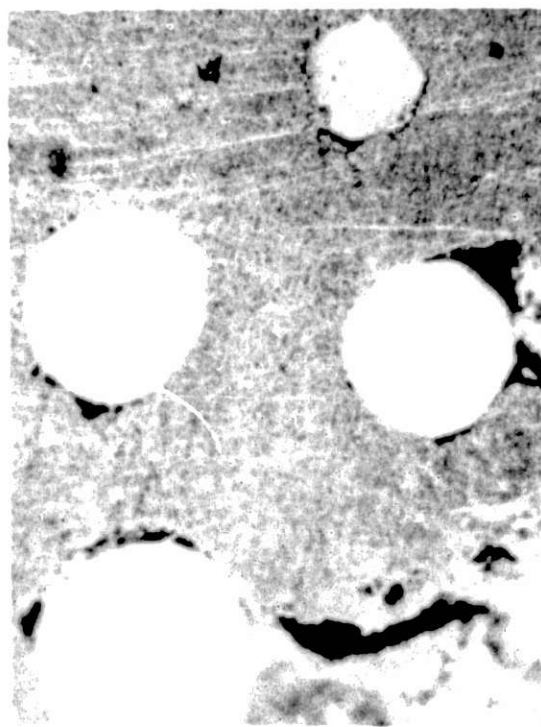
Waste Oxide	Pb Metal Matrix						Al-Si Metal Matrix		Al-Si Metal Matrix	
	PbO ^b		PbO ₂ ^b		Pb ₂ O ₃ ^b		Al ₂ O ₃ ^b		SiO ₂ ^b	
	600 K	700 K	600 K	700 K	600 K	700 K	600 K	1000 K	600 K	1000 K
Eu ₂ O ₃	---	---	---	---	---	---	---	-28.2	---	46.3
Gd ₂ O ₃	115.0	119.4	267.2	275.7	492.2	509.3	103.5	158.8	122.1	156.0
U ₃ O ₈	56.5	56.9	150.1	150.7	257.9	259.4	-72.3	-65.9	5.0	6.2
NpO ₂	72.4	72.8	181.9	182.5	321.5	323.0	-24.6	-19.2	36.8	37.3
PuO ₂	72.4	72.8	181.9	182.5	321.5	323.0	-24.6	-19.2	36.8	37.3
Am ₂ O ₃	89.7	90.4	216.7	217.7	391.2	393.3	27.7	35.3	71.6	73.6
Cm ₂ O ₃	---	---	---	---	---	---	---	26.2	---	82.6
Na ₂ O	41.7	40.6	120.6	118.2	198.9	194.4	-116.5	-128.1	-24.6	-35.3
Fe ₂ O ₃	14.9	15.3	66.9	67.5	91.6	92.9	-197.0	-190.7	-78.2	-77.0
Cr ₂ O ₃	40.1	40.5	117.4	117.9	192.6	193.8	-121.3	-115.8	-27.7	-27.1
NiO	6.1	6.4	49.4	49.8	56.5	57.6	-223.3	-218.1	-95.8	-95.3
P ₄ O ₁₀	21.9	28.0	80.0	78.9	119.6	115.8	-176.0	-174.5	-64.2	-66.2
Al ₂ O ₃	80.5	73.0	198.3	197.9	354.2	353.7	---	---	53.1	50.1
K ₂ O	27.2	26.0	91.6	88.8	140.9	135.6	-160.0	-175.2	-53.6	-66.7
Co ₃ O ₄	1.4	3.9	40.0	40.5	37.7	39.0	-237.4	-231.7	-105.2	-104.4
B ₂ O ₃	51.1	51.6	139.4	140.0	236.5	238.0	-88.3	-80.7	-5.75	-3.7
ZnO	31.05	31.15	99.3	99.2	156.3	156.4	-148.5	-148.2	-45.9	-48.7
CaO	99.05	99.05	235.3	235.0	428.3	428.0	55.6	56.4	90.2	87.7
MgO	90.51	90.5	218.2	217.8	394.1	393.6	29.9	29.0	73.1	69.4

^aExample: $\text{Pb} + \text{Rb}_2\text{O} \rightarrow \text{PbO} + 2\text{Rb}$; $\Delta G_R = 20.6 \text{ kcal/mol}$ at 600 K.

^bReaction product oxide. Free energy data based on reaction of pure aluminum or silicon, not from an alloy.



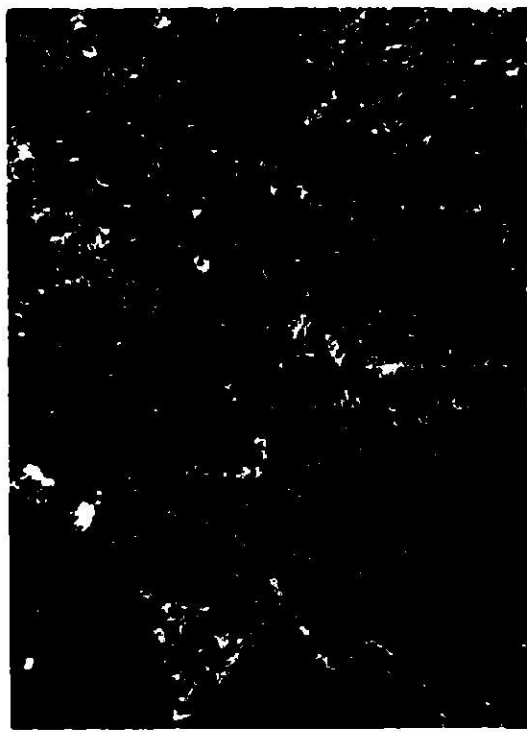
a



b



c



d

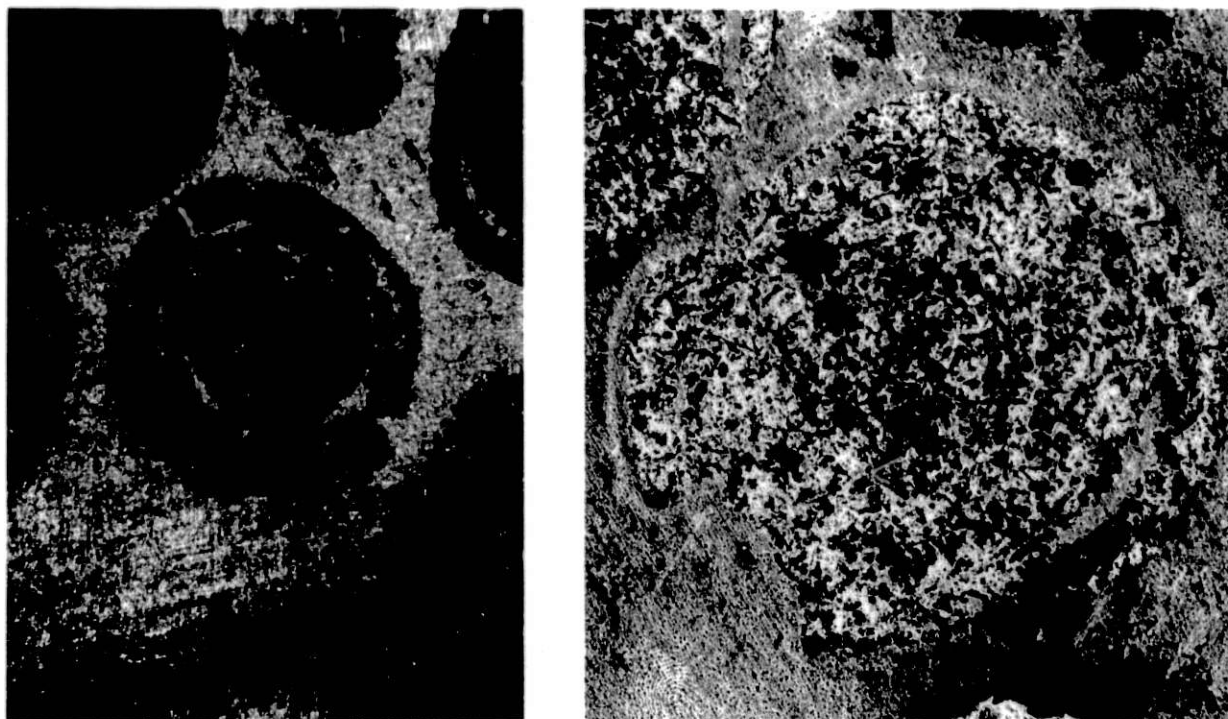
Fig. 16. Photographs of Simulated HLW Forms Encapsulated in Metal Matrices: (a) Al_2O_3 beads in lead (12X) (b) Al_2O_3 beads in aluminum-12 wt % Si alloy (12X) (c) agglomerated PW-7a spray calcine and 15 wt % glass frit (SWF) sintered beads in lead (12X) (d) agglomerated PW-7a spray calcine and 15 wt % glass frit (SWF) sintered in aluminum-12 wt % Si alloy (12X)

Composites were initially examined using a combination of several of four techniques (optical microscopy, scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDXRA), and ion microprobe analysis) in order to determine the extent of contact between the dispersed, simulated HLW forms and the continuous metal phase, as well as the occurrence and extent of chemical reactions at the interface of the dispersed waste form and metal. Optical microscopy (Fig. 16) revealed that the metal came into very close contact with the waste form. No large voids or gaps were generated during cooling at the waste particle-metal interface. In the cases of the SWF-lead and the SWF-aluminum alloy composites, the metal was observed to have partially penetrated the pores of the SWF beads (Fig. 16). Analysis of the Al_2O_3 -lead casting using the ion microprobe (not shown) indicated an interface width of 40-80 μm .

Since no reaction is thermodynamically possible between Al_2O_3 and the encapsulating metals used (Table 12), SWF (PW-7a)-metal composites were used in determining the limits of interface reaction rates. In the SWF-lead system, a "halo" of $\sim 80 \mu\text{m}$ was visible (Fig. 17) surrounding each dispersed SWF bead in the lead, using both optical and scanning electron microscopy. However, EDXRA revealed no significant differences between the "halo" composition and that of the bulk metal phase. The "halo" is concluded to be merely an artifact of cooling and not evidence of a reaction between the SWF and the lead. In the case of the SWF-aluminum alloy system, however, optical microscopy does reveal a zone at the interface of the SWF and metal (Fig. 18). This zone uniformly penetrates the SWF bead and was found to have a thickness of approximately 20 μm for a casting which had been kept at 750°C for 160 min. However, 20 μm is the approximate resolution obtainable from the ion microprobe for these samples, and so the composition of this zone at the interface could not be determined.

A number of differential thermal analysis (DTA) spectra were made for matrix metals (*i.e.*, Al, Al-Si, and Pb), INEL fluid-bed calcine, PNL spray calcine and various mixtures thereof. Sample sizes of 1-2 g were used. Samples of metal filings were prepared by filing newly cast ingots in an inert-atmosphere (N_2) glove box. The metal filings were mixed with calcine powder and/or various additives (typically PNL glass frit, INEL flux [SAMSEL-1977]), and DTA spectra were obtained over the temperature range of 50-900°C in an inert-atmosphere (Ar) apparatus. At heating rates of ~ 5 -10°C/min, no significant exothermic reactions were observed with the mixtures selected (instrument sensitivity estimated as $< 0.5 \text{ cal/g}$ of sample). These results are consistent with DTA results reported by [BERRETH] and [SAMSEL-1977]. For mixtures of calcine and aluminum, these results may imply that the kinetics of any reactions may be somewhat inhibited when complex mixtures of calcine are heated. Such observations are also consistent with the preliminary results in the chemical interaction studies.

The ion microprobe was also used to determine the distribution in the metal phase of elements that had been originally contained in the SWF bead. However, it still had to be established whether elements were transported to the metal phase by reaction or were transported by other means (as by pieces of the SWF bead breaking off during sample polishing or while the composites were being made). In an attempt to determine the manner of transport, the relative elemental distribution in the metal phase and in an unencapsulated SWF bead was measured. If reaction had occurred, it was assumed that the



a

b



c

Fig. 17. Photographs of Agglomerated Simulated (PW-7a) Spray Calcine Mixed with 15 wt % Glass Frit Granules (sintered at 1050°C) and Dispersed in a Lead Matrix: (a) 12X with optical microscopy (b) 24X on SEM, and (c) 110X on SEM



Fig. 18. PW-7a-15 wt % Glass Frit Bead/Al-12 wt % Si Alloy Interface. Lightest area is aluminum alloy; the darkest area is a bead (100X)

amount of a reactive element in the metal phase compared with that in an unencapsulated SWF bead would increase.

SWF bead-metal composites, SWF beads, and the encapsulating metals (Pb and Al) were analyzed for eight representative elements (Ca, Cr, Fe, Sr, Zr, Ba, La, Ce) present in the SWF bead, using the ion microprobe with an O_2 -ion beam. Samples were taken at three locations in the metal phase: (1) in metal inclusions entirely within SWF beads, (2) 25 μm from the optical SWF bead-metal interface, and (3) 400 μm from the optical interface. To eliminate surface contamination, each sample location was cleaned prior to examination by rastering the ion beam over the $\sim 300 \mu\text{m}^2$ sample area to a depth of ~ 0.5 -1.0 μm . Table 13 shows (1) mean values (relative to the encapsulating metal) and their standard deviations, each calculated from several scans of the representative SWF elements in the continuous metal phase and (2) mean values (relative to calcium) in an unencapsulated SWF bead. The large standard deviations in data for the elements in the metal phase preclude any definite statements concerning changes in the relative amounts of these elements due to chemical reactions. Although the mean values of representative elements from the SWF bead seem to decrease with increasing distance from the bead, it is not impossible to establish which mechanism transported these elements into the metal phase. These deviations might be due in part to inhomogeneities in the SWF beads which might have been detected by the high resolution in the microprobe.

Table 13. Relative Mean Values for Representative Elements of SWF Found in Metal Phase of SWF Bead/Metal Castings and in Unencapsulated SWF Beads Using Ion Microprobe Analysis. SWF (PW-7a) + 15 wt % glass frit^a

Element	No Metal	Metal Inclusion	25 μ m into metal	400 μ m into metal
<u>SWF Bead Dispersed in Pb (element values relative to lead)</u>				
Ca		(2.0 \pm 1.2)E-1 ^b	(1.6 \pm 0.8)E-1	(1.2 \pm 1.1)E-2
Cr		(6.1 \pm 5.7)E-2	(1.2 \pm 1.5)E-1	(4.1 \pm 3.5)E-2
Fe		(1.5 \pm 1.2)E-1	(1.0 \pm 1.2)E-1	(3.2 \pm 2.8)E-2
Sr		(9.7 \pm 3.9)E-2	(6.5 \pm 1.7)E-2	(5.6 \pm 4.0)E-3
Zr		(1.7 \pm 2.0)E-2	(1.0 \pm 0.3)E-2	(7.1 \pm 2.0)E-3
Ba		(9.1 \pm 10.0)E-2	(3.5 \pm 0.1)E-2	(2.4 \pm 0.9)E-2
La		(1.1 \pm 0.9)E-1	(3.6 \pm 1.9)E-2	(1.3 \pm 0.6)E-2
Ce		(7.1 \pm 7.3)E-2	(3.0 \pm 0.7)E-2	(2.8 \pm 1.3)E-2
<u>SWF Bead Dispersed in Al-12 wt % Si (element values relative to Al)</u>				
Ca		(5.0 \pm 3.4)E-3	(1.6 \pm 1.3)E-3	(6.6 \pm 7.2)E-4
Cr		(4.1 \pm 5.4)E-2	(1.3 \pm 1.0)E-3	(1.0 \pm 0.8)E-3
Fe		(6.1 \pm 8.1)E-2	(1.2 \pm 0.6)E-3	(1.2 \pm 2.0)E-3
Sr		(9.1 \pm 4.3)E-4	(7.0 \pm 6.4)E-4	(8.5 \pm 6.9)E-5
Zr		(5.8 \pm 8.8)E-4	(5.9 \pm 8.1)E-4	(1.0 \pm)E-5 ^c
Ba		(1.2 \pm 1.7)E-3	(2.1 \pm 2.2)E-4	(3.9 \pm 3.4)E-5
La		(3.6 \pm 4.8)E-3	(6.8 \pm 5.8)E-4	(1.0 \pm 0.8)E-4
Ce		(6.4 \pm 8.5)E-4	(3.3 \pm 4.6)E-3	(1.8 \pm 0.7)E-5
<u>Unencapsulated SWF Bead (element values relative to Ca)</u>				
Cr	(5.2 \pm 1.9)E-2			
Fe	(1.5 \pm 0.5)E-0			
Sr	(1.2 \pm 0.9)E-0			
Zr	(1.6 \pm 0.7)E-0			
Ba	(2.3 \pm 1.8)E-0			
La	(3.2 \pm 1.1)E-0			
Ce	(3.5 \pm 1.5)E-0			

^aThe errors shown are standard deviations, each calculated from several measurements.

^bRead as 0.20 \pm 0.12.

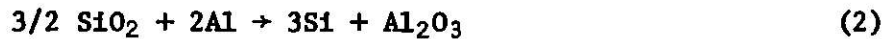
^cBased on one measurement.

On the basis of the above experimental results, it is difficult to make any statements concerning the nature or extent of reactions at the interfaces of the simulated solidified HLW form and metal. In the systems studied, reactions (if they occurred at all) were at or below the limits of detection of the techniques used. It is believed that a simpler system based on a model for solidified HLW oxide-metal reactions should be selected for study by ANL. In the reaction model assumed, whose basis is discussed in the following paragraphs, reactions between the oxides and metals of the following form are postulated:



where M is the matrix metal and AO is an oxide contained initially in HLW. The reaction product oxide (AO) is assumed to adhere to the HLW oxide and to constitute a reaction zone. The reaction is further assumed to be diffusion-controlled--either in the solid state or at temperatures where the matrix metal is in the liquid state. A consequence of this latter assumption is that the long-term solid state behavior of the system can be inferred from reasonably short-term liquid metal phase experiments.

This model has an experimental basis suggested from studies of the reactions of rare earth sesquioxides with aluminum [GVELESIANI] and of reactions of SiO_2 with aluminum in the solid state [GERSHINSKII] and the liquid state [STANDAGE, BRONDYKE]. In the case of the reaction of SiO_2 with aluminum:



the kinetics of reaction in reaction 2 have been thoroughly studied, and Arrhenius parameters for both the solid state [GERSHINSKII] and the liquid state of aluminum [STANDAGE] have been determined. Reaction 2 proceeds by the formation of various phases of Al_2O_3 (γ , η , θ) in a reaction zone of uniform thickness which adheres to the silica and penetrates into the silica sample with time (Fig. 19). A plot of the log of penetration rate, K (cm/h), of this

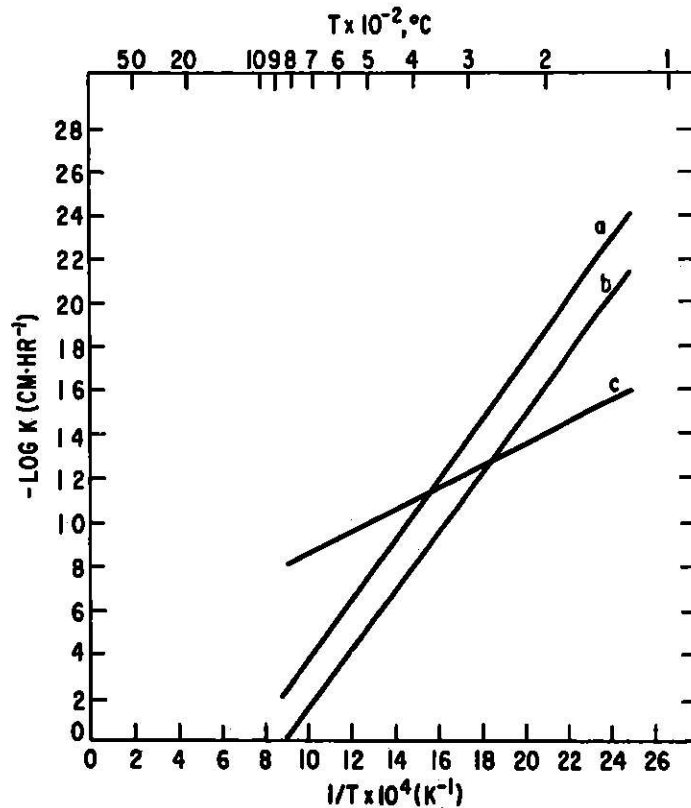


Fig. 19. Log of the Rate of Penetration (K) into Silica vs. T^{-1} Using Arrhenius Parameters Determined for (a) $\gamma\text{-Al}_2\text{O}_3$ [GERSHINSKII], (b) $\theta\text{-Al}_2\text{O}_3$ [STANDAGE], (c) $\eta\text{-Al}_2\text{O}_3$ [STANDAGE]

layer vs. $1/T$ (K^{-1}) based on the previously determined [GERSHINSKII, STANDAGE] activation parameters is shown in Fig. 19. It should be noted that the activation parameters were determined only for fixed-temperature regimes, solid aluminum [GERSHINSKII], and liquid aluminum [STANDAGE]. The penetration rates in Fig. 19 were extrapolated to include the solid and liquid aluminum temperature regimes for all Al_2O_3 phases. [BRONDYKE] has concluded that reaction 2 is controlled by aluminum and silicon diffusion. The extrapolated dependence of the penetration rate for θ - and η - Al_2O_3 is higher than for γ - Al_2O_3 in the region below the melting point of aluminum ($660^\circ C$). This would indicate that the assumption, that rates of solid state reactions may be inferred from reaction rates in systems where the metal is molten, is probably valid for the SiO_2/Al reaction.

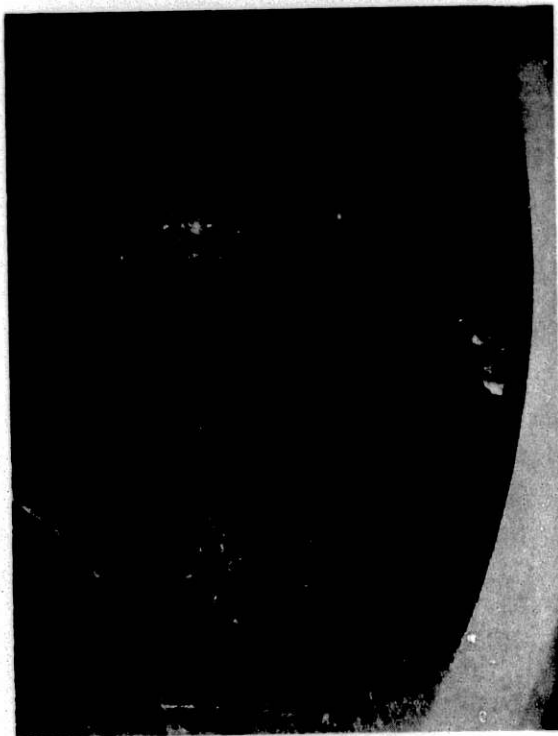
The reaction of quartz with aluminum is particularly applicable to the problem of reactions at the solidified HLW form/ metal interface since SiO_2 is likely to be present as an additive in most solidified HLW forms. An experiment was performed in which (1) quartz rod (10-mm dia) and (2) pellets containing 30, 50 and 70 wt % SiO_2 with the remainder INEL fluid-bed calcine were immersed in a molten aluminum-12 wt % silicon alloy at $700^\circ C$ for 10 h. The pellets (14-mm dia) had been previously cold-pressed to 7×10^4 kPa and sintered for 2-3 h at $900^\circ C$.

The results of this experiment (Fig. 20) were somewhat surprising. The quartz rod showed extensive reaction (reaction zone of ~ 2 mm or 0.2 mm/h) with the reaction layer consisting of mainly θ - Al_2O_3 as determined by X-ray diffraction. However, all the sintered pellets of SiO_2 and INEL fluid-bed calcine showed a very thin reaction zone of approximately the same thickness (~ 0.06 mm).

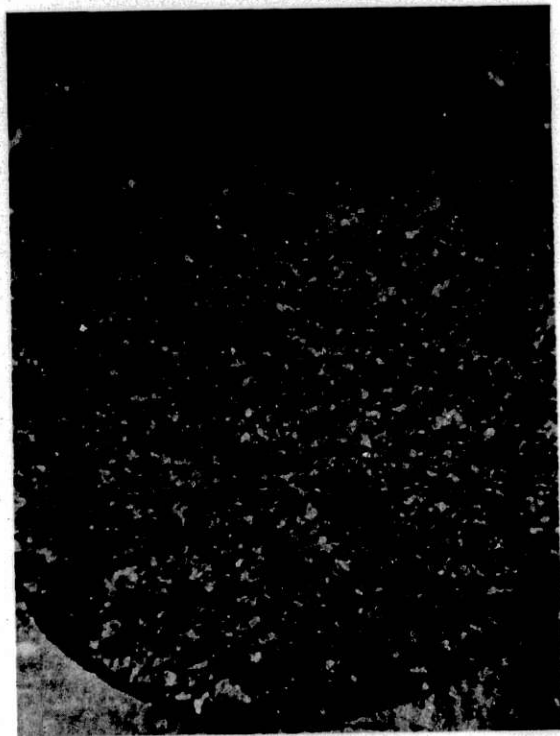
The experiment was repeated using 50 wt % quartz-50 wt % INEL calcine pellets prepared in the same way. The pellets were held in the aluminum-silicon alloy for 91 and 187 h at $700^\circ C$ in order to determine the extent of reaction more precisely and to determine the nature of the reaction zone.

The pellet that had been reacted for 91 h contained a rather uneven reaction zone; maximum penetration was ~ 0.5 mm. The cause of this irregularity is not known but may be the surface characteristics of the particular pellet. This sample was examined using optical microscopy and EDXRA. The reaction zone is apparent in the optical micrograph (Fig. 21a) as a discoloration which penetrated the pellet beginning at the pellet-metal interface. By use of EDXRA, the discolored area was found to be enriched in aluminum (Fig. 21b) and depleted in silicon (Fig. 21c). This data is consistent with the formation of Al_2O_3 and the corresponding reduction of the silicon in the SiO_2 to metallic silicon via a mechanism similar to that for aluminothermic reduction of pure silica [STANDAGE, BRONDYKE] at a much lower reaction rate.

The pellet reacted for 187 h was used to obtain an accurate estimate of the reaction rate by measuring the reaction zone width (using optical microscopy). In this case, the reaction zone was distributed evenly around the circumference of the pellet (Fig. 22), similarly to distribution in the quartz rod experiments. The appearance of the reaction zone itself



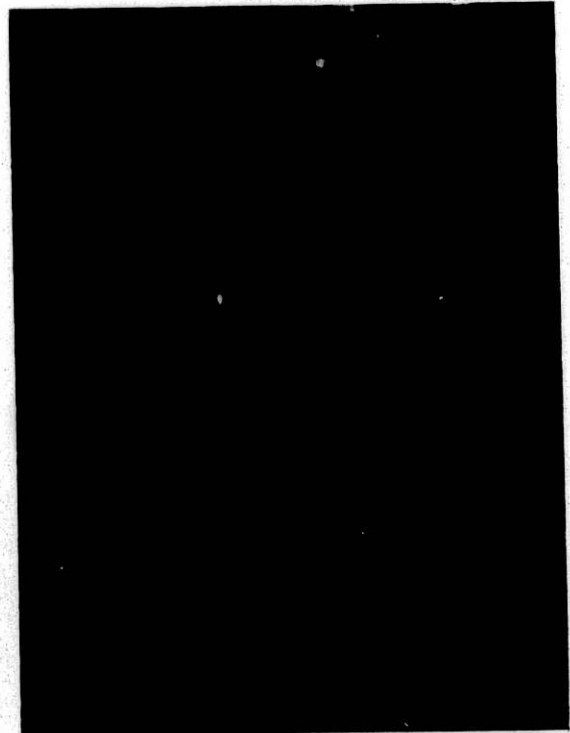
a



b

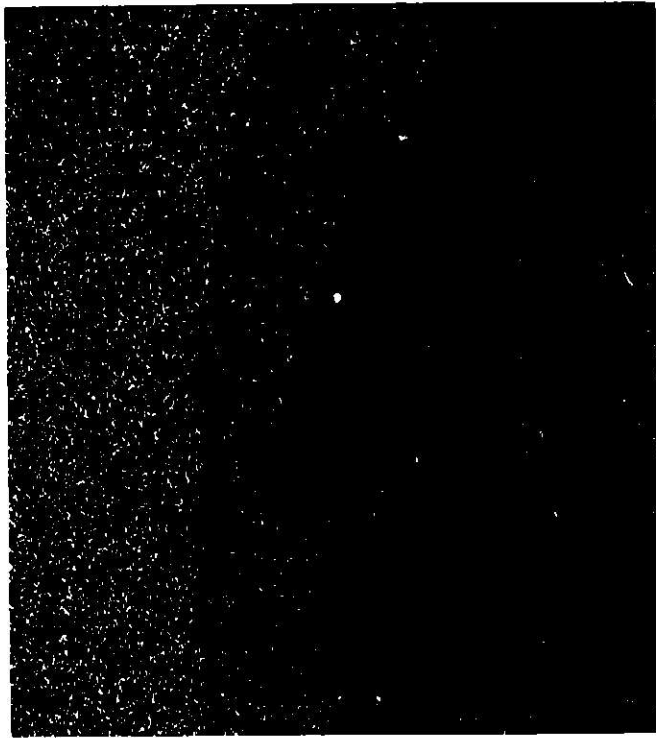


c



d

Fig. 20. Photograph of 91-h Experiment of Reactivity with Al-12 wt % Si Alloy of SiO_2 Diluted with INEL Fluid-Bed Calcine. Reaction temperature 700°C ; 10-h experiments. All calcine/ SiO_2 pellets pressed at 7×10^4 kPa and sintered at 900°C for 2 h. (a) pure SiO_2 , 10-mm rod (6X), (b) 70 wt % SiO_2 -30 wt % calcine pellet (6X), (c) 50 wt % SiO_2 -50 wt % calcine pellet (6X), (d) 30 wt % SiO_2 -70 wt % calcine pellet (6X)



b



a



c

Fig. 21. 50 wt % SiO_2 -50 wt % Fluid-Bed Calcine Pressed and Sintered Pellet Immersed in Al-12 wt % Si Matrix 91 h. Reaction temperature, 700°C . (a) 25X (darkest area is aluminum alloy). (b) 39X EDXRA scan for aluminum. (c) 39X EDXRA scan for silicon.

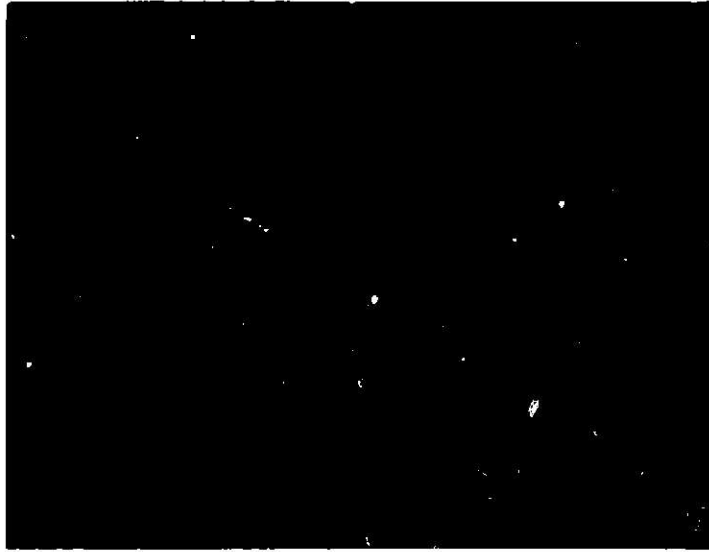


Fig. 22. Reaction Zone after Reacting Aluminum-12 wt % Si with a Mixture of 50 wt % SiO_2 and 50 wt % Fluid-Bed Calcine Made into a Pressed 7×10^4 kPa) and Sintered (900°C for 2 h) Pellet at 700°C for 187 h (25X)

was quite similar to that for the previously described 91-h experiment. The depth of penetration of this zone was measured to be 0.2 mm, which gives a value of K of $\sim 10^{-4}$ cm/h at 700°C . This rate is more than two orders of magnitude lower than that observed for the quartz rod-aluminum experiments (2×10^{-2} cm/h). Surprisingly, this rate is very nearly the same as one would obtain assuming that the zone surrounding the SWF bead using optical microscopy in the previously described SWF-aluminum alloy experiment (Fig. 18) was a reaction zone (8×10^{-4} cm/h). It should be noted that since the "reaction" temperature in the SWF-aluminum alloy experiment (Fig. 18) was about 50°C higher than that for the 50% SiO_2 -50% INEL fluid-bed calcine/aluminum alloy experiment, an increase in the rate would have been expected.

The data obtained to date suggest a lowering of the reaction rate in the SiO_2 -calcine-aluminum alloy system as compared with the SiO_2 -aluminum alloy system. [STANDAGE] also observed a lowering of the reaction rate for reaction 2 when group V elements (bismuth and antimony) were added in small amounts to the system. The lower reaction rates were interpreted as an increase in the activation energy due to coordination of these elements with either the silica or the water bonded to silica, which inhibited the diffusion of aluminum, which is the rate-determining step. Also, a large number of different cations are available for coordination in the silica-calcine pellets studied. This might explain not only the observed lowering of the reaction rate in the presence of calcine but also the relative insensitivity of the rate to silica concentration in the pellet. Experiments have been begun to determine activation parameters for the SiO_2 -calcine-aluminum alloy system in order to see if the activation energy for this system is significantly higher than in the absence of calcine.

c. Conclusions

Waste-metal reactions appear to proceed at a very low rate when compounds such as SiO_2 are present in a simulated HLW form, although the individual waste constituents may be quite reactive with the encapsulating metal. The proposed model for these reactions apparently is a reasonable first approximation and merits further examination. Results of short-term studies at elevated temperatures of a simulated (or actual) solidified HLW form/metal composite might be a reasonable measure of the long-term, low-temperature behavior of the system from the standpoint of making "worst case" estimates of its stability. Finally, it is clear that of the techniques used to study these interactions, optical microscopy was the most valuable in identifying changes due to reaction in the simulated solidified HLW/metal systems.

C. Determination of Leach Rates of Simulated Radioactive HLW Forms

Evaluations of concepts for managing the high-level waste (HLW) from the reprocessing of commercial nuclear fuel must include an assessment of the rate of dispersal of radioactivity from the solidified waste form to the environment. For most waste management scenarios, a probable mechanism for release of radioactivity from a solidified waste form is via the aqueous leaching of radionuclides. The objective of these leach rate determinations is to produce background information which can allow others to evaluate the rate at which specific hazardous radionuclides will return to the ecosystem if and when the waste form becomes dispersed.

The basic leach rate determinations involve the exposure of a solid specimen of a known initial composition and premeasured surface area to a leachant medium for a fixed time interval. This is followed by analysis of the leachant for the quantity of a specific material which has been leached. Difficulties arise in trying first to define and then to duplicate in the laboratory the leachant composition and conditions (pH, temperature, time, oxygen concentration, etc.) present in the natural environment.

The leach rates are usually reported as grams of material leached per square centimeter of initial specimen surface area per day ($\text{g}/\text{cm}^2\text{-day}$). The total surface area of the solid material can be estimated either (1) by assuming a particle shape (*i.e.*, spherical, etc.) and estimating the number and size distribution of particles or (2) by accurate measurement using the Brunauer-Emmett-Teller (BET) (gas absorption) technique [BRUNAUER]. The mass of material leached can be determined either by any standard gravimetric method or, in the case of radwaste, by measurement of the radioactivity dissolved in the leaching medium. Since different ions can be leached at different rates, it is important to specify the specific ion analyzed when quoting leach rate results. To avoid confusion on this matter, it has been suggested [GODBEE] that long-term leaching rate results be reported as

$$(\text{fraction of A leached}) (\text{cm}^2/\text{g})^{-1} (\text{day})^{-1},$$

where A is the specific ion analyzed.

1. Analytical Procedure

The technique by which leach rates were determined in this work is based on a neutron activation analysis (NAA) method. Neutron irradiation of solid waste forms of simulated high-level waste (see Table 14) for a typical composition [BONNER] will produce activation products which can be readily measured by radiochemical and/or instrumental techniques. In order to be useful for these purposes, the activation product must have a sufficiently energetic and abundant radiation (either β^- or γ) to be easily detected and a sufficiently long half-life (*i.e.*, ~ 10 days or more) to be useful for relatively long-term (5 days or more) leach rate studies. The elements in high-level waste considered in this study and their associated measurable radioactive isotopes (see Table 14) are strontium (^{85}Sr), cesium (^{134}Cs), a stand-in for the trivalent actinides, and a stand-in for the tetravalent actinides. A trivalent rare earth (^{152}Eu) has been shown to be a satisfactory substitute in waste studies [BONNER] for the trivalent actinides (americium and curium), and tetravalent cerium (^{141}Ce) has been suggested to be a satisfactory substitute for the tetravalent actinides (uranium, neptunium, and plutonium).

Gamma ray analysis of the neutron-irradiated solidified waste form, using a lithium-drifted germanium (GeLi) detector, provides an assay of the various gamma-emitting radioisotopes present. After leaching of the waste form under a given set of conditions for a suitable time interval, the leaching media can be assayed by gamma ray analysis. If greater sensitivity is required, radiochemical analysis by conventional radiochemical separation techniques [FLYNN] and low background beta counting of the radiochemically separated species can be used. The fraction of the particular isotope (or element) of interest which has been leached from the matrix can be determined from these measurements with great sensitivity. Such measurements require no destruction of the solid waste form prior to leaching and also have the advantage of determining the concentration of the leached ion in the leaching medium when the concentration is insignificant.

2. Calculational Methods

Leach rate measurements have been made by neutron activation analysis on several waste forms. Leach rates were calculated with the equation:

$$L = \frac{A_t}{A_0} \frac{W_0}{St} \quad (3)$$

where L = leach rate ($\text{g}/\text{cm}^2\text{-day}$)

A^t = amount of material A removed in time t

A_0 = initial amount of material A in solid

S = surface area of the solid material (cm^2)

W_0 = initial weight of the solid material (g)

t = leaching period (day)

A_t/A_0 = fraction leached.

Table 14. Typical Composition of High-Level Radioactive Waste

Elements in Waste	Relative Molar Abundance	Selected Activation Products and their Half-Lives	
<u>Fission Products</u>			
Rb	0.015	^{86}Rb	18.7 d
Cs	0.079	^{134}Cs	2.05 y
Zr	0.155	^{95}Zr	65.5 d
Mo	0.139	--	--
Tc	0.032	--	--
Ru	0.086	^{103}Ru	39.5 d
Rh	0.015	--	--
Pd	0.047	--	--
Ag	0.003	$^{110\text{m}}\text{Ag}$	225 d
Cd	0.003	$^{115\text{m}}\text{Cd}$	43 d
Te	0.018	$^{129\text{m}}\text{Te}$	34.1 d
Sr	0.039	^{85}Sr	64 d
Ba	0.040	^{131}Ba	11.5 d
Y	0.020	--	--
La	0.035	--	--
Pr	0.034	--	--
Nd	0.104	--	--
Pm	0.003	--	--
Sm	0.020	--	--
Eu	0.004	^{152}Eu	13.2 y
Gd	0.003	--	--
Ce	0.075	^{141}Ce	32.5 d
<u>Actinides</u>			
U	0.016	--	--
Np	0.012	--	--
Pu	0.000 15	--	--
Am	0.002 6	--	--
Cm	0.000 59	--	--

It might be noted that leach rates are sometimes measured as total weight loss of the solid sample. This method is often too insensitive to give meaningful values for the low leach rates desired for the fixation of radioactive waste. Also, such a procedure measures only the leach rate for total dissolution; hence, specific elements that diffuse from well within the solid boundary can have significantly greater leach rates than are measured with this technique. The unit of $\text{g}/(\text{cm}^2\text{-day})$ implies the "total destruction" type of a leach rate and hence can be misleading when measurements are made on specific elements. Results quoted as the fraction of a specific material leached per day per cm^2 surface area (*i.e.*, A_t/A_0St) can be more descriptive. However, these units can also be misleading if the surface to volume ratio is large. In this latter case, a total volume effect rather than a "skin" is being measured. In any case, conversion between these two values can easily be made if the specific area (cm^2/g) of the waste form is known.

Another method of expressing long-term leach data is cumulative penetration [MENDEL] *i.e.*, the theoretical thickness of glass from which the element of interest has been completely leached away. Cumulative penetration is calculated from the equation:

$$\text{Cumulative Penetration} = \frac{A_t}{A_0} \frac{V}{S} \text{ [cm]} \quad (4)$$

where V is the volume of the solid waste form. The other units are defined for Eq. 3.

3. Leaching of Spray Calcine-10 wt % Silica-10 wt % Glass Frit (PW-4b)

Initial studies were done on sintered waste form (SWF) beads consisting of agglomerated mixtures of 80 wt % spray calcine PW-4b simulated waste, 10 wt % silica, and 10 wt % glass frit. The mixture was sintered at 1100°C . These SWF beads were produced by PNL with a disc pelletizer [MCELROY] and were used with the intent of testing the procedures described below. The SWF beads were about 0.5 cm in diameter, weighed about 370 mg each, and are denoted SWF (PW-4b). The surface area, based on the assumption that the beads had a solid impervious (*i.e.*, hard) spherical shape, was calculated to be $1.1 \text{ cm}^2/\text{g}$. Distilled water (25°C) was the only leachant used in studies with SWF (PW-4b).

Several of these beads were irradiated in the isotope tray (flux $\sim 6 \times 10^{12} \text{ n}/\text{cm}^2\text{-s}$) of the Argonne CP-5 Research Reactor for 24 h (total neutron fluence of $\sim 5 \times 10^{17} \text{ n}/\text{cm}^2$). After about three weeks cooling, which allowed short-lived activities to decay away, the neutron-induced radioactivities present in the SWF beads were determined by γ -ray analysis, using a lithium-drifted germanium (GeLi) detector and computer-programmed gamma spectrum analysis. Isotopes of particular interest that were identified were ^{85}Sr (514-keV γ), ^{131}Ba (496-keV γ), ^{141}Ce (145-keV γ), and ^{160}Tb (879-keV γ). After an initial gamma ray analysis, a single SWF bead was immersed in 100 ml of room-temperature distilled water for seven days with no stirring. (Stirring was generally avoided in these experiments since it was assumed that stagnant water would approximate the slow-moving groundwater encountered in natural situations.) The water was then decanted from the SWF bead and was analyzed radiochemically [FLYNN] for the elements barium, strontium, cerium, and lanthanum.

The barium and strontium were determined in order to measure leach rates for the alkaline earth metals. The measured cerium leach rates should reflect the leaching characteristics of the tetravalent actinides. The lanthanum fraction (containing all of the rare earths) should reflect the leaching characteristics of the trivalent actinides and of the rare earths themselves. The radiochemically separated samples were counted in a low-background beta proportional counter (background of ~ 0.8 count/min), as well as in a GeLi detector. The results of these measurements calculated from Eq. 3 are given in Table 15. The results of the two different counting methods agreed within experimental error (*i.e.*, about 10%). Two successive seven-day leach tests were performed on each SWF bead. The agreement between these two tests indicated no significant change in leach rate with time (on this short time scale) for the particular elements studied (*i.e.*, Ba, Sr, Ce, and La). Cesium was not determined for these SWF beads because we were unable to resolve the ^{134}Cs gamma rays from the gamma spectrum.

Table 15. Leach Rates^a as Determined for SWF (PW-4b) Beads

Isotope	Radiation Counted	Fraction Leached Per Day	Fraction Leached Per Day	g/cm ² day
^{85}Sr	γ	$1.1\text{E-}4^{\text{b}}$	$1.0\text{E-}4$	$3.8\text{E-}5$
^{89}Sr	β	$9.8\text{E-}5$	$8.8\text{E-}5$	$3.3\text{E-}5$
^{131}Ba	β	$1.0\text{E-}4$	$9.4\text{E-}5$	$3.5\text{E-}5$
^{141}Ce	γ	$3.3\text{E-}6$	$3.0\text{E-}6$	$1.1\text{E-}6$
	β	$2.9\text{E-}6$	$2.6\text{E-}6$	$1.0\text{E-}6$
Rare Earths	γ	$1.3\text{E-}5$	$1.2\text{E-}5$	$4.4\text{E-}6$

^a Assumes a hard impervious sphere with an area of 1.1 cm^2 per bead. These beads were observed (with optical microscopy) to be somewhat porous. Thus, these leach rates are upper limits to the actual leach rates.

^b Read $1.1\text{E-}4$ as 1.1×10^{-4} .

4. Leaching of Spray Calcine-15 wt % Glass Frit (PW-7a)

More detailed leach studies have been done on agglomerated SWF beads containing 85 wt % spray calcine (PW-7a) and 15 wt % glass frit. These granules, also obtained from PNL of about 4-mm diameter and 100 mg (average weight), have been identified as SWF (PW-7a). The surface area, based on the assumption that the beads had a solid impervious (*i.e.*, hard) spherical shape, was calculated to be about 0.5 cm^2 per 100 mg bead or $5\text{ cm}^2/\text{g}$. All measurements were based on gross gamma counting, using high-resolution GeLi detectors (*i.e.*, no radiochemical separations were made); hence, there was a significant decrease in sensitivity (gamma counting *vs.* beta counting), as well as some increase in uncertainty as a result of analyzing and resolving extremely complex gamma spectra containing many gamma rays of similar energy. However, this method allows a much larger number of samples to be analyzed per unit time.

Since groundwater characteristically covers a pH range of about 5 to 9, three somewhat arbitrary aqueous leachants covering this pH range were studied. These were (1) distilled water from the tap (pH \sim 5.5), (2) distilled water saturated with CO₂ (pH \sim 4), and (3) distilled water containing NaOH-NaC₂H₃O₂ buffer (pH \sim 9) (0.006M NaOH-0.012M NaC₂H₃O₂). Some tests were also made using saturated salt (NaCl) solutions and a standard buffer solution of pH 4.* Tests were conducted at room temperature (25°C) and at the boiling point (\sim 100°C). Two successive one-week (approximately) tests were performed on the same beads for each set of experimental conditions. The specific isotopes amenable to measurement in these studies and their associated gamma rays are given in Table 16. The isotopes ⁸⁵Sr, ¹³¹Ba, ¹⁴⁷Nd, and ¹⁷⁰Tm were

Table 16. Isotopes Resolvable from GeLi Gamma Spectrum

Isotope	γ Energy, keV	Half Life
⁵¹ Cr	320	27.7 d
⁵⁹ Fe	1099, 1291	44.6 d
⁶⁰ Co	1173, 1332	5.26 y
⁶⁵ Zn	1116	244.0 d
⁸⁵ Sr	514	65.2 d
^{110m} Ag	885	253.0 d
¹²⁴ Sb	1691	60.2 d
¹³¹ I	365	8.0 d
¹³¹ Ba	496	11.7 d
¹³⁴ Cs	605, 796	2.06 y
¹⁴¹ Ce	145	32.5 d
¹⁴⁷ Nd	91, 531	11.0 d
¹⁵² Eu	964, 1408	13.2 y
¹⁷⁰ Tm	84	130.0 d

subject to significant uncertainties because of difficulty of resolving closely associated and/or low-intensity gamma rays from the complex gamma ray spectrum. This difficulty can easily be resolved by introducing radiochemical separations and, if necessary, low-background beta counting. The gram equivalent leach rates (g/cm²-day) based on the fraction of activity leached and calcined from Eq. 3 for each isotope considered are tabulated in Table 17.

* Beckman standard pH 4 buffer solution, diluted 10:1.

Table 17. Leach Rates as Determined for SWF (PW-7a) Beads under Conditions Described in Text. Approximate pH of each leachant is given in parentheses

Isotope	Leach Rate, ^a g/cm ² -d							
	H ₂ O(5.5)		CO ₃ ²⁻ -H ₂ O(4)	Buffered H ₂ O(4)		Na Acetate-H ₂ O(9)		NaCl-H ₂ O
	25°C	100°C	25°C	25°C	100°C	25°C	100°C	25°C
¹³⁴ Cs	5.4 E-3 ^b	5.5 E-3	1.6 E-3	6.0 E-3	5.0 E-3	7.0 E-3	6.0 E-3	6.0 E-3
⁸⁵ Sr	3.0 E-6	5.0 E-6	2.4 E-5	2.2 E-4	2.4 E-4	4.0 E-6	1.2 E-5	2.5 E-5
¹⁴¹ Ce	5.2 E-6	5.7 E-6	2.4 E-6	4.0 E-6	1.0 E-5	2.3 E-6	1.2 E-5	4.0 E-6
¹⁷⁰ Tm	2.8 E-5	5.6 E-5	--	6.1 E-6	2.3 E-5	7.7 E-5	1.2 E-5	5.8 E-5
¹²⁴ Sb	2.2 E-5	2.2 E-5	--	2.0 E-5	2.4 E-5	2.8 E-5	3.8 E-5	1.0 E-5
^{110m} Ag	1.5 E-5	4.5 E-5	1.3 E-5	3.5 E-4	1.8 E-5	1.9 E-5	3.5 E-5	4.7 E-3
⁶⁰ Co	1.1 E-5	2.8 E-5	7.0 E-6	9.0 E-4	9.9 E-4	9.0 E-6	1.8 E-5	2.0 E-5
⁶⁵ Zn	7.0 E-6	5.3 E-5	5.0 E-6	2.0 E-3	1.8 E-3	1.0 E-5	9.3 E-5	2.6 E-5
¹³¹ I	3.4 E-3	3.5 E-3	--	3.7 E-4	4.0 E-3	1.5 E-3	7.0 E-3	3.1 E-3
⁵¹ Cr	1.6 E-2	--	7.6 E-3	9.2 E-3	--	8.8 E-3	--	7.5 E-3

^aAssumes a hard impervious sphere. However, these beads were observed with optical microscopy to be somewhat porous. Hence, these leach rates are upper limits of the actual leach rates.

^bRead 5.4 E-3 as 5.4×10^{-3} .

Total mass leach rates were also determined for the SWF (PW-7a) beads by weighing the sample before and after successive 24-h leachings. The weight loss followed an unusual pattern. During the first 24-h period, a large loss was observed (*i.e.*, about 25 wt % of the total weight of the sample). Thereafter, weight losses decreased to a level where they could not be measured. Such behavior probably indicates the presence of two phases in the waste form, one of them highly soluble.

Leach rates for ten isotopes were determined in these measurements (see Table 17). The elements most relevant to radioactive waste systems were cesium (¹³⁴Cs), strontium (⁸⁵Sr), cerium (¹⁴¹Ce), and the rare earth thulium (¹⁷⁰Tm). The other elements in the table (*i.e.*, Sb, Ag, Co, Zn, I, and Cr) were determined for general information purposes since the data were easily extractable from the analyses. Cesium had a sufficiently high leach rate to be identified, at least partly, with the highly soluble phase referred to above. That is, greater than 20% of the total amount of cesium was leached out during the first leaching period. The other elements studied (*i.e.*, Sr, Ce, Tm, Sb, Ag, Co, and Zn) had sufficiently low leach rates to adequately test the method, as well as to identify the attributes of the waste form for the retention of these elements.

For the elements studied, changes in the leach rates as a function of temperature, time, and leaching media were not dramatic. However, in some cases they were significantly outside of experimental error (*i.e.*, changing by about a factor of 2). More detailed studies would, of necessity, include radiochemical separations and beta counting.

5. Leaching of Metal Matrix Materials

This method was also used to evaluate the leaching characteristics of potential metal matrix materials. Lead was initially selected for these studies. Reagent grade lead shot (2.2-mm dia weighing 75 mg each) having a specific hard sphere surface area of about $2 \text{ cm}^2/\text{g}$ was irradiated for 24 h at a neutron flux of about $6 \times 10^{12} \text{ n/cm}^2\text{s}$. After an appropriate cooling time (about two weeks), the lead shot was gamma counted. Sufficient ^{124}Sb activity was produced by neutron capture of the antimony impurity in the lead to be used as a tracer in leach rate studies.

The irradiated lead shot was immersed in water (25°C) for one week, after which the leachant was analyzed for ^{124}Sb by gamma counting. The lead shot was also weighed before and after leaching to assess the total weight loss. A sample of fifty beads was used in order to increase the sensitivity of the measurement. The leach rates as calculated from Eq. 3 were $3.6 \times 10^{-4} \text{ g/cm}^2\text{-day}$ from the weight loss and $3.2 \times 10^{-4} \text{ g/cm}^2\text{-day}$ from the ^{124}Sb determination. These two numbers agree within experimental error (*i.e.*, $\pm 10\%$) and hence indicate that ^{124}Sb is a representative tracer for measurement of the total mass leach rates for lead.

A preliminary irradiation of some aluminum samples led to the conclusion that the concentration of iron impurity in aluminum is probably sufficient that ^{59}Fe can be used as a tracer in aluminum leach studies.

6. Discussion and Conclusions

The series of measurements delineated in Table 17 were each based on the leaching of a single SWF (PW-7a) bead weighing 100 mg with 0.5 cm^2 surface ($5 \text{ cm}^2/\text{g}$) which had been irradiated for one day at a flux of $\sim 6 \times 10^{12} \text{ n/cm}^2\text{s}$. These conditions easily allowed leach rates of the order of $10^{-5} \text{ g/cm}^2\text{-day}$ to be measured, using one-week leach tests without radiochemical separations. The introduction of radiochemistry and low background beta counting, as was done with SWF (PW-4b) waste form (see Table 15), provides at least two orders of magnitude more sensitivity (*i.e.*, $10^{-7} \text{ g/cm}^2\text{-day}$). The sensitivity can be increased further by increasing the sample size and/or the neutron fluence. With these modifications, leach rates of $\sim 10^{-10} \text{ g/cm}^2\text{-day}$ would be readily detectable.

Leach rates for isotopes other than those listed in Table 16 can also be determined by this method. In fact, any element in the periodic table that is solid at room temperature and has an activation product with a half-life sufficiently long to allow leach testing can be studied using this technique. This method can also be applied to the study of the leach rates of any actinides present in the waste form. In this case, standard carrier-free radiochemical procedures coupled with low-background alpha counting would be used.

Relatively large uncertainties can creep into these measurements when gross gamma counting is relied on in the absence of radiochemical separations. Low-energy gamma rays, such as those associated with ^{147}Nd (91 keV) and ^{170}Tm (84 keV), are particularly difficult to resolve, as well as ^{85}Sr (514 keV) whose gamma ray energy is very close to the usually abundant annihilation radiation (511 keV). Low intensity gamma rays also are difficult to detect above the Compton continuum from high-intensity high-energy gamma rays. For

these reasons, as well as those of sensitivity, radiochemical separations (while time-consuming) represent an invaluable adjunct to the general procedure.

The data reported here are based on the assumption that the waste forms studied were hard (impervious) spheres. Although this approximation is probably adequate for the lead shot, it is conservative for the sintered waste forms. The latter species probably have significantly larger surface areas because of surface irregularities and porosity; hence, the leach rates reported must be assumed to be upper limits. Also, the leach rates reported here are based on one- or two-week tests and must be considered relatively short term. On a long time scale, leach rates of certain species have been shown to decrease with time [*i.e.*, KELLEY, MENDEL-1977, SAMSEL-1975]. The reason for this effect has not been firmly established. It could be the result of either a surface phenomenon or the presence of two phases, one of which is significantly more leachable than the other. In any case, this effect would on a long time scale again serve to decrease the leach rates.

This nondestructive technique for measuring leach rates offers several advantages over current methods. Possible advantages are: preservation of the physical characteristics of the solid matrix, small sample requirements, insignificant buildup of the leached ion in the leaching medium, and greatly increased sensitivity. Applications of this technique to metal matrix composites are currently being studied.

V. ESTABLISHMENT OF TENTATIVE CRITERIA FOR HULL TREATMENT
(L. E. Trevorrow, B. J. Kullen, and Milton Ader)

A. Introduction

The goal of this ERDA program is to develop criteria for handling and disposing of waste hulls and fuel element hardware. The need for such criteria arises from the hazards associated with this metallic waste, which include the potential pyrophoricity of Zircaloy and the radioactivity from neutron-activated metals and residual undissolved fuel. Associated with the radioactivity are the potential hazards of ingestion of radioactivity-laden particles and exposure to penetrating radiation. The potential pyrophoricity is associated with the threat of fires or explosions which, in turn, could result in physical harm or dispersal of radioactivity.

The waste, consisting of metallic fragments from the processing of spent fuel assemblies, is expected to be produced at a rate of about 15 tons ($\sim 15 \text{ m}^3$ uncompacted) per GWe-yr of energy generated by light water reactors. Although Zircaloy (fuel cladding tubes) is the primary constituent of this waste, the waste also includes items of stainless steel (fuel assembly end fittings) and Inconel (fuel assembly spacers).

A variety of technologies for handling and disposing of this waste have been proposed. The criteria to be developed in this program are intended to provide guidelines for safely practicing the technologies for handling the waste and also to provide a reference for the development of rules and regulations.

The product of this program is expected to be a set of criteria and accompanying appendixes. The criteria will include a number of guidelines for procedures and material attributes. The appendixes will provide an explanation or justification for each criterion and a collection of existing regulations that can be interpreted as being applicable to hulls.

A rough draft of this work is to be circulated, for comment, to members of regulatory and energy development agencies and also to industrial organizations that have proposed commercial reprocessing ventures. The final document of this work will be assembled by revising the draft on the basis of the comments received.

Although the scope of these criteria will include anticipated operations and procedures from the point of shearing to the point of receipt at a Federal repository for terminal storage, operations at the fuel reprocessing plant will be emphasized since it is likely to be the site of all operations that result in a hulls waste in a form and packaging suitable for transportation and terminal storage. Criteria are therefore intended to be applicable to the operations of (1) shearing, (2) leaching, (3) rinsing, (4) drying, (5) packaging or containment for interim storage, (6) movement to interim storage, (7) interim storage in primary form, (8) movement from interim storage to operations that change the physical or chemical form of waste, (9) operations for conversion of waste form, (10) final packaging, and (11) transport to terminal storage.

A preliminary step in criteria development was the selection of a list of topics to be addressed (reported in ANL-77-36). Criteria should be: (1) conducive to safe operations, (2) technically feasible, (3) economically feasible, (4) relevant to actual operations planned and described by organizations proposing commercial nuclear fuel reprocessing ventures, and (5) not restrictive of the processor's choice of unit operations.

This work also required the selection of the degree of specificity of the criteria. A set of criteria can be conceived of as a tree, branching from the basic criterion, which is the extreme generality that hulls handling be carried out without undue risk to the safety of operating personnel and the public. Primary branches from this basic general criterion consist of several categories of criteria such as operations, building and equipment, maintenance, accident prevention and mitigation, and shipping and transport. From each primary branch, secondary branches, and from each secondary branch, tertiary branches, etc. can be developed; each stage of branching adds more specificity and detail. If the criteria are not to be dictatorial, however, this "tree" must be truncated just before the degree of specificity begins to infringe on the operator's choice of equipment, procedures, and conditions.

One basis for criteria is the collected knowledge from literature sources [LEVITZ, KULLEN] of conditions that are claimed to encourage pyrophoric behavior. These conditions include: (1) small particle size, (2) high surface/volume or high surface/mass ratio, (3) roughened metallic surfaces, (4) mixtures of metallic zirconium with water in the range of 3-25% water, (5) exposure of zirconium metal to oxidizing environments, (6) storage of zirconium metal in contact with combustible materials, (7) perturbing mechanical forces, (8) accumulation of zirconium metal, (9) formation of zirconium aerosols, (10) high temperatures (except in controlled processes), and (11) exposure to ignition sources.

The development of criteria was begun with the assembly of a large number of possible criteria, which were then culled to produce 17 criteria, previously listed in ANL-77-36, pertinent to the special problems of hulls handling that are not covered by existing regulations applicable to hulls handling. These criteria deal with (1) the definition of hulls wastes, (2) appropriate building areas and equipment for hulls operations, (3) containment and packaging barriers, (4) limits of zirconium metal fines accumulations, (5) isolation of hulls from flammable or reactive materials, and (6) isolation of hulls from static electricity sources.

Another basis for criteria development is existing regulations, directed generally to handling of radioactivity or reactive metals, but adaptable to hulls handling. In this report, statements by the Nuclear Regulatory Commission (NRC) are listed that appear to be applicable to hulls handling. Also presented for comparison with these regulations are statements on fuel reprocessing and waste handling intentions from the Barnwell and Exxon safety analysis reports (SAR) which either specify or permit inference of hull-handling procedures.

Also presented here is a similarly treated list of regulations assembled from the Code of Federal Regulations on transportation, which are not specifically aimed at hulls handling, but are considered applicable to the type of wastes that hulls represent.

In support of the development of suitable hull-handling procedures, an operation to change the form of zirconium is being investigated on a laboratory scale. Hydrochlorination or chlorination to convert the zirconium in Zircaloy to $ZrCl_4$ is being investigated as a means of (1) decontamination from trans-uranium elements, (2) consolidation, and (3) elimination of the hazard of zirconium pyrophoricity. The results of a number of experiments testing this scheme on systems involving zirconium and plutonium are reported here.

B. Criteria Development
(B. J. Kullen)

1. Fuel Reprocessing Plant Criteria Applied to Hulls Management

Although the NRC has not issued regulations specifically addressed to hulls, a general viewpoint of the NRC on hulls management can be assumed to be implicit in the tentative set of general design criteria for fuel reprocessing plants given in proposed Appendix P to 10 CFR 50 [FEDREG-1974A]. If it is assumed that any criteria that guide the design of the plant as a whole also guide the design of specific components or systems within the whole, these criteria can be taken as existing guides for handling hull waste. They are quoted below in Section B.1.a.

The viewpoint of industry on the management of hull wastes, on the other hand, can be taken from descriptions of proposed operating procedures in safety analysis reports of organizations planning fuel reprocessing ventures. Therefore, pertinent statements have been collected from study of safety analysis reports on the intended operations at Barnwell [AGNS] (Plant "A") and Exxon [EXXON] (plant "E") and are presented below in Section B.1.b. To aid comparison of NRC criteria with industrial intentions, each criterion in Section B.1.a is accompanied by a cross reference that identifies the statement in Section B.2.b that could be interpreted as compliance with the criterion. For example, the cross reference for apparent compliance of plant E with criterion 1 would be E1 representing statement 1 of plant E.

a. General Criteria of the NRC

Criterion 1. Quality Standards and Records

*(Hull-Handling)** Structures, systems, and components shall be designed, fabricated, erected, and tested in accordance with quality assurance criteria in Appendix B of 10 CFR 50. Appropriate records of the design, fabrication, erection, and testing of structures, systems, and components shall be maintained by or under the control of the fuel reprocessing plant licensee throughout the life of the plant.

Plant A[†] compliance

A1, A2

* Italicized words in parentheses are those of the author.

† Allied-Gulf Nuclear Services' Barnwell Nuclear Fuel Plant Separations Facility.

Plant E* compliance

E1

Criterion 2. Protection Against Environmental Conditions, Natural Phenomena, and Missiles

(*Hull-Handling*) Structures, systems, and components shall be designed to withstand the effects of and to be compatible with the plant environmental conditions associated with operation, maintenance, plant shutdown, testing, and accidents.

(*Hull-Handling*) Structures, systems, and components shall be designed to withstand the effects of natural phenomena such as earthquakes, tornadoes, lightning, hurricanes, floods, tsunami, and seiches without impairing their capability to perform safety functions. The principal design criteria for these structures, systems, and components shall include: (1) Resistance to the most severe of the natural phenomena reported for the site and surrounding area, with appropriate modifications to take into account the limited quantity of the historical data and the period of time in which the data have been accumulated; (2) safety features to cope with the combinations of the effects of accident conditions and the effects of natural phenomena; and (3) features which provide for safe shutdown under emergency conditions, confinement of radioactivity during the emergency, and safe startup following unscheduled shutdown.

Capability for determining the intensity of natural phenomena which may occur for comparison with design bases of (*Hull-Handling*) structures, systems, and components shall be provided.

(*Hull-Handling*) Structures, systems, and components shall be appropriately protected against dynamic effects, including seismic motion and the effects of missiles and discharging fluids, that may result from equipment failure and from other similar events and conditions both inside and outside the fuel reprocessing plant.

Plant A compliance

A3, A4, A5, A6, A7, A8, A9

Plant E compliance

E2, E3

Criterion 3. Protection Against Fires and Explosions

(*Hull-Handling*) Structures, systems, and components shall be designed and located so as to continue to perform their safety functions under fire and explosion exposure conditions. Noncombustible and heat-resistant materials shall be used wherever practical throughout the facility, particularly

* Exxon Nuclear Company's Nuclear Fuel Recovery and Recycling Center.

in locations vital to the functioning of confinement barriers and systems, to methods of controlling radioactive materials within the facility, and to the maintenance of safety control functions. Explosion and fire detection, alarm, and suppression systems shall be designed and provided with sufficient capacity and capability to minimize the adverse effects of fires and explosions on structures, systems, and components. The design of the fire suppression system shall include provisions to protect against adverse effects in the event of system operation or failure.

Plant A compliance

A5, A10, A11, A12, A13, A14, A15, A16, A17, A18, A19

Plant E compliance

E5, E6, E7, E8, E9, E10, E11, E12, E13, E14, E15, E16, E17, E18, E19, E20, E21, E22, E23, E24

Criterion 4. Sharing of Structures, Systems, and Components

(*Hull-Handling*) Structures, systems, and components shall not be shared between a fuel reprocessing plant and plants of any type unless it is shown that such sharing will not impair the capability of the fuel reprocessing plant to perform its safety functions, including the capability for orderly and safe shutdown in the event of an accident or incident.

Plant A compliance

A20, A21, A22, A23, A24, A25, A26

Plant E compliance

E25, E26

Criterion 5. Proximity of Sites

Fuel reprocessing plants located near other nuclear facilities and other activities licensed under 10 CFR 50 shall be designed to assure that the cumulative effect of discharges (*accumulation of hull waste*) resulting from their operation will not result in undue risk to the health and safety of the public.

Plant A compliance

No direct compliance found in the design analysis.

Plant E compliance

No direct compliance found in the design analysis.

Criterion 6. Testing and Maintenance of Systems and Components

(Hull-Handling) Systems and components that have safety-related functions shall be designed to permit inspection, maintenance, and testing to assure their continued functioning for the life of the facility.

Plant A compliance

No compliance specific to hulls handling procedures was found in the design analysis. However, compliance in terms of the overall plant design is indicated.

Plant E compliance

No compliance specific to hulls handling procedures was found in the design analysis. However, compliance to the criteria in terms of the overall design is indicated.

Criterion 7. Emergency Capability

(Hull-Handling) Structures, systems, and components shall be designed to assure capability for safe shutdown of plant operations and handling of an emergency. The design shall assure capability for use, as necessary, of onsite facilities and available offsite facilities and services such as hospitals, fire and police departments, ambulance service, and utility personnel.

Plant A compliance

A5, A18, A28

Plant E compliance

E15, E24

Criterion 8. Confinement Barriers and Systems

The total *(Hull-Waste)* confinement system shall consist of one or more individual confinement barriers and systems which successively control against the release of radioactivity to the environment. The confinement system shall be designed to protect against the effects of accidents or external natural phenomena and shall be fabricated, erected, tested, and maintained to assure prevention of abnormal leakage, rapidly propagating failure, or gross rupture during the design life of the plant.

Plant A compliance

A22, A24, A25, A26, A27, A28, A29, A30, A31, A32, A33, A34, A35, A36, A37, A38, A39, A40

Plant E compliance

E3, E4, E5, E25, E27, E28, E29, E30, E31, E32, E33, E34, E35, E36

Criterion 9. Ventilation and Offgas Systems

The (*Hull-Handling Containment*) ventilation and offgas systems shall be designed and tested to assure the confinement of radioactive materials during normal or abnormal conditions. To accomplish this objective, these systems shall be designed to meet the following requirements:

- The proper ventilating air flow direction shall be maintained across the confinement barriers, that is, between areas inside the barrier and the general atmosphere outside, under operating and accident conditions.
- The ventilation system shall accommodate changes in operating conditions such as variations in temperature or pressure and shall be capable of safely controlling all radioactive releases that could be associated with normal or accident conditions.
- The continuity of necessary ventilation shall be assured by means of redundant equipment, fail-safe control systems, or other provisions.
- Provisions shall be made for testing all safety-related components during normal operation of the systems to demonstrate their ability to perform at design efficiency and to function during emergency conditions and during transitions between normal and emergency conditions.
- Ventilation systems shall be designed to permit the continued occupancy of any and all areas where such occupancy is required for normal plant operations, for safe shutdown or maintaining the plant in a safe shutdown condition. The design shall include protection against the intake or accumulation of radioactive materials. The design shall also permit the timely and safe evacuation of personnel from all areas.
- Vessel and dissolver offgas systems shall be designed to confine the radioactive materials during normal operation and to assure that the concentration of radioactive materials in the effluent gases is as low as practicable. Such systems shall also be designed to retain their confinement and separation capability to reduce releases resulting from an accident condition to levels consistent with the regulations contained in 10 CFR 50.

Plant A compliance

A19, A31, A41, A42, A43, A44, A45, A46, A47, A48, A49

Plant E compliance

E3, E9, E10, E11, E16, E17, E18, E19, E20, E21, E23, E29, E32, E33, E37, E38, E39, E40, E41, E42

Criterion 10. Protection Systems

Protection systems (*for Hull-Handling Operations*) shall be designed; to initiate action that will assure that specified acceptable operating design limits are not exceeded as a result of operational occurrences, and to sense potential hazardous or accident conditions and to activate systems and components required to assure the safety of operating personnel and the public or to give audible and visible alarm so that action can be taken in a timely manner to assure such safety. Protection systems and components shall be activated automatically where this mode is compatible with the safety requirements to be satisfied.

Protection systems (*for Hull-Handling Operations*) shall have reliability and *in situ* testability. The design of protection systems shall provide for redundancy and independence at least sufficient to assure that; no single failure results in loss of the protection functions, and removal from service of any component does not result in loss of the required redundancy unless it can be otherwise demonstrated that the protection system will operate with acceptable reliability. The protection systems shall be designed to permit the periodic testing of its functions and efficiencies while the plant is in operation, to determine whether failures or losses of redundancy may have occurred.

Protection systems (*for Hull-Handling Operations*) shall be designed to fall into a safe state or into a state demonstrated to be acceptable on some other defined basis if conditions such as disconnection of the system, loss of energy or motive power, or adverse environments are experienced.

Plant A compliance

A19, A48, A49, A50, A51, A52

Plant E compliance

E15, E22, E24, E42, E43, E44, E45

Criterion 11. Instrumentation and Control Systems

Instrumentation and control systems shall be provided to monitor safety-related variables and operating systems over anticipated ranges for normal operation, for abnormal operation, for accident conditions, and for safe shutdown. These systems shall be provided with engineered safety features in the redundancy required to assure adequate safety of process and utility (*Hull-Handling*) operations. The variables and systems that require constant surveillance and control include parts of the process, the overall confinement system, each confinement barrier and its associated systems, and other systems that affect the overall safety of the plant. Controls shall be provided to maintain these variables and systems within the prescribed operating ranges under all normal conditions. Instrumentation and control systems shall be designed to be fail safe or to assume a state demonstrated to be acceptable on some other basis if conditions such as disconnection, loss of energy or motive power, or adverse environments are experienced.

Plant A compliance

A53

Plant E compliance

E15, E45, E46

Criterion 12. Separation of Process Safety Features and Control Systems

The (*Hull-Handling*) process safety features shall be separated from control systems to the extent that a change or failure in either leaves intact a system which satisfies all reliability and independence requirements of the process safety systems.

Plant A compliance

No compliance specific to hull-handling procedures was found in the design analysis. However, compliance in terms of overall plant design is indicated.

Plant E compliance

No compliance specific to hull-handling procedures was found in the design analysis. However, compliance in terms of overall plant design is indicated.

Criterion 13. Control Room

A control room or control area shall be designed to permit occupancy and actions to be taken to operate the plant (*Hull-Handling Operation*) safely under normal conditions and to maintain the plant in a safe condition under accident or other abnormal conditions.

Instrumentation and control in the control room or control areas shall be designed with sufficient redundancy to allow the plant to be put into a safe condition if any one control room or control area is removed from service.

Plant A compliance

A54

Plant E compliance

No compliance specific to hull-handling procedures was found in the design analysis. However, compliance to the criteria in terms of overall plant design is indicated.

Criterion 14. Process Systems

(*Hull-Handling*) Process components and systems are the first confinement barrier. The design of each process system shall provide capability for the system to maintain its integrity and operability to protect the public

health and safety under all normal process conditions and abnormal conditions, including the maximum expected inventories of fissile materials and other radionuclides. Provisions shall be included for the safe handling of anticipated nonroutine process requirements.

Plant A compliance

A27, A32, A33, A34, A35, A36, A37, A38, A39, A55, A56, A57

Plant E compliance

E25, E34, E40, E46, E47

Criterion 15. Utility Services

The design of each utility service system required for emergency conditions shall provide for the meeting of safety demands (*of Hull-Handling Operations*) under normal and abnormal conditions. The design of safety-related utility services and distribution shall include redundant systems to the extent necessary to maintain, with adequate capacity, the ability to perform safety functions assuming a single failure.

Emergency utility services (*for Hull-Handling Operations*) shall be designed to permit testing of their functional operability and capacity, including the full operational sequence, of each system for transfer between normal and emergency supply sources, and the operation of associated safety systems.

Provisions shall be made so that, in the event of a loss of the primary electric power source or circuit (*to Hull-Handling Operations*), reliable and timely emergency power will be provided to instruments, confinement systems, utility service systems, and process systems in amounts sufficient to allow operations to be shut down safely and to be maintained in a safe shutdown condition with all safety devices essential to safe shutdown functioning. The onsite emergency power sources and the electrical distribution circuits shall have independence, redundancy, and testability to assure performance of their safety functions in the event of a single failure or an accident.

Plant A compliance

A58, A59

Plant E compliance

E31

Criterion 16. Safety Margins

The design of (*Hull-Waste*) process and storage systems shall include margins for the nuclear criticality* parameters that are commensurate with the uncertainties in the process and storage conditions, in the data and methods used in calculations, and in the nature of the immediate environment

* It is recognized that leached cladding hulls will not pose a criticality hazard. Hence, criteria 16-19 are presented only for the sake of completeness.

under accident conditions. All process and storage systems shall be designed to be maintained subcritical and to assure that no nuclear criticality accident can occur unless at least two unlikely, independent, and concurrent or sequential changes have occurred in the conditions essential to nuclear criticality safety.

Plant A compliance

A60, A61, A62, A63

Plant E compliance

E36

Criterion 17. Methods of Control

Favorable geometry, in which (*Hull-Handling*) equipment or system are subcritical by virtue of neutron leakage under worst credible conditions, is the preferred method of nuclear criticality control.

Where the favorable geometry method of nuclear criticality control is not practical, the use of permanently fixed neutron-absorbing materials (poisons) is the next preferred method of control.

Where both favorable geometry and the permanently fixed neutron-absorbing materials (poisons) methods of nuclear criticality control are not practical, administrative controls of moderation, fissile material concentration, total fissile material, or the use of soluble neutron-absorbing materials (poisons) shall be employed when combined with margins of safety measurements or appropriate analysis and engineered safety features.

Plant A compliance

A60, A61, A62, A63, A64, A65

Plant E compliance

E48, E49, E50, E51

Criterion 18. Neutron Absorbers

Where solid neutron-absorbing materials (poisons) are used for the prevention of nuclear criticality, the design shall provide for positive means to verify their continued efficacy. Soluble neutron-absorbing materials may be used as a primary nuclear criticality control provided: two independent methods are provided to assure the presence of the required concentration of neutron absorber; and the equipment containing the fissile material is located behind sufficient barriers and shielding to reduce the probability and extent of accidental contamination of the environment and accidental radiation exposure to personnel in the event of a criticality accident.

Plant A compliance

A65

Plant E compliance

E49, E50

Criterion 19. Ancillary Criteria for Nuclear Criticality Safety

(Hull-Waste) Process and storage systems shall be designed to assure that no mechanisms that could cause segregation of fissile materials can be present in components whose nuclear criticality safety is dependent on the homogeneous distribution of fissile material.

(Hull-Handling) Components whose nuclear criticality safety is dependent on a limiting concentration of fissile material shall be designed so that either; mechanisms that could cause critical concentrations of fissile materials are not present, or concentration is controlled by positive instrumental means.

(Hull-Waste) Process and storage systems shall be designed to assure that the transfer of fissile materials from safety systems to unsafe systems is not possible as a consequence of any single failure or operating error.

(Hull-Process) Confinement system components shall be designed to assure that leakage from equipment or from one confinement zone to another confinement zone cannot result in a condition that would result in nuclear criticality.

The spacing between discrete accumulations of fissile materials shall be controlled so as to maintain a subcritical state.

Plant A compliance

No compliance specific to hulls handling procedures was found in the design analysis. However, compliance to the criteria in terms of the overall plant design is indicated.

Plant E compliance

No compliance specific to hulls handling procedures was found in the design analysis. However, compliance to the criteria in terms of the overall plant design is indicated.

Criterion 20. Access Control

The design of the facility (*Hull-Handling Operation*) shall provide for control of access to the facility and to areas of potential contamination or high radiation within the facility. The facility shall be designed so that the spread of contamination can be monitored and controlled.

Plant A compliance

A66, A67, A69, A70, A71, A72, A73, A74, A75, A76

Plant E compliance

E52, E53

Criterion 21. Radiation Shielding

(*Hull-Confinement*) Shielding shall be designed to assure that dose rates in accessible areas are consistent with the regulations contained in 10 CFR 50.

Plant A compliance

A21, A22, A23, A24, A25, A26, A27, A28, A32, A33, A34, A55, A77, A78

Plant E compliance

E53, E54

Criterion 22. Radiation Alarm Systems

Radiation alarm systems shall be provided to warn plant personnel of significant increases in radiation levels in normally accessible spaces and of excessive radioactivity released in plant effluents. Such systems shall be designed with redundancy and with capability to permit testing their efficiency of operation.

Plant A compliance

A87

Plant E compliance

No compliance specific to hull-handling procedures was found in the design analysis. However, compliance in terms of overall plant design is indicated.

Criterion 23. Effluent Monitoring

All plant effluent (*Hull-Handling*) systems shall be designed to include means for measuring and recording the amount of radionuclides in any effluent. In order that the data thus measured and recorded can be used, the flow of environmental diluting media, either air or water, shall be determined.

Plant A compliance

A52, A78, A79, A80, A81, A82, A84

Plant E compliance

E41, E45, E46, E51, E55, E56

Criterion 24. Effluent Control

The design of the plant (*Hull-Operations Confinement*) shall include means to control the release of radioactive effluents, whether gas, liquid, or solid, during normal operations and under accident conditions. Systems provided to guard against the release of radioactive materials shall be designed to be monitored and tested, and shall be provided with alarms. Capability shall be provided for prompt cessation of the flow of contaminated liquid effluents or for retention of such effluents as is necessary to assure that the concentrations of radioactive materials in liquid effluents are maintained as low as practicable.

Plant A compliance

A5, A6, A7, A8, A9, A81, A85

Plant E compliance

E46, E57

Criterion 25. Fuel and Radioactive Waste Systems

Fuel storage, radioactive waste (*Hulls*) storage, and other (*Hulls*) systems that might contain or handle radioactive materials shall be designed to assure adequate safety under normal and accident conditions. These systems shall be designed; with a capability to test components important to safety, with suitable shielding for radiation protection under normal and accident conditions, with confinement systems, and with a heat removal capability having testability and reliability that reflects the importance to safety.

Plant A compliance

A27, A35, A36, A37, A38, A39, A40, A52, A55, A77, A86

Plant E compliance

E25, E27, E35

Criterion 26. Waste Disposal Systems

The waste (*Cladding-Hull*) disposal systems shall be designed so that their performance will comply with the regulations in 10 CFR 50.

Plant A compliance

No compliance specific to hull-handling procedures was found in the design analysis. However, compliance in terms of the overall plant design is indicated.

Plant E compliance

No compliance specific to hulls handling procedures was found in the design analysis. However, compliance in terms of the overall plant design is indicated.

Criterion 27. Decommissioning

In accordance with Appendix F of 10 CFR 50, a design objective for fuel reprocessing plants shall be to facilitate removal of all significant radioactive (*Hull*) waste at the time the facility is permanently decommissioned.

Plant A compliance

No compliance specific to hull-handling procedures was found in the design analysis. However, compliance in terms of the overall plant design is indicated.

Plant E compliance

E58

b. **Statements by Commercial Organizations that Specify or Imply Hulls Management Procedures**

The safety analysis reports of the Barnwell Plant (Plant A) [AGNS] and the Exxon Plant (Plant E) [EXXON] were searched to find construction and operation descriptions relevant to the 27 general NRC design criteria of proposed Appendix P, 10 CFR 50 [FEDREG-1974A], listed above in Section B.1.a. The general philosophy of hull handling differs for the two plants.

Plant A plans to dump entire (chopped) fuel assemblies into its dissolvers. Undissolved metal wastes from the dissolvers are placed (along with collected metal fines) in flanged storage containers, which are subsequently closed with bolted-down, gasketed covers. The closed containers are then removed from the process plant in shielded casks and deposited in an outdoor storage area.

Plant E, on the other hand, plans to saw end fittings from fuel assemblies prior to fuel chopping and dissolution. Leached cladding hulls are dumped into metal storage containers. The containers are sealed by welding a cover in place, and are stored underwater in a combined spent-fuel/solid-waste storage pool. Hull waste-handling operations for both plants are summarized in Fig. 23 and 24, and quotations of statements that specify or imply hulls handling procedures follow in Sections B.1.b(1) and B.1.b(2).

(1) **Statements of Plant A [AGNS]**

A1 "Structures, systems, and components important to safety have been designed, fabricated, erected, and tested to quality standards commensurate with the importance of the safety functions to be performed. A quality assurance program has been implemented to provide assurance that these established quality standards have been fulfilled. Appropriate records will be maintained throughout the life of the unit."

A2 *(In specific reference to hull-waste storage, the analysis cites a requirement that waste containers be uniquely identified and that records be kept on container identification, contents, and storage location.)*

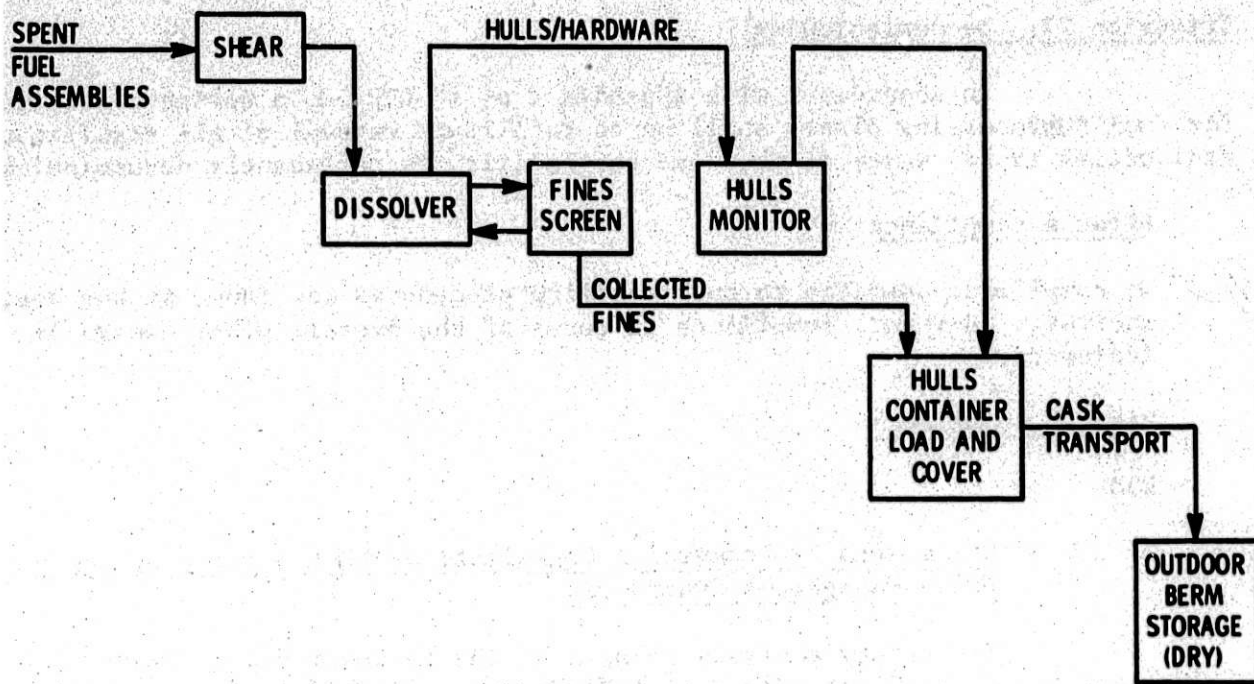


Fig. 23. Plant A Hulls-Handling Flow Diagram [AGNS]

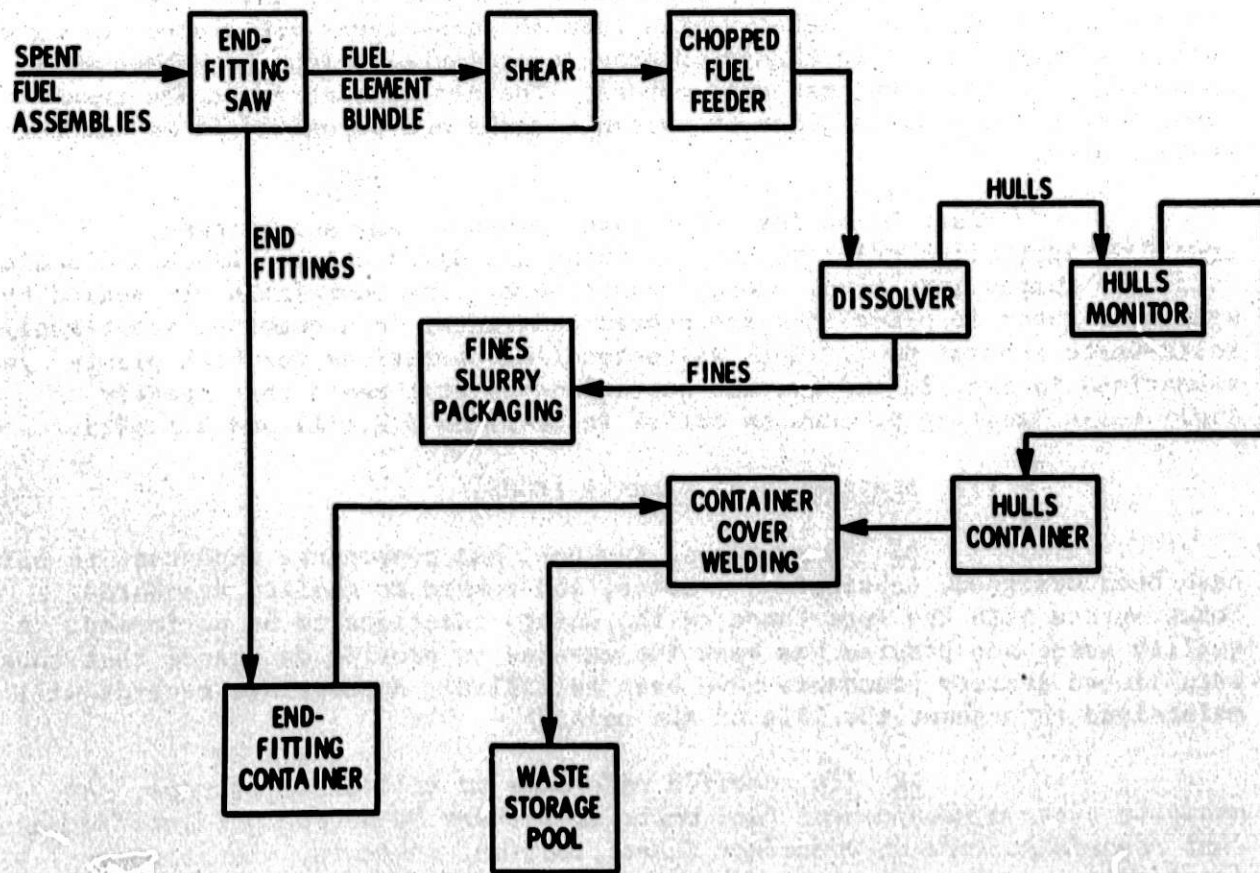


Fig. 24. Plant E Hulls-Handling Flow Diagram [EXXON]

A3 "Critical structures, systems, and components important to safety are designed to withstand effects which are worse than the most severe natural phenomena historically recorded at the site and surrounding area, including earthquake, tornado wind and related missiles, and related accidents."

A4 "Critical structures, systems, and components are designed to be compatible with the environmental conditions associated with normal operation, maintenance testing, and postulated accidents. Such structures, systems, and components are appropriately protected against dynamic effects, including the effects of missiles such as pressure vessel bolts, metal parts, etc."

A5 "The facilities and procedures for solid waste handling and storage are designed to minimize the occurrence and the effects of accidental radioactivity releases to the environment.--Six accident modes involving solid waste handling and storage (*i.e.*, criticality, hydrogen explosion, fire, transportation, earthquake, and tornado) have been postulated; each of these has a very low probability of occurrence."

A6 "A postulated accident mode involving a hulls container handling accident was analyzed in depth."

A7 "The HCS (Hulls Container Storage) caisson storage facility is a static system except during periods when containers are being added or removed. Since the storage caisson and cask can only handle one container at a time, an accident can only affect a single container (approx. 1.5 metric tons). The postulated accident involves dropping a loaded Hulls Transfer Cask a distance of 16 ft into the sand pit that surrounds the vehicle unloading zone at the HCS area."

A8 "The radioactivity in the hulls container prior to the accident is based on (1) hulls from processing of 5 tonnes of fuel at 35,000 MWD/T and cooled 160 days, (2) isotopic spectrum from the ORIGEN code, and (3) 0.5% undissolved fuel per MTU. The accident analysis assumes that 35% of the hulls escape the container and cask as a result of the drop. Furthermore, it is assumed that (1) 40% of the exposed fraction is available for entrainment, (2) the release fraction coefficient equals 5×10^{-4} , and (3) 50% of the release occurs in the first hour following the accident."

A9 "This postulated accident could release approximately 0.24 curies of actinides and 8 curies of fission products over a 24-hour period. The resultant off-site dose would be approximately 110 mrem to the whole body, 3350 mrem to the bone, 260 mrem to the lung, and 53 mrem to the skin. The whole body dose from this postulated accident is 0.4% of 10 CFR 100. The bone dose is 2% of the inferred bone dose limit of 10 CFR 100."

A10 "Structures, systems, and components important to safety are designed to minimize the probability and effect of fires and explosions. Confinement structures for all critical areas are constructed of fire-resistant materials (predominantly reinforced concrete). Automatic fire detection and automatic and manual extinguishing systems are provided and designed to minimize adverse effects of fires on critical components and to limit the spread of contamination."

A11 ". . . windows (*the Remote Process Cell*) are high-density lead glass filled with oil. They are designed to maintain confinement for an in-cell blast of 6 psi static load for all windows except the east wall center window which is designed for 8.6 psi static load. (*The postulated explosion involves*)

- Blast effects equivalent to 3 lb of TNT.
- Liberation of 5700 Btu of energy.
- Hot gas evolution of 100 ft³.
- Shock wave with a pressure of 800 lb/ft² and an energy of 230 ft-lb/ft² at a distance of 15 ft."

A12 "Possibility of zirconium alloy fines combustion is minimized by:

- Preventing accumulation of large quantities of fines in the shear and the diverter by gas purge and intermittent poisoned water flush;
- Keeping the fines (in the dissolver solution) in suspension prior to removal by the feed clarification centrifuge;
- Retaining the wet fines (separated from dissolver solution in the centrifuge) and slurring the fines during removal and handling."

A13 ". . . The shear sweep-air system provides an airflow in excess of 250 scfm down the shear outlet chute. This sweep action channels radioactive gas and particulate matter within the magazine, through the shear, and down the diverter chute to the dissolver--thereby preventing the release of radioactive dust and gas to the RPC (Remote Process Cell) during shearing. The shear design forms an air channeling path through the cutting point. Its sweep-air channeling system, which air sweeps particulate matter, also prevents excessive accumulation of Zircaloy fines (a potential fire hazard) and backup of dissolver solution entrainment or gases to the shear."

A14 "The greatest zirconium fire potential exists during dumping of the hulls and shearing fines into hulls containers or during transportation to the HCS (Hulls Container Storage) area, where the freshly cut, acid sensitized metal surfaces are exposed to potential impact sparking. The massive metal (hulls) represent minimal risk of ignition due to small surface area to mass ratios; however these are the primary source of sparking. The shearing fines (40 mesh/~350 μ) from the dissolver screen pot are pyrophoric, and represent fire risk, particularly during dumping when the fines are dispersed in air."

A15 "Zircaloy fines can be pyrophoric under certain conditions. In the case of sparking, sand can be added to prevent ignition. If fines ignite after closure, the temperature increase in the container would be less than 60°C in the absence of sand (and even less if sand were present)."

A16 "Zirconium fire potential during dumping, transportation, and storage is minimized by administrative controls that isolate the fines from massive metal. This is accomplished by requiring dumping of a screen pot into empty hulls containers. This procedure reduces dispersion of the fines within the hulls due to subsequent dumping. Fire detection and suppression in the RMSC (Remote Maintenance and Scrap Cell) are discussed. . ."

A17 "Once a hulls container is placed in caisson storage at the HCS area, the potential for impact sparking is eliminated. At elevated temperatures of the hulls in storage (500°F nominal to 650°F maximum at steady state), the zirconium will slowly oxidize, resulting in a passive zirconium oxide film. Hence, it is concluded that conditions are unfavorable for ignition and burning of zirconium scrap in the HCS area."

A18 "Fire hydrants and hose houses are located within 300 ft of all buildings and the LLS (Low Level Storage) area. Portable fire extinguishers are provided at each hose house, at several locations in the central personnel facilities, and on all mobile equipment that carry personnel. Fire alarm systems within the WSA (Waste Storage Area) facility will signal a common alarm in a continuously occupied area of the Separations Plant."

A19 "The presence of moisture with the solid waste might possibly result in the generation of molecular hydrogen due to radiolysis. At relatively low radiation source terms, self-shielding properties of the solid waste and low linear energy transfer (LET), the rate of molecular hydrogen generation will be extremely low. However, a caisson vapor space that indicates pressurization is periodically sampled and/or purged with air through the portable filter station . . . This administrative control, coupled by absence of ignition source, negate a hydrogen explosion incident in the caissons."

A20 "Separate structures are provided to house fuel receiving and storage systems, process components, control room, waste storage, and critical ventilation and utility components. These structures are designed to minimize passage of radioactive material into the environment or between structures during any design condition. The failure of any noncritical structure will not endanger the confinement function of any critical structure."

A21 "The hulls cask containing one hull container arrives at the HCS (Hulls Container Storage) area on a trailer. A special platform is located over the storage caisson. This platform includes a shielding door and is designed to position the hulls cask directly over the hole and to support the weight of the loaded cask. A bridge crane is used to remove the loaded cask from the trailer and set it in position on the platform."

A22 "An adapter frame containing the shielding plug is then positioned on the platform. The platform door is opened remotely and the shielding plug is lowered into position. Finally, the platform is removed. A metal plate is placed over the caisson opening."

A23 "With the platform door open, the bottom door of the cask is opened and the hulls container is then lowered into the hole with the internal cask hoist. The hook is released from the bail by remote means and drawn up into the cask. The cask door is then closed and the platform door is closed to shield the workers while the cask is removed from the platform."

A24 ". . . The confinement system consists of a primary container, a secondary container, and the engineered soil berm."

A25 "The radioactive materials associated with the solid waste are principally confined by the primary container, except for potential surface contamination on the primary container."

A26 "The . . . areas for storage of the hulls containers . . . are equipped with galvanized steel caissons which provide secondary confinement of the radioactivity. These caissons are closed to minimize breathing directly to the atmosphere. Each caisson is provided with an internal probe for monitoring pressure, for sampling, and for controlled venting of the caisson. . ."

A27 "The hulls container storage facility is an engineered soil structure in the form of an above grade berm. Within this berm, galvanized steel caissons are set in an array on 10 ft centers. A hulls container holding low level solid waste is placed in the caisson and the caisson is covered with a concrete shielding plug and metal cover plate."

A28 "All equipment in the (remote process) cell is designed to resist either an OBE/DBE or a DBE (Q or ER requirements).^{*} Special efforts have been made to prevent multiple equipment failure from falling debris in case of either natural phenomenon. Among items designed to the criterion are the structural concrete walls, floor, and ceiling, the structural brackets supporting the process equipment, and the supports and retainers for the cranes. The process equipment and cranes are designed to the second criterion. All five RPC (Remote Process Cell) shielding windows and frames are designed to withstand an OBE/DBE or an in-cell blast and still maintain confinement. The 5-foot thick structural concrete provides shielding to personnel in normal operating areas surrounding the RPC so as to limit exposure to not more than 1 mrem/hr."

A29 "Critical confinement structures are provided to prevent unacceptable release of radioactivity to the environment under all postulated normal, abnormal, or accident operating conditions and natural phenomena (such as tornadoes, earthquakes, explosion, and fire).

● Solids from shearing operation

Barriers--single

Confinement Method--channeling, treatment

● Solids (hulls, process wastes, and failed equipment)

Barriers--multiple

Confinement Method--channeling, engineered storage berm [see A35]

* OBE, Operation Basis Earthquake
 DBE, Design Basis Earthquake
 Q, Highest Classification of Confinement
 ER, Extremely Reliable (non-Q)

● Hulls during transport

Barriers--multiple (container, though vented and contaminated, considered primary confinement)."

A30 "The remote process cell structure is designed and constructed to Q requirements and to withstand the simultaneous combination of all normal loads, plus any one of several abnormal loadings. The failure of penetration sleeves and plugs (which are an integral part of this structure) will not cause the protective function of the structure to fail. All structural steelwork, crane rails, fittings, anchorage, clips, and embedded metal items are type 304L stainless steel, 304L stainless steel clad carbon steel, or carbon steel coated with an acid resistant phenolic system such as Phenoline 305* or Amercoat 90*. The floors and lower walls are lined with a 304L stainless steel pan and the walls and ceiling are finished with a phenolic system. Penetrations through the walls and equipment installed in, or through, the penetrations are designed with particular concern to confinement, shielding, air in-leakage, and contamination control. The ventilation system maintains a negative pressure of two inches of water between the operating aisle and the cell interior. This provides confinement by maintaining an air in-leakage through the clearance between penetrations and their inserts, periscopes, master-slave manipulators, K-plugs, shielding windows, shear hydraulic drive, mechanical drives, and pass-through ceiling port. Critical equipment supports in the cell are Q and are designed to withstand an OBE/DBE. The equipment is ER and is also designed to withstand DBE to ensure that it will stay in place under this loading. The cell liner is a reliable leak-proof barrier to any radioactive solutions which reach the floor on this cell."

A31 "The remote maintenance and scrap cell is designed and constructed as is the remote process cell above."

A32 "The cask loading station (CLS) contains the facilities for safely removing loaded scrap disposal containers from the remote maintenance and scrap cell (RMSC) and securing them in a shielding cask for transport to the underground solid waste storage area. Empty disposal containers also enter the RMSC from the CLS. When a cask is in the CLS, personnel traffic is administratively controlled. All personnel and equipment are surveyed before leaving the area."

A33 "The shielding cask cavity is approximately 10 feet high, 4 feet ID, 5.5 feet OD, and weighs approximately 51 tons empty. It is used to transfer hull disposal containers from the process building to the solid waste storage area. The main body of the shielding cask is stainless steel inner and outer shells filled with lead. Shielding is 7.2-in. lead equivalent in all directions. It is designed to limit the maximum dose rates to 100 mR/hr at 18 in. from the surface of the cask."

A34 "The bottom of the cask is equipped with electrically operated, screw-driven, bi-parting shielding doors. The hulls disposal container will be supported on the cask doors during transport. Containers will be raised into and lowered out of the cask with an enclosed, shielded hoist attached to the top of the cask body."

* Registered trademark.

A35 "The berm is constructed by first laying a clay pad at the existing grade level. A layer of porous material is placed over the clay pad, and this layer in turn is covered by another clay layer. The remainder of the berm is constructed of a homogeneous fill having measured ion exchange properties. Finally, the top and sides of the berm are capped with a moisture barrier, such as clay. Any moisture which might penetrate the cap of the berm would be directed horizontally by the upper clay layer and exit through the toe of the berm. The toe of the berm is made up of porous material for this purpose."

A36 "Thus constructed, the berm is isolated from the vadose zone by the two clay layers and the porous layer, which prevents liquid movement between the berm and vadose zone."

A37 "Any moisture from within the berm is channeled by drainage ditches surrounding the berm. The channeled run-off is continuously sampled prior to discharge to the surface drainage system. Dry wells and an underlying network of monitoring tubes provide the primary means of detecting the spread of any radioactivity through the berm."

A38 "Each caisson is set in the berm approximately two ft above the upper clay layer and is surrounded by porous material. This material isolates the caisson from the berm fill and prevents capillary migration of moisture from soil to caisson. The caisson is covered by a concrete shielding plug to prevent entrance of moisture into the caisson."

A39 "A capped monitoring tube extends from outside the top of the berm into the bottom of the caisson for monitoring activity, moisture, pressure, etc., within the caisson."

A40 "This specification establishes the requirements for the storage of retrievable solid radioactive waste. . . . If confinement is lost, corrective action shall be taken to restore confinement as soon as practicable."

A41 "The process confinement structure (including vaults, buildings, etc.) ventilation systems will provide isolation, cleanup, and control of released fission products during normal operation or following any credible accident within the process building. The system will reduce the quantities of radioactivity released to the environment to values as low as practicable and well below the acceptable limits defined in 10 CFR Parts 20 and 100. Systems are designed to operate on the emergency power system and maintain their function upon failure of the normal electrical power system."

A42 "All critical components of the process confinement structure ventilation system are designed to allow appropriate periodic inspection. The design also allows appropriate periodic functional and pressure testing to assure structural and containment integrity, operability, and performance of both the normal and emergency critical components."

A43 "Process, waste storage, and ventilation gases are treated to remove significant noxious or radioactive materials prior to release to the environment. The process building ventilation system will maintain a flow of air through all spaces in the building subject to radioactive

contamination in the desired direction without backflow, and will maintain the applicable limits for normal and accident conditions."

A44 "The sweep-air system on the shear coupled with limited air inflow (except at the controlled inlet valve) provides a positive flow of air (250 cfm) from the cell into the magazine and shear. This flow of air sweeps radioactive gas and particulate matter down the diverter chute into the dissolver system thus preventing their release to the cell during shearing."

A45 "Gases emitted during the dissolution are confined and channeled to the DOG (dissolver offgas) system. The poisoned water seals (on the dissolver and diverter) permit operation of the off-gas system under a negative pressure of from 5 to 10 inches of water. A controlled air sweep within the diverter of 2.5 ft/sec, originating at the inlet to the fuel shear diverter, carries dust, fission product gases, and corrosive vapors away from the shear head into the dissolver system."

A46 "A sintered stainless steel filter (a 3-element, 20 micron porosity unit) removes dust particles leaving the dissolver (prior to collection by the DOG system). The filter is provided with a timed cycled blow-back to discharge collected dust back to the dissolver."

A47 "The remote process cell structure is designed and constructed to Q requirements and to withstand the simultaneous combination of all normal loadings, plus any one of several abnormal loadings. The ventilation system maintains a negative pressure of two inches of water between the operating aisle and the cell interior. This provides confinement by maintaining an air in-leakage through the clearance between penetrations and their inserts, periscopes, master-slave manipulators, K-plugs, shielding windows, shear hydraulic drive, mechanical drives, and pass-through ceiling port."

A48 ". . . the HCS (Hulls Container Storage) - caissons will be closed to minimize direct venting to the atmosphere. This closure minimizes contamination of the operating area and minimizes release of radioactivity to the environment."

A49 "As a result of the closed caisson concept, residual moisture associated with the solid waste could result in pressurization of the caisson at elevated temperatures. Therefore, a pressure indicator is provided on the monitor/sampling tube in each caisson. If pressurization is detected, the caisson is vented through a portable filter station."

A50 "Process systems containing radioactivity are designed with appropriate confinement or treatment components, heat removal capability, radiation shielding, and capability to permit appropriate periodic inspection and testing of components important to safety. Radiation protection in process operating areas is provided by suitable shielding, ventilation systems, monitoring instruments, and appropriate access and administrative controls. The release of radioactive material to the environment will be maintained as low as practicable by the process confinement systems. A minimum of two independent safety features are provided to prevent excessive radioactive release. Radioactive material release will not exceed the limits set forth in 10 CFR Part 20 during normal or abnormal conditions, nor the limits of 10 CFR Part 100, as the result of a design basis accident."

A51 ". . . Sand can be added to the hull disposal container after dumping if the spent hull fines should become ignited. Possible ignition of spent hull fines will be monitored by remote viewing through the shielded window located adjacent to the dumper operating station."

A52 "This specification establishes the requirements for the storage of retrievable solid radioactive waste. . . Monitoring of the WSA (Waste Storage Area) shall be such as to detect a loss of confinement before radioactive material reaches the environment. The frequency of monitoring shall be approved by the operational safety committee based on results of isotope migration studies."

A53 "Instrumentation is provided to monitor variables and systems over anticipated ranges for normal, anticipated variations, and accident conditions as appropriate to assure safety. Safety-related instrument systems are designed to the applicable portions of IEEE-279."*

A54 "The control room is designed as a Q structure which houses the instruments and controls necessary to operate the plant safely under normal conditions, and to permit a safe, orderly shutdown under any credible accident or environmental condition. Adequate radiation protection is provided to ensure that personnel in the control room will receive less than 5 rem whole-body or its equivalent to any part of the body during any credible plant accident. Equipment is provided outside the control room to allow safe plant shutdown in the remote event the control room is inaccessible."

A55 "Shielding windows in the RMSC (remote maintenance and scrap cell) allow direct viewing of the majority of remote hull handling, remote maintenance, and remote decontamination operations--while providing shielding to limit exposure to not more than 2.5 mrem/hr. Television, periscopes, and front surface mirrors supplement the windows for viewing these remote operations. The periscope has a photographic capability and sufficient magnification to facilitate remote maintenance. The interior of the RMSC is adequately lighted to permit remote viewing of cell operations."

A56 "The stainless steel cell liner retains radioactive liquids resulting mainly from decontamination, direct drain from hulls during monitoring, and jetting out of the monitor sump drain to the RMSC sump and sand trap for jetting back to the general purpose concentrator feed tank."

A57 "The dissolver system baskets have a perforated section located near the top to allow liquid overflow, meanwhile retaining the hulls within the basket. The basket is perforated at the bottom to permit upflow liquid feed through the basket. The overflow from each of the dissolver barrels has a 40-mesh titanium screen which limits passage of cladding fines to the feed surge tank."

A58 "The normal commercial electric power system is supplemented with an on-site emergency power system for critical loads. The emergency power system is powered by two independent diesel-drive generators. The emergency system provides (regardless of cause or duration of normal power

* Institute of Electrical and Electronics Engineers Standard No. 279-1971.

outage) that the plant can be shut down and maintained in a safe condition. A battery-powered uninterruptible power supply is provided for starting the emergency generators, maintenance of safety-related instruments, and emergency lighting. The emergency electrical system is designed to withstand accident and environmental design basis events."

A59 "All electric power supply systems and components (critical to safety) are designed to permit appropriate periodic inspection and testing to ensure operability and functional performance."

A60 "Hulls containers are used for packaging spent fuel cladding (hulls) and high level general process trash. For a single container filled with hulls, the total undissolved fuel is limited to 75% of the minimum critical mass . . . "

A61 ". . . A leached hull monitor is used to assess the amount of undissolved fuel, and a suitable margin for safety is included to account for the uncertainties in the measurement technique."

A62 "Based on conservative estimates of the type, volume and origin of High Level Process Trash (e.g., SAC waste, filters and small failed equipment packaged in hulls containers), not more than 80 grams of fissile material is expected in any single hulls container. This amount is 16% of a minimum critical mass for ^{239}Pu ."

A63 "In caisson storage, the hulls containers are neutronically isolated from each other. The caissons are placed on 6 ft edge-to-edge spacing in the soil berm, which is adequate shielding to achieve neutron decoupling between adjacent containers."

A64 "Vigorous acid leaching of the chopped fuel with 8M HNO_3 normally results in the dissolution of about 99.9% of all fuel material. Leached hulls are monitored to determine the amount of undissolved fuel contained therein prior to transferring the content of the basket to a hull disposal container. Normally, no more than about 3 kg of unrecovered fuel is present in a filled disposal container. However, in no instance is the measured quantity of fissile material (^{235}U , ^{239}Pu , ^{241}Pu) present permitted to exceed 1170 g. Thus, nuclear criticality safety of individual disposal containers is assured by mass control. Furthermore, safe spacing of these subcritical units in the solid waste storage area assures that arrays of disposal containers remain subcritical in the event of flooding."

A65 "Leached hulls are rinsed with hull rinse solution (9.2M HNO_3 - 7.5 g/liter Gd). The rinse solution is collected in the hull rinse surge tank to be blended with recycle nitric acid."

A66 "The BNFP Industrial Security Program comprises those measures taken to:

- Deter or discourage entry into or penetration of the plant site or portions of the plant by unauthorized persons.
- Detect such penetrations promptly in the event they occur.

- Minimize the probability of industrial sabotage or theft by promptly apprehending unauthorized persons, or authorized individuals acting in such a manner as to constitute a threat.
- Identify appropriate civil authorities who would take custody of violators."

A67 "The means by which these measures are implemented fall into the following major subject areas:

- Physical and administrative control of access to the plant site or portions thereof. These controls increase in stringency as sensitive portions of the plant are approached.
- Selection and retention of reliable personnel and detection of aberrant behavior of authorized personnel.
- Monitoring the status of vital area, vital equipment, isolation zone, and material access areas.
- Augmentation of the operating staff and security force in the event of threats of actual or potential sabotage.
- Design features of the facility."

A68 "The BNFP Security Plan is 'Allied-General Proprietary' and was submitted to the Nuclear Regulatory Commission as Report AG-L 109, 'Nuclear Materials Safeguards Supplement'."

A69 "The BNFP site (exclusion area) is enclosed by a perimeter fence, except where the main and alternate access roads enter the site. Such fence does not constitute a physical barrier as defined in the Glossary; however, it is a deterrent to accidental trespass. Signs are placed (facing outward) at intervals on the perimeter fence warning that the area within the fence is private property and trespassing is prohibited."

A70 "The process building complex, the Emergency Utility Area and the Blower Station and the Waste Tank Equipment Gallery (WTEG); the Central Alarm Station; and the Solid Waste Area (SWA) are each located on site within a protected area. The protected areas are encompassed by physical barriers the integrity of which is not compromised by natural bodies, structures, or access points. Physical barriers meet the requirements outlined in the Glossary and an isolation zone is adjacent to each such physical barrier. Access to protected areas is controlled by security officers, and all unmanned personnel and vehicle entrances are locked and protected by intrusion alarms."

A71 "Access authorization for employees to enter protected areas is provided by photo-identification badges. Personnel and vehicles entering the protected area are identified and access authorizations are checked at points of entry."

A72 "Personal vehicles are normally excluded from the protected areas. When portals to protected areas are not manned, such portals are protected by intrusion alarms. Surveillance of protected areas, including

barriers, is by security patrol at least once per shift. Isolation zones are illuminated during hours of darkness as to detect the presence of personnel or vehicles."

A73 "The security force is deployed so that one or more security officers can arrive at any point within the protected areas within five minutes. Records and reports of admissions, apprehensions, searches, inspections, patrols, alarms, and tests of intrusion alarms are maintained."

A74 "Security personnel training emphasizes control of access to authorized personnel, familiarization with plant locations, prevention of sabotage, fire prevention, electronic surveillance equipment, radiation safety and emergency procedures."

A75 "Leached hulls, and other waste in stainless steel hull disposal containers are transported to the storage area in shielded casks."

A76 "Management of the storage site as an engineered soils structure (with low permeable berm covers, porous beds for drainage, and adequate slopes for runoff) prevents rainwater saturation of soil around and directly below the hull containers. The site is fenced to prevent unauthorized admittance."

A77 "With a filled hulls container the routine dose rate is approximately 10 to 50 mR/hr 18 in. from the surface of the cask. The dose rate from an unshielded container is greater than 5000 R/hr at contact."

A78 "Instrumentation is provided for monitoring the status of the plant confinement systems, to provide early detection of leakage from the primary confinement systems, and for continuous monitoring of effluents for radioactivity. An environmental monitoring program is provided. Continuous monitoring of radiation and airborne contamination levels is also provided for all normally occupied areas of the facility where contamination exposure could rise above permissible limits."

A79 "Hull handling and monitoring equipment provides the capability of handling and determining residual fissile content of the hulls from the dissolver in a manner which ensures the safety and protection of plant personnel, the public, and the environment. Dissolver baskets can be scanned by the hull monitor to detect undissolved fuel. The monitor rotates the basket as it descends and rises past a NaI crystal gamma detector. Rotational speed is variable from 1/2 to 3 inches per minute."

A80 ". . . The dissolver basket, containing rinsed hulls, is lifted by the 5-ton basket handling crane from the barrel and replaced with an empty basket. On the next cycle, the barrel containing the empty basket receives fresh fuel and operates in the dissolve mode. The basket of rinsed hulls may be monitored in the hull monitor to determine the total fissile material of spent fuel left undissolved, expected to be less than 0.5%. The hulls are transferred to a burial container for transport to the underground solid waste storage area."

A81 "The (hull) monitor sump and jet base is a collection point for condensate, etc. (no fissile material) drained from the hull monitor drive mechanism. Any residual liquid, drained from the hulls within the hull monitor well drains directly to the RMSC floor and to the RMSC sump. Any liquid collected in the hull monitor drive mechanism collects in the hull monitor sump and is indicated on a level indicator in the LVOS (viewing station). The hull monitor sump is jetted directly to the RMSC floor and drains to the RMSC sump."

A82 ". . . In addition to the SNM content measurements, the ratios of uranium to ^{144}Ce and uranium to plutonium in the dissolver solution are determined. These ratios are used in conjunction with the ^{144}Ce determined in the leached hulls by nondestructive monitoring with an NaI(Tl) crystal to calculate the SNM quantity in the hulls. The sum of the solution and hull measurements represent the input to the Separations Process Area."

A83 "Analysis of the leached hulls for undissolved uranium and plutonium after leaving the dissolver is performed by a gamma spectrometry technique. This method involves the detection of the 2.18 MeV gamma of ^{144}Pr which is in equilibrium with the fission product ^{144}Ce . Based upon the ratios of plutonium and uranium to ^{144}Ce which is determined from accountability tank samples, the amount of undissolved uranium and plutonium can be directly calculated from the quantity of ^{144}Ce remaining in the leached hulls after dissolution."

A84 "A five inch iodide crystal is used to scan the entire volume of a hull basket as it is lifted and lowered and rotated past a collimated view port. The electronics have been optimized by means of a fast/slow combination and gating technique to enhance the ^{144}Pr gamma peak and suppress the other fission product and induced cladding activities. Detection sensitivity and accuracy measurements have been performed in the Laboratory simulating anticipated plant conditions using standard sources. It was found that as low as 50 grams of uranium could be detected in a hull basket. During normal plant use of the hull monitor, a standard ^{144}Ce source is used prior to each basket scan to establish that the detection system is functioning properly and within calibration limits."

A85 "The stainless steel cell liner retains radioactive liquids resulting mainly from decontamination, direct drain from hulls during monitoring, and jetting out of the monitor sump drain to the RMSC sump and sand trap for jetting back to the general purpose concentrator feed tank. The sand trap is included because of the possible presence of sand which may be mixed with the hulls as they are dumped into the burial containers. The sand trap is removable for cleaning, and is monitored periodically by remote viewing (i.e., mirrors or TV) for sand accumulation."

A86 "Leached hulls are handled remotely in the RPC (Remote Process Cell) and RMSC until the decontaminated hull disposal container is secured in a shielding cask in the CLS (Cask Loading Station) for transfer to the solid waste storage area by truck. The container is lowered from the shielding cask into the caisson with the cask hoist, and the hole is covered with a concrete plug. A portable shielding platform protects the operator from radiation between removal of the cask and placement of the plug."

A87 "Appropriate instrumentation is provided in the storage and radioactive processing equipment to detect, alarm, and initiate appropriate corrective action in the event of a loss of coolant capability, or excessive increase in radiation level."

(2) Statements of Proposed Plant E [EXXON]

E1 *(This analysis establishes a provision for inspection and inventory of hull-waste material. The design also calls for ultrasonic inspection of the welds on cladding storage container covers. Implied is the recognition of quality assurance for the entire plant design.)*

E2 "There are no site-related factors which are so unusual as to require protection systems beyond those normally required for a facility of this type. There are no site-related factors that require special design attention beyond that normally required for a facility of this type."

E3 "Barriers shall be designed to withstand loadings due to pressure differentials imposed by the process off-gas and building ventilation system, as well as pressure differentials caused by natural phenomena."

E4 "The confinement barriers shall be designed to maintain their functional integrity under the hypothesized major and design basis accidents."

E5 "Design criteria established specifically to avoid damage by combustion-type mechanisms are given below:

- To the extent practicable, only nonflammable or flame resistant materials shall be used in the construction of plant facilities.
- Finely divided metals, such as those produced by sawing zirconium, shall be oxidized or such particles shall be maintained in an inert environment to preclude uncontrolled combustion.
- Hydrogen, as produced by the radiolysis of water and the electrolysis of HF, shall be diluted to a noncombustible concentration."

E6 "Three discrete types of fuel assembly waste are generated . . .

- End-fittings from the fuel preparation.
- Saw fines from end-fitting removal.
- Hardware and leached cladding from the fuel dissolution and cladding rinse operations."

E7 "The Fuel Assembly Waste System includes the separate collection, monitoring, and storage (in a retrievable form) of the waste fractions. Safety-related considerations in the design of the system are fire prevention, nuclear criticality, hydrogen explosion, and contamination and personnel exposure."

E8 "The self-heating and pyrophoric characteristics of the leached cladding requires that special considerations be given to their handling and storage. While being handled in air, the geometry of the dissolver baskets maintains the leached cladding at a safe temperature. The sealed Cladding Disposal Containers are stored in the Fuel Storage Pool which has a normal water temperature of less than 120°F. Cooling of both assembly waste fractions is provided by the Fuel Storage Pool water cooling system. Saw fines are collected and stored underwater until they are mixed with a solid matrix and sealed in engineered storage containers."

E9 "The radiolytic generation of hydrogen gas and its flammability and detonation properties are discussed in . . . The hydrogen gas explosion hazard is minimized in the Fuel Storage Pool and Solid Waste Barrel Storage Area by continuous dilution with air from the ventilation systems such that the atmosphere above these areas is maintained at less than 4 volume percent hydrogen."

E10 "Zirconium fires . . . would involve fines and bulk pieces mixed together. Because of its pyrophoricity, zirconium powder in bulk quantities can burn rapidly; a highly concentrated aerosol could be expected in such a case. Solid pieces of zirconium, however, burn more slowly. As in the case of plutonium, only a small part (<1 percent) becomes airborne, mostly in a particle size range below 5 μ . Therefore, an assumption that one percent is made airborne as particulates is used in this analysis."

E11 "As burning zirconium becomes very hot, volatilization of radionuclides can be expected. No measurements of radionuclide releases from burning zirconium cladding have been reported. However, studies of fission product release from overheated reactor fuels provide an insight into the extent of volatilization to be expected. ORNL (Oak Ridge National Laboratory) reports that 60 percent of Te, Se, Sb; 90 percent of Ru, Mo, Pd, Rh, Tc; and 1 percent of other low-volatility elements volatilize from melting fuel. While these release estimates appear conservatively high considering the lower releases measured by other experimenters, they are used for the . . . accident analysis."

E12 ". . . Ignition of zirconium fines is prevented by handling them in an inert atmosphere or underwater. Accumulation of fines is minimized by periodic flushing of fines handling components."

E13 "The (zirconium) fire is assumed to start with the spontaneous combustion of zirconium fines and to spread to the cladding fragments in a leached cladding container. Zirconium particles, generally in the size range below 10 μ and containing interstitial amounts of water, can undergo self-oxidation and ignite spontaneously. The self-ignition mechanism is a function of particle size, size distribution, mass, temperature, humidity, and surface characteristics. Researchers have found that particles which have a large surface-to-volume ratio are most reactive."

E14 "A fire in the leached cladding containers is considered to have a low probability because of administration and engineering safety features involved in the transfer, handling, and packaging of the leached cladding. The processing systems are designed to prevent heating of the cladding above the ignition temperature."

E15 "A zirconium fire in a leached cladding container in the FHPC (Fuel Handling and Preparation Cell) would activate one of the fire detection systems. The cell contains fire detectors located adjacent to the leached cladding operations and in the cell ventilation exhaust system. The smoke or temperature rise accompanying a zirconium fire would activate one of the fire detectors which would alarm to alert personnel in the Control Room of the situation. The stack monitoring instrumentation might indicate a rise in the radioactivity in the gas stream."

E16 "For the purpose of this analysis it is assumed that the zirconium fire would spread throughout the entire container. The heat from the fire would vaporize some of the radionuclides present in the cladding. In addition, the smoke and particulates released during the fire would contain non-volatile radionuclides."

E17 "The quantity of leached cladding present in a Storage Container is equivalent to the amount associated with 4 tonnes of fuel (normal dissolver batch size). Approximately 2700 pounds of zirconium (cladding plus hardware) are present. For this accident, the leached cladding is assumed to contain 0.1 percent of the original core material as surface contamination, 100 percent of the tritium as zirconium tritide, and 100 percent of the activation products dispersed in the zirconium metal."

E18 "The releases would occur in three forms: vaporization of the volatile species, aerosol entrainment of smoke and other particulates by the combustion gases, and aerosol re-entrainment from the floor during cleanup. At the relatively high temperatures of a zirconium fire, significant volatilization of certain radionuclides, not normally volatile, would occur. Release estimates are based on Oak Ridge measurements of fission product release during fuel oxidation in air at elevated temperatures. All of the volatilized radionuclides, except tritium, Kr, Xe, and the halogens, are assumed to be condensed and susceptible to removal with other particulates by the ventilation system filters."

E19 "The fire in the leached cladding container is assumed to burn for approximately eight hours and consume all the zirconium. During this period, the quantity of non-volatile airborne particulates dispersed is estimated at 1 percent of the zirconium inventory. This estimate is based on experiments with plutonium fires, . . . Most of the particulates are trapped in the filtration system."

E20 "Plugging of the ventilation filters from a leached cladding fire is not possible. If the entire inventory of zirconium were reduced to particulates and carried from the cell to the ventilation filters, the loading on the Deep-Bed Fiberglass Filter would only be approximately 10 percent of its maximum capacity. The filters (deep-bed fiberglass followed by two HEPA filters in series) would remain operable during the fire and provide a particulate DF of 10^5 ."

E21 "The heat from the fire would not produce temperatures which would damage the HEPA filters. The heat produced by burning all the zirconium metal over an eight hour period (1.4×10^7 Btu) could result in an average cell ventilation air temperature of 270°F and a combined ventilation

air temperature of 106°F. The Deep-Bed Fiberglass Filter is protected by water sprays which activate automatically at excessive air temperatures. . ."

E22 "After the fire is extinguished, the material used to extinguish the fire would be removed--by flushing or other means--and transferred to the appropriate radioactive waste system. Release during the cleanup operations would be insignificant, compared to those accompanying the fire."

E23 "Estimated quantities of radionuclides that would be released from the Reprocessing Facility Stack following this accident are given. . . The potential whole body doses from external exposure to, and inhalation of, these radionuclides by an individual at or beyond the site boundary are 4.5×10^{-7} and 6.8×10^{-4} rem, respectively. The maximum 50-year organ dose received by the individual is 1.2×10^{-3} rem to the lung. Radionuclides contributing most (>90 percent) of the organ dose are H-3, Ru-106, and Cm-244."

E24 "Immediately upon receipt of an alarm indicating that a fire is present in a Leached Cladding Container, operating personnel would verify that the fire extinguishing system is operating, shutdown other operations in the FHPC and notify appropriate administrative/safety personnel."

E25 "The Fuel Storage Pool provides space for the interim storage of up to 7000 tonnes of irradiated fuel from light-water reactors. When the Fuel Reprocessing Facility becomes operational, the function of these pools will be extended to include the storage of scrap fuel assembly hardware, leached cladding, krypton gas in storage bottles, and encapsulated solidified high-level waste."

E26 "The principal function of the FHPC (Fuel Handling and Preparation Cell) is to provide space for the processing operations associated with

- Mechanically (*e.g.*, by shearing) exposing the fuel core for subsequent chemical processing, and
- Dissolving the core material in acid, in preparation for downstream solvent-extraction processing.

Associated process operations include the receiving of fuel assemblies from the FSP (Fuel Storage Pool) and the disposal of waste hardware (assembly end fittings and cladding) resulting from the operations."

E27 ". . . Solid wastes, including leached cladding fragments, fuel-end sections, miscellaneous fuel hardware, . . . , shall be packaged and stored in a manner to insure the safe confinement of the associated radioactivity."

E28 "The total confinement system shall consist of one or more individual confinement barriers and systems which restrict releases of radioactive material to the environment or into areas normally occupied by plant personnel. The design of the confinement barriers and systems shall conform to the guidelines of NRC Regulatory Guide 3.18, 'Confinement Barriers

and Systems for Fuel Reprocessing Plants,' dated February 1974. In order to limit the spread of radioactive materials, the facility shall be separated by confinement barriers into areas or zones of various levels of contamination."

E29 "Two types of confinement barriers are used in the facility. 'Total barriers' . . . are those fabricated of material which shall prevent penetration of all confined material without regard to that material's physical or chemical nature. 'Selective barriers' are mass transfer devices or filters which shall be employed to remove selected chemicals or particulate matter from a process or ventilation stream while allowing the bulk amount of the stream to pass through."

E30 "Confinement systems shall be constructed of nonflammable materials except where this is not possible because of special functional requirements."

E31 "Emergency power shall be provided to those confinement barriers and systems where loss of confinement capability could result from loss of primary electrical service."

E32 "Process off-gas systems shall be designed and installed to confine hazardous chemical and radioactive materials evolved during process operations and radioactive waste storage, to reduce their concentration in gaseous process effluents to levels as low as reasonably achievable. NRC Regulatory Guide 3.20, 'Process Off-Gas systems for Fuel Reprocessing Plants,' dated February, 1974, will be followed."

E33 "Ventilation systems shall be designed and installed to confine, channel, and control airborne radioactive contaminants and provide normal ventilation requirements. NRC Regulatory Guide 3.32, 'General Design Guide for Ventilation Systems for Fuel Reprocessing Plants,' dated September, 1975, will be followed. NRC Regulatory Guide 3.12, 'General Design Guide for Ventilation Systems of Plutonium Processing and Fuel Fabrication Plants,' dated August, 1975, will be followed as applicable."

E34 "The waste treatment systems shall be designed to insure adequate confinement of the wastes under normal and accident conditions in accordance with the safety classification criteria . . . "

E35 "The waste storage facilities shall provide adequate confinement of activity in the event of container failure. Provisions shall be made for detection, retrieval, isolation, and repackaging of leaking waste containers."

E36 "The Fuel Preparation and Cladding Handling System provides for end-fitting removal, core (UO₂ or mixed oxide) exposure, fuel cooling and in-process storage, transfer of core material, and cladding and end-fitting handling. Safety-related considerations in the design of this system are nuclear criticality, zirconium fines ignition, and loss of confinement."

E37 "The building ventilation and process off-gas systems shall control the spread of airborne contamination through openings in barriers by regulating the direction of air or gas flow between these zones so that gas

leakage shall be successively from zones of low potential to zones of higher potential for contamination."

E38 "The capacity of the ventilation system shall be adequate in relation to confinement system requirements to assure that the velocity of the gas flowing through any barrier opening is sufficient to prevent back flow of airborne contaminants through such openings and that air flow patterns are not disrupted by winds, movement of equipment or personnel, or temporary opening of passageways through confinement barriers."

E39 "The fuel assembly is placed in a magazine and is fed into one of two shears which cuts the fuel rods into lengths of 1/2-inch to 2-inches. The feed magazine and shear housings are maintained at slightly negative pressure relative to cell atmosphere, and a sweep of inert gas is maintained within the shear system enclosure to prevent fires with zirconium fines and to remove fission gases released during core exposure of the fuel rod. Fission gases released during fuel shearing are vented to the Dissolver Off-Gas System for subsequent processing and recovery. The cut sections of fuel are transferred by gravity through a dust-tight chute and airlock to the Fuel Cooler/Surge Drum."

E40 "Leached cladding is loaded into stainless steel storage containers approximately 3 feet in diameter by 10 feet long (91-cm diam x 2.4-m long, 0.5-cm wall thick.). The cladding storage containers are partially filled with water (covering the cladding) to provide ballast, to prevent combustion of zirconium fines, and to enhance heat transfer to the storage container wall. Filled containers are closed and transferred to the Fuel Storage Pool for long-term storage. The containers are equipped with 10 psig rupture discs that can relieve to the Storage Process Vent system."

E41 ". . . Both the ventilation air above the Fuel Storage Pool and the pool water are continuously monitored for radioactivity to detect possible leaks."

E42 "Personnel exposure is reduced to as low as reasonably achievable and below 10 CFR 20 requirements by using remote handling techniques and remote maintenance or decontamination followed by contact maintenance. In addition, the Fuel Receiving and Storage Facility and the Process Building have ventilation systems to maintain air flow toward potentially higher contamination zones."

E43 "Zirconium particles partially wet with water can burn violently, possibly because hydrogen is produced via metal-water reaction. Zirconium metal can be considered nonflammable when its surface area is less than 0.1 m²/g and/or its thickness is more than 0.025 cm. Zirconium fines produced by sawing in air are oxidized as they are produced and so are not flammable. Inert gas can be used to suppress ignition; the oxygen content must be reduced to 3, 4, or 5 percent when argon, nitrogen, or helium, respectively, is used as the diluent."

E44 "Zirconium fragments from the shearing operations are potentially flammable because of feather edges produced by the shearing operation. Commercial power reactor oxide fuels have been chopped for 6 years in the Nuclear Fuel Services Plant at West Valley, New York, with no known instance

of zirconium combustion. Zirconium burning is avoided in the fuel assembly sawing operation by performing the sawing underwater with saw fines collected and stored underwater. This technique avoids having to handle a heavy load of radioactive fines via an off-gas system. The burning of chopped fuel cladding fragments is prevented by blanketing the equipment with inert gas until fuel is charged to the dissolvers."

E45 "Fissile materials are measured in the solid wastes leaving the plant. The concentration of transuranics in the high-level wastes are measured prior to solidification; other solid wastes are measured by non-destructive assay methods. Sophisticated instrument systems will be selected from those being developed for ERDA activities and other commercial operations. Additional development effort will be performed as required to improve upon available technology."

E46 "Effluents from waste treatment systems are treated to reduce contaminant releases to the lowest practicable level. Cooling systems are provided for the removal of radioactive decay heat as required to protect the integrity of confinement systems. Instrument monitoring and control systems are provided to prevent or control conditions that could lead to explosions, leaks, uncontrolled chemical reactions, or criticality."

E47 "Upon completion of the fuel dissolution cycle, the leached cladding is rinsed and the dissolver basket is transferred to a monitoring station to measure the amount of undissolved core material remaining with the cladding. Cladding within the allowable core contamination levels is transferred to the basket dumper for subsequent canning. If the cladding contains fuel above allowable quantities, it is recycled through the dissolver."

E48 "Special design considerations, such as safe geometry, concentration control, sump and vent system design, etc., are required to prevent inadvertent criticality."

E49 "Safe spacing during the movement and storage of fissionable materials shall be accomplished by design so that safe spacing will be maintained under all credible accident conditions."

E50 "Fixed neutron absorbers, if incorporated in racks to assure safe storage, shall be resistant to corrosion or other loss, and their presence shall be capable of periodic verification."

E51 "The primary criticality control parameter in the Cladding Disposal Containers is fissile mass. The leached cladding is assayed before being transferred to the Cladding Disposal Container to insure that mass limits are met; cladding containing excess amounts of fuel core is returned to the Fuel Dissolver for an additional leach cycle. No criticality potential is postulated for the handling and storage of saw fines or fuel assembly end-fittings."

E52 "Access controls shall be designed to meet the following;

- The area within the site boundary shall be enclosed by an agricultural-type fence (minimum of three strands of barbed wire on metal posts) and shall be legally posted to prohibit trespassing.
- Only the minimum number of penetrations shall be provided and these shall be posted.
- For the effluent control purposes and protection of the general public, and in accordance with 10 CFR Part 100.3(a), the area within this boundary fence shall be considered an Exclusion Area.
- All roads, railroads, and waterways crossing the site boundary shall be appropriately posted at the fence line.
- Operating areas containing radiation sources and/or safety-related structures and components shall be enclosed by a barrier fence.
- At all roads and railroads into operating areas, the fence shall be equipped with normally locked gates.
- For radiation protection purposes, operating area fences shall be used to control personnel access to facilities containing and/or processing radioactive materials, and in which personnel safety and protection are largely dependent upon cognizance of specific procedures."

E53 "Radiation shielding shall be designed to assure lowest reasonably achievable dose rates in areas essential to safe operation, such as pipe and operating galleries, by taking into consideration: (1) maximum transient conditions against which protection must be provided, (2) possible exposure of personnel who perform functions in other areas. Both gamma and neutron radiation shall be considered in the shielding design. The levels of gamma and neutron radiation shall be additive in the design when determining personnel exposures, and (3) the radiation dose to personnel during maintenance activities shall be minimized to the extent reasonably achievable through the use of techniques, such as remote handling and shielding placement."

E54 "Shielding shall be designed to limit radiation levels in noncontrolled areas, such as the control room, cable spreading room, etc., such that personnel cannot receive whole body radiation exposure rates in excess of 0.2 mrem/hour."

E55 "The Fuel Assembly Waste System separately collects an end-fitting fraction, a saw fines fraction, and a leached cladding and hardware fraction; each fraction is assayed for fissile material content, packaged in retrievable containers and stored with capability for future retrieval."

E56 "Following leaching in the Fuel Dissolver, the rinsed cladding and hardware are transferred in the Fuel Dissolver Basket to the Fuel Dissolver Leached Cladding Monitor for fissile material assay using a remotely operated bridge crane. At the Fuel Dissolver Leached Cladding Monitor, the

amount of fuel remaining in the leached cladding is measured to determine if the cladding should be returned to the Fuel Dissolver for an additional leach cycle or transferred to the Cladding Disposal Container Closure Station. Leached cladding, with less than 0.1 percent of the fuel core remaining, is transferred to the Fuel Dissolver Basket Dumper by the remotely operated bridge crane . . ."

E57 "For effluent control purposes and protection of the general public, and in accordance with 10 CFR Part 100.3(a), the area within (the) boundary fence shall be considered an 'Exclusion Area.'"

E58 ". . . Storage capability is provided initially for 5 years' accumulation, at forecasted rates, of high-heat and high gamma wastes and 3 years' accumulation of low-gamma wastes. These waste storage areas are expandable to accommodate wastes from up to 30 years of plant operation in the event shipment off site is delayed."

2. Federal Regulations on Packaging and Transportation Applied to Hulls Management

Review of Federal Regulations [CFR 71] dealing with packaging and shipping disclosed several standards that might be appropriately adapted to the management of hulls. These standards are summarized below. Commercial plans for the packaging and shipping of hulls, obtained from a search of the safety analysis reports [AGNS, EXXON] of the Barnwell and Exxon plants, are also summarized below. In the latter summary, the apparent relevance of commercial plans to Federal standards is indicated.

Packaging Standards - Large-Quantity Shipments [CFR 71]

- a. Materials and construction of the package shall be such that no reactions, chemical or galvanic, occur between package components or between the packaging material and the contained waste.
- b. The package shall have positive closure to prevent inadvertent opening.
- c. Lifting devices integral with the package shall support three times the loaded weight without stressing the package in excess of yield strength.
- d. Lifting devices for the package cover shall support three times the weight of the cover and attachments without stressing the cover in excess of yield strength.
- e. Lifting devices integral with the package shall be designed so that failure of the device does not impair the containment or shielding properties of the package.
- f. As a simple beam supported at both ends, the package shall uniformly support five times its loaded weight without being stressed in excess of yield strength.

- g. The package shall maintain containment of contents under external pressures up to 25 psi gauge.
- h. The package shall (1) suffer no shielding reduction beyond that increasing the external dose rate to a limit of 1 rem/hr at three feet from the surface, (2) not release radioactive material other than gases or contaminated coolant not exceeding 0.1% of the total radioactivity in the package or 0.01 Ci Group I,* 0.5 Ci Group II, 10 Ci Group III, and 10 Ci Group IV nuclides, and 1000 Ci of inert gases: as a result of:
- a free drop of 30 feet (9.1 m) to any unyielding horizontal surface,
 - a free drop of 40 inches (1 m) to the end of a vertical cylindrical mild steel bar mounted on an unyielding horizontal surface,
 - exposure to heat at 1475°F (800°C) for 30 min.

Barnwell Plant [AGNS] Packaging Plans Related to Federal Standards a through h

Standard a. AGNS plans to use hull disposal containers fabricated of 304L stainless steel so as to resist corrosion from the dissolver rinse solution retained by the leached hulls and hardware. The container wall thickness would include a nominal corrosion allowance[†] of 0.062 inch (0.16 cm).

Standard b. The hull disposal containers would have covers equipped with captive bolts for securing to the shells of the containers.

Standard c. AGNS hull container bodies are not to be equipped with lifting devices.

Standard d. The cover of the AGNS hull container is to be fitted with a mating fixture (lifting device) to allow lifting and lowering of the entire hull container by the transfer cask hoist. No data could be found regarding the strength characteristics of the mating device.

Standard e. In a model postulated accident, a 16-ft (5 m) drop of a hull container encased in a hulls transfer shielding cask into a sand pit would result in the following:

- 35% of the hulls escape the container and cask,
- 40% of the exposed fraction is exposed to the atmosphere, with an estimated release fraction of 5×10^{-4} ,

*"Transport group." Any one of seven groups into which radionuclides in normal form are classified according to their toxicity and their relative potential hazard in transport . . . [CFR 0-199].

[†]It is assumed that a corrosion allowance is that amount of wall thickness loss that is allowable before the structural strength of the container begins to deteriorate.

- 50% of the total release occurs in the first hour after the incident,
- 0.24 Ci of actinides is released in 24 h,
- 8 Ci of fission products is released in 24 h,
- resulting off-site doses would be
 - 110 mrem, whole body (0.4%) [CFR 100]
 - 3350 mrem, bone (2%) [CFR 100]
 - 260 mrem, lung
 - 53 mrem, skin.

Standard f. No specific relevance found.

Standard g. No specific relevance found.

Standard h. See relevance to Standard e. Otherwise, there is no indication that the hull disposal container could qualify as a shipping package.

EXXON Packaging Plans Related to Federal Standards a through h

Standard a. Exxon cladding-storage containers are to be constructed of stainless steels, and the contained hulls will be covered with water before closure. Container walls will be 0.48 cm thick. It is not claimed in the SAR that these containers could be used for shipment to final disposal.

Standard b. After they are filled, the cladding storage containers will be fitted with covers and seal-welded closed. It is planned to equip each cover with a 10-psig rupture disk assembly.

Standard c. On the container bodies, trunnions are attached as lifting devices for crane transfer from the loading area to the fuel/waste storage pool. No analysis of the strength characteristics of the trunnion device could be found.

Standard d. The container cover would be fitted with a lifting eye designed for the raising and lowering of only the cover. No analysis of the effects of lifting on the yield strength of the cover could be found.

Standard e. No analysis of the effects of trunnion (lifting device) failure on the containment capabilities of a sealed cladding storage container could be found.

Standard f. No analysis of the effects of weight loading on strength capabilities of the cladding storage container could be found.

Standard g. No analysis of the effects of external pressure on the containment capabilities of the cladding storage container could be found. However, the design calls for storage of sealed containers in a pool. If a

mean water depth of 6 m is assumed, an external pressure of 0.6 kg/cm^3 (~ 9 psi gauge) can be expected on the walls of the container, the implication being that the container is designed to withstand at least that pressure. There is no claim that the container can withstand 25 psig pressure (stated in Packaging Standard g listed above).

Standard h. No analysis of the effects of accident tests on the integrity of the cladding storage container was presented. There was no implication that the container might be suitable as a shipping package. On the contrary, it was implied in the SAR that prior to off-site shipment, repackaging of the stored hulls would be necessary.

C. Chlorination of Hulls
(M. Ader)

Chop-leach processing of LWR oxide fuel leaves a residue of $\sim 0.1\%$ undissolved fuel with the Zircaloy hulls. The TRU content of this residue plus that from activation of the ~ 1 ppm of tramp uranium in Zircaloy cause the hull waste to exceed the proposed limit [FEDREG-1974B] of <10 nCi of TRU elements per gram of solid. Accordingly, this voluminous waste must be packaged in a retrievable manner and consigned to a Federal repository for disposal rather than to a commercial burial site. Considerable savings in packaging, interim storage, shipping, and burial costs can be realized if the volume can be reduced. One proposed method is separation of zirconium (constituting ~ 98 wt % of the Zircaloy) from transuranic elements by volatilization of ZrCl_4 . Conversion to ZrCl_4 (and eventually to ZrO_2 by pyrohydrolysis) would also eliminate the pyrophoric hazard of handling Zircaloy. The chemical feasibility of the ZrCl_4 volatilization concept has now been tested, using laboratory-scale equipment that was described in the preceding progress report in this series (ANL-77-36).

The general experimental procedure involved, first, displacing air in the system with nitrogen as the furnace temperature was raised. Then gaseous HCl/N_2 or Cl_2/N_2 (2/1 vol ratio, $45 \pm 5 \text{ cm}^3/\text{min}$) was passed over various solids that are representative of hull waste. The solids were supported in quartz or Vitreosil* boats within a Pyrex*-tube reactor held at 400 to 410°C. Gaseous products were swept through a quartz-wool filter into a Pyrex condenser, a portion of which was at room temperature. At the end of an experiment, the apparatus was cooled while being flushed with N_2 , and condensed solids were dissolved in 100 cm^3 of 2M HNO_3 and were analyzed for plutonium alpha activity. Each experiment employed a small fragment of $\text{UO}_2\text{-PuO}_2\text{-fissia}$, referred to as $(\text{U,Pu,Fs})\text{O}_2$, and some combination of Zircaloy-2 tubing, high-purity arc-melted zirconium, 304 stainless steel rod, or Inconel 718 rod. The solids were positioned so that the gas stream flowed over Zircaloy-2 or pure zirconium first, then over 304 stainless steel or Inconel 718, and finally over $(\text{U,Pu,Fs})\text{O}_2$.

The $(\text{U,Pu,Fs})\text{O}_2$ is from a batch of high-fired pellets made at CEN in 1964 from a mix of UO_2 , PuO_2 , fissia (19 inert fission product oxides), and a binder. According to Special Materials (SPM) accountability records, the fired pellets contain 86 wt % U, 0.422 wt % Pu, and ~ 2 wt % fissia. SPM also provided what

*Trademark.

they believe to have been the isotopic composition of the plutonium in 1962, namely (in wt %), ^{239}Pu (91.53), ^{240}Pu (7.71), ^{241}Pu (0.73), and ^{242}Pu (0.032). From this, a current specific plutonium alpha activity of 1.64×10^8 d/(min)(mg) may be calculated. We have had the $(\text{U,Pu,Fs})\text{O}_2$ assayed for plutonium alpha activity, *i.e.*, after alpha-active ^{241}Am was removed. By combining this result with the above-calculated specific plutonium activity, we obtain a value of 0.43 ± 0.01 wt % Pu in the $(\text{U,Pu,Fs})\text{O}_2$, which agrees with the SPM information. The ratio of $(\text{U,Pu,Fs})\text{O}_2$ to Zircaloy used in these experiments is roughly twentyfold greater than that expected for LWR hull waste.

Results of the volatilization experiments are given in Table 18. The data are divided into four groups to indicate the use of one $(\text{U,Pu,Fs})\text{O}_2$ charge for several successive experiments. In Expts. 1A, 1B, and 1C, a $(\text{U,Pu,Fs})\text{O}_2$ fragment weighing 0.0955 g was successively hydrochlorinated for 45, 46, and 90 min. Its appearance and weight remained unchanged during each period, and no solids were observed in the condenser. Assay of the condenser washings for alpha activity gave a counting rate close to the background level, indicating that virtually no plutonium (*i.e.*, <0.05 nCi) had volatilized.

In Expt. 2, 1.706 g of Zircaloy-2 was included in the boat with the $(\text{U,Pu,Fs})\text{O}_2$, and about 88% was converted to ZrCl_4 , as indicated by the quantity of zirconium in the residue, but no plutonium appeared with the ZrCl_4 condensate. The experiment was repeated in Expt. 3 with a larger amount of Zircaloy being added to $(\text{U,Pu,Fs})\text{O}_2$ in the boat; however, again no plutonium was found in the condensate.

Since stainless steel and Inconel alloys are also constituents of the hull waste, it was of interest to determine whether or not their presence would affect plutonium volatility. In Expt. 7A and 7B, high-purity zirconium was substituted for Zircaloy-2, and either 304 stainless steel or Inconel 718 was charged into the boat with the $(\text{U,Pu,Fs})\text{O}_2$ fragment. The data show that these alloys are essentially inert to HCl at 400°C and have no effect on plutonium volatility.

These results indicate that of the major constituents of hull waste, only Zircaloy reacts with HCl at $\sim 400^\circ\text{C}$, and that the zirconium in Zircaloy is readily separable from TRU oxides. Despite the exaggerated $(\text{U,Pu,Fs})\text{O}_2/\text{Zircaloy}$ ratio employed, less than 0.05 nCi of plutonium accompanied the 1- to 2-g portions of volatilized zirconium. Neptunium, americium, and curium are expected to behave similarly to plutonium. TRU metals present in Zircaloy from transmutation of trace uranium will, in all likelihood, be converted to trichlorides, which are only slightly volatile at 400°C . The implication is that zirconium ultimately to be disposed of (*e.g.*, in the form of ZrO_2) would contain much less than 10 nCi of TRU elements per gram of solid and therefore would not have to be disposed of at a Federal repository.

Instead of HCl, chlorine can be used to convert zirconium to ZrCl_4 . However, since chlorine is an oxidizing agent, it is expected to react more aggressively than HCl with UO_2 , TRU oxides, and other constituents of the hull waste. In fact, the combination Cl_2/CCl_4 has been applied in several volatility processing schemes [CONF] for decontaminating $\text{UO}_2\text{-PuO}_2$ and $\text{ThO}_2\text{-UO}_2$ fuels. These chlorinations, however, have usually been carried out above 550°C , which is considerably higher than the temperature needed for the present purpose of

Table 18. Results of Chlorination Experiments (400-410°C)

Expt. No.	Duration, min	Gas ^a	(U,Pu,Fs)O ₂ , ^b g		Zircaloy-2, ^c g		Pu Condensed, ^d nCi
			Charge	Residue	Charge	Residue	
1A	45	HCl/N ₂	0.0955	0.0956	--	--	<0.05
1B	46	HCl/N ₂	0.0956	0.0955	--	--	<0.05
1C	90	HCl/N ₂	0.0955	0.0955	--	--	<0.05
2	90	HCl/N ₂	0.0955	0.0954	1.706	0.238	<0.05
3	95	HCl/N ₂	0.0954	0.0953	2.951	0.793	<0.05
4A	60	Cl ₂ /N ₂	0.1921	0.218	--	--	6.0
4B	90	Cl ₂ /N ₂	0.218	0.215	--	--	0.1
5	90	Cl ₂ /N ₂	0.215	0.236	2.157	0.107	9.8
6A	120	Cl ₂ /N ₂	0.2218	0.249	--	--	7.4
6B	70	Cl ₂ /N ₂	0.249	0.263	2.317	0.072	17
6C	70	Cl ₂ /N ₂	0.263	0.265	0.072	0.062	<0.05
6D	70	HCl/N ₂	0.265	0.257	--	--	<0.05
6E	120	HCl/N ₂	0.257	0.304	2.452	0.581	0.2
6F	70	Cl ₂ /N ₂	0.304	0.299	0.581	0.044	12
6G	80	Cl ₂ /N ₂	0.299	0.305	1.581 ^e	0.019	16
7A	90	HCl/N ₂	0.2030	0.2032	1.853 ^e 1.679 ^f	0.467 1.679	<0.05
7B	90	HCl/N ₂	0.2032	0.2032	1.262 ^e 2.043 ^g	0.182 2.043	<0.05
7C	90	Cl ₂ /N ₂	0.2032	0.2101	2.219 ^e 2.043 ^g	0.094 2.043	20
7D	90	Cl ₂ /N ₂	0.2101	0.2143	2.062 ^e 1.678 ^f	0.338 1.678	2.3

^aVolume ratio, 2:1; flowrate, 45 ± 5 cm³/min.

^b86 wt % U; 0.42 wt % Pu (3.2 × 10⁵ nCi/g); remainder, 0, Fs.

^cZirconium alloyed with 1.5 wt % Sn, 0.15 wt % Fe, 0.1 wt % Cr, 0.05 wt % Ni.

^dLimit of detection = 0.05 nCi.

^eHigh-purity zirconium.

^f304 SS.

^gInconel 718.

volatilizing $ZrCl_4$ to separate zirconium from the TRU elements. Accordingly, the chlorinations described below were done at $\sim 400^\circ C$, the same temperature used for the hydrochlorinations.

In Expt. 4A, 0.1921 g of $(U,Pu,Fs)O_2$ was treated with Cl_2/N_2 for 60 min, after which very thin deposits of white and orange substances were found inside the condenser. These may have been volatilized fissium constituents (e.g., Mo, Ru). The condenser washings contained 6.0 nCi of plutonium, which is about 100 times the amount volatilized with HCl. It was evident that chlorine had reacted with the $(U,Pu,Fs)O_2$: the originally hard black fragment had begun to crumble and turn dark green. Moreover, its weight had increased, presumably due to the formation of UO_2Cl_2 . In fact, the solid gained weight while being weighed, indicating a rapid pickup of moisture. Subsequently, the $(U,Pu,Fs)O_2$ residues were kept in a desiccator over Drierite and exposed to the atmosphere only when being weighed or loaded into the reactor. Despite this precaution, moisture always appeared in the condenser during warm-up of the residues to $400^\circ C$, until swept out of the system by flowing N_2 . In Expt. 4B, chlorination of the $(U,Pu,Fs)O_2$ residue for another 90 min volatilized only 0.1 nCi of plutonium. However, when 2.157 g of Zircaloy-2 was added to the reactor boat in Expt. 5, 9.8 nCi of plutonium was found with the $ZrCl_4$. Because this result suggested that plutonium volatility is enhanced by $ZrCl_4(g)$ in the Cl_2/N_2 stream, the experiments were repeated.

Chlorination of 0.2218 g of $(U,Pu,Fs)O_2$ in Expt. 6A volatilized 7.4 nCi of plutonium, about 23% more than in Expt. 4A but not twice as much, as might be expected from doubling of the reaction time. The addition of 2.317 g of Zircaloy-2 to the reactor boat in Expt. 6B resulted in 17 nCi of plutonium being volatilized with the $ZrCl_4$, a substantial increase over that in the previous experiment (in which no zirconium was added). The residue of Expt. 6B was further chlorinated in Expt. 6C, and the result was similar to that of Expt. 4B--namely, virtually no plutonium transport. In Expts. 6D and 6E, HCl was substituted for chlorine and, consistent with the earlier hydrochlorinations, little or no plutonium volatilized whether Zircaloy-2 was present or not. With the resumption of chlorine (and $ZrCl_4$) flow in Expt. 6F, plutonium was again volatilized to the extent of 12 nCi. An even larger amount of plutonium, 16 nCi, was volatilized in Expt. 6G, when the amount of zirconium chlorinated was increased from ~ 0.5 g to ~ 1.6 g.

The results of Expt. 7C and 7D give no clear-cut indication that the volatilization of plutonium by chlorine is influenced by the presence of 304 stainless steel or Inconel 718. Although the weight changes for these alloys were negligible, some reaction with chlorine or $ZrCl_4$ was inferred from blackening of their surfaces.

Overall, the experiments with chlorine suggest that volatilization of plutonium from $(U,Pu,Fs)O_2$ is enhanced by $ZrCl_4$ in the Cl_2 stream, although the mechanism is not apparent. This effect was not seen in the hydrochlorination experiments, presumably because HCl does not react with $(U,Pu,Fs)O_2$ at $400^\circ C$ to yield the volatile plutonium species $PuCl_4$, whereas Cl_2 does. Another effect, the marked drop in plutonium transport observed in Expt. 4B, 6C, and 7D, may be a surface phenomenon. Plutonium at the surface of a hard $(U,Pu,Fs)O_2$ fragment could be rapidly depleted, so that there would have to be breakup of the UO_2 substrate before further transport.

Insofar as treatment of LWR hull waste with chlorine is concerned, these experiments indicate that reaction with chlorine would produce $ZrCl_4$ with a TRU content just at or slightly over the proposed limit of 10 nCi/g. Certainly, some of the metallic plutonium in the Zircaloy matrix would be oxidized to $PuCl_4$ and thus be transportable. Disadvantages of chlorine (as compared with HCl) are difficult control of reaction rate and temperature and greater reactivity toward fission products, activation products, and materials of construction. Some of these disadvantages were apparent in the following experiments with irradiated Zircaloy.

Work was done to find out how fission products and neutron activation products in the hull waste behave during chlorination at $\sim 400^\circ C$. Accordingly, one experiment with HCl and one with chlorine were carried out with segments (1 cm dia by 1.9 cm long) of irradiated Zircaloy-2 cladding. This cladding had originally been part of a General Electric experimental subassembly irradiated to 6600 MWd/MTU at Dresden, Illinois, and Vallecitos, California. The UO_2 fuel encased in the Zircaloy-2 was removed by mechanical means rather than by leaching with nitric acid. At the time of the present experiments, the Zircaloy-2 had cooled about 6.5 y. Thus only the concentrations of long-lived nuclides could be determined. Disintegration rates were determined by gamma-ray spectroscopy, using a Ge(Li) detector and counting at selected energies (>120 keV) for about 1000 min. The experimental procedures were similar to those previously described for the studies with inactive Zircaloy-2 except for two conditions: No $(U,Pu,Fs)O_2$ was included in the HCl experiment, and the reaction zone in the chlorine experiment became hotter by about 10 degrees than the 400 to $410^\circ C$ usually maintained by the furnace controller. In fact, with chlorine, glowing red spots on the surface of the Zircaloy-2 were occasionally observed, denoting localized temperatures above $500^\circ C$.

Table 19 lists the data obtained for several gamma-emitting fission products and activation products. With HCl the chlorinating agent, virtually none of the radionuclides were volatilized except for 1% of the antimony and 2% of the cesium. When chlorine was used, substantially more radioactivity was volatilized, namely, 75% Sb, 15% Ru, 11% Cs, 8% Co, and 3% Mn. Only the rare earths cerium and europium were nonvolatile. Comparison of the results of the two experiments suggests that the oxidizing power of chlorine caused certain species (*e.g.*, Co, Ru) to be volatile; and that the higher reaction temperature with chlorine enhanced the volatility of all species (*e.g.*, Cs, Sb). The effect of reaction temperature was also discerned in the amount of plutonium, 314 nCi, volatilized from the $(U,Pu,Fs)O_2$ fragment included in Expt. FP-2. This is about 15 to 30 times more than that volatilized in the comparable experiments listed in Table 18.

It should be realized that both mild and strong chlorinating agents will volatilize not only normal zirconium, but also all the beta-active ^{93}Zr ($t_{1/2} = 9.5 \times 10^5$ y) induced in the Zircaloy cladding. Part of the tin, inactive and active (250-d ^{119m}Sn , 50-y ^{121m}Sn), will also be transported. Consequently, the $ZrCl_4$ condensate must be considered radioactive in any event, and any zirconium metal salvaged could only be used in the nuclear industry. Zirconium recovery would be particularly unattractive if chlorine or another strong chlorinating agent were used because numerous fission products and activation products besides those already mentioned would volatilize with the zirconium. For example, chlorine will volatilize all inactive and active iron

Table 19. Results of Chlorination Experiments With Irradiated Zircaloy-2

Gamma Emitter	Half-life, y	Energy, keV	Expt. FP-1 (HCl/N ₂) ^a			Expt. FP-2 (Cl ₂ /N ₂) ^a		
			Activity Charged, ^b dpm	Activity Condensed, ^c dpm	Percent Volatilized	Activity Charged, ^d dpm	Activity Condensed, ^c dpm	Percent Volatilized ^e
¹⁰⁶ Ru	1.00	512	1.06 E8 ^f	<8 E4	<0.08	9.98 E7	1.54 E7	15
¹²⁵ Sb	2.73	427	7.64 E8	7.91 E6	1.0	7.13 E8	5.33 E8	75
¹³⁴ Cs	2.06	796	4.86 E7	8.59 E5	1.8	3.54 E7	3.74 E6	11
¹³⁷ Cs	30.2	662	9.23 E8	1.66 E7	1.8	7.08 E8	7.44 E7	11
¹⁴⁴ Ce	0.78	133	1.13 E8	<5 E4	<0.04	1.04 E8	<2 E6	<2
¹⁵⁴ Eu	8.5	1274	6.34 E6	<3 E3	<0.05	4.09 E6	<5 E4	<1
⁶⁰ Co	5.26	1332	2.97 E7	<3 E3	<0.01	2.58 E7	2.05 E6	8
⁵⁴ Mn	0.86	835	3.66 E6	<2 E3	<0.04	3.08 E6	9.0 E4	3

^aVolume ratio, 2/1; flowrate, 45 ± 5 cm³/min; duration, 120 min; temperature, 400-410°C.

^bZircaloy-2: charge, 2.742 g; residue, 0.551 g. No (U,Pu,Fs)O₂ charged.

^c< denotes estimated lower limit of detection.

^dZircaloy-2: charge, 2.464 g; residue, 0.040 g. (U,Pu,Fs)O₂: charge, 0.227 g; residue, 0.259 g.

^e³¹⁴nCi Pu volatilized.

^fRead 1.06 E8 as 1.06 × 10⁸, etc.

(2.7-y ^{55}Fe) in Zircaloy (but not necessarily the iron in 304 stainless steel or Inconel). Thus, the TRU-free volatilized-and-condensed fraction might require disposal as a highly radioactive material.

Regardless of which chlorinating agent is used, the nonvolatile TRU-containing residue may present some disposal problems. If this residue is to be combined with other high-level wastes, *e.g.*, as a glass or calcine, the massive pieces of unreacted stainless steel and Inconel would have to be sorted out. Also, it would be prudent to convert all chlorides in this residue to oxides, thereby avoiding potential problems with moisture pickup and corrosion.

Operationally, a mild chlorinating agent like dilute HCl is preferable because the reaction is readily controlled and appears to be adaptable to simple, transpiration-like equipment and procedures (*e.g.*, HCl flow over heated trays containing the hull waste, and downstream condensation of ZrCl_4). With a strong chlorinating agent like chlorine, it is difficult to control reaction rate and temperature. This problem can probably be circumvented by using a fluidized bed, but entrainment of particles in the gas stream may prevent achievement of the <10 nCi/g limit.

Although there are economic and other incentives [ZIMA-1976, ZIMA-1977] for reducing the volume of hull waste destined for a Federal repository, the costs and advantages of zirconium volatilization must be compared with competing processes. For example, compaction of hulls [LEVITZ] appears to be a simple procedure capable of yielding a volume reduction (~70%) roughly comparable to that for hydrochlorination (~85%). However, compaction has not been demonstrated with irradiated chop-leach-processed hulls, nor does it eliminate entirely the potential hazard of zirconium pyrophoricity.

VI. DEEP-WELL DISPOSAL OF NOBLE GASES (L. E. Trevorrow)

This project involves the evaluation of proposals to dispose of noble gas wastes by underground injection. The noble gas nuclide of main concern with respect to environmental impact is ^{85}Kr , which has a half-life of 10.7 y. Four concepts are being considered in this study: (1) storage in the gaseous phase, (2) storage in solution, (3) disposal between shale layers as bubbles entrapped in grout, similar to the method (termed hydrofracturing) developed for intermediate-level liquid wastes at ORNL, and (4) the possible use of presently existing, abandoned wells for either type of storage. A number of factors which have to be considered in evaluating this concept were listed in the preceding report in this series, ANL-77-36.

The study is expected to require inputs from several disciplines: the physical chemistry of solutions, geology, geological engineering, radiation chemistry, and engineering economics. The project was subcontracted to a consulting firm, Dames & Moore, which has a staff experienced in these fields.

A draft of the details of the study is not yet available, but some qualitative conclusions are given below:

Storage in the gas phase in capped formations in the manner of natural gas storage has been evaluated. This approach is technically feasible, but most capped formations are much larger than would be needed to serve the volumes of gas released in fuel reprocessing. Therefore, they represent resources that would be better used for other purposes. The leak rate from this type of storage is difficult to estimate, first because of industrial secrecy on leakage experience and second because each formation has individual characteristics that are better predicted by examination than by extrapolation from the behavior of other formations.

Gas phase storage in deep, noncapped formations was also evaluated. It was concluded that gases might be retained for some time in these formations in the interstices between small particles that are held together by strong cohesive forces derived from the surface tension of water.

Storage in solution in deep wells has the advantage that high hydrodynamic pressures reduce the gas volumes to very small values. However, the reliability of any conclusions is lessened by the lack of data on noble gas solubilities at pressures much in excess of 100 kPa.

Analysis of the concept of disposing of noble gases by storing them as bubbles trapped in grout indicated that the storage medium is apt to be highly permeable and that there would be no dynamic forces in hardened grout to prevent the gases from being replaced by natural fluids.

The use of abandoned oil wells has the disadvantages that the fields containing them typically have a large number of wells, all providing potential escape routes. Therefore, all wells in a field would have to be located and plugged. Also, a rather large area might have to be dedicated to storage. The concept offers the advantage that residual crude oil in an abandoned field is thought to be a good solvent for the krypton and therefore to offer a mechanism for retaining it.

VII. SUPPORT FOR THE ENVIRONMENTAL IMPACT STUDY OF WASTE MANAGEMENT
(K. F. Flynn, L. J. Jardine, B. J. Kullen, M. J. Steindler,
and L. E. Trevorrow)

The development of a section for the Environmental Impact Statement on waste management in the commercial LWR nuclear fuel cycle was completed during this period. This Environmental Impact Statement is being assembled at the request of ERDA. A number of national laboratories and other organizations are contributing to it, and the entire effort is coordinated by Battelle-Pacific Northwest Laboratories. The aims, expected structure, and expected contents of this impact statement have been briefly outlined (UNRUH).

The section contributed by ANL describes the expected characteristics of waste types (from the generation of power by LWRs) that will emerge at reactors, spent fuel storage facilities, fuel reprocessing plants, and mixed oxide fuel fabrication facilities. These characterizations included descriptions of the volumes, radioactivity (in terms of both totals and isotopic compositions), densities, and chemical identities. Information on radioactivities was obtained from ORIGEN calculations by Battelle. Data on other properties was derived from calculations, estimates, and published information.

VIII. TRANSPORT PROPERTIES OF NUCLEAR WASTES IN GEOLOGIC MEDIA

(M. G. Seitz, P. G. Rickert,* S. M. Fried,*
A. M. Friedman,* and M. J. Steindler)

A. Introduction

The Waste Isolation Safety Assessment Program (WISAP) being managed by the Pacific Northwest Laboratory Laboratory was set up to provide technical support for the National Waste Terminal Storage Program (NWTSP). The overall objective of WISAP is to evaluate potential interactions between emplaced radioactive waste and surrounding rocks which might affect the integrity of long-term confinement. Task 5 of WISAP was formulated to develop quantitative data describing radionuclide-geologic media interactions that control the transport of radionuclides. The experimental program being conducted at Argonne National Laboratory is designed to meet the objectives of Task 5. The experimental program has utilized three types of experiments (column infiltration experiments, static absorption and desorption experiments, and batch partitioning measurements, described in Table 20) designed to give information on the migration behavior of nuclides in aqueous solution-rock systems. The purposes of using different approaches are to establish nuclide behavior under a variety of experimental conditions and to identify the characteristics of nuclide adsorption that are important for an understanding of nuclide migration in natural systems (recently fractured rock, weathered rock, porous rock, etc.).

B. Column Infiltration Experiments

Column infiltration experiments were performed to determine relative migration rates of nuclides in some geologic media and to examine the effects of different procedures on the experimental results. Several experimental designs were employed. Low-pressure (0-1.4 kPa, 0-0.2 psi) to moderate-pressure (345 kPa, 50 psi) water columns were used over columns of rock aggregate or permeable rock. The experiments can accommodate rocks such as shales that disaggregate in water.

1. Experiments with Rock Aggregate

Experiments were performed to investigate the migration of cesium through Pierre shale and Selma chalk. Cesium-135, a fission-product nuclide, is a long-lived (2.0×10^6 y half-life) isotope, and its containment is therefore of concern for any permanent waste storage concept. The possibilities of locating terminal storage facilities in both Pierre shale and Selma chalk have been considered [NWTSP, BROOKINGS].

One experimental approach employs granulated material and may be relatable to migration behavior of radionuclides in fractured rocks that are otherwise impermeable to water. Supplies of homogeneous granulated material can be produced for use in different experiments, avoiding the problems of heterogeneity that exist for many solid rock samples.

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Table 20. Experimental Methods Used to Investigate Migration Behavior of Nuclides^a

Method	Material	Description	Experimental Measurement	Potential Relation to Nuclide Migration
Column infiltration	Solid rock columns	Aqueous solutions are forced through columns of permeable rock.	Dispersion of V_n	Migration behavior in solid rock
	Rock aggregate	Aqueous solutions percolate through crushed rock.	Dispersion of V_n	Migration behavior in fresh regolith
Static absorption and desorption	Rock tablets	Tablets of rock react with static solutions of minerals and nuclides and nuclide-containing rock react with mineral water.	Kinetics of the reaction; reversibility; K_D	$V_n = \frac{V_w}{1 + (K_D \rho / \epsilon)}$
Batch partitioning measurements	Rock Aggregate	Granulated rock is reacted with stirred solutions of minerals and nuclides.	Surface saturation limits; dependence of K_D on particle size, nuclide concentration, and concentration of dissolved salts	$V_n = V_n \text{ (grain size, } C_n, fCl^-)$

^aSymbols: V_n , velocity of nuclide in rock, cm/s.

V_w , velocity of aqueous solution in rock, cm/s.

K_D , partition coefficient, equal to nuclide concentration per gram of rock, divided by nuclide concentration per milliliter of solution.

ρ , density of rock, g/cm³.

ϵ , porosity of rock, fraction.

C_n , concentration of nuclide, ppm.

The experimental apparatus consisted of a Buchner funnel, glass tubes, and a 100-mL solution reservoir, as depicted in Fig. 25. Rock aggregate* (20 g) was placed in the funnel and packed against the glass frit with a metal rod. Mineral water† (25 mL) was poured into the funnel to wet the rock column and was allowed to drain through the rock column. Expansion of the rock (particularly of the shale) occurred during wetting. The wet columns had a height of 1.8 cm for the shale and 2.3 cm for the chalk.

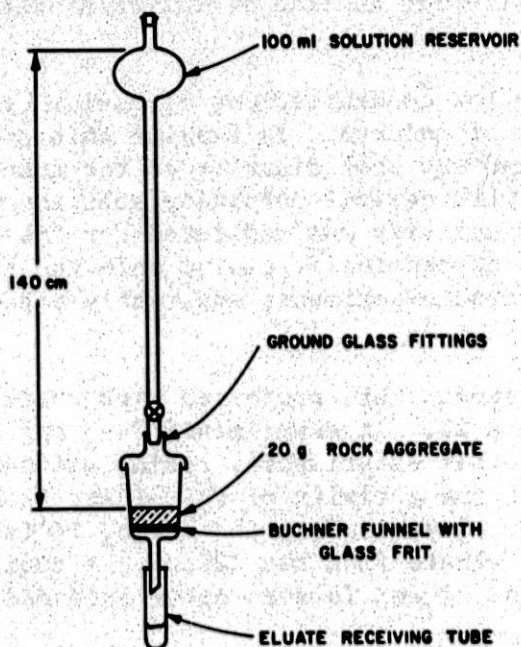


Fig. 25.

Apparatus for Column Infiltration Experiments with Rock Aggregate. ANL Neg. No. 308-77-497

* The rock was crushed and sieved to 18 mesh and then ground for 10 min in an automatic mortar and pestle. This treatment was chosen to separate the particles of shale without fracturing a large amount of individual grains.

† Mineral water or "rock-equilibrated water" (REW) mentioned in this report was prepared by allowing distilled water to react at room temperature for an extended period of time with aggregate of the rock to be studied. The mineral water used with the rock aggregate columns was prepared by mixing with a magnetic stirrer 10 g of rock aggregate and 1 L of distilled water for one week in a polyethylene or Teflon bottle. The mixture was then allowed to settle for one week, and the liquid was decanted and filtered through two No. 1 Whatman filters to remove floating material (mainly Teflon from abrasion of the bottle). The preparation of the REW solutions was selected to allow extensive reaction of the water with rock prior to experimentation in order to establish a chemical content in the water of all elements (except the nuclide being studied) that would change little during the course of an experiment.

In the experiments, the cesium was either added to the eluent to produce a low cesium concentration (0.01 $\mu\text{Ci/mL}$) in the eluent or it was added directly to the rock as small volumes (1 mL) of more concentrated solution (5.7 $\mu\text{Ci/mL}$). The former method is thought to be more typical of conditions hypothesized for a repository, where solutions of low nuclide concentration would continually infiltrate a geologic body. On the other hand, the latter method is more readily interpreted in terms of simple models of nuclide migration. The experiments established that both methods lead to similar results and that results from the second method, preferred because of its simplicity, could be generalized in considering nuclide migration at the expected repository conditions.

When solutions containing very low concentrations of cesium are used, the absorption of cesium on glassware is of concern. To examine this point, two glass tubes (each 140 cm in length and the same diameter as the tube in the infiltration apparatus) were filled with cesium-containing solution of chalk and shale REW water. The solution activity was monitored for the duration of all the infiltration experiments. No adsorption of cesium onto the glass was detected. Thus, the glass used in these experiments apparently performed satisfactorily.

Five column infiltration experiments were performed with chalk or shale aggregate and are described in Table 21. In experiments 24-3 and 24-5, cesium was added to the eluent. In the other experiments, cesium was added directly to the rock column. In Fig. 26, the activity of the eluate from experiment 24-3 is given versus volume of eluate. From the curve, it is seen that there is no activity in the initial eluate from the column. A small amount of activity relative to that in the eluent is seen after extended infiltration of the column.

Table 21. Rock-Aggregate Column Infiltration Experiments with Cesium-135

Expt.	Expt. No.	Rock	Range of Column Elution Rate, mL/h	Elution Volume, mL	Activity on Column, ^a dps	Cesium in Eluent, Fraction of Total
1	24-3 ^b	Selma Chalk ^c	4.2-20	2 312	7.5×10^5	0.013
2	24-4	Selma Chalk	1.9-9	3 531	2.1×10^5	<0.007
3	14-1	Pierre Shale ^d	0.7-0.9	562	2.1×10^4	<0.04
4	24-5 ^b	Pierre Shale	0.2-0.5	368	1.5×10^5	<0.002
5	24-6	Pierre Shale	0.4-1.1	527	2.1×10^5	~0.013

^aBased on the measurement of the activity in the CsCl solution used for the five column experiments.

^bCesium added to the eluent, rather than to the rock in these experiments.

^cPorosity of the chalk was measured to be 0.40 by a water saturation method.

^dPorosity of the shale was measured to be 0.27 by a water saturation method.

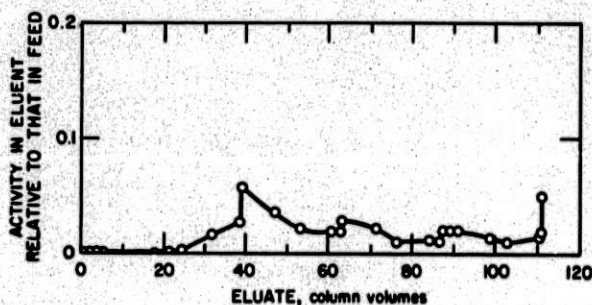


Fig. 26.

Cesium Activity in the Eluent Relative to the Activity in the Feed Versus the Eluate Volume. Experiment 24-3, ^{134}Cs in solution, Selma chalk column

In three experiments (24-4, 14-1 and 24-5), the column eluates did not contain detectable radioactivity, and upper limits to the amount of activity that might have been in the eluates are given (Table 21). In one experiment (24-6), the activity detected in the eluate is believed to be a consequence of a wetting and drying sequence that preceded addition of the cesium solution to the rock and produced fissures in the shale material. The fissures closed after the radioactive eluent solution was applied. The concentration of cesium in the eluate decreased gradually during this experiment.

After these experiments were terminated, the rock-aggregate columns were sampled at six depths and the samples analyzed by counting gamma rays to determine how far the cesium had penetrated. The activity levels for the four columns in which cracking had not occurred are plotted in Fig. 27. A small sample was taken at the top of each column to locate the position of maximum concentration within the column. These top samples had the highest concentrations of cesium, indicating that the peak of the activity did not perceptibly move within the columns. However, all samples analyzed contained low but measurable concentrations of cesium. The resulting distribution of cesium in the columns is strongly skewed, with the maximum near the surface of the column and a long tail of activity extending in the direction of the water flow.

On the basis of the distributions of cesium seen in the columns, cesium is seen not to behave as predicted by models which employ simple ion-exchange mechanisms and conditions of local equilibration. These models predict a single nuclide velocity relative to the velocity of the water infiltrating the rock. However, the skewed distributions of cesium imply a large dispersion in the relative migration rate of cesium in these columns. Much of the cesium moved with low velocity as evidenced by the large peak in distribution near the top of the columns. However, cesium was present at the bottom of the columns, implying a much greater relative migration rate for some of the cesium. Migration rates, based on the absence of visible migration of the peak activity and the migration rates based on detection of cesium in the eluate or in the bottom of the columns, are given in Table 22.

A large range in measured migration rate is seen in Table 22. This dispersion is an important feature of cesium migration and must be considered in modeling the movement of cesium in a uniform and homogenized material such as the rock aggregate used in these experiments. One such model is a dispersive model of fluid flow that accounted for observations in large field experiments which traced the advancing water front from one well to another [WEBSTER]. The dispersion was attributed to the channeling of water in the many cracks present

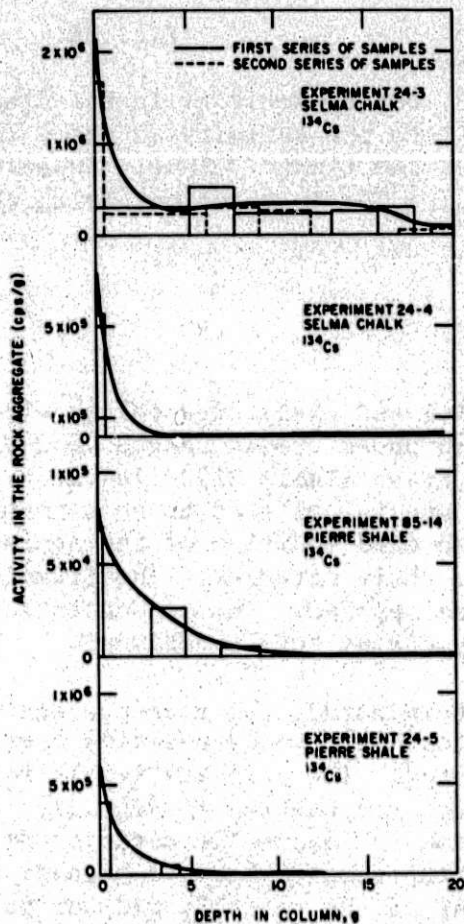


Fig. 27.

Column Infiltration Experiments. Activity in the rock versus depth in the columns. All columns had measurable ^{134}Cs concentrations on the bottom (20-g) level.

in the permeated medium. A similar model describing dispersive effects on a finer scale could be invoked to model the results observed in these experiments. However, it is not yet known whether the dispersion is due to channeling between aggregates or to some other dispersive effect (such as nonequilibrium behavior).

Distributions of activity in columns of chalk were similar, even though the concentration in one column was four times greater than in the other (Table 21). This suggests that cesium concentration did not measurably affect the behavior of cesium. A similar conclusion is reached from observation of the shale columns, for which concentrations differed by an order of magnitude. Furthermore, the similarity of the cesium distribution in the chalk and shale columns in spite of differences in chemical composition and elution rates (see Table 21) suggests that neither of these variables affects the amount of dispersion seen in the experiments.

2. Experiments with Solid Rock

In experiments with columns of solid rock, the migration of plutonium, americium, and neptunium through Salem limestone and Ohio barrier sandstone was investigated. Long-lived radioactive isotopes of these elements are present in reactor wastes, and the migration properties of these elements are of concern in relation to permanent waste storage concepts. The nuclides plutonium-237, americium-241, and neptunium-239 were used in these experiments and were analyzed by gamma counting.

Table 22. Relative Migration Rates of Cesium Measured in Selma Chalk and Pierre Shale

Expt. No.	Material	Relative Migration Rate ^a of Peak Activity ^b V_{Cs}/V_w	Maximum Relative Migration Rate Detected V_n/V_w
24-3	Chalk	1×10^{-5}	0.16×10^{-2}
24-4	Chalk	0.6×10^{-5}	0.24×10^{-2}
14-1	Shale	9×10^{-5}	0.8×10^{-2}
24-5	Shale	6×10^{-5}	0.2×10^{-2}
24-6	Shale	70×10^{-5}	$50^c \times 10^{-2}$

^aThe relative migration rate is the velocity of the nuclide divided by the velocity of the infiltrating water. The calculation of relative migration rate uses the porosity given in Table 21 and assumes that all pores are subject to water flow.

^bThese values each represent the maximum possible migration rate for the activity in the peak activity. No evidence of migration of the activity in the peak was detected. The peak migration rates were estimated by assuming that the activity had traveled the thickness of the sample taken from the top surface of the column.

^cRapid migration of some cesium occurred through large cracks in the column for experiment 24-6.

Circular rock columns were cut from rocks and fastened in polyethylene tubes with epoxy. The rock columns were wetted with rock-equilibrated water, and nuclides were added to the top surface of the columns in small volumes (1 mL) of water. After the radioactive water soaked into the rock, the columns were pressurized with water. In one method, standing tubes of water approximately 150 cm high were used as a source of pressurized water. In another method, a regulated-pressure air supply was used to provide pressures up to 2.8×10^2 kPa (40 psi). The air was separated from the water solutions by a movable rubber piston in a cylinder; this prevented air from dissolving in the water.

Rocks and elements (Table 23) were studied in nine column experiments (listed in Table 24) performed with plutonium, americium, and neptunium nuclides. The eluates were collected from each experiment and analyzed for nuclide activity.

In Table 24, some of the results are given, expressed as percent of a nuclide transmitted at relative migration rates greater than the stated ratios to the water front velocity. In most experiments, the bulk of the activity remained in the rock even after a hundred or more column volumes of eluent passed through the columns. For example, for the first experiment listed in Table 24, it can be seen that only 2.6% of the activity was eluted

Table 23. Rocks and Elements Studied by Infiltration Experiments with Solid Rock Columns

Rock Type	Porosity, ^a Percent by Volume	Density, g/cm ³	Elements and Valence States
Limestone, Salem Formation	13.6	2.27	Am ³⁺ , Np ⁵⁺ , Pu ⁴⁺ , Pu ³⁺
Sandstone, Ohio Barrier	19.4	2.10	Am ³⁺ , Np ⁵⁺

^aPorosity measurements were made by weighing a sample before and after water saturation. The weight difference is indicative of the pore volume of the sample.

from the column. The relative velocity of 0.0014 corresponds to an eluate volume of about 100 column volumes in this experiment. However, it was seen that in all experiments, nuclide activity was detected in the initial one or two column volumes of eluate that passed through the columns and was present in all eluate samples. This behavior is indicative of a large dispersion in the relative migration rates of each of the nuclides, plutonium, americium, and neptunium, in the rocks studied. This result is similar to that seen for cesium in shale and chalk and suggests that a model involving a single migration rate for a nuclide cannot accurately represent its migration behavior in common rocks.

C. Static Absorption Experiments

Static absorption experiments were run on a series of rock types. In an experiment, a tablet of rock was suspended from platinum wire and immersed in a solution containing radionuclides of plutonium, americium, or both. Because each solution was prepared in air, plutonium was presumed to be in the 4⁺ valence state and americium in the 3⁺ valence state. During the period of immersion of the rock tablet in solution, the rock was removed from the solution at intervals and the activity remaining in solution was monitored by gamma counting. Generally, the activity associated with the solution was seen to decrease very rapidly during the first few hours or days of contact with the rock. Later, it attained an activity that stayed constant for the remainder of the experiments. A typical plot of the activities in solution during experiment 32 (corrected for nuclide decay, background, Compton scatter, and interference from decay of other nuclides) versus the reaction time is given in Fig. 28. The curve shows an initial rapid decrease in plutonium and americium activities of the solution to a value that remained constant in the subsequent part of the experiment.

Experiments were found to require contact times sometimes in excess of 500 h for absorption to cease. The activity, A, in solution as a function of time was approximated by the formula

$$A = A_f + (1 - A_f)e^{-(t/t_r)} \quad (1)$$

Table 24. Cumulative Percentages of Nuclide that Moved with a Velocity Greater than the Stated Velocities as Determined in Column-Infiltration Experiments with Solid Rock

Sample	Experiment	Nuclide and Valence	Nuclide Passing Through the Core, % Cumulative	Ratio of Velocity of Nuclide to Velocity of Water Front
Limestone, Salem Formation	B-Series	Pu ⁴⁺	0.007	1
			0.01	0.5
			0.11	0.006
			2.6	0.001
Limestone, Salem Formation	C-Series	Pu ³⁺	0.05	1.00
			0.23	0.3
			0.50	0.05
			1.0	0.003
Limestone, Salem Formation	C-Series	Am ³⁺	0.002	0.3
			0.005	0.05
			0.024	0.01
			0.031	0.007
Limestone, Salem Formation	D-Series	Np ⁵⁺	0.030	1.0
			0.053	0.5
			0.092	0.02
			0.69	0.009
Limestone, Salem Formation	123-77-Series Extended Test	Am ³⁺	0.0004	0.42
			0.008	0.008
			0.068	0.003
			0.28	0.001
Limestone, Salem Formation	123-77-Series	Np ⁵⁺	0.04	0.4
			0.11	0.1
			1.1	0.003
			6.1	0.001
Sandstone, Ohio Barrier	E-Series	Am ³⁺	0.0002	0.3
			0.002	0.05
			0.024	0.04
			0.033	0.001
Sandstone, Ohio Barrier	E-Series	Np ⁵⁺	1.3	1
			12.3	0.10
			61.3	0.01
			69.7	0.005
Sandstone, Ohio Barrier	123-77-Series	Np ⁵⁺	0.45	0.4
			12	0.09
			28	0.03
			45	0.005

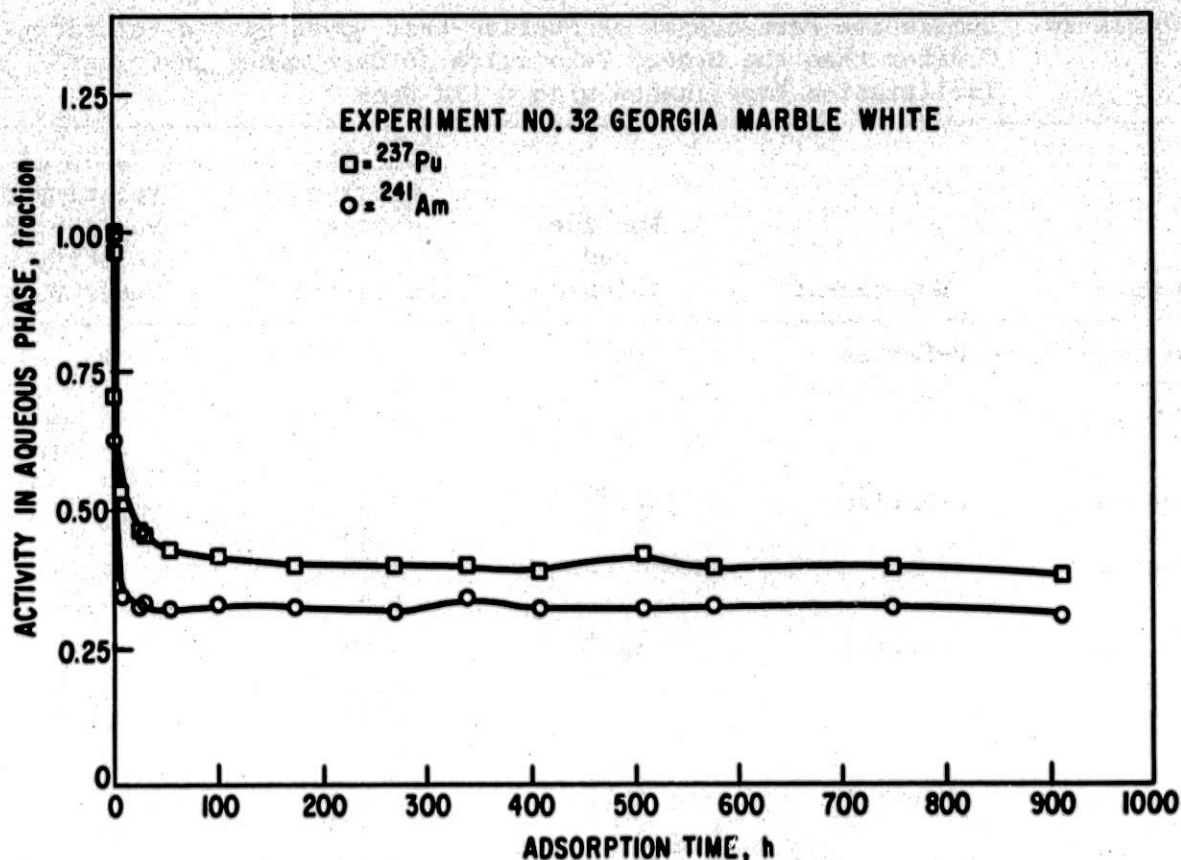


Fig. 28. Static Absorption Experiment. Activity of plutonium and americium in solution versus contact time with a rock tablet of marble.

where A_f is the final activity remaining with the solution and t_r is defined as the characteristic time of the reaction. The sum of the activity remaining with the rock, A_r , and the activity remaining with the solution, A_f , is equal to 1.

Some activity remained associated with polyethylene tubes used in the experiments. This activity was subtracted from the total radioactivity of the tube and solution to obtain the activity of the solution, A_s . The latter radioactivity was used to determine the distribution coefficient, K_D , by the equation:

$$K_D(\text{mL/g}) = \frac{A_r/\text{g of rock}}{A_s/\text{mL of solution}} \quad (2)$$

Results from some of the experiments in each of which two isotopes were added simultaneously are listed in Table 25. Nearly all of the experiments (29 out of 31) exhibited the behavior expressed by Eq. 1, for which a characteristic time of reaction, t_r , could be determined. The values of t_r were estimated from absorption curves, and the values of K_D were calculated from the counting data; these values are listed in Table 25.

Table 25. Typical Results from Static Absorption Experiments with Plutonium and Americium

Rock Type	Expt.	Characteristic Reaction Time, h			Partition Coefficient, K_D			Element
Georgia White Marble	30, 31, 32	5	5	8	77	180	51	Pu ^a
		5	5	5	162	160	220	Am ^a
Colitic Limestone	33, 34, 35	5	5	5	540	710	210	Pu ^a
		<5	<5	<5	415	520	690	Am ^a
Barrier Sandstone	36, 37, 38	50	n.d. ^b	50	8.2	20	6.4	Pu
		25	15	15	11	12	7.7	Am
Soapstone	39, 40, 41	15	15	20	8.4	23	28	Pu ^a
		10	15	25	23	67	105	Am ^a
Culebra	42, 43, 44	<5	1	1	16	19	20	Pu ^a
		<5	1	1	58	84	59	Am ^a
Gneiss	45, 46, 47	75	150	100	10	17	16	Pu
		~600	~600	~600	18 ^c	8.3 ^c	4.4 ^c	Am
Dolomite	48, 49, 50	<5	<5	<5	3.4	34	13	Pu ^a
		<5	<5	<5	10	150	26	Am ^a
Chalcopyrite	51, 52, 53	100	150	200	25	3	4.7	Pu
		75	n.r. ^d	n.r. ^d	0.6	0.3	0.5	Am

^aIn these experiments, a considerable amount (<50%) of the radionuclide associated with the solution was retained on the walls of the polyethylene tube. The activity in the solution was determined by subtracting the activity on the walls from the activity of the tube and solution. The corrections are large and may have led to errors in the calculated partition coefficients.

^bn.d. indicates that the activity curve did not fit the behavior indicated by Eq. 1.

^cPartition coefficients were measured after a 1000-h experiment and do not represent equilibrium conditions.

^dn.r. indicates that there was insufficient reaction to allow the characteristic reaction time to be measured.

The characteristic time of reaction for different nuclides and rocks shows a considerable spread in these experiments, ranging from about 1 h to in excess of 600 h. However, the time of reaction appears to be constant and well defined for a particular nuclide and rock, as indicated by the consistency of results from duplicate experiments. With some rocks (e.g., gneiss), the reaction times were long and steady-state behavior could not be attained, even in the 1000-h experiments.

In most of the experiments, the plutonium and americium nuclides were absorbed into the rock. This effect is indicated by partition coefficients in excess of one. Often the isotopes were strongly fractionated, particularly onto rocks of oxide composition, leading to partition coefficients in excess of 100.

From the experimental observations described, the reaction rates are seen to vary considerably for different rock-nuclide systems (by three orders of magnitude among the 30 rock-nuclide systems). Fluid flow velocities in rock columns for which local equilibrium conditions would be attained are expected to differ for different rock-nuclide systems. Therefore, models of nuclide migration which assume local equilibration during fluid flow are not, in general, valid for all elements simultaneously.

In some static absorption experiments, the experiments were initiated with one element, plutonium or americium, in solution. The solutions were reacted with rock, and the activity of the solutions was monitored as a function of time. After about 1000 h of contact of the solutions and rocks, the second element was added to the solutions. The solutions were again contacted with the rock and the activities of both nuclides in solutions were monitored.

For experiments in which plutonium was the initial nuclide in solution, the absorption behavior seen for the rocks is consistent with that seen for experiments listed in Table 25.

However, in the experiments in which americium was the initial nuclide, the presence of plutonium often had a significant effect on the behavior of the americium. In three of five experiments, the adsorption of americium on rock was enhanced by the addition of plutonium. In one experiment, addition of plutonium resulted in the transfer of americium from the rock to the solution. In one experiment, the addition of plutonium had no effect on the behavior of americium.

From the experimental results, the presence of synergistic effects was seen to be confined to cases in which a plutonium spike was added to a solution containing americium. This suggests that something associated with the plutonium affects the adsorption equilibrium of americium. It is unlikely that the plutonium itself is the source of the synergistic behavior because the concentration of plutonium is low. One possibility that will be examined is that the agent for the synergistic behavior is an auxiliary chemical used in the preparation of the plutonium-237 and still present in the spike. Such an agent may affect the adsorption of plutonium as well, a point that would not be apparent from these experiments.

D. Batch Partitioning Experiments

Two sets of batch partitioning experiments are described in this report. The first set of experiments was performed to test the reversibility of the sorption process. The second set was performed to determine whether sorption increases with decreasing particle size.

The migration behavior of nuclides depends sensitively on whether absorption processes are reversible. Ion-exchange models used to predict nuclide migration generally assume that the sorption process is reversible.

To test whether this assumption is valid for americium in a common rock, batch experiments were done with granulated Columbia River basalt of graded mesh sizes (16-20, 30-40, and 50-70 mesh) and americium-bearing solutions.

Rock samples of 0.1 to 0.3 g were agitated with 2 or 3 mL of solution in test tubes for 500 h. One or two milliliters of solution was then removed from the test tubes and analyzed for americium-241 activity. The partitioning of americium between solution and rock during absorption was then determined from the initial and final activities of the solution. The sample of active solution that had been removed from the test tubes was then replaced with rock-equilibrated water having no activity, and the system was agitated for an additional 500 h. The activity of the solution after this period is indicative of the partitioning of americium during desorption. The experimental results are given in Table 26. The results indicate that americium desorbed from the basalt and thus that the reaction is reversible. However, the partition coefficients are higher on desorption than on adsorption, indicating that americium is preferentially retained by the rock. This effect is not large--greater than 90% of the americium activity was retained by the rock in both cases.

Table 26. Partitioning of Americium in Columbia River Basalt After Absorption and Desorption^a

Expt.	Mesh Size	Partitioning After Absorption, K_D	Partitioning After Desorption, K_D
1	16-20	83	156
4	16-20	70	124
7	16-20	95	121
2	30-40	138	247
5	30-40	148	336
8	30-40	121	164
3	50-70	147	316
6	50-70	164	322
9	50-70	115	215

^a500-h equilibration times for adsorption and for desorption. Temperature was 24°C.

The existence of reversibility in these experiments contrasts with results obtained in static absorption experiments (not discussed above) when rock tablets were allowed to dry between absorption and desorption of plutonium or americium. In 18 desorption experiments, 11 showed no measurable desorption of plutonium or americium, 6 experiments showed slight desorption of americium, 1 experiment (with marble) showed slight desorption of plutonium, and 1 experiment (with galena) showed complete reversibility of americium during

desorption. These results indicate that reversibility of the reactions depends upon the history of the rock-nuclide system.

Batch absorption experiments were done to determine whether decreasing the particle size of a sample would increase its absorptivity. If adsorption is a surface phenomenon, the amount of absorption per gram of material may increase as the surface area of the material is increased.

To test this theory, a fine-grained basalt (Columbia River basalt) was ground and divided into the three particle size ranges, 16-20, 30-40, and 50-70 for batch partitioning experiments. Basalt was chosen because of its moderate partition coefficients for plutonium(IV) and americium(III) and its presumed low permeability. However, the measurements of large surface areas made using the Brunauer-Emmett-Teller (B.E.T.) method indicated that the basalt may have a fine pore structure and may not be of low permeability. This pore structure may account for a large surface area relative to the calculated fracture surface.

In each experiment, between 0.1 and 0.5 g of basalt was allowed to react under slight agitation with 2 or 3 mL of water solutions to which plutonium(IV) or americium(III) tracers had been added. Six measurements were made for each nuclide reacted for the same length of time with each of the three mesh sizes used. No systematic change in the partitioning with mesh size was noted for either nuclide with materials between the two smallest mesh sizes (30-40 and 50-70 mesh). However, the partitioning of americium to the rock was seen to increase with particle size between 16-20 and 30-40 mesh sizes. This particle-size effect for americium is also evident from the data in Table 26. Partitioning of plutonium to the solid was also seen to increase with particle size for the two largest mesh sizes but was less than for americium (plutonium partitioning values increased from ~85 to ~115 when particle size was decreased from 16-20 to 30-40 mesh).

The changes seen for different particle sizes do not correlate with either the calculated fracture surface or the measured surface area of the materials of the three particle size ranges. One explanation of the data is that the penetration depth of the solution in basalt is comparable to the particle radius of the material of moderate-mesh size but lower than the average size of the largest-mesh fraction. Thus, the material of largest particle size is only partially reacted with the solution, resulting in less partitioning than for the smaller-size material.

E. Discussion

In most static absorption experiments, plutonium and americium were seen to be strongly absorbed into the rock. A strong affinity of nuclides for the rock phases would be expected to retard the migration of nuclides during infiltration. In column infiltration experiments, nuclides of cesium, plutonium, and americium were seen to migrate much more slowly than did the infiltrating fluid. Much of the cesium moved with low velocity, as evidenced by the peak concentration of cesium remaining near the top of the columns during infiltration. Similarly, from the results in Table 24, very little of the plutonium and americium was eluted from the columns, and therefore most must have moved only a fraction of the distance of the water front.

One approach used in the past to understand transport of waste nuclides in geologic media has been to mathematically describe possible reactions of nuclides between rocks and solutions and then to calculate the migration resulting from water flow. In order to model the transport phenomena, simplifying assumptions concerning nuclide-rock reactions have been made [DEMARSILY, INOUE, BURKHOLDER]. These assumptions generally include the following: (1) that exchange reactions of nuclides between rock and solution are reversible, (2) that the nuclide-rock reactions are instantaneous and so the equilibrium of the nuclide between solution and rock is locally maintained within the rock, (3) that the rock formation can be represented as a continuous homogeneous medium, and (4) that the concentration of each nuclide is sufficiently small that nuclides react independently of each other and do not affect macroscopic properties of the water.

Given these simplifying assumptions, nuclides are expected to migrate down the column with a well defined velocity. For a nuclide concentrated initially in a narrow band at the upper end of the column, continued elution of the column will move the band down the column. As the band moves down the column, it widens and assumes the shape of a Gaussian curve. The velocity of the peak of the nuclide band V_n relative to the velocity of the water front V_w is given by

$$V_n/V_w = \frac{1}{1 + (K_D \epsilon/\delta)} \quad (3)$$

where ϵ is the porosity and δ the density of the rock and K_D is the ratio of the nuclide in the solid to nuclide in the solution as defined in Eq. 2.

Where diffusion is small in relation to the migration rate of the band, the band width due solely to the exchange reactions will be proportional to the square root of the distance the peak had traveled. Nuclide migration has also been modeled to include dispersion of the type produced by diffusion of nuclides within the fluid. Diffusion of nuclides within the fluid will increase the width of the band but will not destroy the Gaussian shape of the band. This model of nuclide migration appears to accurately describe the movement of strontium in a column of glauconite aggregate [INOUE].

However, the simplified model of nuclide migration does not, in general, accurately describe the results of nuclide migration obtained here experimentally. From results of the static absorption experiments, the reaction rates appeared to be well defined for a particular nuclide-rock system. It was seen from the data, however, that the characteristic reaction time for different nuclides and rocks varied considerably. The reaction time varied from about 1 h for some systems to in excess of 600 h for others. With some rocks (e.g., gneiss), the reaction times were long and steady state behavior was not attained, even in the 1000-h experiments.

These results indicate that in different rock-nuclide systems, the attainment of local equilibration would require different time periods and consequently different velocities of an infiltration fluid. Therefore, models of nuclide migration may need to consider conditions other than local equilibration during fluid flow such as non-equilibration on the local scale and to employ the various reaction rates for different rock-nuclide systems.

Based on the distribution of nuclides in the rock columns or in the eluates during infiltration experiments, it is seen that the nuclides do not behave in general as predicted by models based on simplifying hypotheses. For example, the skewed distributions of cesium seen in rock aggregate columns imply a large dispersion in the relative migration rates of cesium in chalk and shale. Although a low migration rate of most of the cesium is evidenced by the high cesium concentrations at the top of the column at the end of experiments, the presence of cesium at the bottom of the columns is indicative of much higher migration rates for some of the cesium. The dispersion in migration rates is evident from the different migration rates in rock aggregate seen in Table 22. Similar dispersive characteristics were seen for plutonium, americium, and neptunium in solid rock columns; in all infiltration experiments, nuclide activity was detected in the initial one- or two-column volumes of eluate that passed through the columns and was also present in all eluates sampled. Similar skewed distributions were observed for plutonium migration in tuff; the plutonium concentrations were in the form of tails decreasing exponentially with depth in the direction of fluid flow [FRIEDMAN, FRIED-1976]. The experimental results suggest that models involving a single migration rate for these nuclides would not accurately represent their migration behavior in common rocks.

The great range in the observed relative velocities implies that the movement of nuclides, even in a uniform and homogenized material such as the rock aggregate used with cesium, has to be described by a model that accounts for this dispersion. Large field experiments which traced the advancing water front from one well to another [WEBSTER, INOUE] required a dispersive model of fluid flow to account for the observations. The dispersion was attributed to the channeling of water in the many cracks and subsequently in many pathways in the permeated medium. Similar dispersive effects may exist in the column infiltration experiments due to a void structure in the rock columns. Fluids moving through a rock aggregate or within rock pores would be continuously subdivided into finer offshoots and would be recombined into larger streams at intersecting flow paths. Variations of path lengths and fluid velocities in the different paths from one location to another would cause a peak to spread as it migrates through the column. This type of dispersion, as determined in simply characterized media, increases with the distance the peak has traveled but preserves the peak symmetry [DEJOSSELIN DE JONG]. Therefore, this model cannot account for the skewed nuclide distributions seen in the infiltration experiments.

Several conditions may have existed in the infiltration experiments that could have contributed to the nonidealized behavior seen. Possibly, for example, the dispersion in nuclide migration was a result of large heterogeneities in the columns. Visible cracks in one column were found to result in greatly increased velocities of cesium migration. Channeled flow in similar but smaller cracks or in pores within the rock columns may have contributed to the observed nuclide distribution by allowing solutions to pass through columns with little reaction with the rock. Alternatively, dispersion may have been due to the flow rates used in the experiments being high enough to prevent equilibration of the solution and rocks. This would allow some of the nuclide to be washed through a column without the retardation effect produced by partitioning on the solid rock phase. The flow rates within pores, calculated from porosity and column elution rate (Table 21), are comparable to flow rates found for some groundwaters, and effects caused at these flow rates could be expected to be found also in natural systems.

The dispersive characteristics seen in the column infiltration experiments are likely to be important in assessing nuclide retention in geologic storage facilities. For example, plutonium is considered (from results of laboratory experiments) to have a strong affinity for lithic material and therefore a low migration rate relative to that of an advancing water front. From static partitioning measurements, plutonium in Salem limestone would be expected to have a relative migration rate of 4×10^{-4} . This calculated value is based on the simplifying assumptions stated previously and is consistent with the observation (from column infiltration experiments) that most of the plutonium was retained by limestone even after continued infiltration. However, it is seen in Table 24 that 2.6% of the plutonium travels with a relative migration rate greater than 0.001. This small but finite amount of activity may present a radiological hazard, and the greater velocity associated with this activity than with the remainder of the activity may be a limiting factor in nuclide retention. This assessment of the importance of the dispersion of relative velocities differs from recent viewpoints which suggest that dispersion is not a governing factor in the confinement of waste [DEMARSILY].

F. Conclusions

In the column infiltration experiments with shale and chalk aggregate, the peak concentrations of cesium were seen to move with low velocity, which is consistent with a strong partitioning of the nuclide onto rocks. However, cesium activity was also seen in a long tail extending from the cesium peak in the direction of water flow as a result of relative migration rates up to three orders of magnitude larger than that for peak concentrations. Nuclide activity downstream from the peak activity was also seen for plutonium, americium, and neptunium in solid rock columns of limestone and sandstone. Thus, dispersion in the relative migration rates of these elements in the common rocks studied is large, and the behavior of these elements cannot be accurately described by models that predict a single migration rate based on simple absorption properties and local chemical equilibration. For similar reasons, partition coefficients measured in batch experiments are not adequate to characterize the migration of these nuclides in geologic media.

When rocks of oxide composition were studied in static absorption experiments, plutonium and americium were found to be strongly absorbed by the rock tablets. Relative migration rates for plutonium and americium by fluid flow calculated from the results of the static absorption experiments are considerably lower than the velocity of the infiltrating water. The experiments also indicate that the reaction rates of nuclides in solutions and rocks vary considerably for different rock-nuclide systems. Therefore, for a solution containing several nuclides and moving through rock, conditions of local equilibration may exist for some nuclides and not others. Thus, models of nuclide migration need to provide for the reaction rates of the individual nuclides.

Drying out of rocks after absorption was seen to drastically alter subsequent nuclide partitioning behavior. This effect may be important in assessing the evidence of limited nuclide migration at the fossil reactor site in Oklo, Gabon, where a sequence of water infiltration, criticality, and dry out cycles is suggested to have occurred that would be expected to make nuclide absorption irreversible.

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