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**CHEMICAL ENGINEERING DIVISION
FUEL CYCLE PROGRAMS**

October—December 1976

by

**M. J. Steindler, M. Ader, G. Bernstein,
K. Flynn, T. Gerding, L. Jardine, B. Kullen,
W. Mecham, B. Saunders, W. Seefeldt,
M. Seitz, A. Siczek, and L. Trevorow**

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ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

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**Materials Science Division.

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	2
I. SALVAGE OF ALPHA-CONTAMINATED METALS	5
A. Introduction	5
B. Experimental Techniques	6
1. Autoradiographic Analysis	8
2. Neutron-Activation Analysis	9
C. Experimental Conditions and Results	10
D. Conclusions and Plans for Future Work	21
II. DEVELOPMENT OF ADVANCED SOLVENT EXTRACTION TECHNIQUES	23
A. Developments for the Processing of LWR Fuel	23
1. Introduction	23
2. Development of 10 Te/day Contactor	24
3. Development of a Mini-Contactor	26
4. The Chemistry of Ruthenium and Zirconium in the Purex Process	26
B. Developments for Reprocessing of FBR Fuel	33
1. Introduction	33
2. Development of a 0.5 Te/day Centrifugal Contactor	33
3. Solvent Cleanup	34
III. ENVIRONMENTAL EFFECTS	37
IV. METAL MATRIX ENCAPSULATION OF HIGH-LEVEL WASTES	40
A. Introduction	40
B. Results	40
C. Experimental	48
D. Conclusions	48
V. ESTABLISHMENT OF TENTATIVE CRITERIA FOR HULL TREATMENT	50
A. Introduction	50
B. Topics to be Treated in Criteria	51
C. Topics to be Excluded from Consideration in Criteria	53
D. Preliminary Criteria	54

E. Hydrochlorination of Hulls	56
VI. DEEP-WELL DISPOSAL OF NOBLE GASES	59
VII. SUPPORTING EFFORT FOR THE ENVIRONMENTAL IMPACT STUDY OF WASTE MANAGEMENT	61
REFERENCES	63

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Metal and Slag Prior to Melting	6
2.	Crucible and Contents after Melting and Resolidification	7
3.	Ingot Sectioning	7
4.	Arrangement of Samples and Detectors for Neutron-Activation Analysis	9
5.	Alpha-Radiographs of Samples from Steel Ingots	14
6.	Fission Tracks in Muscovite from Metal Samples	17
7.	Types of Plutonium Associations Identified in Melt-Refining Metal	19
8.	Annular Centrifugal Contactor (10 Te/day)	25
9.	Extended Casing for Annular Contactor	35
10.	HLW Canister Surface Temperature <i>vs.</i> Total HLW Canister Heat Generation Rate for Different Canister Diameters	42
11.	Waste Solidification Flow Sheet for 5 MTU/Day Plant	46
12.	Sectioned Castings in Thin-Walled Stainless Steel Beakers of (a) 5-mm glass beads and (b) 1-4 mm Al ₂ O ₃ pellets, each dispersed in a lead matrix	49
13.	Hydrochlorination Apparatus	57

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Experiments to Melt-Refine Plutonium from Mild Steel	11
2.	Experiments to Melt-Refine Plutonium from Nickel and Stainless Steel	12
3.	Melt-Refining of Plutonium from Mild Steel--Analytical Results for Bulk Samples	13
4.	Plutonium in Metal Samples Analyzed by Alpha Radiography	16
5.	Plutonium in Metal Samples--Neutron Activation Analysis	18
6.	Plutonium Distribution in Slags--Alpha Radiographic Analyses	20
7.	Extraction Coefficients of Ruthenium Nitrosyl Complexes	29
8.	Extraction Coefficients, D_{Zr} , of Zirconium	32
9.	Comparison of Maximum Total Heat Generation Rate of Reference HLW Canisters: Lead Alloy Metal Matrix of Calcine or Glass Beads Cooled in Water or Air	44

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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. The actinides are partitioned to a high degree into slags that are contacted by the molten metal. Studies of advanced solvent extraction techniques 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. Review of literature on the process chemistry of zirconium and ruthenium has been carried out to aid in improving the process when fast contactors are used. A review of information on the dispersion of reagents during accidents in reprocessing 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 has been initiated. The data will be used to identify the state of the art and the importance of selected features of this process. 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 together with the necessary technical rationalization, into a package for review by interested parties. A brief program to explore the disposal of noble gas fission products by deep-well injection has been started.

SUMMARY

Salvage of Alpha-Contaminated Metals

Large amounts of plutonium- and americium-contaminated metals are generated from equipment replacement and the decommissioning of process facilities. The metals are relegated to retrievable storage, with no plans regarding their ultimate disposal. The purpose of the present study is to demonstrate a method of cleaning and assaying the contaminated metals for economic disposal or even recycle of the metals.

In the experimental program, steels "contaminated" with PuO_2 and Am_2O_3 were melted (*i.e.*, melt-refined) in the presence of silicate liquids (slags). The slag-extraction process produced a steel product with a very low residual plutonium and americium content. Most of the plutonium is extracted from the steel. Incomplete separation of the silicate slag from the steel constitutes the major source of activity remaining in the ingots. Plutonium in large defects within the ingot is also a source of activity in the product steel. A small amount of plutonium occurs throughout the ingots in the form of tiny clusters. These results indicate that a high degree of decontamination can be obtained by limiting the amount of slag carried with the steel product and by limiting the formation of large defects in the ingot. The process does not appear to be sensitive to the metal or slag compositions.

Development of Advanced Solvent Extraction Techniques

A program was initiated during this quarter aimed at the development of advanced solvent extraction techniques for Purex reprocessing of LWR fuels. This program is being carried out in cooperation with the Savannah River Laboratory. Purex type extraction systems are to be improved by using short-residence annular centrifugal contactors which will take advantage of differences in extraction kinetics of uranium-plutonium and fission product elements.

Design criteria have been developed for a contactor to process 10 Te/day of LWR fuel. A requisition has been issued to procure a 5-hp motorized milling spindle which will be used to drive the contactor rotor.

A single-stage miniature contactor is being fabricated and will be used to evaluate the performance of a very small annular contactor after which a multistage unit will be designed. The miniature multistage contactor can be used to study extraction kinetics of selected fission products and reduction kinetics of plutonium.

A literature review of the solvent extraction chemistry of ruthenium and zirconium in the Purex process was completed. The chemistry of these two elements in nitric acid solutions and their extractability by tributyl phosphate (TBP) has been reviewed. Possible methods of improving the decontamination of uranium and plutonium from ruthenium and zirconium are discussed.

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 initial phases of the work include a series of reviews of the mechanics of formation of aerosols, dusts, and mists during accident events; the behavior of aerosols, dusts, and mists during transport to an air-cleaning system; and the modification of airborne material during passage through an air-cleaning system.

In this early work, the accident event emphasized has been explosions. Literature related to nuclear and nonnuclear explosions is being examined. Particular attention is being given to the concentrations and particle size distributions of airborne material shortly after an event.

Metal Matrix Encapsulation of High-Level Waste

Metal matrix encapsulation has generally been applied to high-level waste in the calcine form, although encapsulation of glass beads has been tested in foreign work. Dispersion of calcined or glass waste in metal (*e.g.*, lead) produces a two-phase composite that may contain 60-70 vol % high-level waste. Experiments have shown that the metal can be made to occupy only the volume between close-packed calcine or glass particles, so that the net waste volume is little increased compared to the unencapsulated form. The thermal conductivity of lead-matrix waste composite is more than ten times that of glass or calcine. If the temperatures of the center and the canister wall are fixed, this increase permits either a higher volumetric heat loading and thus solidification sooner after reactor discharge, or larger and hence fewer canisters in comparison to either the calcine or glass form. Further, the high thermal conductivity reduces the detrimental effects (*e.g.*, outgassing, devitrification) which would be enhanced by large temperature gradients.

Encapsulated waste is expected to be dispersed less than unencapsulated waste because of the low corrosion rate of lead in water and the relatively high mechanical strength of the composite. The corrosion rate of lead in salt water is as low as or lower than that of most glasses; one centimeter of lead is expected to resist penetration for about 3000 yr. One proposal that would utilize this low corrosion rate specifies that the waste encapsulated in lead be surrounded by a layer of lead in which there are no waste particles. Resistance to leaching due to such a protective metallic envelope should be adequate to allow the fission products to decay to very low levels before leaching. The metal matrix is also expected to add some intrinsic mechanical strength and adequate ductility to retard dispersal, particularly in comparison to either the glass form or the untreated calcine form of waste.

Establishment of Tentative Criteria for Hull Treatment

Criteria are being developed for ERDA for safe handling and disposal of fuel-assembly hulls and hardware that will be discarded after chopping and leaching of spent fuel at fuel reprocessing plants. In this program, a set of tentative criteria is to be assembled, they are to be distributed

to appropriate industries, ERDA, and the NRC for review and suggestions, and revised versions based on comments by reviewers are to be issued. In this report, preliminary versions of criteria for handling of hulls are presented, together with an outline of some of the bases for criteria development.

Volatilization of zirconium as $ZrCl_4$ is being examined as a means of reducing the volume of the hull waste which, because of contamination by transuranic elements, is likely to require disposal in a Federal repository. Equipment has been set up to hydrochlorinate or chlorinate Zircaloy-(U, Pu) O_2 mixtures at $\sim 400^\circ C$ and to measure Zr/Pu separability. The results of shakedown trials with inactive material (Zircaloy- UO_2) indicate that the equipment is satisfactory for the intended study.

Deep-Well Disposal of Noble Gases

An evaluation of the feasibility of deep-well injection as a means of disposing of fission product noble gases released in fuel reprocessing is being organized. The evaluation will cover three possibilities: (1) disposal as a gas or a solution in abandoned oil and gas wells, (2) underground disposal as a gas, and (3) storage in a deep well as an aqueous or non-aqueous solution. The investigation of solution storage will be the main effort of the project. Because of the diversity of disciplines needed to properly make this assessment, contract arrangements are being made to obtain the help of a consulting firm with a staff experienced in geological engineering, chemistry, nuclear science, and engineering economics.

Supporting Effort for the Environmental Impact Study of Waste Management

An environmental impact statement being prepared by a number of contractors for ERDA addresses the effect of waste treatment operations associated with reactors and the post-fission end of the light water reactor (LWR) fuel cycle. The ANL task in this study is to define the characteristics of the primary waste forms to be expected from LWRs, spent fuel storage basins, fuel reprocessing plants, and mixed oxide fuel fabrication plants. A first draft of this waste characterization section was submitted to the coordinator of the study, Battelle-Pacific Northwest Laboratories on September 2, 1976; a revision reflecting the needs of other task groups for waste information was distributed on October 18, 1976.

Current work consists of (1) supplying to other task groups additional details on expected waste properties and (2) re-expressing the waste characteristics in a standard format--radioactivities as fractions of the values in reference tables. The reference tables consist in most cases of amounts of radioactivity per unit quantity of spent fuel from ORIGEN calculations.

I. SALVAGE OF ALPHA-CONTAMINATED METALS (M. Seitz* and T. Gerding)

A. Introduction

Nuclear operations involving direct or suspected contact with trans-uranium elements generate waste streams that, because of existing and proposed regulations, require special treatment. The metals (contaminated with plutonium and americium) that are generated by equipment replacement and the decommissioning of process facilities constitute a large volume of this waste stream. Further, detection of very low levels of contamination in convoluted metallic waste is not feasible. The purpose of the present study is to demonstrate a method of cleaning and assaying for contaminated metals (predominantly mild steel and stainless steel) aimed at more efficient disposal or even recycle of the metals. Prior work on this topic has been reported in previous reports [STEINDLER-1975].

The contaminated metals exist in various forms and with various levels of plutonium contamination. The origin of the metals is obsolete equipment and tools and scrap from operations such as fabrication and reprocessing of nuclear materials. The quantity of material is extensive and increasing. In one study [STEINDLER-1974], it was estimated that $6.5 \times 10^4 \text{ m}^3$ of contaminated equipment was stored at one facility operated by the U.S. Energy Research and Development Administration.

Under a proposed federal regulation [FEDERAL REGISTER], material that is contaminated with plutonium in excess of 10 nCi/g cannot be disposed of in commercial burial facilities but must be stored in a retrievable fashion. Costs are incurred in proportion to the length of time the retrievable storage facilities are maintained. Retrievable storage in any case is thought of as only a temporary repository for transuranic-contaminated metals. A more permanent solution involving decontamination, contaminant fixation, or both is required.

Some transuranic-contaminated metals may meet proposed federal requirements for commercial burial with no decontamination step. In addition, chemical and mechanical surface cleaning offers a possible method of reducing plutonium levels of some of the remaining contaminated metals. However, the uncertainties associated with measuring low levels of plutonium on irregularly shaped objects preclude reliable assay.

In previous work [LEVITZ-1976], literature surveys of decontamination methods for metals and an inventory of existing plutonium-contaminated metals revealed a need for a process to reduce the volume of contaminated metals and provide material that is easily assayed. Therefore, a method is desired of converting the material to standard homogenized forms, as well as decontaminating the material. Melt-refining techniques were selected to achieve these objectives. These techniques are feasible for the large-scale processing required to handle the quantities of presently existing contaminated metals.

* Materials Science Division, Argonne National Laboratory

The work performed this quarter was part of an experimental program to determine the chemical behavior of plutonium in melt-refining processes, using different experimental conditions with various metals and slags.

B. Experimental Techniques

Steels, plutonium oxide-ameridium oxide, and slag were loaded into an alumina crucible, as depicted in Fig. 1. One of the following metals was

Fig. 1. Metal and Slag Prior to Melting

used in each experiment: a cold-rolled mild steel (analysis: Fe >99%, C 0.08-0.23%, P 0.24%, Si 0.03%, Mg <0.001% by weight), 304 stainless steel, and nickel-200. The oxide consisted of 83.81 wt % plutonium (isotopic composition: ^{238}Pu 0.050%; ^{239}Pu 86.46%; ^{240}Pu 11.84%; ^{241}Pu 1.48% by weight) and 0.528 wt % ^{241}Am . The slags were glasses, industrial slags from steel-making processes, or were constituted by fusing mixtures of metal oxides.

As seen in Fig. 1, the plutonium oxide was contained in a cavity in the steel sample, with a metal plug to restrict its accessibility and to simulate contamination in cracks or embedded on wear surfaces of metals. The furnace was loaded either with one relatively large crucible (100-ml capacity) containing about 200 g of metal or with three small crucibles (5-ml capacity), each containing about 10 g of metal.

Two experiments (experiments 113 and 115) were performed in which the plutonium was introduced differently from the way depicted in Fig. 1. Experiment 113 was used to examine whether staged extraction (*i.e.*, successive decontamination steps) produced a cleaner steel ingot; it employed clean slag along with steel that had been previously decontaminated by melt-refining. Experiment 115 was performed to determine whether plutonium would enter the metal from the slag; it employed clean steel with contaminated slag.

The furnace contained dry helium at a pressure of ~ 400 mm Hg (5.4×10^4 Pa) during each experiment. The contents of the crucibles were melted in a tungsten-mesh resistance furnace by maintaining furnace power for 1 to 2 hr during which time the temperature was approximately 1500°C . The appearance of the metal and slag after cooling and solidification is shown schematically in Fig. 2. The crucibles often cracked, probably during cooling due to differential thermal contraction of the crucible, metal, and slag.

Fig. 2. Crucible and Contents after Melting and Resolidification

The slag was bound to the crucible and had to be fractured to obtain samples free of crucible material for analysis. The ingot easily separated from the crucible but generally had fragments of slag adhering to it. Each metal ingot was cut into five sections as shown in Fig. 3. The slags and the top, middle, and bottom metal samples were analyzed by chemical dissolution and radiochemical counting techniques.

Fig. 3. Ingot Sectioning

Chemical analyses of massive samples (~ 10 g) are useful for determining the average plutonium concentrations in bulk material but do not identify how plutonium is actually associated with the metals and slags. Consequently, two methods (described in detail below) were used to reveal the microdistribution of transuranic elements in the solid phases. An autoradiographic technique, sensitive to alpha particles, was used to obtain representations of the plutonium and americium distributions in the metals and slags. The technique is adaptable to high or low alpha activities simply by adjusting the exposure time. In addition, a neutron-activation technique was employed that recorded fission particles from neutron-fissioned isotopes. The technique is highly sensitive to plutonium, and there is little interference from other elements in these analyses.

1. Autoradiographic Analysis

In the alpha-radiographic technique, cellulose-nitrate plastic (Kodak-Pathe, LR 115, Type II) was used for the registration of alpha particles. The paths of the alpha particles were etched by use of a sodium hydroxide solution; a microscope was used to view alpha tracks and hence the distribution of plutonium and americium within the samples. The technique has been determined to be sensitive to ~ 2 ppb ^{239}Pu concentrations when the exposure time is 1 week. Based on the specific activities of the nuclides in the americium-bearing plutonium oxide mixture used, it is calculated that 77.3% of the alpha activity is from plutonium and 22.7% is from americium. Measured alpha-track densities in the plastic, reduced by 23% to adjust for the contribution of americium, were used to calculate plutonium concentrations (based on an alpha-particle range of $11.3\text{ }\mu\text{m}$ in steel and an efficiency of 25% for registration in plastic of alpha disintegrations from a $11.3\text{ }\mu\text{m}$ thickness of steel).

The range in steel was calculated from the range of 5.14-MeV alpha particles in air, using the Bragg-Kleeman relationship of ranges in materials of different atomic weights. The efficiency of registration was determined by calculating the fraction of alpha particles that originated within the range of the surface of the metal and crossed that surface.

This treatment assumes that the alpha tracks are etchable within the plastic along their full length and that the etching rate of tracks (v_T , in m/s) is larger than the general attack rate of the plastic surface (v_G). This treatment is consistent with experimental observations that (1) tracks emanating from a highly radioactive plutonium particle are immediately adjacent to the particle, as well as several micrometers away, indicating that the tracks are etched independently of the energy of the particle and (2) the tracks are narrow right cylinders, indicating that $v_G/v_T \ll 1$ [FLEISCHER]. Measured maximum track lengths are short, ranging from ~ 5 to $9.2\text{ }\mu\text{m}$, as compared with a calculated alpha range of $\sim 35\text{ }\mu\text{m}$ in cellulose nitrate. The track lengths appear to increase with increased etching time with no measurable increase in the track density, indicating that the tracks are not etched to their full "etchable" length.

An alternative behavior suggested by the short tracks but not consistent with other etching characteristics is that the tracks are only etchable at the end of their range, where the energy loss rate is high. With this behavior, a shorter maximum track length and a lower efficiency (estimated to be a $9.2\text{-}\mu\text{m}$ maximum track length and a 20% efficiency based on estimated track lengths) would be used to calculate plutonium concentrations, resulting in plutonium concentrations 50% higher than those reported here. While this is an unlikely possibility, it cannot be eliminated. However, because the plutonium concentrations measured are generally used in this work in a comparative manner to detect variations over several orders of magnitude, more detailed study of the analyses is not warranted.

The americium concentration may be determined from the measurements by multiplying the plutonium concentration by 0.0063. This treatment assumes that there has been no chemical fractionation of plutonium and americium.

Although the alpha particles from ^{241}Am are more energetic than most of the alpha particles from the plutonium and produce tracks of greater length, it is not possible to distinguish the two elements from the radiographs alone because the tracks are not etched to their full lengths in these analyses. Chemical fractionation of plutonium and americium may be recognized from discrepancies in plutonium concentrations determined by alpha radiographs and by neutron activation. No discrepancies have been noted in measurements performed to date. Hence chemical fractionation, if present, is not large.

2. Neutron-Activation Analysis

In neutron activation analysis, the distribution of plutonium is mapped by inducing fission of plutonium and stopping the fission fragments in a solid detector that is in direct contact with the sample. The detector is then etched to reveal fission tracks and is viewed with an optical microscope. The distribution of the fission tracks corresponds to the distribution of plutonium within the sample.

The detectors are located between two samples as shown in Fig. 4. They maintain their position with respect to the samples during irradiation. Sheets of muscovite are used as the fission-fragment detectors and after exposure to fission fragments are etched in HF (48% HF, for 12 min at 26°C).

Fig. 4. Arrangement of Samples and Detectors for Neutron-Activation Analysis

Normally, a glass containing a known concentration of ^{235}U is included as a dosimeter sample [SEITZ] and the plutonium concentration is determined by the ratio of track density of the sample to that of the standard glass. The plutonium isotopes 238, 239, and 241 have significant cross sections for thermal neutron fission (17, 746, and 1025 barns, respectively) [HUGHES]. The average fission cross section is 660 barns for plutonium having the isotopic composition used in these experiments. The plutonium concentration, C_{Pu} , of the sample is given by the formula

$$C_{\text{Pu}} (\text{ppm}) = \frac{\delta_{\text{sample}}}{\delta_{\text{std}}} \times C_{\text{std}} (\text{ppm}) \times \frac{\sigma_f(\text{U})}{\sigma_f(\text{Pu})}$$

where δ_{sample} and δ_{std} are track densities for the sample and the standard glass, respectively, C_{std} is the concentration of ^{235}U in the standard [CARPENTER-1972], and $\sigma_f(\text{U})$ and $\sigma_f(\text{Pu})$ are the thermal neutron fission cross sections for ^{235}U and the plutonium, respectively [$\sigma_f(\text{U}) = 580$] [HUGHES].

This treatment assumes that the ratio of effective fission cross sections for uranium and plutonium is equal to the ratio of cross sections for thermal neutrons, an assumption that is not valid if a large fraction of the neutrons from the reactor are nonthermal. Fission of ^{241}Am is negligible, being $\sim 2.5 \times 10^{-5}$ that of plutonium. The treatment also assumes that the ranges (in kg/m^2) of fission fragments from ^{235}U and plutonium in glass and steel are the same, an approximation valid to $\sim 30\%$ or better. Because measured plutonium concentrations in different samples are used in a comparative manner, no effort will be made to refine the treatment to reduce any systematic error. The numbers of tracks within areas were counted to determine the track densities, δ_{sample} and δ_{std} , for the samples and standard glass. When the tracks were uniformly distributed, as in the standard glass, an area was selected that gave a sufficient number of tracks for the statistical accuracy desired. For nonhomogeneous track densities, an area was selected that was representative of the material being measured. This was done by moving the detector under the microscope and counting the tracks in fields of view at random intervals. The statistical accuracy of the measurements depended upon the number of tracks counted, as well as on the distribution of tracks in the detector, because the tracks were clustered. A sufficient number of tracks were counted in many instances so that any statistical inaccuracy was due primarily to nonhomogeneities in plutonium distribution.

Because the fission track method analyzes material at or near the surface of a sample, it is sensitive to surface contamination (which may be a result of cross contamination). With very high partitioning coefficients between steel and slag (in excess of 10^6), cross contamination of the steel with even traces of slag is of concern.

The presence and extent of surface contamination may be determined in several ways. One useful method is to measure the track densities from the epoxy of the metallurgical mount. The epoxy is free of fissionable isotopes (< 0.002 ppb ^{235}U equivalent) and is not a source of fission tracks. If cross contamination occurs after mounting in epoxy (e.g., during sample preparation such as by grinding and polishing), tracks from contaminants will be seen on the epoxy.

C. Experimental Conditions and Results

Table 1 lists the conditions for experiments performed with "contaminated" mild steel, and Table 2 lists the conditions for experiments with nickel and stainless steel. In the experiments with mild steel, the amount of slag and its composition were varied to determine the effect on the cleanup

Table 1. Experimental Conditions Used to Melt-Refine Plutonium from Mild Steel. Reaction temperature: $\sim 1500^{\circ}\text{C}$

Experiment Number	Weight of Steel, g	Weight of Pu, mg	Steel Contamination, ppm Pu ^a	Slag Material	Weight of Slag, g	Slag/Steel Weight Ratio	Time at Temperature, hr
53	204	82	400	none	none	----	1
73	204	92	450	CaSiO ₃	10.0	0.049	1
76	197	83	420	CaSiO ₃	22.5	0.11	1
78	203	82	400	CaSiO ₃	41.7	0.20	1
80	205	87	420	B ₂ O ₃ Glass ^b	20.4	0.10	1
82	206	89	430	B ₂ O ₃ Glass	39.9	0.19	1
101	206	83	400	CaMgSi ₂ O ₆	20.0	0.10	1
103	205	93	450	Ca-Al silicate ^c	20.1	0.10	1
105	205	83	400	Hearth Slag ^d	20.7	0.10	1
107	205	83	400	Ca-Al silicate	20.1	0.10	2
109	209	85	410	B ₂ O ₃ Glass	20.1	0.10	2
111	203	87	430	B ₂ O ₃ Glass	40.0	0.20	2
113	240	0.03 ^e	~ 0.1	B ₂ O ₃ Glass	20.1	0.084	1
115	207	59	280	B ₂ O ₃ Glass	19.9	0.096	1
121a	12.2	5.0	410	B ₂ O ₃ Glass	1.29	0.10	1
121b	11.4	99.7	8750	B ₂ O ₃ Glass	1.31	0.12	1
121c	12.0	164	13700	B ₂ O ₃ Glass	1.27	0.11	1
124a	11.8	7.8	660	CaMgSi ₂ O ₆	2.20	0.19	1
124b	13.1	93	7100	CaMgSi ₂ O ₆	1.94	0.15	1
124c	13.2	189	14300	CaMgSi ₂ O ₆	1.96	0.15	1

^aWeight ratio of plutonium charged to mild steel.

^bNominal composition of B₂O₃ glass is 81.0% SiO₂, 13.0% B₂O₃, 4.0% Na₂O, 2.0% Al₂O₃, and 0.5% K₂O by weight.

^cCa-Al silicate is a commercial blast furnace slag with minor amounts of Mg, Ti, V, and Mn and possibly Fe as determined by microprobe analysis. Gehlenite crystal (Ca₂Al₂SiO₇) with some ackermanite (Ca₂MgSi₂O₇) were detected by X-ray diffraction.

^dHearth slag is a commercial open hearth furnace slag containing CaFeSiO₄ crystal and melilite (solid solution of gehlenite and ackermanite) with a minor amount of α -SiO₂, as determined by X-ray diffraction.

^eThe weight of plutonium was calculated from the measured plutonium concentrations of the steel (from experiments 80 and 82) used in staged extraction experiment 113.

Table 2. Experiments to Melt-Refine Plutonium from Nickel and Stainless Steel^a

Exp. Number	Metal	Weight of Metal, g	Weight of Pu, mg	Metal Contam., ppm Pu	Weight of Slag, g	Slag/Metal Weight Ratio
117	Nickel	222.1	82	370	20.2	0.091
119	304 Stainless Steel	190.8	85	445	19.9	0.10

^a Reaction temperature, 1500°C. Time at temperature, 1 hr. The slag material was borosilicate glass.

of metal. The metal contamination was held at about 400 ppm by weight for most experiments but was increased to as high as ~14,000 ppm in experiments 121 and 124 to determine the effects of higher levels of plutonium on the melt-refining process.

After melting and solidification, the slag was often a transparent glass of uniform coloration. The ingots had shiny surfaces, varying from smooth to pitted with voids or slag inclusions. The experiments of one-hour duration with borosilicate glass (experiments 80, 82, 113, and 115) resulted in slags with marbled coloration. The final slag from the one-hour run with Ca-Al silicate (experiment 103) consisted of several dark spherules embedded in a greenish transparent glass. Experiment 119 with stainless steel produced a slag having two distinct colors.

The plutonium and americium analyses obtained by chemical dissolution of the samples and radiochemical counting are given in Table 3. The analyses available thus far indicate extensive fractionation of the plutonium to the slag. Generally, the center sections of the ingots showed lower actinide concentrations that did the tops or the bottoms, suggesting that significant amounts of plutonium and americium may be associated with the surface of an ingot. Some metal samples had plutonium concentrations lower than the 10 nCi/g (~0.1 ppm plutonium) level currently used to define transuranic-contaminated wastes. The low plutonium levels were achieved without special treatments (such as trimming or electropolishing of the ingot surface) to separate slag from metal.

Alpha radiographs were made of metal samples cut from ingots in the manner depicted in Fig. 3. The radiographs showed that the alpha activity was predominantly on the perimeter and associated with slag material either on or near the surface of the ingot. All ingots analyzed showed this effect. As determined from the radiographs, plutonium also occurred in the interior of some ingots and, where present in concentrated form, was associated with visible defects. The plutonium was found to be in patches, which were often grouped in isolated areas and constituted most of the plutonium in the steel matrix. Occasionally, a point source of high alpha activity appeared in an area of the steel having no observable defect. Photomicrographs showing alpha activity at the surface of ingots and at visible defects are given in Fig. 5. Plutonium at the metal surface or in visible defects accounted for most (>99%) of the plutonium associated with the metal.

Table 3. Melt-Refining of Plutonium from Mild Steel--Analytical Results for Bulk Samples^a

Exp. No.	μg Actinide/g Steel After Melting							Fraction of Initial Pu in Slag
	Top		Middle		Bottom		Slag	
	Pu	Am	Pu	Am	Pu	Am	Pu ^b	
53	Very High	Very High	1.03	1.47×10^{-4}	0.77	5.3×10^{-3}	----	-----
73	6.4	4.9×10^{-2}	0.54	1.1×10^{-4}	0.27	4.8×10^{-5}	4.78×10^3	0.52 ^c
76	20.0	0.15	0.26	1.61×10^{-3}	9.0×10^{-2}	4.5×10^{-4}	2.69×10^3	0.74
78	7.56	7.6×10^{-2}	6.5×10^{-2}	3.5×10^{-4}	0.12	9.3×10^{-4}	2.06×10^3	1.05
80	2.9×10^{-2}	3.8×10^{-5}	0.22	2.0×10^{-3}	1.7×10^{-2}	2.5×10^{-5}	4.04×10^3	0.95
82	6.0×10^{-2}	$<1 \times 10^{-6}$	4.1×10^{-2}	$<1 \times 10^{-6}$	0.32	1.8×10^{-3}	1.96×10^3	0.88
101	21.0	0.1	0.18	1.8×10^{-4}	0.69	1.8×10^{-3}	N/A	-----
107	1.6	0.20	0.10	2.6×10^{-4}	0.09	2.7×10^{-4}	N/A	-----
109	2.0×10^{-3}	$<1 \times 10^{-6}$	1.2×10^{-3}	$<1 \times 10^{-6}$	3.1×10^{-3}	$<1 \times 10^{-6}$	N/A	-----
111	5.0×10^{-3}	$\approx 1.6 \times 10^{-6}$	9.6×10^{-3}	$\approx 5 \times 10^{-5}$	2.0×10^{-1}	2.5×10^{-3}	N/A	-----
113	1.7×10^{-3}	$<1 \times 10^{-6}$	1.1×10^{-3}	$<1 \times 10^{-6}$	2.3×10^{-3}	$<1 \times 10^{-6}$	N/A	-----
115	1.9×10^{-3}	$<1 \times 10^{-6}$	2.8×10^{-3}	$<1 \times 10^{-6}$	5.7×10^{-3}	$<1 \times 10^{-6}$	N/A	-----

^aAnalyses by aqueous dissolution and radiochemical determination.

^bAnalysis based on μg Pu/g slag. N/A indicates the sample was not analyzed.

^cBecause a portion of this sample was lost during analysis, the reported value (0.52) is lower than the real value.

Fig. 5. Alpha-Radiographs of Samples from Steel Ingots. Alpha tracks appear dark in transmitted light. (a) Alpha activity from inclusions at the ingot surface can be seen at the upper left, and low activity from the metal at the lower right. The curved boundary is along the surface of the ingot. (b) Region of high alpha activity from visible defects within ingot. The scratch is a fiducial mark approximately at the ingot surface.

Large areas of the interior of the steel, with the exceptions stated above, were found to be low in alpha activity. After exposure for several days to plastics, no alpha tracks were found at the interior of some samples, and hence only upper limits to the plutonium concentrations could be determined. The concentrations of plutonium determined from alpha radiographs of the steel matrices which were devoid of silicate inclusions or other visible defects are given in Table 4. Except for the nickel sample (experiment 117), all metal samples generally have concentrations below 10 ppb plutonium, with some samples well below 1.0 ppb. Because several different compositions of slag were used in the experiments, the results in Table 4 indicate that plutonium extraction by melt refining is not strongly dependent upon slag composition within the range of compositions explored in these experiments. The counting error is given for data in Table 4 when it is believed to be the effect that limits the precision of the measured value.

The neutron activation analysis performed in this program has a much higher sensitivity than either radiochemical analyses or alpha-track counting and is particularly useful for examining the concentrations and distribution of plutonium at the low levels found in the steel matrix. Neutron activation analyses were performed on small (approximately 1-cm by 2-cm) slabs of the metal. A metal sample was usually taken along the radius and included material from the center to the surface of an ingot. The fission-track maps made by neutron activation generally showed high fission-track densities from tiny bits of slag that adhered to the surface of the metal samples. In comparison, relatively few fission tracks were generated in the bulk steel. The tracks from the steel were clustered, indicating localized concentrations of plutonium. Photomicrographs showing fission tracks from plutonium associated with the metal ingots are given in Fig. 6.

The types of plutonium associations seen with the metal ingots from alpha radiographs and from neutron activation analysis are depicted in Fig. 7. The sizes of "plutonium-amerium" particles near the metal surface were calculated from the number of tracks in a star, using the neutron fission cross section and the measured neutron fluence. The dispersed plutonium-amerium particles contained $\sim 2 \times 10^9$ atoms plutonium, and the clusters of plutonium throughout the metal matrix ranged from $\sim 10^5$ to $\sim 8 \times 10^6$ atoms of plutonium per cluster in all experiments. Differences in cluster size were seen between experiments, however (*e.g.*, clusters in metal from experiment 109 varied from a lower limit to $\sim 1 \times 10^6$ and in experiment 109 from a lower limit to $\sim 8 \times 10^6$).

In Table 5, the plutonium concentrations determined from fission-track densities are given and are consistent with the very low concentrations of plutonium determined by alpha radiography. The origin of the variations in the concentration of plutonium in metals from different experiments is not apparent. For example, the plutonium concentration in metal from experiment 109 is lower by about a factor of 10 than in metal from experiment 111. These experiments were performed with similar weights of steel and plutonium but with about half as much slag being used in experiment 109 as in experiment 111 (20 g *vs* 40 g). The metal from experiment 111 would therefore be expected to have a lower contamination if a constant partitioning ratio between slag and steel was assumed. Possibly, a partitioning coefficient that is sensitive to experimental parameters such as temperature or trace

Table 4. Plutonium in Metal Samples
Analyzed by Alpha Radiography

Exp.	Sample	Concentration of Plutonium, ^a ppb
53	Mid Top	<2.4
73	Mid Top	<2.4
76	Mid Top	<2.4
78	Mid Top	<2.4
80	Mid Top	<3.5
82	Mid Top	<2.0
101	Top	1.2
107	Top	2.9
	Bottom	1.3
109	Top	0.4 ± 0.1
	Center	0.4 ± 0.1
	Bottom	0.4 ± 0.1
111	Top	3.4 ± 0.3
	Center	3.0 ± 0.3
	Bottom	5.5 ± 0.5
113	Top	0.02 ± 0.02
	Center	0.06 ± 0.03
	Bottom	0.09 ± 0.04
115	Top	0.04 ± 0.04
	Center	0.08 ± 0.04
	Bottom	0.07 ± 0.04
117	Top	26 ± 1
	Bottom	39.3 ± 0.4
119	Top	2.5 ± 0.4
121a	Top to Bottom	0.6 ± 0.1
121b	Top to Bottom	5.9 ± 0.4

^aPlutonium concentrations were determined in the metal matrix but not at the surface of the ingot or within large visible defects. The errors associated with the concentrations were calculated from the total number of tracks counted, N . $\text{Error} = \text{Concentration} \times 1/\sqrt{N}$. The error thus represents a one sigma variation on a normal distribution. No error due to track clustering was calculated, but it may be significant.

(a)

(b)

(c)

Fig. 6. Fission Tracks in Muscovite from Metal Samples. (a) Micrograph showing track clusters from plutonium in metal corresponding to ~ 10 ppb Pu, experiment 111. (b) Micrograph showing high plutonium concentration along the surface of ingot (bottom, left to right) with few tracks from the metal matrix (upper) corresponding to ~ 0.5 ppb Pu, experiment 109. (c) High-magnification of a track cluster, showing individual tracks from plutonium fission.

Table 5. Plutonium in Metal Samples--Neutron Activation Analysis

Exp No.	Sample	Pu Concentration, ppb	Comments
101 ^a	---	1.8	Plutonium was concentrated in clusters in metal matrix. Very high fission-track densities from the ingot surface correlate with tiny glass fragments adhering to metal. The concentration is consistent with that measured by alpha radiography.
107 ^b	Top	---	The track density in clusters was too high to resolve for an accurate plutonium measurement. The density is consistent with the plutonium concentration measured by alpha radiography.
109 ^b	Top	0.5	Plutonium is in resolvable clusters.
111 ^b	Top	---	Track density in clusters too high to resolve. Reliance on estimates of plutonium concentration by alpha radiography.
113 ^b	Top Interior	0.2 to 5.5	Pu finely distributed in small clusters and in aligned patterns in some areas; contamination from sample preparation is probable.
	Epoxy, adjacent to steel sample	0 to ~10	Highly variable concentrations. Obvious contamination.
115 ^b	Steel, Top Interior	4.1	Pu in clusters.
	Epoxy	~5.4	Average Pu concentration. Pu occurs in clusters. High track densities at small bubbles in epoxy. Obvious contamination.
Blank ^a	Uncontaminated Steel	<0.01	

^a Sample was activated with a thermal neutron dose of 8.1×10^{19} neutrons/m².

^b Sample was activated with a thermal neutron dose of 6.1×10^{20} neutrons/m².

Fig. 7. Types of Plutonium Associations Identified in Melt-Refining Metal

impurities may be responsible for the observed behavior. In any case, it appears on the basis of the experimental results that increasing the slag to metal weight ratio does not necessarily result in improved decontamination of the metal. Samples 113 and 115 were cross-contaminated during sample preparation, as evidenced by the readily detectable plutonium associated with the epoxy of the mounts.

Analyses by radiochemical counting of dissolved metal samples (Table 3) are expected to show higher plutonium concentrations than are seen in the metal matrix by alpha- and fission-track analyses because the former includes plutonium from the surface and from ingot defects as well as plutonium from the metal matrix. The plutonium content determined by radiochemical counting is sometimes greater than autoradiographic analyses of the metal matrix (Table 3) by as much as a factor of 10^4 , presumably due to this effect (see samples 73, 76, 78, 80, 82, 101, and 107). This large difference emphasizes the importance of obtaining a metal product that is free of large plutonium-bearing defects and is low in slag material in order to attain maximum benefit from the melt-refining process.

Other samples are found to be low in plutonium by both radiochemical counting and radiographic techniques, indicating that the samples had no defects containing plutonium and had few surface inclusions. This is the case for some samples from experiments 80 and 82 and for all samples from experiments 109, 111, 113, and 115.

Alpha radiographs were also made to determine the distribution of plutonium in slag and crucible samples. The radiographs indicate high plutonium concentrations in all slags radiographed. Thin layers of slag, rich in plutonium, were found to separate the sides and bottoms of ingots from the crucibles. Slag fragments of uniformly blue glass contained homogeneous distributions of plutonium. In slag of marbled coloration (*e.g.*, from 1-hr experiments using a borosilicate slag), concentrations of plutonium varied locally.

Zones where slags had reacted with crucible material were observed in cross section. In the reaction zone (*i.e.*, the narrow band between the slag and the crucible), the plutonium concentration would decrease nearer the crucible. Slivers of material depleted in plutonium were seen parallel to the crucible, indicating an undercutting and floating-off of the crucible wall material. Results of analyses of the slags, along with comments, are given in Table 6.

Table 6. Plutonium Distribution in Slags--Alpha Radiographic Analyses

Exp No.	Sample	Comment
107	Slag, light and dark colored	Uniform concentration of plutonium throughout slag.
113	Slag	Pu concentrations correlate with blue-grey portions of marble-colored glass. ~160 ppm Pu average concentration glass.
115	Slag	Dark-colored clear glass with opaque glass above it. Both layers show uniform, high concentrations of Pu, ~2000 ppm. Slag near the crucible contains strips that have low Pu concentrations and that may be crucible material that was undercut from the wall. A small amount of floating material on the top edge of the opaque glass is higher in alpha activity than the remainder of the glass but represents only a minute fraction of the total alpha activity of the slag (<0.1%).
119	Slag, different colorations	High plutonium concentrations in the alumina-rich silica-deficient phase. Low plutonium concentrations in the alumina-deficient, silica-rich phase.

Experiment 113 was performed with steel from previous experiments (experiments 80 and 82) and clean borosilicate glass. In experiment 113, approximately equal amounts of steel from experiments 80 and 82 were used; the steel was that adjacent to the middle sections (for which analyses are given in Table 3). The slag was found to contain 160 ppm plutonium (Table 6), a result that is in significant disagreement with the calculated value of 1.5 ppm based on plutonium concentrations in the steel (measured by radiochemical counting). The unexpectedly high plutonium concentration observed in the slag may have resulted from inclusions in the steel from experiments 80 and 82 (the total amount of plutonium in the inclusions would have to equal 5% of the total plutonium used in either of the initial experiments). Slag from previous experiments that adhered to the steel surfaces is not a probable source of plutonium since one gram of slag from

experiment 80 or two grams of slag from experiment 82 would have been required to account for this quantity of plutonium in the slag from experiments 113.

The results of experiment 113 do, however, indicate a significant benefit to staged extraction. The concentration of plutonium in the slag suggests that a strong partitioning of plutonium to the slag occurred and, as a result, decontamination of the steel. Low concentrations of plutonium in the bulk samples of steel (Table 3) point to staged extraction being an efficient decontamination step.

Slags from experiments 107 and 119 each contained two materials of distinctly different colors; this suggests the coexistence of two silicate phases in the slag. However, the plutonium distributions in the two slags were different; slag from experiment 107 had a uniform concentration of plutonium, and slag from experiment 119 had distinct Pu-rich and Pu-absent areas that corresponded to the two apparent phases.

These two slags were studied with an electron microprobe to determine which silicate phases were present and to gain an understanding of the behavior of the plutonium in these phases. The slag from experiment 107 was found to be homogeneous, with no detectable variations in major or minor element composition in the slag. It is concluded that the slag consisted of a single liquid phase having a uniform plutonium distribution despite differences in coloration. The slag from experiment 119 (in which stainless steel was melt-refined with borosilicate glass) was found to consist of two phases; their different chemical compositions corresponded to the areas distinguished on the basis of color and plutonium concentration. The phase having the higher concentration of plutonium is high in alumina and low in silica in comparison to the phase having the lower concentration of plutonium. The high-plutonium phase also has detectable quantities of potassium and sodium, which are absent from the low-plutonium phase. Minor amounts of iron and chromium, presumably from the stainless steel, are found in both phases, with the chromium concentration being higher in the alumina-rich phase.

The process by which these two phases originate from a homogeneous glass may be due to liquid immiscibility which occurs, for example, in the sodium borosilicate system. Possibly, similar immiscibility exists in the more complex system employed here, and the high-silica and high-alumina phases may separate upon cooling. During the formation of phases, plutonium remained almost entirely with the phase high in alumina along with the alkali metals, sodium, and potassium. This suggests that plutonium, as well as other large ions, may be more compatible with a slag having a lower silica concentration than with the borosilicate glass used in these experiments.

D. Conclusions and Plans for Future Work

Plutonium is seen to fractionate strongly into the silicate liquid phase in preference to liquid steel. More than 99.9% of the plutonium is extracted from the steel and retained by the slag. Incomplete separation of the silicate slag from the steel is the major source of activity in the ingots. The second most important source of activity in the steel is plutonium at

visible defects in the ingot and plutonium at points in the steel without visible defects ($\sim 2 \times 10^9$ atoms Pu/point). There is a small amount of plutonium throughout the ingot in the form of tiny clusters ($\sim 10^5$ to $\sim 8 \times 10^6$ atoms/cluster). These results indicate that a high degree of decontamination can be obtained by limiting the amount of slag carried with the steel and eliminating the formation of visible defects in the ingot. The process does not appear to be limited by the chemistry of plutonium oxide in metal-slag systems.

Plutonium throughout the ingot in the form of small clusters may be precipitates produced upon slow cooling of the metal ingot. This is suggested by the uniform average concentration of plutonium in molten steel that would occur as a result of precipitation under near-equilibrium conditions. Verification that the plutonium-bearing clusters are precipitates is important because it would suggest a mechanism for dispersion of plutonium in the steel, generating a metal of uniform composition for assay.

Because of the low concentrations of plutonium in melt-refined metal, equilibrium partitioning coefficients of plutonium between silicate slag and metal [(concentration in slag) $\div$ (concentration in metal)] are equal to about 2.0×10^6 for mild steel. The partitioning coefficient for stainless steel was estimated to be just as high. The partitioning coefficient of plutonium between slag and nickel was estimated to be considerably smaller than this ($\sim 5 \times 10^4$), although it may still be high enough for the process to be useful for decontaminating nickel.

In all experiments, the plutonium was strongly fractionated into the silicate phase. Although slags were noted to differ in appearance, ease of separation from the ingot, and so on, no large differences in the chemistry of the slags with respect to plutonium were observed. However, one slag was observed to have two distinct chemical phases as well as large variations in plutonium concentration, suggesting that a slag lower in silica content than the borosilicate glass (81% SiO_2 by weight) would have better extraction properties for plutonium.

Experiments have been initiated to define more closely the material balance and process variables. A conceptual process outline for a full-scale application of this technique will be developed to further identify the areas needing study.

II. DEVELOPMENT OF ADVANCED SOLVENT EXTRACTION TECHNIQUES (G. Bernstein, A. Siczek, B. Saunders)

A. Developments for the Processing of LWR Fuel

1. Introduction

A program was initiated at the start of this quarter to develop advanced solvent extraction techniques for Purex reprocessing of light water reactor (LWR) fuel. One feature of the program is the development of an improved centrifugal contactor design that can be adapted to a plant-scale multi-stage extractor system with a capacity of 10 Te/day of LWR fuel. The program is being carried out in cooperation with the Savannah River Laboratory (SRL).

The use of compact, centrifugal contactors, particularly in the first solvent extraction cycle, is desirable in order to reduce solvent damage due to irradiation and to reduce the amount of heavily shielded cell space. Based on earlier work [BERNSTEIN] at Argonne National Laboratory (ANL), Savannah River Plant (SRP) centrifugal contactors of modified design are being developed that are expected to be easier to maintain and less costly to fabricate.

The scope of this program includes design, construction, and testing of a full-scale centrifugal contactor to ensure operability under various plant conditions, the capability of remote maintenance, and adequate service life of critical components. Life and operational testing of the unit will result in a reference design for multi-unit banks of contactors that can be fabricated by commercial concerns thereby ensuring transfer of technology to industry. It is expected that cold testing of a bank of full-scale centrifugal contactors will be done at SRL in existing facilities suited for such work.

Along with the advantages of fast contactors, there are additional requirements of flow sheet performance that do not exist when, for example, pulse columns or mixer-settlers are used in a Purex process. Waste management considerations make it desirable to use nonmetallic reducing agents for the partition of plutonium and uranium. One of the leading candidates, hydroxylamine nitrate (HAN), has been briefly investigated to determine the rates of reduction of plutonium under a variety of conditions.

The kinetics of plutonium reduction will be studied in miniature contactors that are being designed and built as part of this program. The basic design features of the mini-contactors, and the plant-scale units will be similar to ensure that data obtained in these units can be safely extrapolated.

Processes in the Purex process other than the reduction of plutonium have also been identified as relatively slow compared with residence times in fast contactors. These processes, particularly the transfer of ruthenium and zirconium between solvent and aqueous acid, are important factors in the attainable decontamination of desired elements from fission products. Short residence contactors can be used to take advantage of the low rates of transfer of these troublesome fission products to improve the degree of their separation from uranium and plutonium.

The three basic elements of the program were initiated during this quarter: design of the 10 Te/day contactor, design of the minicontactor and a literature review of ruthenium and zirconium extraction data. Each of these items is described separately below.

2. Development of 10 Te/day Contactor (G. Bernstein)

A plant-scale centrifugal contactor is being designed which is based on the annular centrifugal contactor designed at ANL several years ago [BERNSTEIN, 1973]. The annular design is an outgrowth of the centrifugal contactor currently in operation at SRP [WEBSTER, 1967]. It retains the basic features of the SRP design, differing principally in the mixing mode employed.

In the SRP design, incoming aqueous and organic process streams are fed into a chamber where they are mixed by a paddle attached to the shaft that carries the separating bowl or rotor. The mixture is then discharged through a nozzle which delivers it to an orifice in the bottom of the rotor. The phases are separated by centrifugal force as they move up through the rotor and are guided by a weir system to separate discharge ports.

In the ANL design, the mixing chamber and paddle are eliminated and the process streams are fed into the annulus between the rotating bowl and casing where they are mixed as they flow downward toward the rotor inlet. This change simplifies the construction of the rotor assembly, making it lighter, shorter, and easier to dynamically balance.

In addition, remote maintenance is greatly simplified by making the rotor readily removable from the housing. In the SRP design, the mixing paddle is held captive in the mixing chamber so that removal of the rotor assembly requires disassembly of the housing. A complex drive shaft, spindle, and circumferential air seal on the shaft (for the air-controlled weir) are needed to permit remote replacement of a motor or spindle should the need arise. In the ANL annular design, the rotor is attached directly to a motorized spindle which has a hollow shaft. A simple rotary air seal is mounted at the top of the motor to admit air for control of the aqueous-organic interface in the weir system. The entire rotor-motor assembly can be removed and replaced without disturbing the contactor housing, thus greatly simplifying maintenance. The design is adaptable to commercially available components, a feature which should contribute to the reduction of fabrication costs.

Based upon a Purex solvent extraction process flow sheet provided by SRL, a capacity of about 250 L/min will be required for the contactors in a 10 Te/day plant. This is essentially the same size as the contactors currently operated at SRP [WEBSTER, 1967]. This unit requires a rotor 25 cm (10 in.) in diameter and a separating zone 36 cm (14 in.) long. The general configuration of the rotor and casing for the large-capacity annular contactor are shown in Fig. 8. A contactor this large cannot be critically safe for all concentrations of ^{239}Pu and ^{235}U . However, since the concentrations of these elements in LWR fuel are quite low (~ 1 g/L for ^{235}U and ~ 1 g/L for ^{239}Pu), any criticality risk would be the result of possible increases in plutonium concentration due to refluxing. The

Fig. 8. Annular Centrifugal Contactor (10 Te/day)

maximum attainable plutonium concentration under normal and abnormal process operations will be checked by computer codes for Purex processing, and criticality hazards will then be evaluated.

Calculations have been made of critical speed and power requirements and show that the required unit can be driven by a 5-hp (3.73 kW) motorized spindle at ~ 1800 rpm, which is well below its critical speed. Detailed design of this unit will be done after the fabrication and testing of a smaller unit of the same type, described in a later section (Section B. 2). In the meantime, specifications have been prepared and an invitation to bid has been issued to several manufacturers of precision motorized milling spindles.

3. Development of a Mini-Contactor (G. Bernstein)

A multistage miniature annular centrifugal contactor is being developed. This unit retains some of the general design features of the earlier SRL unit [JENNINGS, 1962] and the Hanford Engineering Development Laboratory (HEDL) unit [RICHARDSON, 1970]. The major changes are elimination of the separate mixer assembly, conversion of the separating rotor into a combination annular mixer and separator, and elimination of the bottom bearing on the separating rotor.

A single-stage mini-contactor is being fabricated to test the performance of the annular design in a small unit such as this. This contactor is being made with a stainless steel rotor (~ 2 cm diameter and ~ 3 cm long) that rotates in a methacrylate housing to permit observation of phase mixing in the annulus. The unit is calculated to have a capacity of about $100 \text{ cm}^3/\text{min}$ and, at that throughput, a residence time of ~ 2 sec in the mixing zone and ~ 4 sec in the separating rotor. Operation will be at about 3600 rpm.

The multistage mini-contactor that will be built next will be of all-stainless steel construction with eight stages arranged in a rectangular block. The rotors will be driven by a common motor, and their speed will be adjustable up to about 7000 rpm. The multistage unit will be designed for remote operation to permit tests with solutions containing plutonium and fission products. Provision will be made for the addition and removal of aqueous and organic phases at any stage. Eventually, several of the eight-stage banks will be operated together in tests designed to measure the kinetics of plutonium reduction and fission product extraction.

4. The Chemistry of Ruthenium and Zirconium in the Purex Process (A. Siczek)

a. Introduction

In the Purex separation process, the uranium and plutonium are coextracted into the organic solvent, tri-n-butyl phosphate (TBP), from nitric acid medium in the first solvent extraction cycle, while most of the fission products remain in the aqueous phase (raffinate). Potentially, complete separation can be achieved with the aid of multistage contactors.

However, two elements, ruthenium and zirconium, complicate the satisfactory decontamination of the products in the reprocessing of irradiated fuel by Purex solvent extraction [BROWN, 1958A]. These elements accompany the fissile materials (uranium and plutonium), get into the subsequent extraction cycles, and consequently into the low activity waste stream.

The inability to effect a complete separation of products from ruthenium lies in (1) the diversity of ruthenium compounds and their extraction coefficients, and (2) the sensitivity of equilibria between the compounds to even slight differences in extraction conditions.

Zirconium and its daughter, niobium, create difficulties because they are extracted to a higher degree by small quantities of radiolytic and hydrolytic degradation products of TBP (*e.g.*, di- and mono-butyl phosphate) and of diluents and are retained in the organic solvent.

The literature on ruthenium and zirconium compounds relevant to the Purex process is reviewed in this report.

b. Ruthenium

During the dissolution of irradiated nuclear fuel in nitric acid, the ruthenium passes into the aqueous solution in the form of various nitrate, nitro, and mixed nitro-nitrate complexes of trivalent ruthenium nitrosyl (RuNO^{+3}) as extraordinarily stable species. They are complexed with hydroxo- and aquo- ligands and have the general formula:*

The formation and interconversion reactions among these complexes are slower for complexes containing the nitro ligands than for complexes with nitrate groups [BROWN, 1960]; thus, slow reactions ($t_{1/2} = 1$ to 30 days at 20°C) characterize substitutions involving the nitro ligand. In contrast, reactions with nitrate ligands occur with a $t_{1/2} = 10$ to 60 min at 20°C . Once formed, however, nitro complexes show greater stability than their nitrate analogues.

In nitric acid solutions, the fractions of different nitrate complexes of RuNO^{3+} , $[\text{RuNO}(\text{NO}_3)_x(\text{H}_2\text{O})_y(\text{OH})_{5-x-y}]^{-2+y}$, will depend upon the nitrate ion concentration in the solution. The existence of tetra, tri-, di-, and mono-nitrate complexes has been established [FLETCHER-1955, WALLACE, SCARGILL-1965].

Pentanitrate complexes are not known, contrary to some earlier beliefs [FLETCHER, 1959].

* A prefix nitro- denotes the presence of the monovalent $-\text{NO}_2$ radical; a nitrate-compound contains the monovalent $-\text{NO}_3$ radical.

In presence of nitrous acid, the rather weakly bound nitrate groups on ruthenium nitrosyl can be slowly replaced with the more nucleophilic nitro groups and form nitrocomplexes or mixed nitro-nitrate complexes of ruthenium nitrosyl. Mono-, di-, tri-, and tetra-nitrocomplexes are known, but not penta-nitrocomplexes [BROWN, 1960, PICHKOV]. However, hexanitrocomplex of the RuNO^{3+} can be formed by treating ruthenium nitrosyls with KNO_2 [PICHKOV]. No nitro-nitrate complexes species with four ($\text{NO}_2^- + \text{NO}_3^- = 4$) nitro-nitrate groups have been found--only complexes with one type of ligand present [JOON, BROWN, 1960].

Under typical plant conditions (2 to 4M HNO_3 , 10^{-2} to 10^{-3} M HNO_2), 30 to 70% of the total ruthenium in the dissolver solution used as feed to the first cycle may be in the form of nitro or nitro-nitrate rather than nitrate complexes [SCARGILL, 1963]. It has been observed that nitrate complexes are generally about twice as extractable into the organic phase as nitro complexes.

Among the nitrate complexes of RuNO , tri- and tetra-nitrate complexes have been found to be the most extractable. Mono- and di-nitrate complexes have been reported not to be extracted readily.

In the case of the nitro complexes of RuNO , the dinitro complex is more extractable into the TBP phase than higher nitro complexes but even then its extraction coefficient is low [JOON]. As seen in Table 7, mixed nitro-nitrate species are more extractable than are nitro compounds.

To obtain the optimum conditions for ruthenium decontamination, the ruthenium complexes should be converted to less extractable forms by adjusting (1) acidity (concentrations of nitric acid and nitrous acid), (2) concentration of solvent, (3) temperature, and (4) aqueous-solvent contact time.

Since the maximum of D_{Ru} occurs at 0.5M HNO_3 [RUDSTAM, MARTIN], operating at higher concentrations of nitric acid seems to be desirable. Treatment with nitrous acid leads to improvement of ruthenium decontamination by as much as a factor of 50 in laboratory solutions (20% TBP, 0.5 to 1M HNO_3) because it converts nitrate species to much less extractable nitro complexes [SCARGILL, 1965].

An increase in the temperature of the extraction process leads to a decrease of the extraction coefficient, D_{Ru} [SCHLEA, ORTH-1963] as does diluting the TBP to 3% instead of 30% [ORTH-1965]. Reduction in residence time in the solvent extraction contactors seems to be promising [ORTH-1971] since in short-residence contactors, extraction of ruthenium is diffusion-controlled, not controlled by chemical equilibria.

c. Zirconium

The chemistry of zirconium is complicated by its ability to form coordination bonds and by the variety of different modes of bonding in the complexes formed [BAILAR]. In aqueous solutions, depending on the total zirconium concentration, the zirconium complexes may undergo hydrolysis and/or polymerization to produce polynuclear complexes of differing extractability. Hydroxopolymers of zirconium are extractable by TBP, whereas

Table 7. Extraction Coefficients of Ruthenium Nitrosyl Complexes

Expected Complex	Temp, °C	[HNO ₃], mol L ⁻¹	TBP, vol %	Diluent	[Ru], mol L ⁻¹	D _{Ru} ^a	Reference
dinitrato	20	1	21.0	Nysolin 160/200 ^b	<10 ⁻⁷	0.18	Rudstam
	20	1	30.0	Nysolin 160/200 ^b	<10 ⁻⁷	0.22	Rudstam
	20	1	31.2	Nysolin 160/200 ^b	<10 ⁻⁷	0.39	Rudstam
	20	1	40.9	Nysolin 160/200 ^b	<10 ⁻⁷	0.54	Rudstam
	20	1	50.0	Nysolin 160/200 ^b	<10 ⁻⁷	0.63	Rudstam
dinitrato	0	1	30	kerosene	10 ⁻³	12.5	Brown, 1958A
	0	3	30	kerosene	10 ⁻³	0.5	Brown, 1958A
trinitrato	0	1	10	kerosene	~10 ⁻⁴	11.0	Fletcher 1965A
	0	3	15	kerosene	~10 ⁻⁴	0.9	Fletcher 1965A
	0	3	20	kerosene	~10 ⁻⁴	1.5	Fletcher 1965A
	0	4	30	kerosene	~10 ⁻⁴	0.95	Fletcher 1965A
	0	3	30	kerosene	~10 ⁻⁴	3.5, 2.6	Fletcher 1965A
trinitrato	20	1	10.0	Nysolin ^b	<10 ⁻⁷	2.4	Rudstam
	20	1	21.0	Nysolin ^b	<10 ⁻⁷	19.5	Rudstam
	20	1	30.0	Nysolin ^b	<10 ⁻⁷	39.0	Rudstam
	20	1	31.2	Nysolin ^b	<10 ⁻⁷	45.1	Rudstam
	20	1	40.9	Nysolin ^b	<10 ⁻⁷	88.0	Rudstam
	20	1	50.0	Nysolin ^b	<10 ⁻⁷	150.0	Rudstam
	--	1	20	kerosene	5·10 ⁻²	0.15	Martin
	--	2	20	kerosene	5·10 ⁻²	0.09	Martin
	25	3	20	kerosene	-----	0.3	Fletcher 1965B
	37	3 ^d	30	"Adakene 12" ^c	-----	0.42	Schlea
	65	3 ^c	30	"Adakene 12" ^c	-----	0.1	Schlea
tetranitrato	0	3.05	30	kerosene	~10 ⁻⁴	8.2, 12	Fletcher 1965A
	0	2.95	10	kerosene	10 ⁻⁴	2.1	Fletcher 1965A
	25	3.00	20	kerosene	-----	0.9	Fletcher 1965B
tri- and	--	3	10	n-dodecane	5·10 ⁻⁵	0.131	Tsuboya
tetra-nitrato	--	3	15	n-dodecane	5·10 ⁻⁵	0.422	Tsuboya
	--	3	20	n-dodecane	5·10 ⁻⁵	0.548	Tsuboya

Table 7 (Contd)

Expected Complex	Temp, °C	[HNO ₃], mol L ⁻¹	TBP, vol %	Diluent	[Ru], mol L ⁻¹	D _{Ru} ^a	Reference
tri- and tetra-nitrato	0	4	30	kerosene	8.5·10 ⁻³	1.2	Fletcher 1965A
	0	3	30	kerosene	2.5·10 ⁻⁴	4.2	Fletcher 1965A
	0	3	20	kerosene	2.5·10 ⁻⁴	1.8	Fletcher 1965A
	0	3	15	kerosene	2.5·10 ⁻⁴	1.1	Fletcher 1965A
	0	1	10	kerosene	8.5·10 ⁻³	15.0	Fletcher 1965A
dinitro	20	0.1	30	kerosene	5·10 ⁻³	2.04	Brown, 1960
	20	1.0	30	kerosene	5·10 ⁻³	1.70	Brown, 1960
	20	3.0	30	kerosene	5·10 ⁻³	0.506	Brown, 1960
dinitro (cis)	20	1.0	30	n-dodecane	5·10 ⁻⁵	0.0155	Joon
dinitro (trans)	20	1.0	30	n-dodecane	5·10 ⁻⁵	0.0477	Joon
dinitro-mononitrato	--	3	10	n-dodecane	5·10 ⁻⁵	0.0078	Tsuboya
	--	3	15	n-dodecane	5·10 ⁻⁵	0.0141	Tsuboya
	--	3	20	n-dodecane	5·10 ⁻⁵	0.0467	Tsuboya
1 nitro -2,3-dinitrato	20	1	30	n-dodecane	5·10 ⁻⁵	7.28	Joon
mononitro-dinitrato	20	5	30	kerosene	5·10 ⁻³	0.8	Brown, 1960
1,2 dinitro-3-nitrato	20	1	30	n-dodecane	5·10 ⁻⁵	5.25	Joon
1,3 dinitro-2-nitrato	20	1	30	n-dodecane	5·10 ⁻⁵	10.74	Joon

^a Extraction coefficient, $D_{Ru} = [Ru]_{Org} / [Ru]_{Aq}$.

^b Mainly paraffinic kerosene.

^c Straight-chain paraffins.

^d Additional component, 1.5 M UO₂(NO₃)₂.

oxopolymers, formed in nitric acid solutions with high zirconium concentrations (greater than $10^{-2}M$) do not extract into TBP under any conditions [YAGODIN]. The hydroxopolymers change into oxopolymers with time. Differing amounts of the unextractable forms of zirconium in the nitric acid solution studied by various investigators are difficult to study and are responsible for the irreproducibility of the data [FOMIN].

In contrast to UO_2^{2+} , $RuNO_3^+$, PuO_2^{2+} , Pu^{4+} , or Pu^3 , the extraction coefficient of zirconium by TBP shows a continuous increase as the acidity of the aqueous phase increases. Thus zirconium apparently does not compete with HNO_3 for TBP as the former ions do [TSVETOVA]. The controlling factor in the extraction is actually the total nitrate ion concentration; in the presence of uranyl nitrate, the extraction of zirconium decreases considerably.

The values of the extraction coefficients of zirconium by TBP, D_{Zr} , are shown in Table 8. The distribution coefficients indicate that a satisfactory decontamination from zirconium should be achieved in the Purex process; in reality, however plant data show an incomplete separation. This may be partially due to the chemical additives and impurities and the kinetics of extraction. Residence times in the solvent extraction contactors determine how closely equilibrium is approached and affect the decontamination from zirconium.

The decontamination from zirconium decreases with time due to degradation products that form in the solvent (dibutyl phosphate, DBP, and monobutyl phosphate) and diluent (hydroxamic acids, nitroparaffins and others) which complex zirconium very strongly and are responsible for its retention in the solvent [FAUGERAS, HARDY, BLAKE 1963A, STIEGLITZ, LANE, HUGGARD, HEALY, CAO]. The formation of radiolytic degradation products can be reduced by limiting the irradiation of the solvent and diluent--possibly by using centrifugal extractors with short contact times. Zirconium can also be excluded from the organic phase by complexing it as the fluoride [BOUDRY, SWANSON, BRESCHET] or with oxalic acid or EDTA [SWANSON] before the extraction.

d. Conclusions

Process conditions which should lead to optimum decontamination from zirconium and ruthenium* include:

1. The adjustment of acidity. Unfortunately, although the ruthenium extraction coefficient decreases with increased nitric acid concentration, the zirconium extraction coefficient increases. A feed solution of $2M HNO_3$ should be optimum.

2. A low concentration of the extractant, TBP. In more dilute solvents, the D_{Ru} and D_{Zr} are both lower; additionally, the radiolytic and chemical degradation of extractant is reduced and therefore less zirconium is retained.

*The presence of DBP does not change the ruthenium contamination, as [BRUCE] and [BROWN 1958B] have shown.

Table 8. Extraction Coefficients, D_{Zr} , of Zirconium

Temp, °C	TBP, vol%	Diluent	HNO ₃ mol L ⁻¹	D _{Zr}	Reference
	19	kerosene	0.98	0.0015	Alcock
			2.02	0.045	Alcock
			3.01	0.120	Alcock
			4.01	0.23	Alcock
			4.96	0.49	Alcock
			6.04	0.90	Alcock
23	20	saturated hydrocarbons (fraction boiling at 170-240°C)	0.05	0.0089	Adamskii
			1.04	0.019	Adamskii
			1.94	0.044	Adamskii
			2.84	0.084	Adamskii
			3.74	0.167	Adamskii
			5.7	0.58	Adamskii
			9.0	4.7	Adamskii
40	20	saturated hydrocarbons	0.4	0.004	Adamskii
			1.1	0.019	Adamskii
			2	0.053	Adamskii
			2.9	0.121	Adamskii
			5.58	0.64	Adamskii
70	20	saturated hydrocarbons	0.58	0.012	Adamskii
			1	0.04	Adamskii
			1.82	0.099	Adamskii
			3.5	0.38	Adamskii
			5.4	0.78	Adamskii
	50	white spirit	4	0.48-0.52	Stern
			5	1.5-1.7	Stern
			6	5.1-5.4	Stern
			7	8.8-9.3	Stern
	5	benzene	3	0.007	Shevchenko
3			0.026	Shevchenko	
3			0.07	Shevchenko	
3			0.17	Shevchenko	
5	decane	3	0.01	Shevchenko	
		3	0.032	Shevchenko	
		3	0.13	Shevchenko	
		3	0.24	Shevchenko	

3. An increase in temperature.

4. The use of short-residence-time contactors. The ruthenium is extracted to a much lesser degree if the phase contact time is less than 60 sec. Although not affected as much, the zirconium distribution coefficient is also lower [PUSHLENKOV].

5. A two-solvent system. It has been tested successfully and consists of (1) TBP, which gives good decontamination from ruthenium and (2) methyl isobutyl ketone (MIBK), which separates zirconium from uranium [LEWIS].

6. Any chemical treatment which is independently effective for ruthenium or zirconium could be used, since it would not influence the total decontamination negatively. Specific effects of such a treatment on the recovery of uranium and plutonium must be considered, including possible operational difficulties such as product reflux in scrubbing sections.

7. Owing to the deleterious effect on decontamination of small amounts of solvent degradation products, frequent and efficient solvent cleaning should result in improved removals of zirconium.

Of all the possibilities, the use of short residence time contactors seems to be the most effective and practical method.

B. Developments for Reprocessing of FBR Fuel

1. Introduction

A program has been undertaken to develop improved solvent extraction techniques for use in Purex processing of Fast Breeder Reactor (FBR) fuel in a 0.5 Te/day pilot plant. This work is being carried out in cooperation with the overall Oak Ridge National Laboratory (ORNL) program for FBR fuel reprocessing. The main objectives of the ANL program are development of an annular centrifugal contactor of 0.5 Te/day capacity, adaptation of a Purex flow sheet for use with short residence centrifugal contactors, and a study of solvent cleanup techniques aimed at improving the cleanup process and reducing the impact of solvent cleanup upon waste handling.

2. Development of a 0.5 Te/day Centrifugal Contactor (G. Bernstein)

Many of the design features of the 0.5 Te/day contactor are similar to those of the 10 Te/day unit described in the previous section. The smaller unit will have a rotor 9 cm in diameter and 27 cm long. A request-to-bid has been issued for a 3/4-hp, (0.56-kW) 1800-rpm motorized milling spindle to drive the rotor. The smaller unit is scheduled for early development and fabrication and will be tested to demonstrate that direct coupling of the rotor to a commercial motorized spindle is a practical basis for construction.

The low throughput required for a 0.5 Te/day plant (~10 L/min for a flow sheet based upon high concentrations of plutonium) should permit the dimensions of the contactor to be within the limits of geometrical criticality safety for all concentrations of plutonium. However, the effect of interaction of adjacent units of a bank of contactors on criticality will be evaluated.

The studies on kinetics of fission product extraction and plutonium reduction referred to in the previous section will be of value in studies of the FBR flow sheet. The higher plutonium concentrations encountered in the FBR fuel make the selection of reduction conditions and kinetics a more critical factor than in the processing of LWR fuel.

Possibly, the kinetics of fission product extraction and plutonium reduction will make it desirable to have longer residence times in the mixing zones of selected contactors in a multistage contactor bank. For example, longer residence times may improve fission product scrubbing in the scrub section of an extraction bank or may improve plutonium reduction in a uranium-plutonium partition bank. One method of increasing residence time is to extend the length of the casing below the rotor, as shown in Fig. 9. With this design, the mixed phases will flow out of the annulus into pipes and will be reintroduced near the bottom of the extended casing. It is anticipated that the turbulence caused by the impingement of the inlet streams will maintain a mixed condition within the extended mixing zone until the mixed phases enter the rotor orifice. Since no change would be required in the construction of the motor-rotor assembly, replacement motor-rotor assemblies would be identical for units with long or short casings.

The test facility which was used for the development of the ANL annular centrifugal contactor is being reactivated. It will be used to examine the feasibility of employing a contactor having an extended casing. An extension section is being fabricated to fit the existing annular contactor. It will be made of acrylic plastic to permit observation of the quality of mixing in the extended casing.

3. Solvent Cleanup (B. B. Saunders)

a. Introduction

The radiolytic decomposition of tri-n-butyl phosphate (TBP) and the hydrocarbon diluents used in the Purex process for separation of uranium and plutonium from fission products is known to cause various problems in the plant process: clogging of contactors, retention of fission product in the solvent, reduced decontamination factors, and plutonium losses. These problems are expected to become more severe as reprocessing is applied to higher burnup fuels, which contain larger concentrations of the radioactive fission products responsible for most of the radiation of the solvent. Alkali washes have been used to regenerate the solvent but have not been very successful. In addition, alkali metals should not be used since the introduction of alkali metals into the radioactive waste stream causes difficulties when the wastes are reduced to a solid form.

The literature review has been completed of the mechanisms of the radiolytic decomposition of the TBP and hydrocarbon diluents used in the Purex process. A separate report describing both the mechanism of degradation and methods of regeneration will be issued in the near future. Di-n-butyl phosphoric acid (HDBP) is the predominant decomposition product. Mono-n-butyl phosphoric acid (H₂MBP) is formed in much smaller yields. Other degradation products include ketonic phosphates [NOWAK], nitroparaffins, and hydroxamic acids [BLAKE 1963B, LANE]. The yields of the various degradation products depend upon: (1) HNO₃ concentration, (2) type of hydrocarbon diluent,

Fig. 9. Extended Casing for Annular Contactor

(3) TBP concentration, (4) the presence of O_2 , and (5) the presence of metal ions (U, Zr, and Pu). There is considerable dispute within the literature over the applicability of the laboratory experiments to the actual reaction in the plant process.

HDBP appears to be the component in the irradiated solvent which is responsible for most of the fission product retention in the solvent and hence low decontamination factors and high plutonium losses. It forms strong complexes with Pu(IV) and Zr(IV) and a weaker complex with U(VI). The Zr(IV) complexes of HDBP, *e.g.*, $Zr(NO_3)_2(DBP)_2$ and $Zr(NO_3)_2(DBP)_2 \cdot (HDBP)_2$, are believed by some to be the major components of the oils, emulsions, and precipitates which cause clogging problems in the process [BRESCHET].

Various methods have been tried in the laboratory to purify or regenerate the solvent after it has been subjected to different amounts of radiation under different conditions. The most effective methods are distillation and the use of anion-exchange resins [DAVIS, SCHULZ]. Numerous other workers have tried sorption, complex formation, neutralization, organic extraction, and filtration. There is considerable discrepancy in the literature over the use of alkali washes. HDBP is soluble in both TBP and water, but recent experiments [NOWAK, HEALY] leave no doubt that, even when uncomplexed with Pu, U, or Zr, HDBP is not completely removed by washing the organic phase with an alkali solution. To date, apparently, no methods other than alkali washing (with either NaOH or Na_2CO_3) have been tried on a plant scale.

Not only is an alkali wash unable to successfully remove HDBP (and H_2MBP) or the metal complexes of HDBP with Pu, Zr, and U, it cannot remove the other products of radiolytic decomposition. Hydroxamic acids are known to form unusually strong complexes with Zr(IV) and even Pu(IV) [BARONCELLI], but it has not been proved to exist in the solvent under plant conditions. Various ketonic phosphates have been identified [STIEGLITZ], but their complexing power has not been established.

A new method for solvent cleanup has been proposed which takes advantage of the complexing ability of formic acid and the inextractability of the resulting complexes in the TBP/dodecane system. Formic acid is known to successfully strip plutonium from its DBP complexes [GERMAIN]. The anion-exchange resins of Schulz, used with a prewash of formic acid, eliminate the alkali metal from the radioactive waste stream, deliver a pure solvent, allow the resin material (a quaternary ammonium hydroxide) to be regenerated, and extend the life of the resin. The prewash with formic acid removes some of the nitric acid from the solvent and thus reduces the amount of nitric acid passing through the anion-exchange resin. Nitric acid forms a very strong complex with the resin material which is difficult to displace. The corresponding formate is much easier to displace with a strong organic base; thus, the resin can be regenerated. Literature data is still being collected concerning the stability, extractability, and solubility of zirconium, plutonium, uranium, thorium, and ruthenium complexes with formate. This data will appear in the forthcoming report on solvent degradation and regeneration.

III. ENVIRONMENTAL EFFECTS (W. Seefeldt and W. Mecham)

An objective of this study of the literature is to provide a compilation of data to aid in the prediction of accident consequences (*i.e.*, source terms and filter penetrations) in LWR fuel reprocessing facilities. The scope encompasses (1) the definition of source terms for hypothetical accidents in reprocessing plants in terms of the physical and chemical properties of materials released to the first stage of air cleaning, (2) quantitative estimation of the penetration of radionuclides through various stages of air cleaning, and (3) the definition of properties of the products of accidents as they are released to the environment at the stack or similar boundary of the plant.

Information will be compiled on (1) accidents that have occurred in fuel reprocessing and related facilities, (2) the state of the art of gas-cleaning equipment in relation to its performance under normal and abnormal operating conditions, and (3) the results of research to elucidate the behavior of materials and equipment under accident conditions.

An application for a Part 50 license to construct and operate a fuel reprocessing facility must include a Preliminary Safety Analysis Report and a Final Safety Analysis that, in addition to other requirements, must present analyses and evaluations of the design and performance of structures, systems, and components with the objective of assessing the risk to public health and safety from operation of the facility. The application must include a determination of (1) the margins of safety during normal operations and during transient conditions anticipated and (2) the adequacy of structures, systems, and components provided for the prevention of accidents and the mitigation of the consequences of accidents.

Regulatory Guide 3.26, Standard Format and Content of Safety Analysis Reports for Fuel Reprocessing Plants, suggests the inclusion of a chapter on Accident Safety Analysis in which the response of a facility to postulated accident events is described. This should include identification of such events, their causes, the quantitative identification and mitigation of the consequences, and the capability of coping with each situation.

Essentially no coherent compilation of data exists that would aid in the prediction of accident consequences (*i.e.*, source terms and filter penetrations) in light water reactor (LWR) fuel reprocessing facilities. As a result, accident analyses for various fuel cycle facilities are highly variable and frequently contain assumptions that may be regarded as conflicting. The use of a conservative assumption that has little relationship to a real event may serve well in the accident analysis of one plant, but its use in a second plant may result in unrealistically large calculated releases. An example of such a conservative assumption is 100 percent of the inventory becoming airborne for a particular event. An assumption may lead to acceptable releases being calculated for one plant, but unacceptable releases for a second. The need to relate assumptions to the mechanisms of real events is evident.

Thus, one objective of this work is to relate the assumptions to the realities of a plant. The basic fundamental processes occurring during an accident event must be understood. Confidence in the theoretical basis can

be strengthened by experiments or by analysis of actual accident events. In the absence of data from closely related systems, information from non-related systems may be helpful in confirming theoretical bases, from which extrapolations to the systems of interest may be possible.

It is convenient to divide the mechanisms that lead ultimately to a release from a stack into three phases: the accident event itself, which results in material becoming airborne at the accident site, the behavior (both physical and chemical) of the airborne material enroute to an air-cleaning system, and the modification of airborne material in its passage through the air-cleaning system. The actual design of the plant and its processes, including those features incorporated to reduce accident probability or to ameliorate accident consequences, influence each of the three phases. Thus, an accident analysis can begin only after a description of the plant and its design features has been provided.

In the case of accidents at fuel reprocessing plants, little experimental work has been performed that would lead to an understanding of fundamentals or of the character and quantities of material that would become airborne. Information can be gained from accidents that have occurred in fuel cycle facilities. If none of these are available, technologies in non-nuclear fields may be helpful.

To undertake the first phase (the accident event) requires the identification of significant failure events. The generic events most frequently identified in environmental reports and safety analyses are explosions, fires, and criticality. A review will be made to ensure that all significant events are included in our study.

Current efforts have been focussed on examining the literature related to explosion events. Our interests in explosions are narrow, centering principally on the history of aerosol and dust clouds immediately following the events (*i.e.*, during a period extending to several hours). This is the time period of greatest concern in terms of the challenge to an air-cleaning system.

In the nuclear area, essentially no experimental work of this type has been directed toward accidents in fuel reprocessing or related facilities. However, a number of experiments involving explosions have been performed in support of the Plowshare program. These experiments used both nuclear devices and high explosives as the detonation mediums. Though our examination of the literature in this area is not yet complete, in general, we have found that the early time history of the characteristics of the resulting aerosols and dust clouds apparently was not a principal concern in the analysis of experimental results. Partial results of the survey follow.

Some data identified as being potentially applicable was obtained in project Schooner, a nuclear event conducted in 1968 [GUDIENSEN]. Concentration maps and particle size distributions were measured for samples taken by aircraft passing through the cloud soon after the detonation (twelve minutes to several hours after detonation). The earliest samples (taken 12 minutes after the event) showed concentrations ranging up to 240 mg/m^3 , with mass median diameters of $30 \mu\text{m}$. As would be expected, these decreased rather rapidly with time after detonation due to settling from the atmosphere.

Freeman *et al.* [FREEMAN] conducted tests (using TNT as a detonation medium) that yielded some information on dust concentrations immediately after an event. Although the principal purpose of the tests was to develop instrumentation for measuring dust parameters, some results were reported for periods extending to several seconds after the event. Dust concentrations up to 1100 g/m^3 were observed, an unusually high value. After several seconds, dust concentrations decreased to several hundred grams per cubic meter.

Literature concerning explosions in various nonnuclear activities is also being examined. Examples of such activities are mining and quarrying for minerals.

IV. METAL MATRIX ENCAPSULATION OF HIGH-LEVEL WASTES (L. J. Jardine and K. F. Flynn)

A. Introduction

Disposal of nuclear wastes ranks as an important problem which must be solved before nuclear power will be acceptable. High-level waste (HLW), containing most of the fission products and unusable transuranium elements, is to be transferred to a Federal waste repository for final disposal. The waste is to be solidified prior to deposition, and the currently favored approach seeks to minimize dispersibility of the solid waste by either aeolian or hydraulic means.

The high-level waste is formed as an aqueous solution, and the first product of solidification is a calcine produced from this solution by evaporation and heating. The calcine product is thermally stable, but it is in a dispersible form because of its relatively high solubility in water and the type of powder usually produced. Poor thermal conductivity of the calcine and low inherent mechanical strength are additional disadvantages.

Considerable effort has been expended on a national scale to convert high-level waste to glass by additional steps or steps taken concomitantly with calcination. The glass product has low dispersibility and improved thermal conductivity and mechanical strength, which advantages are offset by severe conditions for its formation and its being in thermodynamically unstable form.

Another form of high-level waste that may be acceptable is calcined waste dispersed in a metal matrix. A program was initiated to review the use of metal matrix encapsulation, to identify the attributes of the product, and to define the status of technology.

The work on metal matrix waste forms includes development of a program plan and recommendations for its implementation. As part of the program plan, areas in need of experimental work will be identified, and some experimental work is being planned. A report is in preparation assessing the state of the art of the metal encapsulation concept. The assessment includes evaluation of (1) the increase in thermal conductivity of encapsulated waste, (2) and to a lesser extent the integrity of encapsulated waste, and (3) the resistance to dispersion compared with either glass or calcine waste forms. The goal is to identify the conditions under which the additional solidification steps required for metal encapsulation would yield further net advantages to HLW management.

B. Results

To provide the basis for a technical assessment of the state of the art, a literature review was made of previous and current work on the encapsulation of radioactive waste in a metal phase. Some of the high-lights are briefly summarized below.

Developmental work on metal matrix encapsulation has been actively pursued at three laboratories. They are (1) the Pacific Northwest Laboratory (PNL) of Battelle Memorial Institute at Richland, Washington, (2) the Idaho

National Engineering Laboratory (INEL) of the Allied Chemical Corporation at Idaho Falls, Idaho, and (3) the Eurochemic Laboratories at Mol, Belgium. Data in the literature from these institutes has been supplemented with visits to PNL and INEL, reported in detail in [JARDINE-1976A] and [JARDINE-1976B].

The major work done by Eurochemic consists of encapsulation of phosphate glass beads into a lead alloy matrix, using a casting technique [VANGEEL-1975, VANGEEL-1976]. In 1976, 2 kg of "hot" (9,000 Ci) 5-mm glass beads were successfully encapsulated [VANGEEL-1976]; these specimens are currently under evaluation. Eurochemic has done some work with calcine also. U.S. encapsulation work is currently limited to "cold" simulated waste forms.

Fluidized-bed or spray calcine, because of its small particle size and wide range of particle size distributions (~ 0.01 - 0.4 mm), cannot always be directly encapsulated by casting encapsulation techniques under development at INEL and Eurochemic. For calcine it has been found [ICP-1976A, VANGEEL-1975] that if the content of calcine "fines" (*i.e.*, particles ≤ 0.1 mm) is greater than about ~ 10 wt %, casting techniques will not work. Nonwetting of the calcine by the alloys (primarily aluminum and lead have been used) has been concluded to be the reason [ICP-1976A]. Particles larger than ~ 1 mm present no difficulty. Consequently, to allow casting techniques to be employed with calcine, PNL [BNWL] and INEL [ICP-1976B] have added a particle - agglomeration step in order to enlarge calcine particle sizes to ~ 1 - 100 mm.

The agglomeration stage of calcine is an ideal opportunity to add materials that improve the product's resistance to leaching. INEL has found that ~ 10 wt % additions of metakaolin to calcine (with H_3PO_4 and HNO_3 used as binder) produces calcine granules that, after firing at $800^\circ C$, have leach rates approximately as low as that of glass [IC-1976B]. Such a treatment, followed by metal encapsulation in a metal having good corrosion resistance, thus appears to be a very attractive alternative to high-temperature ($>1000^\circ C$) glass making for HLW solidification. One of the most important advantages in comparison to glass making is perhaps the elimination of corrosion (due to liquid phases at $>1000^\circ C$) and the uncertainty of material life (*i.e.*, glass furnace liners). Encapsulation experiments at INEL have involved both powder metallurgical and molten metal casting techniques. Limited data have been reported on thermal conductivities, leach rates, and mechanical strengths of encapsulated waste [ICP-1976A, ICP-1976B].

The PNL agglomeration process consists of blending a glass frit and calcine, using a water binder [BNWL]. Sintering at $\sim 800^\circ C$ produces dense (~ 2.6 g/cm³) granules that possess a leach resistance similar to that of glass. The current concept is to coat the sintered granules with impermeable coatings and to encapsulate these in a porous sintered-metal matrix. A direct in-canister powder metallurgical gravity sintering encapsulation process is under development. Candidate matrix materials are higher melting metals such as steel and copper alloys. Similar encapsulation of borosilicate glass beads is planned [BNWL],

With powder metallurgical techniques, it should be possible in principle to use the calcine "fines" directly to fabricate a metal matrix. Sintering operations also allow the use of higher melting metals (*e.g.*, steel, brass, etc.). A general survey has been made of possible powder metallurgical

fabrication techniques. It was concluded that most methods for producing nonporous matrices would require more extensive development for eventual use in hot cells than would casting methods. Preliminary data from metal matrix casting techniques indicate these techniques to be the most directly applicable. For these reasons, a preliminary recommendation is that casting of agglomerated and sintered calcine or glass beads be pursued if an encapsulation process is to be developed on a short time schedule or to conserve resources.

Some steady state heat transfer properties of solid cylinders (representing HLW canisters) in air or water were calculated to evaluate how much advantage is gained by metal encapsulation due to the increased thermal conductivity. Two maximum temperatures impose limits upon the maximum allowable total heat generation rate of HLW canisters. These are the maximum temperature of the outer canister surface (T_s) for an assumed storage environment of air or water and the maximum temperature of the centerline temperature (T_{CL}), which in general is related to the form and thermal conductivity of the waste. These temperatures have been plotted against heat generation rates for cooling in air and water so that the maximum permissible heat generation rates for a desired value of T_s or T_{CL} can be obtained. One such plot is shown in Fig. 10. This shows the steady state surface temperatures of 10-ft-long solid cylinders for different heat generation rates.

Fig. 10. HLW Canister Surface Temperature vs. Total HLW Canister Heat Generation Rate for Different Canister Diameters:
 (1) Natural Air Convection (Vertical) and Radiation Cooling ($\epsilon = 0.7$)
 (2) Water, Natural Convection

Before a canister is filled, its heat generation rate can be controlled by either choosing a waste of appropriate age (after storage as spent fuel or as liquid high level waste or as a combination of these) and/or by diluting the waste with additives (glass-formers, metakaolin, metal) that enhance its physical properties (*e.g.*, leach rate, thermal conductivity, or mechanical strength). After a canister is filled, the heat generation rate decreases as the radionuclides decay.

A much lower limit of the maximum permissible heat generation rate will be imposed upon HLW canisters by the ultimate Federal repository. If a geological repository is selected, the permissible rates are certain to be much lower than is permissible in either air or water (see Fig. 10). A salt repository is likely to impose a limit of about ≤ 5 kW per HLW canister [ORNL]. For example, if a 30.5-cm-diameter canister is filled with waste yielding a 30-kW heat generation rate in order to stay below a surface temperature of 400°C in air (Fig. 10), the canister would have to undergo interim storage until the heat generation rate decayed to 5 kW. Since the rate of decay is roughly inversely proportional to the HLW age, the length of the interim storage period is dependent upon the HLW age at the time of fill.

To evaluate the relationships of spent fuel, liquid HLW, and interim storage times, a series of calculations were done for calcine, glass, and metal-encapsulated waste forms. The results of one such calculation are summarized. Shown in Table 9 are the three storage times required for each heat loading and storage mode of calcine or glass beads in a metal matrix (a typical lead alloy). These are labeled: "to fill," "interim," and "to repository." The storage times are direct consequences of the total heat generation rate of HLW canister. Heat generation rates were obtained from the ORIGEN output for a spent fuel of 25,000 MWd/MTU at 35 MW/MTU specific power, using appropriate waste dilution corrections where required [KEE].

The storage time "to fill" is the minimum time that must elapse between discharge of spent fuel from a reactor and filling of a HLW canister with the indicated waste form while satisfying the indicated T_{CL} and T_S limits. It is assumed that HLW canisters are not filled prior to the elapse of the "to fill" storage time to satisfy the limitations of T_{CL} and T_S . Spent fuel can be stored during the entire "to fill" storage time period (*i.e.*, no high level liquid waste storage) so that following reprocessing, direct solidification and filling of the HLW canister can be done. Alternatively, the time period can be divided into different, or equal, intervals of spent fuel storage and high-level liquid waste storage such that the sum of the storage times equals the "to fill" storage time.

The "interim" storage time is the time interval between filling of HLW canisters and decay of the total heat generation rate of a HLW canister to the level (assumed to be 5 kW) required for acceptance into a Federal repository. During the "interim" storage time, HLW canisters are assumed to be stored in water or air continuously.

The storage time "to repository" is the minimum time between discharge from a reactor and reduction of the total heat generation rate of the solidified HLW in the canister to 5 kW, which is the assumed maximum heat

Table 9. Comparison of Maximum Total Heat Generation Rate of Reference HLW Canisters:
Lead Alloy Metal Matrix of Calcine or Glass Beads Cooled in Water or Air

Q _{max} , kW ^{a,b}	Waste Form	Storage Mode	T _{CL} , ^a °C	T _s , ^a °C	D, cm	Number of HLW Canisters	Storage Time		
							To Fill, ^d yr	Interim ^e yr	To Repository, ^f yr
15	calcine	water	92	53 ^g	15.2	1080	<0.5 ^h	1.3	1.8
15	beads	water	92	53 ^g	15.2	2700	<0.5 ^h	~0	0.5
30	calcine	water	131	53 ^g	30.5	270	1	6.4	7.4
30	beads	water	131	53 ^g	30.5	675	0.6	2.4	3
60	calcine	water	210	53 ^g	61	68	2.2	51.8	54
60	beads	water	210	53 ^g	61	170	0.8	17.2	18
84	calcine	water	300 ^g	80 ⁱ	15.2	1080	<0.5	1.3	1.8
84	beads	water	300 ^g	80 ⁱ	15.2	2700	<0.5	~0	0.5
89	calcine	water	300 ^g	67 ⁱ	30.5	270	<0.5	6.9	7.4
89	beads	water	300 ^g	67 ⁱ	30.5	675	<0.5	2.5	3
93	calcine	water	300 ^g	57 ⁱ	61	68	1.5	52.5	54
93	beads	water	300 ^g	57 ⁱ	61	170	0.7	17.3	18
7.4	calcine	air	300 ^g	280	15.2	1080	1.2	0.6	1.8
7.4	beads	air	300 ^g	280	15.2	2700	0.5	~0	0.5
13	calcine	air	300 ^g	265	30.5	270	3	4.4	7.4
13	beads	air	300 ^g	265	30.5	675	1	2	3
23	calcine	air	300 ^g	240	61	68	6	48	54
23	beads	air	300 ^g	240	61	170	2.5	15.5	18

^a A thermal conductivity value of 10 W/(m)(°C) was used. These are the values at the time of HLW canister filling. A length of 10 ft is assumed.

^b The heat generation rate of a HLW canister was obtained from an ORIGEN output for spent fuel of 25,000 MWd/MTU burnup at 35 MW/MT specific power. [KEE]

^c This is estimate of the number of HLW canisters required to contain the reference metal matrix from the reprocessing of 1500 MTU.

^d "To fill" storage time is the time elapsed between discharge of spent fuel from a reactor and filling of the HLW canister.

^e "Interim" storage time is the time between "to fill" storage and "to (salt) repository" storage.

^f "To repository" storage time is the time elapsed between discharge of spent fuel from a reactor and decay of each HLW canister to a total heat generation rate of 5 kW (so that the HLW canisters can be directly placed in a salt repository).

^g This temperature limits the maximum heat generation rate of a canister.

^h Times less than 0.5 yr may be possible on the basis of a thermal analysis; however, shorter time periods will probably never be of interest since there are additional handling and chemical separation problems with shorter cooled fuel.

ⁱ The limit of T_s ≤ 53°C is temporarily increased so that the centerline temperature T_{CL} becomes the limiting temperature. The result is T_s ≤ 80°C.

generation rate per canister acceptable for a salt repository [ORNL]. During this period, storage may be as spent fuel elements, high level liquid wastes, or solidified HLW in canisters in water or air or any combination thereof. For example, if desired, spent fuel elements may be stored during the entire "to repository" storage time, thereby eliminating all high-level liquid storage and interim storage with water or air cooling; upon reprocessing, the waste can be directly solidified in HLW canisters (5 kW per canister) which can then be immediately placed in the repository.

Also shown in Table 9, are the numbers of HLW canisters that would be needed to contain various forms of solidified HLW from the reprocessing of 1500 MTU.

First, as shown in Table 9, the effect of 53°C outer surface temperature [MECHAM] during storage in water was examined. For a 30.5-cm-dia canister, glass beads-metal matrix can be put into a HLW canister 0.6 yr after reactor discharge, compared with 1 yr for a calcine-metal matrix. The dilution effect of glass beads (waste volume is higher by a factor of ~ 2.5 than for calcine or calcine-metal matrix) also allows the interim storage time to be decreased to 2.4 yr rather than 6.4 yr (required for a calcine-metal matrix). Thus, glass beads-metal matrices can be put into a salt repository after two-fifths as much storage time as calcine-metal matrices. However, 2.5 times as many HLW canisters are needed for glass beads-metal matrices as for calcine-metal matrices. Results for canisters with other diameters are also shown.

Second, the effect of allowing a centerline temperature of 300°C (the melting point of lead is 327°C) to become limiting was examined for water and air storage. For water storage, this requires that the outer surface temperature be $\leq 80^\circ\text{C}$. With these constraints HLW canisters may be filled with calcine-metal matrices or glass beads-metal matrices at times ~ 0.5 yr after reactor discharge; however, there are corresponding increases in the "interim" storage time. Changing the permissible temperature does not change either the time that must elapse before the salt repository heat limit is reached or the number of HLW canisters.

With air storage and the same temperature constraints, the storage time "to fill" is 3 yr for calcine-metal matrices and 1 yr for glass beads-metal matrices (Table 9).

Therefore, if it is desired to fill a 30.5-cm HLW canister in 1 yr with $T_s \leq 53^\circ\text{C}$, this will be followed by 2 yr of "interim" air storage for glass beads-metal matrices or by 6.4 years of "interim" water storage for calcine-metal matrices. In general, larger diameter HLW canisters require longer time intervals between reactor discharge and filling (*i.e.*, "to fill" storage times) and corresponding longer, perhaps undesirably long, "interim" storage times before the salt repository total heat generation rate of 5 kW per canister is satisfied.

A conceptual flow sheet for the encapsulation of HLW in a lead matrix is shown in Fig. 11. It is based on some of the better features of the processes reviewed and some limited scouting experiments. The flow sheet identifies a concept that leaves a protective annulus of minimum thickness or an envelope of pure metal (typically ≥ 1 cm) that completely surrounds the

Fig. 11. Waste Solidification Flow Sheet for 5 MTU/Day Plant

outermost waste particles. Such a fabrication process would provide additional resistance to leaching due to the protective metallic envelope. This should be adequate to allow many fission products to decay to very low levels before they are exposed to a leaching media.

An experiment was carried out to demonstrate this concept using a wire mesh to isolate the outermost waste particles from the wall. It is recommended that such a technique be employed in metal encapsulation with cylindrical waste canisters. This concept should reduce any problems due to a thermal contact resistance associated with the alternative of putting a HLW monolith in a larger-diameter HLW canister (or overpack) and filling the annulus with a molten alloy before sealing.

Process steps (Fig. 11) include a calcine agglomeration, or pelletization step. This is followed by sintering at 800°C, (based on preliminary encouraging results obtained by INEL using metakaolin-H₃PO₄ additives or by PNL using glass frit additives). The granules are then loaded into cylindrical wire mesh baskets, which are sealed so that no waste granules can escape. The wire baskets are at least 2 cm smaller in diameter and height than the final HLW canister. The HLW canisters are prefilled with solid lead, and the alloy is melted. A loaded mesh basket is next positioned in the HLW canister containing the molten alloy so that there is at least 1 cm clearance on all sides. After the entire assembly is heated for a short time, it is allowed to solidify. The product is a high level waste form with a ≥ 1 cm protective envelope of lead surrounding the outermost waste pellets that acts to retard dispersion by leaching.

Preliminary leach rates of agglomerated and sintered calcine granules from the INEL metakaolin-H₃PO₄ additives process have been almost as low as those of borosilicate glass [ICP-1976B]. The lead corrosion rate at 25°C was measured to be $2.3 \cdot 10^{-5}$ g/(cm²)(day) in Egyptian tap water and $2.1 \cdot 10^{-5}$ g/(cm²)(day) in 1M NaCl solution [ABDUL]. If lead is assumed to have a corrosion (leach) rate of 10^{-5} g/(cm²)(day) the corrosion of the 1-cm lead "protective annulus" provided for in Fig. 11 would take ~ 3100 yr after which the first waste particles would be exposed for leaching. A large fraction of the more troublesome isotopes (such as ¹³⁷Cs, ⁹⁰Sr) would decay during the time required to corrode the outer protective lead layer. If the leach rate of the agglomerated calcine can be similarly reduced to 10^{-5} g/(cm²)(day), $\geq 10^4$ years would be required to leach or corrode away an entire 32-cm-dia HLW cylinder. The net effect would be to retard dispersal. This illustrates the time delay yielded by a protective annulus. However, to confirm these statements, additional leach rate and corrosion data for lead composites in other simulated conditions (*i.e.*, hot pressurized saturated brine solutions typical of repository) are needed. The amount (108 liters/day) of lead required to offer this protection to HLW is rather small (0.07% of total U.S. consumption in 1969).

The flow sheet for a 5 MTU per day reprocessing plant (Fig. 11) indicates production of two (~ 32 cm OD x 172 cm) units of encapsulated waste per day. The flow sheet assumes that a shorter canister will be more suitable for handling operations at a reprocessing plant, during transport, and at a repository, even though the number of (remote) welds required is twice that for a single canister. The choice between fewer and longer HLW canisters and more shorter, lighter canisters is entirely arbitrary at this time since no process criteria exist.

C. Experimental

Two scouting-type casting experiments were performed to demonstrate the feasibility of the protective annulus layer concept (illustrated in Fig. 11). Agglomerated calcine (simulated by using 1 to 4-mm-dia Al_2O_3 pellets) and 5-mm glass beads were dispersed in a pure lead matrix. Thin-wall stainless steel beakers filled with pure solid lead were used to simulate high level waste canisters. A 1-mm by 1-mm stainless steel wire mesh was used as basket material. Temperatures were maintained below 395°C , and the concept illustrated in Fig. 11 was carried out. No vacuum or pressure systems were employed.

A 3-in.-OD by 3-in.-long casting of glass beads and a 2.5-in.-OD by 2.5-in.-long casting of Al_2O_3 pellets, each dispersed in lead matrices, are shown in Fig. 12. It can be observed that lead fully penetrated the beds of waste forms. The protective annulus that would isolate the outermost waste granules or glass beads in the event of premature canister failure or accelerated corrosion is clearly observable. Thus, an outer protective layer of lead (illustrated in Fig. 11) presented no difficulties with particle size ≤ 1 mm. More work is needed to further optimize such a process and to establish its limitations with actual waste forms, including consideration of internal heat generation in actual high level waste before introduction of the metal phase.

D. Conclusions

The metal encapsulation concept of waste management is sufficiently attractive as an alternative to glass monoliths to warrant additional research, development, and possible demonstration (RD&D). A detailed report is being prepared that assesses the metal encapsulation alternative and supports this statement. A preliminary assessment of RD&D requirements has also been made. This includes identification of laboratory, cold engineering and hot pilot scale studies that would allow full-scale demonstration of metal encapsulation to be begun in FY79. A recommended program plan has been submitted to ERDA for action.

(a)

(b)

Fig. 12. Sectioned Castings in Thin-Walled Stainless Steel Beakers of (a) 5-mm glass beads and (b) 1-4 mm Al_2O_3 pellets, each dispersed in a lead matrix.

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

A. Introduction

The goal of this program for ERDA 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. The waste which consists of metallic fragments from the chop-leach processing of spent fuel assemblies in the Purex process, 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 a light water reactor.

The waste is primarily Zircaloy (fuel cladding tubes) along with some stainless steel (fuel assembly end fittings) and Inconel (fuel assembly spacers). The hazards include the potential pyrophoricity of zirconium in the Zircaloy and the radioactivity from neutron-activated metals and residual undissolved fuel. The radioactivity can cause harm if radioactivity-laden particles are ingested or if there is exposure to penetrating radiation; the pyrophoricity can lead to fires or explosions which, in turn, could result in physical harm or dispersal of radioactivity.

A variety of technologies for handling and disposing of this waste have been proposed. The functions of the criteria to be developed in this program are to provide guidelines for safely practicing the technologies for handling the waste and, perhaps, to serve as the bases for rules and regulations.

The product of this program is expected to be a set of criteria and an appendix. The criteria will include a number of statements defining specifications for procedures and materials attributes. It is planned that the appendix will provide an explanation or justification for each criterion. The appendix will also give one or more examples of how each criterion can be observed in practice.

The nature of the criteria must be such that they are not only useful in promoting safe operation, but also are compatible with several other needs of plant operation and management: They must not impose severe economic penalties on plant operation; they must avoid, wherever possible, restricting the process designer to specific procedures or materials; they must be relevant to process designs that are likely to be used, (*i.e.*, they must take into consideration plans for handling and disposing of hulls that have been proposed in the past, and they must be developed with some anticipation of plans likely to be proposed in the future). A tentative set of criteria that reflect these constraints and would apply to the general technology areas will be developed and distributed to ERDA, NRC, and subsequently to representatives of appropriate nuclear industries. Finally, the tentative criteria will be revised according to the suggestions obtained in the review, and the resulting set of recommended criteria will be presented to ERDA.

It is expected that these criteria will be developed from (1) accumulated knowledge of conditions that minimize the pyrophoric behavior of zirconium [LEVITZ-1975, LEVITZ-1977], (2) principles for safe handling of radioactive materials developed previously by a number of Federal or international agencies,

councils, advisory bodies, and industrial concerns, and (3) information on physical and chemical properties of waste forms that contribute to the isolation of radioactivity from the environment.

Two major areas will be addressed that are significant to safe handling and disposal of these metals wastes: (1) procedures and (2) materials attributes. The scope of the criteria will include all operations involving discarded fuel-assembly metals (comprising fragments of all sizes from the stage of chopping to the stage of disposal).

Some of the operations on metallic fuel-assembly wastes that may have to be covered by criteria are listed below in the expected order of their application. The individual fuel reprocessor may omit these operations or apply them in a different order:

1. Chopping
2. Leaching
3. Rinsing
4. Drying
5. Packaging for interim storage
6. Movement to interim storage
7. Interim storage in primary form
8. Movement from interim storage to transformation to a different physical or chemical form
9. Transformation
10. Final packaging
11. Transport to disposal site
12. Emplacement in disposal location

The final set of criteria will pertain to not only the operations likely to be carried out on hulls (above), but also to topics important to the handling of reactive metals combined with radioactive material. Presented below, with brief comments, is a preliminary group of topics to be addressed and also a group of topics that after examination have been judged to be best excluded from consideration in the development of criteria. These topics are in the initial stages of formulation, not their final version, and are unlikely to be adequately comprehensive.

B. Topics to be Treated in Criteria

1. Definition of hulls and hardware. A clear and thorough definition of the materials to which the criteria are addressed would be clearly and thoroughly defined to avoid misinterpretations.
2. Accounting for metals by weight. A criterion would be appropriate requiring records of the weights of fuel-assembly metals. This would allow a material balance to be made from the time the material leaves the reactor to final disposal.
3. Number of barriers between hulls and the environment. The smallest number of serial barriers separating hulls from the environment, permitted to be maintained in interim and final storage, would be specified.

4. Labeling of packages or storage sites containing hull wastes. It may be appropriate to specify guidelines for identifying packages or storage sites containing hull waste; existing Department of Transportation (DOT) regulations may be adaptable to this purpose.
5. Safeguards and surveillance. A criterion involving precautions that would prevent the unlawful diversion of hulls may be appropriate, but would most likely be adequately covered by normal plant security measures.
6. Emergency procedures. Specific emergency procedures should not be recommended by criteria, but a listing of unacceptable procedures may be appropriate. Perhaps the most reasonable criterion would simply specify that any emergency procedures must be chosen with the aim of confining radioactivity releases to the site of an accident.
7. Disposition of metallic fines from sawing or chopping. Special attention must be given to handling of metallic fines because of the potential for pyrophoric behavior of zirconium and its alloys having a high surface/volume ratio. A criterion specifically directed at the disposition of fines will be developed.
8. Time limit between immersion and dryness. A criterion will be developed to limit the duration of time that Zircaloy waste can be maintained in a state intermediate between immersion and dryness. Experience indicates that storing zirconium either completely immersed in water or dry prevents or minimizes pyrophoric and explosive incidents. It would be important, therefore, to avoid the practice of storing Zircaloy having wetted (but not immersed) surfaces.
9. Inventory limit on zirconium storage. A criterion would specify an upper limit on the weight of zirconium (not other hardware materials) permitted in a given storage location or compartment. This would be aimed at limiting the size and effects of any incident resulting from its pyrophoricity.
10. Ambient temperature limits. Upper limits for ambient temperature of sites or packages containing hull waste can probably be developed from applicable, existing DOT regulations.
11. Centerline temperature of storage package. This criterion must be chosen with some care; too high a limit may result in packages that are susceptible to combustion, but too low a limit may require container diameters so small that waste handling costs are excessive.
12. Mechanical properties of the storage form. It may be appropriate to develop a criterion prohibiting any readily friable storage form.
13. Permissible properties of a matrix (if used). It is expected that a criterion will be developed that only a material that is inert and non-flammable be used as a matrix in which hulls are dispersed.
14. Permissible residue of reagents on hulls in storage. This criterion would be especially directed to limiting the presence of oxidizing agents and potential gas-forming reagents. The limits for gas-forming reagent will probably be estimated from the pressure limit on the storage package.

15. Handling of secondary wastes from hull decontamination. Several schemes have been proposed to remove the 0.05-1% of total fuel that remains undissolved with hulls after the acid leaching step. These schemes all generate secondary waste streams containing fission products and transuranium elements. Criteria aimed at the control of secondary waste streams may be appropriate, but their disposition will probably be by normal waste handling procedures.

16. Dispersibility or leachability of the storage form. No criterion on this topic may be necessary with respect to disposal, but one may be required for minimizing the effects of any accidents in transporting waste to the disposal site.

17. Shipping cask requirements. Specifications for packages or casks to be used in the shipping of hull waste can probably also be adapted from existing DOT regulations on relevant classes of materials.

C. Topics to be Excluded from Consideration in Criteria

Many safety-related topics appear pertinent to the alternative methods of preparing the hulls waste for final disposal. However, criteria need not be written for each such topic since existing regulations may suffice. Examples of topics for which specific criteria need not be written are listed below, together with the rationale for their exclusion.

1. Limits on radioactivity release. Under current Federal regulations, releases of radioactivity to the biosphere are to be as low as is reasonably achievable.

2. Retrievability of storage mode. Criteria are unnecessary because Federal regulations require disposal of TRU wastes at a site other than the reprocessing plant. Thus, hull wastes must be retrievable from any interim storage arrangements at the reprocessing site.

3. Radiation level of storage form. Existing Department of Transportation (DOT) regulations should specify this.

4. Bulk density of storage form. There is no need to limit density since this is not explicitly applicable to safety considerations.

5. Permissible gross surface/volume ratio of the storage form. The reprocessor's choice of storage form should not be restricted by an arbitrary ratio unless pertinent safety considerations necessitate this.

6. Thermal conductivity of storage form. This property is of importance only indirectly. It should be specified in a criterion specifying maximum centerline temperature of the storage container.

7. Permissible transport modes. This is not a pertinent concern. The mode(s) of transportation selected by the reprocessor must conform to current DOT regulations.

8. Type of acceptable disposal site for hulls. This is already covered by Federal regulations on disposal of TRU and non-TRU wastes.

D. Preliminary Criteria (B. J. Kullen)

Most of the criteria produced in this program are likely to be the result of much revising and refining of preliminary suggestions. Several preliminary criteria are presented below, and additional preliminary criteria will be formulated soon.

1. Hull waste and non-hull waste are defined as follows:

- a. Metallic fuel-assembly components that have been contacted by acidic solutions during the dissolution step of fuel reprocessing are considered to be hull wastes within the scope of these criteria. These wastes may include zirconium alloys, stainless steel, and other alloys and are not limited to metals that have been in direct contact with the spent oxide fuel. These wastes are also considered to be TRU wastes and shall be given the treatment for TRU wastes specified by Federal regulations.
- b. Fuel-assembly components that, during normal reactor operation and fuel-handling procedures, (1) do not contact the oxide fuel (*e.g.*, end pieces, assembly-support members, spacer grids), (2) are removed from the assembly, and (3) are not contacted with dissolver solutions are not considered hull wastes and, therefore, the hull-waste criteria do not pertain to them.

2. Mechanical operations (*e.g.*, sawing, unbolting, shearing, and subsequent handling) on spent fuel assemblies shall be conducted in areas provided with appropriate radiation shielding, ventilation, and equipment for safe, remote handling procedures. The above provisions shall be of such integrity that if accidental ignition and combustion of zirconium should occur, the safety and health of operating personnel and the general public will not be unduly endangered. Hull waste shall not be removed from the areas where the mechanical operations are performed unless first placed in sealed containers offering equivalent protection to operating personnel and the general public.

3. From the time of its generation, hull waste shall be contained within at least two (2) physical barriers. Specifically, this criterion shall apply to (a) the plant containment, (b) packaging for movement outside the plant containment to interim storage, (c) interim storage, and (d) packaging for transport to final disposal.

4. All equipment and mechanisms that handle hull waste, from fuel disassembly to packaging for disposal, shall be so constructed to preclude holdup of fine metal particles in quantities greater than those which, upon ignition and combustion, would impose a hazard to operating personnel and the general public. In cases where fines holdup is not precluded by design, routine operational procedures shall be instituted which keep the amount of retained fines below a quantity which is hazardous to operating personnel and the general public.

5. Materials that can contribute to the extent and intensity of a pyrophoric incident (*e.g.*, flammable or reactive materials) shall be excluded from areas where metallic fuel-assembly components or hull wastes are present and

from areas where metallic fuel-assembly components or hull wastes are present and from equipment or mechanisms that are used to handle metallic fuel-assembly components or hull wastes.

6. All metallic containers, mechanisms, and machinery that might contact metallic hulls waste during handling in the plant shall be designed to prevent discharge of static electricity.

7. Hull waste surveillance shall be included in the general plant-security operation, whether the hull waste is within plant containment or in interim storage outside plant containment.

8. Hull waste materials of particle size smaller than a nominal 6-mm diameter are to be considered fines and shall be separated from the larger-particle hull waste material as soon after the dissolution step as is feasible. These fines shall not be allowed to accumulate to quantities greater than 20 liters, (0.02 m^3), shall be kept in containers under a water cover, and, upon or before reaching the 20-liter accumulation limit, shall be subjected to a process which totally eliminates the pyrophoric potential of the material.

9. Hull waste material from which fines have been removed shall either be (a) dried in such a manner that a moisture content of less than 3 wt % is achieved in the shortest possible time, and maintained in such a condition as to ensure no introduction of water to the waste or (b) totally submerged in water under conditions that ensure no loss of the water cover. This criterion shall apply to hull waste stored for an interim period within the plant containment or outside the plant containment but within the plant boundary. Encapsulation of hulls into a matrix containing bound water (e.g., concrete) could reduce the access of free moisture to the hulls to meet this criterion.

10. The procedure used for drying hull waste shall leave the waste unchanged except for the removal of moisture. No material may be used in the drying procedure which leaves residues or reaction products that may, through secondary reaction or radiolytic/chemical decomposition, jeopardize the package used either for storage or for shipment to the final disposal site.

11. The packaging for hull waste that is to be stored outside the plant containment for an interim period shall provide the same protection as the plant containment, i.e., adequate radiation shielding and the ability to withstand ignition and combustion of the hull waste without endangering the health and safety of the operating personnel and the general public. The provision for combustion containment, however, may be omitted if a packaging or waste-treatment technique is used which ensures that the hull waste can not ignite during the interim storage period.

12. The packaging for hull waste to be stored outside plant containment for an interim period shall conform to Department of Transportation (DOT) accident specifications for radioactive-waste transport containers. These specifications shall apply to packages used (1) for transport to and from the interim storage area and (2) during the interim storage period.

13. The physical form of hull waste transported either to interim storage outside the plant containment or to final disposal shall be such that exposure of the waste to the atmosphere would not result in the release of aerosols, dusts, vapors, or solutions.

14. Any process used to treat hull waste materials with the objective of removing transuranium elements, reducing the waste volume, deactivating the pyrophoricity hazard, or accomplishing any combination of the foregoing, shall be subject to the following requirements:

- a. the products or product forms resulting from such treatments shall not be more pyrophoric than the original hull waste,
- b. the radioactive products or product forms resulting from such treatment shall not be more susceptible to leaching, corrosion, or dispersion or radioactivity than was the original hull waste.

15. During processing for the volume reduction or decontamination of hull waste in which the metallic state of the waste is maintained (e.g., compaction, melting, liquid-metal dissolution, surface decontamination), the amount of hull waste that may be handled at any time is limited to that which could ignite and combust totally without endangering the health and safety of operating personnel and the general public.

16. The packaging of any form of hull waste for shipment to the Federal repository for disposal shall conform to DOT accident specifications for radioactive-waste transport containers.

17. Hull waste, regardless of interim handling, shall be suitably packaged and transported to a Federal (ERDA) repository within five (5) years after its generation.

E. Hydrochlorination of Hulls (M. Ader)

One method proposed for reducing the volume and eliminating the pyrophoric hazard of hulls involves reaction of the major component of hulls (zirconium) and its volatilization from the TRU elements. At about 400°C, Zircalloys readily react with anhydrous HCl to produce $ZrCl_4$, which sublimates at 331°C and 1 atm pressure. Hydrochlorination eliminates the hazard of pyrophoricity; however, it would be desirable to convert the difficult-to-handle $ZrCl_4$ to stable, solid ZrO_2 via pyrohydrolysis. The ZrO_2 would still be beta-gamma active due to presence of the 9.5×10^5 -yr ^{93}Zr , but could be consigned to commercial burial. The residual nonvolatile TRU-bearing waste could be disposed of along with high-level active wastes, e.g., as a calcine or glass.

Examination of the literature did not reveal any experimental measurements on the separation of $ZrCl_4$ from transuranic oxides, although considerable work on hydrochlorination of U-Zr alloy and Zircaloy-clad enriched UO_2 was carried out in the 1960's [RAMASWAMI, CHILENSKAS]. Nevertheless, the general stability of the actinide oxides toward hydrochlorination at approximately 400°C, as well as the low vapor pressure of actinide chlorides, virtually ensures that zirconium volatilized as $ZrCl_4$ will not be contaminated with Np, Pu, Am, or Cm. In fact, entrainment of particulates is likely to be

the limiting factor to achieving a TRU-free waste, which is defined as waste having alpha activity of <10 nCi/g.

A limited experimental effort is now in progress to determine how well hydrochlorination decontaminates the zirconium in Zircaloy from accompanying plutonium (and americium) oxide. Substitution of Cl_2 for HCl will also be tried since chlorination does not produce H_2 and therefore avoids having to deal with a potentially explosive gas mixture. However, chlorine has disadvantages, such as the handling of a more corrosive gas and the possible difficulty [BARGHUSEN] of controlling the reaction with Zircaloy. The apparatus for this study, shown schematically in Fig. 13, has been set up in a vacuum-frame hood and is operated as follows:

Anhydrous HCl (or Cl_2) and N_2 flow through 1/4-in.-OD nickel tubing, passing through shutoff valves (V_1 , V_2), flow control valves (FCV_1 , FCV_2), and flow meters (FM_1 , FM_2). A Monel pressure-relief valve (V_4 , 50 psig) and pressure gauge (G_1) are included in the HCl line. The individual gases mix in a nickel cross, pass through a shutoff valve (V_5), and enter a rubber-stoppered 28-mm-OD Pyrex glass reactor at a pressure (G_2) only ~ 30 torr (~ 4 kPa) above atmospheric.

Fig. 13. Hydrochlorination Apparatus

The reactor is positioned inside a 30-cm-long by 2.5-cm-ID hinged tube furnace. A chromel-alumel thermocouple (TC2) under the reactor is used to control furnace temperature. Inside the reactor, gas flows around a solid nickel cylinder that serves as a preheater and prevents back-diffusion. It then flows over the sample (contained in a nickel or quartz boat resting on a nickel support). The reaction temperature is monitored by a chromel-alumel thermocouple inside a nickel thermowell that passes through holes in the rubber stopper, nickel preheater, and nickel support. Gaseous reactants and products are swept through a quartz-wool particle filter inserted in a constriction that prevents back-diffusion, and then through a standard taper connection to a Pyrex condenser that extends about 20 cm beyond the furnace and is air cooled. Because the connection, a Pyrex 24/40 $\frac{3}{4}$ Clear-Seal joint, lies within the hot zone of the furnace, it does not plug up with ZrCl_4 condensate. Gases that are not condensed pass through a Pyrex-wool filter, a Teflon stopcock, and then, via glass ball joints and sections of glass, nickel, and polyethylene tubing, into rubber-stoppered 1000- and 2000-cm³ glass mixing cylinders. Cylinders A and C are empty anti-suck-back traps; cylinders B and D each contain 3M NaOH to absorb excess HCl (or Cl_2). When the experiment is complete and the furnace has cooled to room temperature, the Clear-Seal joint is easily taken apart, and both the condensate and residue become available for dissolution and analysis.

Several trial experiments have been run under the following conditions: 0.5-3.5 g of Zircaloy-2 tubing; HCl (or Cl_2) and N_2 flow rates of 15-75 cm³/min; a pressure of ~ 105 kPa; reaction temperatures of 400-425°C; and reaction times up to about 70 min. The results indicated that the equipment is satisfactory for the intended study.

In some of these trials, a small fragment (26 mg) of high-temperature-fired UO_2 was included, and its weight and physical characteristics were not altered. Similar behavior is expected from $(\text{U,Pu})\text{O}_2$ --i.e., essentially no volatilization of uranium or plutonium. Therefore, in the Zr/Pu separation experiments to be done next, a fragment of $(\text{U,Pu})\text{O}_2$ containing less than 5 wt % Pu will be used. The amount of plutonium per experiment will be limited to ~ 1 mg, which is approximately the maximum permissible for these non-glovebox experiments. Approval to carry out this study was given following a safety review of the equipment and procedures. The Zr-Pu separations achieved by volatilization of ZrCl_4 will be reported next quarter.

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

A study of the feasibility of disposing of the noble gas fission products from a fuel reprocessing plant by underground injection is being organized. Rough estimates of expected annual volumes from a plant processing 1500 metric tons of uranium per year show that if krypton is separated from off-gases, to be stored alone, the amount of gas to be stored would be 150 m^3 (STP), whereas without separation the amounts to be stored would include 1500 m^3 (STP) of fission-product xenon and perhaps 10^6 m^3 (STP) of air.

The charter for this work suggests considering the possibilities of (1) storing the noble gases underground in the gaseous state, (2) storing the noble gases in solution in deep wells, and (3) using abandoned oil or gas wells for these two states. Storage of the gas underground has already received a good deal of evaluation during the past 10-15 years [KULLEN], but storage underground in solution has not been evaluated.

Plans to pursue this project, which must culminate in a written document (at least in rough-draft form) by October 1, 1977, includes the following:

- I. A very brief treatment of the feasibility of using abandoned oil wells.
- II. A brief survey of previous investigations of the feasibility of underground storage of noble gases in gaseous form, with summary and conclusions.
- III. An evaluation of the feasibility of storing noble gases in solution in deep wells which would be the effort most heavily emphasized in this project. This area offers an opportunity of contributing to the development of concepts for noble gas storage because it has not been pursued in detail previously and because it may offer technological advantages over simple injection for storage of gas.

This project will be a "paper study," not involving experimental work. Time and funding have been allotted accordingly. Among the factors that may have to be considered in determining the feasibility of these methods are the following:

1. estimated rate of escape of gases from stored solutions,
2. estimated radiation dose to public from this practice,
3. estimated radiation dose to operators from this practice,
4. general geologic requirements,
5. U.S. locations that possess the geologic requirements,
6. method and cost of transport from processing plant to storage site,
7. effect of salt content of storage fluid on gas solubility,

8. recommended solvents (water, organics),
9. susceptibility of organic fluids, if used, to bacterial action,
10. magnitude and effects of solvent radiolysis,
11. influence of local and Federal regulations,
12. capital and operating costs,
13. storage space and liquid volumes needed,
14. effect of nonideality of gases at storage pressure,
15. incentives for separating and storing krypton only.

The relative importance of these factors may vary widely, and it may be discovered during the course of this study that other factors not listed here are of major importance.

The diverse nature of the above list of possible significant factors indicates that a variety of disciplines must be applied to this evaluation, perhaps including geology, geological engineering, law, physical chemistry of solutions, radiation chemistry, and engineering economics. In order to bring such a variety of disciplines to bear on this problem with funding of only about 1 equivalent man-year, we plan to have the bulk of the study carried out by a consulting firm with a staff offering experience in the disciplines listed above, and with guidance and coordination by ANL. The program would consist of an attack on the problem (by the consulting firm) in stages that follow an outline of ANL. At the completion of each stage, ANL plans to review progress and to make recommendations for proceeding further. This plan is being pursued by arranging (with the help of the Argonne Procurement Division) for a contract with an appropriate consulting firm.

VII. SUPPORTING EFFORT FOR THE ENVIRONMENTAL
IMPACT STUDY OF WASTE MANAGEMENT

(L. Trevorrow, K. Flynn, L. Jardine, B. Kullen, M. Steindler)

ERDA has commissioned the preparation of an environmental impact statement on the treatment and disposal of waste resulting from commercial reactors and post-fission operations in the LWR fuel cycle. Contributions to the statement will be provided by many of the national laboratories and ERDA contractors, and the entire effort is being coordinated by Battelle-Pacific Northwest Laboratories. The waste management aspects of the statement will be based on available technology as presented in the recently issued document, "Alternatives for Managing Wastes from Reactors and Post-Fission Operations in the LWR Fuel Cycle" [ERDA].

The statement will be generic in nature, discussing typical or hypothetical facilities in typical or hypothetical environments. It is not intended to replace environmental statements required in support of specific projects nor for Nuclear Regulatory Commission licensing procedures. A major purpose of the generic statement is to inform the public and to solicit comments on the ERDA program for: (1) the final disposition of commercial radioactive waste, (2) waste treatment, (3) waste interim storage, and (4) transportation of waste.

The generic statement will not pertain to radioactive waste resulting from U.S. Defense Programs, the mining or milling of uranium, the management of waste from the breeder reactor program, or waste from other nations, nor will it include an evaluation of the impact of waste generated by power sources other than light water reactors.

The analysis of the environmental impact will consider types and levels of waste from light water reactors, reprocessing plants, spent-fuel basins, waste treatment and solidification facilities, mixed oxide fuel fabrication plants, decommissioning activities, interim storage facilities, transportation, waste isolation facilities. The statement will also consider the environmental impact of the use of commercial burial grounds for wastes not required to be delivered to the Federal government.

The contribution of an ANL team to this effort is to characterize the primary waste forms, *i.e.*, to define the properties of the wastes before any treatment operations have been applied to them. In this work, the wastes expected from LWRs, spent-fuel storage basins, fuel reprocessing plants, and mixed oxide fuel fabrication plants have been characterized including at a minimum the volume, composition, and radioactivity of these wastes.

The ANL team includes K. Flynn, L. Jardine, B. Kullen, and L. Trevorrow with M. Steindler as the task leader. The team distributed a first draft of this waste characterization on September 2, 1976, to Battelle and other teams that would use the data in developing concepts of waste treatment operations and the environmental impacts resulting from them. The draft was then revised to accommodate the needs of other task teams for information on waste properties, and the revision was distributed on October 18, 1976.

Current work by the ANL team involves (1) supplying additional information that other teams have specified they will need in order to complete their tasks, and (2) completing the re-expression of all data in a standard format

designed by Battelle. This format expresses the radioactivity in a waste as a fraction of some reference value. The reference values have been chosen in most cases to be radioactivities per unit weight of spent fuel at various cooling times, based on ORIGEN calculations by Battelle. This format, therefore, attempts to account for the distribution of all nuclides in spent fuel among the various waste forms produced by the facilities of the post-fission nuclear fuel cycle, i.e., reactors, fuel storage basins, fuel reprocessing plants, and mixed oxide fabrication plants.

In addition to completion of the reference tables, future work to complete this task is expected to consist of (1) some revision of the standard format tables (based on comments on them by Battelle and other participants in the Impact Statement work) and (2) rewriting of the text to accompany the tabular information. The textual material in previous drafts of this section of the environmental impact statement contained much general discussion of the characteristics of wastes and the facilities that generate them. The new textual material is expected to consist mainly of information to reference, support, and justify the data presented in the tables, which are now the focus of attention in the revised work. When the waste characterization has satisfied the needs of all tasks, the draft is expected to be distributed for review by appropriate representatives of the nuclear industry. A final revision of the draft will be made to include all of these additions and the revisions based on comments obtained in the industrial review.

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