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FEASIBILITY EVALUATION AND R&D  
PROGRAM PLAN  
FOR TRANSURANIC PARTITIONING  
OF HIGH-LEVEL FUEL REPROCESSING WASTE



**Battelle**

Pacific Northwest Laboratories  
Richland, Washington 99352

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FEASIBILITY EVALUATION AND R&D PROGRAM PLAN  
FOR TRANSURANIC PARTITIONING OF HIGH-LEVEL FUEL REPROCESSING WASTE

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SUMMARY

An approach to managing high-level radioactive waste is to separate it into fractions of different half-lives. Short-lived fractions would then decay to become radioactively non-toxic in relatively short times---times short enough to consider storage and to be within man's capabilities to predict events which would cause changes in the earth's crust. The long-lived fraction, much reduced in mass, decay heat output, and penetrating radiation output could be considered for other treatment such as transmutation to non-radioactive or short-lived nuclides, extraterrestrial disposal or special storage.

The objectives for this study were to review existing separations technologies and assess their potential for this application, to define process concepts expected to be capable of these separations, to identify areas where R&D to develop and design an effective process is required, and to prepare an R&D plan for selection and development of a partitioning process.

The scope of this study was partially determined by risk analyses performed as part of the PNL studies on advanced methods for management and disposal of high-level radioactive waste. These risk analyses determined that the actinides, selected fission products (I, Tc, Sm, and Sn), and nickel are the elements with isotopes of highest radioactive toxicity and potential need for removal from high-level waste. Separations techniques for all of these elements were therefore reviewed.

The risk analyses also made preliminary determinations of which of these potentially toxic elements would constitute a risk to man. With assumed repository waste release characteristics and current knowledge of isotope pathways and toxicity as a basis, these analyses indicated that the separations process would have to remove transuranics from waste with decontamination factors on the order of 100 in order to reduce the potential long-term risk to insignificant levels. These estimates are preliminary,

however, and further work should be done to verify and refine the process performance requirements.

A wide spectrum of technologies was initially considered. The review concluded that, of all of the alternatives available, solvent extraction and ion exchange separations of the types already widely used in the nuclear industry offer the best prospects for a cost effective process. Partitioning using these technologies to achieve transuranium element decontamination factors on the order of 100 is expected to be feasible. While these technologies exist, they have generally been applied for recovery purposes rather than for the separations purposes needed for partitioning. An R&D program to select and develop a partitioning processes is therefore needed.

Evaluations to determine the partitioning process R&D program needs determined the following:

- Partitioning of high-level waste produced from conventional reprocessing flowsheets is preferred over revision of reprocessing operations.
- An Am/Cm recovery process proposed by researchers at Karlsruhe shows promise but has alternatives and may encounter operational problems in service.
- Retention of transuranics on suspended solids in process streams may prevent achievement of design performance. Evaluation of the need to account for suspended solids in partitioning process design should be a major R&D activity.
- Analytical measurement capability commensurate with partitioning process needs may not now exist depending on separations requirements.

The results of these evaluations were used for formulate an R&D program plan for waste partitioning. The objective for the plan is to select and develop a partitioning process. Major supporting activities include waste characterization, aimed at determining the significant properties of the

waste feed for the process and their effect on process design; solids removal from waste, aimed at determining needs and methods to accommodate suspended solids in process design; and analytical techniques development, which will provide the laboratory and process instrumentation and procedures needed. These activities will provide information to the separations process development activity which is expected to select partitioning processes for pilot plant demonstration by mid-FY-1975.

The R&D program to select and develop a partitioning process is expected to require five years for completion. Total estimated funding required is approximately 3.0 million dollars.

FEASIBILITY EVALUATION AND R&D PROGRAM PLAN FOR  
TRANSURANIC PARTITIONING OF HIGH-LEVEL FUEL REPROCESSING WASTE

I. INTRODUCTION

This report presents the results of an assessment of the technical feasibility of separating high-level waste from fuel reprocessing plants into fractions with different long-term biological toxicity. A plan for research and development to select and develop a separations process is also presented.

The report includes a review of separations methods and current information, definition of methods that might be used to separate high-level waste, definition of areas where R&D is required, and definition of the R&D activities and schedules.

The basic objective for the separation process would be to eliminate, or reduce to acceptable levels, the potential long-term (after approximately 1,000 years) risk to man from high-level waste in terrestrial storage. The long-lived hazardous isotopes would be isolated as a separate waste fraction suitable for management by methods such as transmutation, disposal to space, or special storage.

This review was restricted to evaluation of technologies that might be used to make such separations for high-level waste. Assessment of practical feasibility (i.e., benefits obtained for costs incurred) can be obtained only by comprehensive analysis of the separations in context as part of the total waste management system. It will require definition and evaluation of trade-off's involving factors beyond the scope of this effort. It also will require, as shown in the report, information not now available.

II. SCOPE AND METHODOLOGY FOR THE STUDY

A. Separations Requirements

Design and selection of a partitioning process require determination of the elements to be removed and the amount of removal needed. These determinations involve three basic factors: (1) definition of toxic isotopes; (2) evaluation

of probabilities of release of toxic isotopes from a waste repository; and (3) evaluation of radiation dose to man. Release probabilities and dose evaluations are combined to estimate the risk to man.

Radiological analyses showed that the actinides, selected fission products (viz., I, Tc, Sm, and Sn), and nickel, which enters the waste as a result of dissolution of non-fuel core components, are the potentially toxic isotopes. Technologies for separating each of these elements from the high-level waste were therefore reviewed.

At the time that this study on waste separation was started, the study basis for separation was to produce a short-lived waste fraction which would decay to negligible radioactive toxicity to man in about 1,000 years. To accomplish this, removal of the elements listed in the previous paragraph from the short-lived fraction would be required. Removal requirements (decontamination factors) needed for these elements were expected to range from 100 to 1,000 for the fission products to the order of  $10^6$  for actinide elements.

Coincident with these waste separation studies, risk and pathway analyses were being made as part of advanced waste management study to evaluate the potential radiation dose to man which might result from a release of radioactive isotopes from a waste repository. These risk analyses have been completed for sample cases only and their use for determining the desired separation of long-lived from short-lived nuclides is not yet established.

Although preliminary and incomplete, these studies provide an indication of the order of magnitude of performance requirements for the waste separation process. Present indications are that only the actinide elements need be removed from the short-lived waste fraction and that removal of these elements by decontamination factors of about 100 may be adequate. There is indication that the only transuranium element of concern is Am and that U-233, U-234 and the daughters of these isotopes are the dominant toxic isotopes for time periods greater than  $10^5$  years. Since Pu-238 is a major source of U-234, removal of Pu might be required.

These studies to determine process performance requirements need to be extended, however, to verify and refine the DF needs. The repository release

studies are incomplete, and factors other than repository release may control the DF requirements. Possible controlling factors include alpha-induced rapid degradation of solidified waste, purity requirements for actinide streams produced from the separation process, and avoidance of problems due to californium in the fuel cycle.

#### B. Basic Separations Concepts

Two basic concepts for partitioning have been defined. One is to perform all operations on the waste as it is produced in existing nuclear fuel reprocessing operations. With this approach, partitioning would not be within, or have any effect on, the reprocessing operations. This concept has been defined as "adjunct partitioning". In principle, it could be applied to the waste any time after it is produced.

The other basic approach for partitioning is to incorporate it within the reprocessing operation. At minimum, this might involve only adjustments to operating parameters and controls. Beyond this minimum, various degrees of revision to the reprocessing operation could be conceived. Implementation of this concept, herein called "repro-partitioning," could require flowsheet and equipment modifications for existing and now-in-design reprocessing plants. The separations would, of course, be done only for fresh waste as it is produced.

Combinations of adjunct partitioning and repro-partitioning may be possible and desirable.

#### C. Guidelines and Methodology

The basic guideline for this study was to obtain a comprehensive, overview evaluation of separations technologies and their applicability for removing the actinides and long-lived hazardous fission products from high-level waste. Major results sought from the review were identification of separations concepts which show promise for high-level waste separations, and identification of areas where R&D is required.

Since waste composition will depend on many factors (e.g., reactor type, fuel exposure history, cooling time, etc.) the study sought to make

the evaluations independent of waste composition. Separations processes will, in practice, have to accommodate wastes of various types. However, most information currently available is based on waste from LWR fuel with relatively low burnup in comparison with exposures anticipated for the future. Results of this study are therefore potentially limited by the possibility that present information cannot be extrapolated reliably to wastes from the mixed nuclear power economy of the future. Present expectations are that this study has identified the problems which should be generic for all types of waste; differences for various fuels are expected to be of degree rather than kind. Additional work is required to verify this, however.

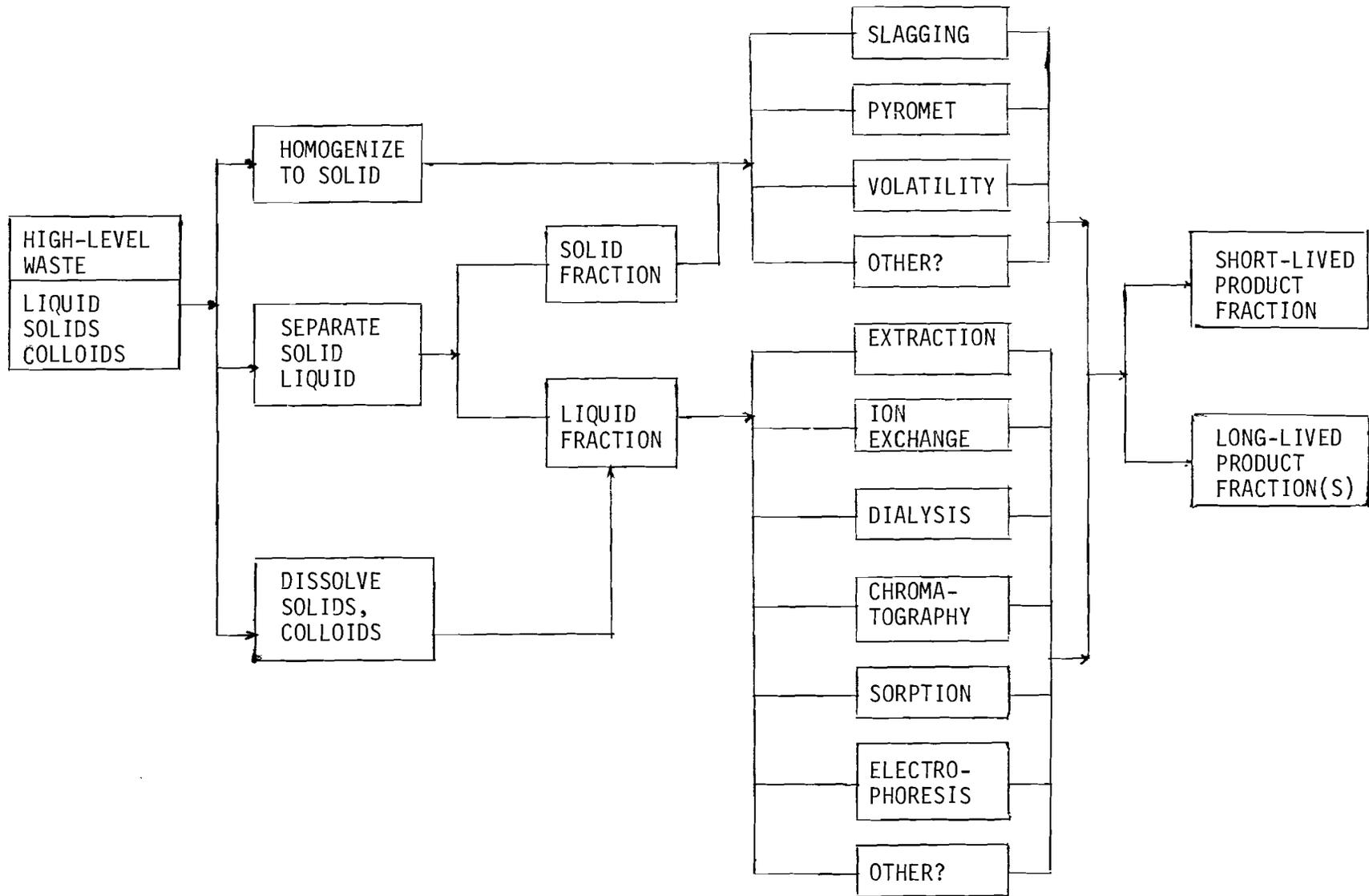
The separations technologies shown in Figure 1 were evaluated. Figure 1 is constructed to illustrate the fact that suspended solids or colloids in the waste are potentially a significant problem which could limit or define the feasible separations technologies (see Section III). Solids are expected to be present in the waste; if treatment of them is needed, operations such as shown in Figure 1 would be needed prior to separations. The possibility that separations would have to be done on a solid waste introduces, as shown in Figure 1, the need to consider pyrometallurgical, slagging, and other solids-based separations techniques within the scope of this study.

Rapid decisions on feasibility of concepts were sought via consultation with acknowledged experts. Approximately twenty-five experts outside BNW were contacted during this study.<sup>(140)</sup> These included individual consultants, personnel of other AEC laboratories, and industrial firms with expertise in special separations techniques. The contributions of these experts are reflected in the contents of this report.

In addition to these contacts with individuals, an exhaustive literature search was conducted by an experienced and highly qualified librarian. The literature on separations is extensive; sources cited in this report are only representative of the information available.

Three major problem areas were defined and evaluated within this review: (1) suspended solids in waste, (2) separations technologies, and (3) analytical measurements. Sections III through VI of the report are devoted to these areas. Individual summaries are given at the end of each of these sections.

FIGURE 1  
BASIC WASTE PARTITIONING OPTIONS



Results of the reviews were analyzed and interpreted to deduce process concepts expected to be feasible for high-level waste partitioning and to define problem areas requiring future R&D. These utilizations of the reviews are reported in Sections VII and VIII.

### III. SUSPENDED SOLIDS IN WASTE

One of the major problems for adjunct (and possibly repro-) partitioning is the presence of suspended solids in the waste. In broad terms, the problem is that suspended solids can greatly reduce or destroy the effectiveness of a partitioning operation. If components to be removed are in the solids (and/or colloids), they will not be "available" for removal by a partitioning agent such as an extracting solvent. Thus, for example, if the suspended solids contain a large fraction of the Pu to be partitioned, a process designed to produce a Pu DF of 100 might actually achieve a DF of only 10 or less.

The solids are known to exist. The typical concentration range is 1-10 weight percent. They may be introduced by two primary sources: carryover from the dissolution operation, or as a result of the reprocessing chemistry (e.g., exceeding solubility limits). If waste is stored (as liquid or a solid to be subsequently redissolved) for some period of time before partitioning, solids would still be present. The physical and chemical characteristics of these solids would, however, be expected to be quite different from those for fresh waste as a result of aging effects.

Another potential source of solids is that they might be generated during the partitioning operation as a result of chemical effects such as for the reprocessing operation.

In summary, solids that may adversely affect adjunct partitioning operations can be produced in several ways. If they contain a significant fraction of the isotopes to be partitioned, or if they would otherwise

interfere with the operation, they would have to be separated from the waste. The removed solids would then be a separate, small-mass waste stream which could be, but might not be, subjected to further treatment prior to storage or disposal.

The present problem is to determine if the solids would interfere with adjunct partitioning. This section reviews available literature on the subject and assesses the status of knowledge. For convenience, the solids problem is divided into several areas of concern:

- A. Dissolution of Spent Fuel Elements
- B. Separation of Solids from Dissolver Solutions
- C. Characterization of Solid Residues
- D. Volume and Characterization of Solids in High-Level Acid-Stored Waste
- E. Summary of Current Knowledge
- F. Major R&D Needs

A. Dissolution of Spent Fuel Elements

Excellent review articles by K. L. Rhode and J. A. Buckham,<sup>(1)</sup> J. H. Goode,<sup>(2)</sup> and W. Baehr and T. Dippel,<sup>(3)</sup> as well as others, provide a state-of-the-art review on the dissolution of fuel materials.

The dissolution of  $\text{PuO}_2\text{-UO}_2$  in nitric acid is affected by (1) the percentage of  $\text{PuO}_2$ , (2) the method of fabrication,<sup>(4)</sup> and (3) the irradiation level.<sup>(5)</sup> Plutonium dioxide<sup>(6)</sup> does not dissolve readily in  $\text{HNO}_3$  (about 15% of the total Pu was insoluble)<sup>(7)</sup> unless it is combined with  $\text{UO}_2$  in a solid solution. Usually a catalyst such as fluoride is required for complete dissolution. However, the use of fluoride causes corrosion problems. The addition of three moles of aluminum nitrate per mole of fluoride to prevent corrosion to the dissolver negates the effect of the fluoride.<sup>(8)</sup>

Solid solutions of  $\text{PuO}_2\text{-UO}_2$  (up to 35%  $\text{PuO}_2$ ) were found to be soluble in  $\text{HNO}_3$ . Studies with unirradiated fuel demonstrated that mechanically blended 15%  $\text{PuO}_2\text{-85% UO}_2$  could be converted to solid solutions with increased

sintering times.<sup>(9)</sup> When 25% PuO<sub>2</sub>- 75% UO<sub>2</sub> fuel was irradiated in the ETR to 20,000 MWd/T the fuel was more soluble; Pu in the residue decreased from about 16% for the unirradiated pellets to less than 5% for irradiated material. Voloxidation (PuO<sub>2</sub>-UO<sub>2</sub> oxidized to PuO<sub>2</sub>-U<sub>3</sub>O<sub>8</sub>) had only a modest effect on the dissolubility of unirradiated fuel.

Hot-cell dissolution of highly irradiated 20% PuO<sub>2</sub>- 80% UO<sub>2</sub>, stainless-steel clad, fast reactor fuel specimens irradiated to levels as high as 99,000 MWd/T was reported.<sup>(2)</sup> More than 99% of the PuO<sub>2</sub>-UO<sub>2</sub> dissolved in less than 5 hours in all concentrations of HNO<sub>3</sub> greater than 3M. No fluoride was required. Undissolved residues consisted of core oxides and fission product Mo, Zr, Pd, Ru, and Rh.<sup>(2)</sup> As the U and Pu became more soluble with increased burnup, the ratio of Pu/(U+Pu) in the residues became smaller. The average ratio of the Pu/(U+Pu) in the residues from the three different fuel specimens was about 0.64, 0.52 and 0.29 at 17,000, 45,700, and 66,300 MWd/T, respectively.

Rhode and Buckham noted that a more complete understanding of the effects of irradiation on the chemical reactivity of these alloys and oxides appears dependent upon a greater understanding of the fundamental changes in composition and structure which occur on irradiation.<sup>(1)</sup> Even if a solid solution of PuO<sub>2</sub>-UO<sub>2</sub> originally exists (providing complete dissolution), these oxides may tend to segregate in the reactor environment to provide, upon discharge, a mixture which is partly a solid solution enriched with respect to UO<sub>2</sub> but which also contains some rather pure PuO<sub>2</sub> in the center of the fuel rod.<sup>(10,11)</sup> This segregation is caused by a migration of UO<sub>2</sub> away from the center of the rod while in the reactor. The dissolution requirements for this material are probably more severe than for the original solid solution.<sup>(12)</sup>

For PuO<sub>2</sub>-UO<sub>2</sub> fuels, it may be attractive to dissolve the major fraction of the fuel by first using a brief leaching step followed by separation of the fuel residue from the solution for a more rigorous treatment.<sup>(13)</sup> Schulz<sup>(14,15)</sup> reports the use of HNO<sub>3</sub>NH<sub>4</sub>F; Divine<sup>(16)</sup> and others<sup>(17-19)</sup>

suggest the use of complexing agents to dissolve  $\text{PuO}_2$ ; Uriarte and Rainey<sup>(8)</sup> review the dissolution of high-density  $\text{UO}_2$ ,  $\text{PuO}_2$ , and  $\text{UO}_2\text{-PuO}_2$  pellets in inorganic acids, and Gilman<sup>(20,21)</sup> refers to many approaches to the dissolution of  $\text{PuO}_2$  using mineral acids, fusion,<sup>(22,23)</sup> halogenation,<sup>(6,24)</sup> and complexing agents.

#### B. Separation of Solids from Dissolver Solutions

As the fuel elements receives higher burnup the amount of fission products will increase. In dissolution tests at ORNL with LMFBR fuel specimens of 20,000 to 73,000 MWd/T burnup, the mass of undissolved residues varied widely but usually was in the range of 1 to 10% of the initial fuel mass. These residues settled fairly rapidly in the fuel solution. Filtration through Whatman No. 42 filter paper was extremely slow.<sup>(25,26)</sup>

The operating experience in La Hague (the AT 1 pilot plant) with highly irradiated (up to 60,000 MWd/T) fuels containing 25%  $\text{PuO}_2$  indicated that the filtration of the feed solution coming out of the dissolver was a major problem. They found a rather high quantity of insoluble material (some g/kg U) which contained some metallic elements such as Mo and Ru, but very few fissile materials.<sup>(27)</sup> In a USSR operation, the initial dissolver solution was treated with a flocculator, heated, and then filtered to prevent the formation of interfacial suspensions.<sup>(28)</sup>

A number of fuels being reprocessed at Idaho Chemical Processing Plant (ICPP) produced considerable quantities of solids after their dissolution. Undissolved solids in the dissolver product solutions have caused line blockage and contributed to interface cruds. A centrifuge has been installed to remove solids from the dissolver solutions before they are fed into the extraction columns.<sup>(29,30)</sup>

Extensive studies of aluminum-uranium-silicon alloys show that dissolved silicon may polymerize forming a gelatinous precipitate. Very little is known about the kinetics of the polymerization of dissolved silicon, and the quantity of this type of solid (or colloid) which may form with different process conditions is not known.<sup>(29)</sup> The aluminum-fuel dissolver solution

is sometimes treated with gelatin to prevent emulsion formation in the extraction columns;<sup>(31)</sup> gelatin has also been used as a flocculant prior to centrifugation to remove silica.<sup>(32)</sup>

During the reprocessing of Zircaloy-clad fuel in the ICPP, considerable zirconium oxide solids were encountered. A centrifugal force of 100 x G removed the bulk of the solids from the solution in less than one minute. Determination of the uranium loss to the solids was not attempted in the simulated process solution.<sup>(29)</sup>

Four laboratory-scale hydrocyclones were evaluated for their efficiency in clarification of product solution from electrolytic dissolution of EBR-II fuel at ICPP. Ninety-five percent removal of stainless-steel solids and 10% removal of EBR-II fission alloy was attained.<sup>(33)</sup> Cyclone separators were used to clean up the fluid of the aqueous homogeneous reactor at ORNL.<sup>(34)</sup>

H. C. Rathvon, formerly of Nuclear Fuel Services, Inc., indicates that 2-5 weight percent solids were found in dissolver solution tests. Plugged lines have been cleaned with  $\text{NH}_4\text{F}$ ; success with this method indicates that the plug was mainly due to Zr fines from the chop-leach step.<sup>(35)</sup>

### C. Identification of Solid Residues

Very few studies have been made to determine the volume and identity of the insoluble residues resulting from the dissolution of various fuel elements. These solids are primarily insoluble cladding oxides and undissolved core materials, such as Mo, Pd, Rh, Nb, Zr, Mn, Al, Ce, Ba, La, Ru, and Si.<sup>(12,36)</sup>

J. H. Goode<sup>(2)</sup> found that the fission products from  $\text{UO}_2\text{-PuO}_2$  irradiated to 99,000 MWd/T were soluble in a  $5\text{M HNO}_3\text{-}0.53\text{M UO}_2(\text{NO}_3)_2\text{-}0.12\text{M Pu}(\text{NO}_3)_4$  solution with the exception of an insoluble residue amounting to 2 to 3% of the weight of the core. Spectrographic and chemical analysis showed that the residues contained 1.5 mg of U, 2.0 mg of Pu, 28 mg of Mo, 24 mg of Zr, 1 mg of Pd, and 3 mg of Rh, totaling 59 mg or 2.2% of the fuel oxide weight. Gamma-ray scanning showed that nearly all the radioactivity was due to  $^{106}\text{Ru}$ .

The gamma spectrum for one of the leach residues from the 4-8M HNO<sub>3</sub> dissolution of a 20% PuO<sub>2</sub>- 80% UO<sub>2</sub> coprecipitated, 50,000 MWd/T specimen supplied by NUMEC, showed the following principal radionuclides with the indicated activity levels (in dis min<sup>-1</sup>g<sup>-1</sup>): <sup>106</sup>Ru, 20.9 x 10<sup>12</sup>; <sup>103</sup>Ru, 8.5 x 10<sup>11</sup>; <sup>144</sup>Ce, 7.2 x 10<sup>11</sup>; <sup>95</sup>Zr-Nb, 5.1 x 10<sup>11</sup>; <sup>125</sup>Sb, <3.0 x 10<sup>11</sup>; and <sup>140</sup>Ba-La, 7.0 x 10<sup>11</sup>.<sup>(13)</sup> The amount of undissolved Pu ranged from 0.08 to 8.3% in other leaching tests with 100,000 MWd/T NUMEC rods in boiling 8M HNO<sub>3</sub>.<sup>(37)</sup>

To reduce the Pu loss to the undissolved residues, use of F<sup>-</sup> is usually required. Dissolution tests were made with voloxidized, mechanically blended 25% PuO<sub>2</sub>- 75% UO<sub>2</sub> fuel.<sup>(38)</sup> After 10 hours of dissolution with 8M HNO<sub>3</sub> the residue contained 5%, 5.5%, 80%, 50%, 4%, and 3.5% of the Pu, U, Ru, Nb, Zr and Ce, respectively. An additional 2 hours of 8M HNO<sub>3</sub>- 0.05M HF treatment reduced the loss to the residue to 0.05% Pu, 0.01% U, 75% Ru, 15% Nb, 0.4% Zr, and 0.17% Ce.

B. C. Musgrave<sup>(39)</sup> indicates that the solid residues resulting from the chemical or electrochemical dissolution of the EBR-II uranium-fissium alloy contained all of the components of the fission alloy except Mo. The Mo was quantitatively dissolved; Ru was about 20% dissolved (i.e., 80% of the Ru remained in the residue). On the basis of these Mo and Ru data, it was estimated that the residues amounted to about 2% of the fissium alloy.

#### D. Volume and Identification of Solids in High-Level Acid-Stored Wastes

Very little information is available on the effects of concentration and long-term storage of boiling high-level acidic wastes on solids content. Hanford and NFS currently store on the alkaline side. No information has been found relating to acid storage experience in Europe.

Cooley, et al., note that in future fuel reprocessing plant designs more emphasis will be placed on routing all radioactive wastes to the high-level waste streams to minimize the amount of intermediate and low-level wastes.<sup>(40)</sup> With this approach will also come additional cations and anions such as Po<sub>4</sub><sup>=</sup> that will effect the ultimate solias-solution relationship.

E. Summary of Current Knowledge

Data on spent fuel dissolution show that the effectiveness of various techniques will depend on many factors, including fuel composition and history. Plutonium has been indentified in the residual solids. Data are quite sparse for present purposes but suggest that the amount of solids in the dissolver effluent and its Pu content may be highly variable (1-10 w/o).

Available data (again sparse) on separation of solids from the dissolver effluent show that separation is frequently difficult. Colloids are indicated to be present. These solids apparently cause problems in the reprocessing operations. However, contributions to these problems via solids formed as a result of process chemistry have not been distinguished.

Few studies have been made to characterize the composition and amounts of solids in the dissolver solution. Plutonium has been identified, however, in the residues examined.

There is no information on the solids content of waste immediately after production in the reprocessing operation.

There is no useful information on the solids content of waste after periods of acid storage.

F. Major R&D Needs

Available data are insufficient to answer adequately either of the two key questions concerning the effect of suspended solids on adjunct partitioning, i.e., will the solids contain significant amounts of elements to be partitioned, and, is removal of solids from the waste necessary? Perhaps most significant, none of the data address the problem of Am, which is expected to be the element most in need of partitioning.

For a variety of reasons (chiefly, to avoid high radiation levels and problem nuclides) adjunct partitioning is preferred to be done several years after the reprocessing. This means that solids that exist after storage and aging of the wastes would be of most significance. At one extreme, such solids might be adequately represented by solids present during the dissolution

and/or reprocessing operations. Data such as those cited above would then be representative. On the other hand, solids present after aging might be markedly different from those in a fresh waste stream. This would be expected especially if the waste is solidified and redissolved prior to partitioning. As noted above, there is no information on solids associated with aged, acid-stored waste.

For practical purposes, then, history provides at best a tentative indication of the solids problem associated with adjunct partitioning. Only if present data on dissolver and reprocessing solutions are assumed representative can any inferences be made. Such an assumption is probably unrealistic. An R&D program to evaluate the existence and resolution of problems that solids might pose for adjunct partitioning is therefore needed.

Basic elements of this program should be:

- Follow on-going work in Europe that is significant to this problem. Coordinate our programs with European effort insofar as possible.
- Devise and implement a program for solids studies derived from calcined wastes now in storage at Idaho Falls. The basic objective for this work would be to characterize problems that might arise for partitioning of waste that had been solidified and redissolved.
- Devise and implement a program of studies on solids present in acid-stored waste. Representative materials might be obtained from existing reprocessing facilities either here or in Europe.
- Attempt theoretical predications of solids formation. The capacity of theoretical concepts (solubility products, etc.) to provide useful information is probably highly limited. A modest effort should be made, however, to test the possibility.

#### IV. WASTE SEPARATIONS METHODS

This section reports the review and evaluation of methods that might be used to accomplish waste partitioning and fractionation. The methods described are in principle applicable to either adjunct partitioning or repro-partitioning. Specific requirements for use probably would differ markedly, however, for the two situations.

The contents of this section reflect the objective of comprehensiveness. Attention has been given to all actinide elements that might be candidates for partitioning and those fission products shown by the risk analyses to be candidates for fractionation. No assumptions concerning level of removal (i.e., DF attained in practice) were made, since actual DF requirements will depend on the outcome of the release and pathways studies referred to in Section II.

Present indications are that the factors involved in waste storage and any escape of isotopes from storage may have risk reduction effects such that the only requirements for partitioning would be to reduce Am, Pu, and possibly Cm concentrations in the waste to be stored by factors of about 100 in comparison with their initial concentrations. Fractionation would not be required. In contrast, in the absence of these waste holdup effects the concentration reductions demanded of partitioning would be on the order of  $10^6$  to  $10^8$ ; fractionation would also be required.

These indications of partitioning requirements in practice are preliminary and limited in scope. More comprehensive risk analyses might change the list of elements to be removed and the DF's required. The comprehensive review reported here is intended to cover all possible needs and to indicate the method alternatives available.

##### A. Partitioning of Solids

A need to partition waste initially in a solid phase could arise either if all waste is solidified or if suspended solids are isolated from the liquid phase (cf. Figure 1).\* A solid consisting of the total would be

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\*A third alternative for primary treatment of the waste is to dissolve all solids (Figure 1). This is considered impractical and not discussed further in this report. The solids are present because of dissolution difficulties; large volumes, perhaps without effectiveness, would be required to complete the dissolution.

produced if, for example, liquid storage was not permitted and storage of waste for some period prior to partitioning was required. It might also be produced as the first step in a partitioning process (which would have to be demonstrably advantageous in comparison with a liquid-based process) which requires a solid as the starting material.

#### A.1 Partitioning Methods for Solidified Waste

Review and evaluation to date indicates that solid-phase partitioning promises formidable problems. Three major problems stand out: high temperatures, and therefore high energy inputs, would be required; the separations are not clean (i.e., good decontamination factors are not inherently attainable); and major R&D, including extension of basic knowledge, would be required to prove and develop a feasible and effective process. Other potential problems include generation of large volumes of slag waste, control of volatile components, and the possibility of higher inherent hazard to operating personnel and the process environs (in comparison with alternatives such as extraction).

These potential problems (defined primarily from consultation with experienced personnel at ORNL, ANL, and the Bureau of Mines) were sufficient to preclude in-depth study of this approach to partitioning. Further evaluation is possible but not recommended. Alternatives based on liquid-phase operations appear much more attractive.

For overall cost effectiveness, partitioning based on solids-phase treatment has therefore been dropped from consideration. A possible need remains, however, to devise treatments for solids that are present.

#### A.2 Waste Solidification Prior to Partitioning

If all waste is solidified prior to partitioning, process concepts for redissolution of the waste prior to the partitioning operations would be needed. A major concern would be to solidify the waste so that it could be easily redissolved by agents that would be compatible with the partitioning process. There is no experience to indicate solidified forms that will optimize the process. Certainly, however, a high-integrity solid such as borosilicate glass would not be appropriate. Calcines such as are formed at Idaho Falls may be satisfactory.

Pursuit of this approach (i.e., solidification of all waste prior to partitioning) does not appear desirable unless all opportunity for liquid storage of waste is banned and partitioning immediately after or during reprocessing is proven infeasible. The concept would introduce waste management costs and operations that need not be incurred unless mandatory. It may be argued that interim storage (i.e., prior to partitioning) of solidified waste is safer than liquid storage, but the validity of this argument would have to be tested via a trade-off analysis. The extra operations and materials required to solidify and redissolve the waste may offset the benefit for the storage form.

### A.3 Treatment of Suspended Solids

If suspended solids are isolated from the waste solution, the solids constitute a separate waste stream. This waste may be managed without further treatment, or partitioning may be applied to it. The choice may depend on the composition and amount of the separated solids (see Section III).

As indicated by the fact that they are present, the suspended solids are expected to be difficult to dissolve. However, fusion followed by dissolution and liquid-phase partitioning were identified during this study as processes which could provide for the solids a partitioning effectiveness comparable to that for the liquid-phase waste. Evaluation of whether such operations should be done is a task for future study. The decision will depend on factors such as the characteristics of the solids and the requirements for the fusion-dissolution operations.

### B. Liquid-Phase Partitioning

As shown in Figure 1, many basic liquid-phase partitioning concepts were considered. A consensus was quickly established, however, among the staff and consultants who participated in the study, that solvent extraction and ion exchange offered far greater promise for effectiveness and flexibility than the alternative concepts. This consensus was confirmed by communication with experts on the other concepts (e.g., flotation, dialysis, etc.). These

other concepts are at this time not sufficiently developed, or are not sufficiently effective for use, or are beset by process problems (e.g., membrane degradation) that would preclude their use. For these reasons, major attention was centered on solvent extraction and ion exchange. Use of these techniques for separations such as would be required by partitioning has been widely explored. Their use would therefore represent relatively straightforward extension of existing technology, maximum compatibility with present operations, and minimum investment in future R&D programs.

Problems which could limit practical application of solvent extraction and ion exchange (e.g., generation of large volumes of low-level liquid wastes or contaminated, waste ion exchange resin) were recognized but not treated in depth. Detailed evaluation of such problems was beyond the scope of this work and can be done with maximum cost effectiveness after actual partitioning requirements are better defined.

Radioisotopes which would be candidates for liquid-phase partitioning or fractionation were identified in the risks study that paralleled this work. The initial risks study was also generic and all-inclusive. It indicated that the isotopes listed in Table I are those most likely to be candidates for fractionation or partitioning. Isotope properties shown in Table I were derived from ORIGEN runs for Diablo Canyon Reference LWR fuel.<sup>(42,43)</sup> Activation products (from cladding, etc.) are included because the potential hazard from some of these is comparable to that for some of the fission products.

Table I provides no indication of the actual ranking of the nuclides as a potential hazard to man. Such a ranking is a complex function of the risk and pathway analyses, as previously noted. Analyses to establish these rankings are at present incomplete but indicate that Am, Pu, and Cm are the actinides of major concern and I, Te, Sm, and Sn are the fission products of most concern. The scope of this study was limited to these fission products, the actinides, and the major problem from neutron activation, nickel. Expected waste concentrations for these elements are shown in Table II.

TABLE I. Radioisotopes Potentially Requiring Partitioning or Fractionation

Basis for Data: ORIGIN Runs for Diablo Canyon Reference LWR Fuel

Nuclide	t 1/2		Ci/T		g/T 10 yr	Ci/g* 10 yr	10 <sup>-3</sup> g/g* 10 yr
	yr		1,000 yr	10,000 yr			
Ni-59**	8x10 <sup>4</sup>		0.394	0.358	5.72	3.98x10 <sup>-4</sup>	5.72
Ni-63**	92		1.48x10 <sup>-6</sup>	0.0	425	60.1	425
Se-79	7x10 <sup>4</sup>		1.89	1.88	736	1.89x10 <sup>-3</sup>	736
Sr-90	28		14.3	13.9	841	1.43x10 <sup>-2</sup>	841
Zr-93	9.5x10 <sup>5</sup>		0.110	0.110	231	1.10x10 <sup>-4</sup>	231
Tc-99	2.1x10 <sup>5</sup>		0.543	0.510	19.2	5.46x10 <sup>-4</sup>	19.2
Pd-107	7x10 <sup>6</sup>		0.0374	0.0374	229	3.74x10 <sup>-5</sup>	229
Sn-126	10 <sup>5</sup>		0.286	0.285	324	2.86x10 <sup>-4</sup>	324
I-129	1.6x10 <sup>7</sup>		9.85x10 <sup>-6</sup>	0.0	974	84.8	974
Cs-135	2x10 <sup>6</sup>		0.435	3.12x10 <sup>-32</sup>	42.3	1.15	42.3
Cs-137	30		1.05x10 <sup>-15</sup>	0.0	30.7	4.45	30.7
Sm-151	93		1.69x10 <sup>-3</sup>	3.10x10 <sup>-3</sup>	22.7	1.44x10 <sup>-6</sup>	22.7
Eu-154	16		0.368	0.374	483	3.41x10 <sup>-4</sup>	483
U-236	2.39x10 <sup>7</sup>		0.222	10 <sup>-19</sup>	5.68	9.59x10 <sup>-2</sup>	5.68
U-238	4.47x10 <sup>9</sup>		2.05	4.03	26.4	1.62x10 <sup>-3</sup>	26.4
Np-237	2.14x10 <sup>6</sup>		8.28	3.29	20.5	4.53x10 <sup>-3</sup>	20.5
Pu-238	87.7		7.60x10 <sup>-3</sup>	8.0x10 <sup>-3</sup>	1.76	6.88x10 <sup>-6</sup>	1.76
Pu-239	2.44x10 <sup>4</sup>		34.7	0.144	45.9	0.157	45.9
Pu-240	6.76x10 <sup>3</sup>		16.1	7.12	91.5	1.76x10 <sup>-2</sup>	91.5
Pu-242	3.79x10 <sup>5</sup>		5.89x10 <sup>-14</sup>	0.0	21.3	1.73	21.3
Pu-244	7.6x10 <sup>7</sup>		0.306	0.144	1.88	3.33x15 <sup>-4</sup>	1.88
Am-241	428		0.0577	0.0153	0.216	6.67x10 <sup>-5</sup>	0.216
Am-243	7.37x10 <sup>3</sup>						
Cm-244	18.1						
Cm-245	9.32x10 <sup>3</sup>						
Cm-246	5.48x10 <sup>3</sup>						

\* 1,000  $\lambda$  waste/ton

\*\*From non-core components.

TABLE II. Candidate Elements to be Isolated -  
Expected Concentrations in Waste

<u>Element</u>	<u>Concentration in Waste</u> <u>(10 Year Storage)</u> <u>g/l<sup>(3)</sup></u>
Np	0.483
Pu <sup>(1)</sup>	0.058
Cm	0.024
Am	0.138
Sm	0.901
Tc	0.841
Sn	0.051
I	0.270
Ni <sup>(2)</sup>	---

Notes: (1) Represents 0.5% of spent fuel value.

(2) Not a fission product.

(3) 1,000 liters/ton.

## B.1 Solvent Extraction

Many thousands of man-years of research and development have been applied to solvent extraction. Much of this work has been for the nuclear industry, with the outcome of making solvent extraction the basic technology for nuclear fuel reprocessing and other nuclear-oriented separations.

As a result of this effort, there is a vast literature on this topic. The specific problem of waste partitioning has not been previously considered, but there are sufficient data available to permit identification of attractive processes and estimation of additional study required.

B.1.1 Iodine --- Iodine can, in principle, be removed by solvent extraction since the elemental form is very soluble in a large number of solvents. Problems exist, however: iodine exists in several valence states and can be difficult to extract from an aqueous phase of high ionic strength. Also, as Purex operating experience has shown, iodine tends to combine chemically (irreversibly) with some solvents.<sup>(44)</sup> Thus, extensive removal of iodine by volatilization in steps prior to or just after fuel dissolution is extremely advantageous not only to the present partitioning problem but to the main fuel reprocessing program. At the present time retention of at least one percent of the iodine in the dissolver solution seems likely.<sup>(45)</sup> This figure is assumed for Table II. Subsequent volatilization studies may prove this value to be high by as much as a factor of 100, i.e., all but 0.01 percent of the I might be blown out of the dissolver. The fact that a very small fraction of the iodine appears to be "refractory" towards volatilization, exchange with cold iodine, etc., suggests that removal by solvent extraction may be equally difficult. On the other hand, the species resisting volatilization could be readily extractable. Further work is needed on the chemistry of iodine at low concentrations in aqueous solutions. Whatever the method, iodine separation may require a separate step from the other partition operations. Isotopic dilution with nonradioactive iodine may be an effective I-waste management method.

B.1.2 Nickel -- Nickel may be a formidable problem. It does form extractable complexes such as the one with dimethylglyoxime. However, to form these complexes requires a unique environment, e.g., buffered acetic

acid solution. Such a solution is not compatible with reprocessing wastes. It is possible that other chelating reagents can be found which will assist extraction. At this time no solvent extraction technique suitable for nickel has been identified.

The source of the nickel is stainless-steel reactor components. It may be possible and desirable to remove this contamination before the fuel reprocessing step if removal of nickel from the waste is actually required.

B.1.3 Actinides, Lanthanides, Technetium and Tin -- The primary target for waste partitioning is expected to be the actinides, the lanthanides, technetium, and tin. Simultaneous removal of neptunium and plutonium will be required, including the Pu which resulted from higher actinide decay during storage. Separation of the lanthanides and the trivalent actinides (Am, Cm) is difficult, but nature is kind in one respect: since samarium is the only lanthanide to be removed and since lanthanides with atomic numbers above samarium are a small fraction of the total lanthanide mass, it may be adequate to separate lanthanides into two groups, Sm and higher atomic numbers, and Pm and lower atomic numbers. Since the actinides and lanthanides are very similar in extraction behavior, and since both show a progression in extraction with atomic number, this abundance distribution with the division line at samarium can be an important factor in separations feasibility and effectiveness.

Americium appears to be the element of major concern as a hazard. Curium, which is present in much smaller concentration, will follow the americium in the partitioning process.

Solvent extraction can be described in terms of solvent types. The attractive ones for the present problem appear to be: (1) neutral organophosphorus compounds; (2) acid organophosphorus compounds; (3) organic amines; and (4) chelating reagents. Other neutral solvents such as ethers and ketones and other acidic compounds such as carboxylic acids may have application.

● Neutral Organophosphorus Compounds -- Tributylphosphate (TBP) is probably the best known solvent in the nuclear industry. The extraction of Np and Pu has been adequately demonstrated with this reagent. Americium and Cm can be extracted from the nitrate solution but a high salting strength and low acidity are required. These conditions can be tempered somewhat by using a high TBP concentration instead of the conventional 15-30% solution. Roberts and Bray at Hanford demonstrated the recovery of Am and Cm from waste from the Redox processing of Shippingport fuels.<sup>(46)</sup>

Fifty percent TBP in "Ultrasene" (purified kerosene) was used for batch extraction of Am-Cm from  $6M\ NO_3^- - 0.4M\ H^+$  solution for the initial transplutonium campaign at Savannah River.<sup>(47)</sup> In addition to the actinides, the lanthanides and a considerable fraction of other fission products such as Zr are also extracted. Thus, although this solvent might be used for a preliminary separation, complete removal of the actinides would be difficult. Also, better selectivity is desired. Stronger complexing solvents, the phosphonates typified by dibutylbutylphosphonate (DBBP) or the phosphine oxides such as trioctylphosphine oxide (TOPO) are better. However, the basic pattern (i.e., the extraction of the lanthanides along with some of the other fission products) remains the same as with TBP. The mechanism of Am extraction has been studied in detail starting with the work of Sheppard<sup>(48)</sup> and a number of separation schemes have been demonstrated for both Am and Cm.<sup>(49-57)</sup>

Other phosphonates that look attractive in tests include 2-ethylhexylphosphonic acid which has been used for transplutonium element extraction by Baybarz.<sup>(52)</sup> Extraction using neutral organophosphone compounds has been studied in detail by workers at Hanford, Savannah River, ANL, and ORNL.<sup>(53)</sup> Peppard has recently reviewed this work in his discussion of extraction of metal ions.<sup>(54)</sup>

TOPO is the most widely used phosphine oxide. Watanabe<sup>(55)</sup> and others have demonstrated its effectiveness in extracting Cm and Am from nitric acid solutions. Goffart and Duyckaerts have compared TOPO with the tributyl homolog for the extraction of the individual actinides and lanthanides.<sup>(56)</sup> Their data show a maximum in distribution coefficient at about  $0.2-0.3M\ H^+$ .

Technetium exists as the pertechnetate ion and hence is extractable either as the acid or as metal salts. The compilation of extraction data of the Japan Atomic Energy Research Institute<sup>(61)</sup> indicates an extraction coefficient greater than unity for both TBP and TOPO systems.

Tin in the 4-oxidation state is extractable by TOPO solutions. The chloride seems to be more highly extractable but even in  $\text{HNO}_3$  solutions extraction coefficients of greater than unity for 5 percent TOPO in toluene are reported.<sup>(57)</sup>

It is thus feasible to carry out at least a preliminary extraction of the actinides and lanthanides with neutral organophosphorus extractants. If desirable, a preliminary extraction with 30 percent TBP from nitric acid solutions would remove Np and Pu (after proper adjustment of Np oxidation state). This would be followed by a low-acid, high-nitrate extraction with DBBP solution to remove the actinides and lanthanides.

Separation of the actinides and Sm from the other lanthanides is more of a problem. Although the first separation may be carried out to some extent with the use of aqueous complexants, it is probably more reasonable to turn to another solvent or to ion exchange if this separation is needed.

Bifunctional organophosphorus compounds have been proposed by Siddall.<sup>(58,59)</sup> His studies indicate that these compounds (for example, methylene diphosphonates) have some promise as efficient extraction agents for the actinides. They are, however, ineffective in distinguishing between actinides and lanthanides in the absence of other complexants.

● Acid Organophosphorus Compounds -- Acid organophosphorus compounds, such as bis(2-ethylhexyl) phosphoric acid and 1-methylheptyl phenylphosphonic acid cover a wide spectrum of structures, acidities and other properties and are excellent candidates for this partitioning task. Like the neutral esters, they have been extensively studied and used for nuclear separations problems. Their versatility as metal ion extractants has been recognized for many years. A decade ago, one-fourth of the papers at the Solvent Extraction Chemistry Symposium at Gatlinburg, Tennessee, were devoted to the study and review of these systems. Since then many detailed investigations have proven the usefulness of the acid organophosphates and phosphonates for fission product recovery and for transuranium element recovery.

As early as 1957, workers at ANL pointed out the ability of di(2-ethylhexyl) phosphoric acid (HDEHPA) to extract lanthanides and actinides.<sup>(60)</sup> Systematic studies by these workers showed that extractabilities of these two groups of metals overlapped and that Am was similar to Pr.<sup>(61)</sup> Demonstration of lanthanide extraction was carried out at Hanford by Bray,<sup>(62)</sup> Schulz,<sup>(63)</sup> and Richardson.<sup>(64)</sup> The feed for these studies was neutralized Purex waste and hence was of low acidity and 2-3M in nitrate ion.

The acid phosphates can be used at higher acidities. Michelson and Smutz<sup>(65)</sup> using HDEHPA found a reduction in extraction coefficient for lanthanides of about five on going from 1M to 2M in either HNO<sub>3</sub> or HCl. A minimum was reached at about 7M. Shaw and Bauer had previously noted a similar effect with cerium.<sup>(66)</sup>

Qureshi and coworkers at the National Bureau of Standards studied the extraction of a number of elements of concern to the present problem.<sup>(67)</sup> Their data for HDEHP extraction from HCl, HClO<sub>4</sub> or HNO<sub>3</sub> solutions indicate a number of problems. For example, Tc extracts very poorly compared to Zr, Nb and Mo.

The coextraction of the lanthanide and actinide groups has already been mentioned as a potential problem for partitioning. A possible solution to this is the use of aqueous complexing agents. These were employed by Bray and others in the fission product recovery program<sup>(62)</sup> and were more extensively developed at ORNL in connection with the transplutonium program. A wide variety of carboxylic acids and polyamino carboxylic acids has been employed.<sup>(68)</sup> Their general effect is to reduce the extractability of the actinides relative to the lanthanides and the scheme provides a method of separating Am and Cm by retaining them in the aqueous phase. This approach has been demonstrated in the TALSPEAK<sup>(69)</sup> process and other work related to the transplutonium production program. Kolarik and coworkers at Karlsruhe have used the same approach to remove Am and Cm from waste solutions.<sup>(70)</sup> One of their concepts (similar to the TALSPEAK process) could be adapted to solve at least part of the partitioning problem. The procedure would be:

- (1) Lower the nitric acid concentration by decomposition with formic acid.
- (2) Complex Zr, Fe, etc., with lactic acid or other acids.
- (3) Extract Am, Cm and lanthanides with an organophosphorus acid.
- (4) Back-extract Am and Cm with polyamino acids.

A very large amount of work has been done in this area and publications are far too numerous to list. Peppard has extensively reviewed the basic extraction chemistry of the various organophosphorus acids.<sup>(53)</sup> Acids other than HDEHP may prove to have better selectivity.<sup>(71)</sup>

The organophosphorus acids could have a significant role in the partitioning of radioactive wastes and may possibly be the best candidates for the removal of Am and Cm. Partitioning of Sm from the other Lanthanides may be achieved if sufficient extraction stages are employed. Alternatively, another technique such as ion exchange could be used. The removal of tin and technetium may require another approach.

- Organic Amines -- Pu and Np are easily extracted from acid solutions by alkyl amines. The chemistry is well understood and a multitude of publications have appeared since Sheppard showed that the hexanitrate complexes of Np(IV) and Pu(IV) were extractable with trioctylamine.<sup>(72)</sup>

On the other hand, the trivalent actinides and lanthanides are very poorly extracted from nitric acid and only moderately well from chloride and sulfate systems.<sup>(73)</sup>

The key factor in these separations is that the anionic complexes of the trivalent states are relatively weak and a high salting strength is required. Thus the "Tramex" process for transplutonium elements requires concentrated LiCl solutions.<sup>(74)</sup> The recoveries of Am and Cm appear good and the rejection of Ru, Zr, and other fission products on stripping the actinides with HCl is good. It is interesting to note that nickel follows Am and Cm. However, the necessity of converting from high HNO<sub>3</sub> concentration to high LiCl concentration and the attendant large new waste volumes make the concept unattractive.

Since amine extraction requires formation of an anionic complex of the metal ion, a search for other promising anions has been carried out. The thiocyanate ion is fairly effective.<sup>(72,75)</sup>

Primary, secondary and tertiary amines have been extensively employed for extraction. Fewer studies have been made with quaternary amines. Moore found, however, that with the thiocyanate, the quaternary amine, tricapryl methyl ammonium chloride (TCMAN) was superior to other amines for Am extraction.<sup>(75)</sup> In this system the +3 actinides extract considerably better than the lanthanides.

Kock found that TCMAN could be used to extract Am and Cm from ammonium nitrate salted systems.<sup>(76)</sup>

Technetium as the  $TcO_4^-$  ion is readily extracted by organic amines. Boyd and Larson<sup>(77)</sup> reported good extraction with both tertiary and quaternary amines.

In summary, amines have a potential application for partitioning by solvent extraction. The major disadvantage is the high salting strength required to form the anion complex. The chloride system is highly corrosive, and the sulfate system adds waste volume. In order to avoid these problems an aqueous phase which can be decomposed (such as ammonium nitrate) would have to be employed.

Actinides generally have higher extracting coefficients than lanthanides. As with the phosphorus-based solvents, it may be necessary to add other complexants to suppress the extraction of other fission products.

● Chelating Extractants -- The acid organophosphorus compounds and, perhaps, the neutral phosphorus compounds previously discussed, form bidentate complexes and hence could be considered chelating extractants. For the present discussion, however, this classification is reserved for organic compounds containing at least two other atoms (C-C, C-N, etc.) between the electronegative atoms forming the metal bond. The  $\beta$ -diketones are good examples and are perhaps the most widely studied for nuclear applications. By using these with thenoyl trifluoroacetone, (HTTA), Pu(IV) and Np(IV) can be extracted from moderately strong acid. If the pH is raised to about 3.5, Am and Cm can be extracted.

Because of the high selectivity of chelating reagents, the development and study of these compounds has been largely directed towards analytical chemistry. In addition to the diketones, many other classes of chelating reagents can be identified. They include hydroxyquinolin derivatives, dioximes and acyl oximes, nitrosophenols, hydroxamic acids, thiocarbazono derivatives, and numerous others.

The great potential of chelating solvents lies in the wide range of properties such as acid strength, solubility, steric hindrance, and nature of the coordinating atoms that are available as a result of virtually unlimited possibilities in molecular structure.

Metal chelates are normally neutral compounds and need no further solvation for extraction into the organic phase. However, at least two possible modifications of chelate extraction can be recognized: (1) solvation of the neutral chelate salt by a strongly polar solvent such as TBP and (2) formation of anionic chelate complexes which in turn form ion-pair complexes with organic amines. Few examples of the latter case have been reported; however, the anionic complexes themselves have been extensively studied in laser chemistry. In extraction, the competition of the reagent itself for the amine often interferes. The polar solvent modification is very common and often leads to enhanced extraction or a synergistic effect.

The dividing line between what some authors describe as simple solvent effects and others as synergism is rather fuzzy. For example, the extraction of Am(III) and Eu(III) by 0.1M dibutyl phosphate (HDBP) in a variety of other solvents (termed "diluent" by some workers) showed distribution factors,  $E_A^0$ , for Eu which varied by a factor of  $10^5$  and a separation factor,  $E_A^0(\text{Eu})/E_A^0(\text{Am})$  which varied over a range from 20 in  $\text{CHCl}_3$  to 2 in hexanol.<sup>(78)</sup>

The TTA-TBP system has received considerable attention. Healy found distribution ratios for Am in this system that varied from  $>10^4$  to less than 1.0 as the diluent was varied from hexane to  $\text{CCl}_4$ , to benzene, to  $\text{CHCl}_3$ .<sup>(79)</sup> Davis, Holt and Tournier have examined the actinide-lanthanide separation problem using this system.<sup>(80)</sup> They worked with low concentrations of HTTA and TBP in kerosene,  $\sim 0.01$  to 0.1M for each reagent, and found

distribution coefficients that ranged from about 0.002 to 20 with essentially the same order as was found for the pure TBP system, i.e., Sm>Am, Cm, Nd>Pr>Ce, La. In agreement with other workers they suggested the complex to be metal  $(TTA)_3(TBP)_2$ .

The combinations of chelating anions and polar solvents are too numerous to list. Many of the systems have been investigated in considerable detail, complexing constants are known, and solvent distribution data are available. This type of solvent extraction is worth further consideration since high extraction coefficients and high selectivity are both inherently possible.

Many other solvent extraction reagents can and should be considered. To indicate the wide choice of types available, a few examples can be listed: sulfonic acids, analogs of organophosphorus compounds such as phenylarsonium derivatives, other oxygen-containing compounds such as ketones and polyethers, sulfur analogs of the oxygen-containing compounds, nitrogen-containing compounds such as amides and hydroxamic acids, and the multitude of other organic analytical reagents.

B.1.5 Summary of Solvent Extraction Review -- This preliminary survey of solvent extraction indicates that the approach can be used to accomplish the partitioning and/or fractionation that might be needed. Extraction of the actinides, Sm, Tc and probably Sn, can be achieved. Tracer experiments have shown that the concentrations can be reduced to low levels at least for the actinides, and conventional techniques employing multistage extraction should accomplish the desired degree of removal and separation (presently undefined). However, selectivity to provide a small package of these elements has not been adequately demonstrated. Complications from radiation damage to the solvent are of some concern, although for a ten-year-cooled waste these do not appear serious at first consideration. Capability to do the partitioning without producing major new waste streams which are either contaminated with the problem elements or so large in volume such that they create new storage problems remains to be demonstrated.

This review has generally assumed that waste which has been stored in the (nitric) acid form would be the feed for solvent extraction. From a materials standpoint, this is the preferred situation. Even though the wastes might be stored for an interim period as lightly calcined solids, as suggested by Rupp,<sup>(81)</sup> they can be reconverted to nitrates. On the other hand, other acid systems should not be ruled out at this time.

Although the long-lived hazardous elements probably can be removed by solvent extraction, there is no certainty at present that the sharpness of separation required can be met with a simple flowsheet and without producing an excessive amount of new waste. Research is required to determine the best solvents to make the separations at the desired points. A several-step process possibly involving several different solvents may be required. A logical approach is to follow one or more solvent extraction steps with another technique such as ion exchange. Nickel may be a special problem and every attempt should be made to keep it out of the feed.

## B.2 Ion Exchange

Ion exchange processes have been used extensively for nuclear separations. As with solvent extraction, there is extensive literature and experience. Also, however, as for solvent extraction, use of ion exchange technology specifically to partition high-level waste has not been explored. But previous work has included investigation of ion exchange as a method to isolate the elements of concern for partitioning.

### B.2.1 Anion Exchange

#### B.2.1.1 Primary Processes

- Neptunium and Plutonium -- Soluble Pu and Np can both be removed directly from typical high-level waste by anion exchange. Anion exchange absorption of both Pu(IV) and Np(IV) is very efficient in the nitrate concentration range expected ( $\sim 8M$ ) for these wastes. Since Np would be expected to be present in typical waste ( $3M H^+$  and  $\sim 8M NO_3^-$ ) as Np(V), reduction to Np(IV) would be required. Processes have been devised to recover Np from nuclear processing wastes and these have used ferrous sulfamate followed by

heat kill,<sup>(82)</sup> ferrous sulfamate and hydrazine,<sup>(83)</sup> or nitrite<sup>(84)</sup> as reducing agent for Np. With the ferrous sulfamate-heat kill and nitrite methods, Np and Pu are co-absorbed. Ferrous sulfamate is probably not the most desirable as reductant because it adds to the total waste. Nitrite (or  $\text{NO}_2$ ) does not completely reduce Np(V) at the acidity of the typical waste. There are undoubtedly several reducing agents (organics), etc., which would reduce Np and not add permanent components to the waste, and some research would be involved in making the best choice. With the proper choice of reductant, possibly followed by heat kill, simultaneous absorption of both Np and Pu would be no real problem in the absence of high radiation levels.

Snyder<sup>(83)</sup> has reported that with high radiation levels and moderately low acid waste ( $\sim 3\text{M}$  was assumed as typical here) it is somewhat difficult to maintain neptunium oxidation control sufficiently well to produce low waste losses in Np recovery by anion exchange. He found that a mixture of ferrous sulfamate and hydrazine performed this function satisfactorily. Since this mixture has been used in nitric acid systems to minimize the absorption of Pu and to elute it from the resin,<sup>(85)</sup> there is some question as to whether both Np and Pu could be co-absorbed and research would be necessary to determine how best to do this. Both Np and Pu could be absorbed separately if maintaining them simultaneously in the tetravalent state and co-absorbing them did not prove feasible. Some work would be needed to determine the optimum reducing agent to use and to determine whether Np and Pu can be co-absorbed.

The anion exchange absorption of Pu(IV) has been thoroughly studied and the effects of process variables are known.<sup>(86)</sup> The concentrated waste is expected (on the basis of 100 gallons of waste per ton of fuel) to be about 2 g/l in Np, and at this concentration high resin loadings would occur. However, the feed may have to be considerably more dilute than this because solids formation may limit the evaporation to waste volumes more than 100 gal/ton. At a concentration of 2 g Np/l or even at only 0.2 g/l, the capacity of the resin will reasonably be of the order of 50 to 60 g Np/liter of resin with absorption of 99 to 99.9% of the Np on the basis of

2 g/l of feed (380 l waste/ton of fuel) this amounts to 25 to 30 bed volumes of feed. The degree of removal of Np and Pu by further cycles of anion exchange will of course depend on the amount of feed fed to the column. For removal of 99% of the Np and Pu per anion exchange cycle at low Pu and Np feed concentrations, feed volumes of about 200 column volumes can probably be used but experimental runs will be needed to establish the optimum feed volume and DF per cycle.

On the basis of feeding wastes concentrated to 380 l/ton directly to anion exchange columns after ten years cooling, the useful life of the resin would be expected to be of the order of 200 to 400 hours of actual feed contact. Discard of used resin should not be too severe a problem since the resin is an organic material of relatively low ash content.

One advantage of anion exchange for recovery of Np and Pu is that they are eluted from the resin with a large concentration factor over the feed ( $\sim 100$  for dilute feeds) by  $\sim 0.5M$   $HNO_3$ . The product can then be concentrated readily much further by evaporation. Another advantage is that the process is very specific for Np and Pu and they are well separated from fission products. The chief disadvantage is that Am and Cm are not recovered. Although Am and Cm absorb to some extent from some highly salted nitrate solutions, the distribution coefficients are only high enough to be of any possible value in  $Mg^{2+}$ ,  $Al^{3+}$ ,  $Li^+$ , and  $Ni^{2+}$  nitrates.<sup>(87)</sup> Even with these nitrates, it is questionable whether the distribution coefficients are high enough to make an efficient process. The absorption of Am and Cm (along with all lanthanides) from such highly salted solutions also requires very low acidities<sup>(88-90)</sup> and the reduction of Np to Np(IV) may be difficult under such conditions. There may be no advantage to removing Pu and Np by anion exchange if Am and Cm are to be removed by a solvent extraction process that would also extract Pu and Np.

● Americium and Curium -- As mentioned above, trivalent actinides<sup>(87,91,92)</sup> as well as trivalent lanthanides<sup>(58,93)</sup> absorb on anion exchange resins from highly salted, low acid, nitrate solutions. Of the various metal nitrates that have been studied,<sup>(88)</sup> it appears that only

in  $\text{Li}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ni}^{2+}$  nitrates are distribution coefficients high enough to be even considered. Even with these nitrates, distribution coefficients are low (<500) and only moderately small volumes of feed can be processed before appreciable breakthrough.

This method has been used for the recovery of Am, Cm, and other trivalent actinides from plutonium process wastes generated by the removal of plutonium from solutions of irradiated Pu-Al alloy.<sup>(94,95)</sup> The absorption kinetics are poor, and low flow rates and resins of small particle size are required. Fairly high pressure drops occur with the viscous solutions. Because of the relatively poor distribution coefficients, not more than 15 column volumes of feed can be processed per cycle. Decontamination factors from iron and fission products other than lanthanides are moderately high. The desired low acidity can be obtained by thermally evaporating the feed to 140°C to remove  $\text{HNO}_3$  followed by dilution back to 2.6M  $\text{Al}(\text{NO}_3)_3$ .

Application of this process to the current problem would require addition of  $\text{Al}(\text{NO}_3)_3$  or another nitrate such as  $\text{LiNO}_3$ , thermal removal of  $\text{HNO}_3$ , and dilution. The chief disadvantage of the process, other than the relatively low efficiency and process problems described above, is the fact that the process requires the addition of a quite considerable amount of nitrate salts to the waste. It is almost certain that the solids content of the waste would be increased several-fold by such a process.

It has been shown that anion exchange resins absorb the trivalent lanthanides and actinides strongly from mixtures of many organic solvents with nitric acid.<sup>(96-98)</sup> Americium distribution coefficients ( $K_D$ ) of as high as 6,000 have been observed in 90 v/o ethanol-10% 5M  $\text{HNO}_3$  (aq.).<sup>(98)</sup> This method has been applied to separations on a tracer scale<sup>(96,97,99)</sup> but not on a macro scale. Data on absorption kinetics are completely lacking but unless kinetics are extremely poor, good resin loading would be expected on the basis of the distribution data. Use of a mixed solvent system would avoid many of the disadvantages of the metal nitrate system (e.g., viscosity, low distribution coefficients, and addition of permanent components to the waste) but would certainly create some problems of its own. Many of the

solvents are flammable, although some that have been studied are perhaps not highly so. Resin stability for prolonged use in such solvents, radiation stability, effects of degradation products, salt solubilities in the mixed solvents, separation factors in the mixed solvents, and as mentioned, absorption kinetics, would all have to be determined before the feasibility of such a process could be defined.

- Technetium -- Technetium is absorbed strongly on anion exchange resins as the pertechnetate ion,  $TcO_4^-$ . It does not absorb to any appreciable extent from strong nitric acid solutions but does absorb strongly from dilute,  $\sim 0.1M$ , nitric acid.<sup>(100)</sup> It is also known that Tc absorbs well from neutral or basic solutions even though these are high ( $\sim 8M$ ) in nitrate and nitrite and this fact is the basis for a method for the recovery of Tc from alkaline high-level wastes.<sup>(101)</sup> Distribution coefficient data have not been measured for Tc as a function of pH and nitrite and nitrate concentration. Because of this, it is not known whether Tc can be loaded from low acid-high nitrate solutions. It has been reported<sup>(102)</sup> that one Russian-made anion exchange resin will absorb Tc from low acid as well as neutral or basic high nitrate solution. With alkaline Hanford wastes, up to 50 column volumes of solution could be passed through a column without significant Tc breakthrough. This value would be smaller under conditions of high Tc feed concentration and limited resin capacity. There are reports<sup>(103)</sup> that Rh and Pd also load to an appreciable extent from Hanford alkaline wastes. The natures of the Rh and Pd species loading are not known, but they are probably nitrite complexes of some type. It appears likely that the Rh and Pd, but not Tc, behavior in freshly neutralized feeds might be quite different. Because of the limited amount of information on Tc anion exchange in nitrate media, considerable research would be needed to optimize the process and determine its efficiency for Tc removal.

#### B.2.1.2 Secondary Processes: Trivalent Actinide-Lanthanide

- Partitioning -- In addition to anion exchange processes directly applicable to nitrate waste solution, there are processes that are applicable to the separation of trivalent actinides, in this case Am and Cm,

from lanthanide elements after both groups have been removed from the waste. Because of the amount of lanthanides present (about one-third of the total fission products) this separation is considered necessary.

- LiCl Anion Exchange -- Anion exchange in concentrated LiCl solution allows a group separation in which the actinides are absorbed and the lanthanides are not appreciably absorbed.<sup>(104-106)</sup> This process has often been used for analytical separations and has been used on a relatively large (multigram) scale for the separation of transplutonium actinides from fission product lanthanides.<sup>(107-110)</sup>

The method, as developed and used at ORNL<sup>(108-110)</sup> for multigram quantities, calls for loading the actinides from 12.5M LiCl-0.1M HCl at 80°C onto not more than the top 20% (~5 to 15 g/l of resin average loading) of a column of Dowex 1, X-10 (200-300 mesh). Nickel and lanthanides are washed off with 10M LiCl-0.1M NH<sub>4</sub>OH·HCl-5 v/o CH<sub>3</sub>OH until alpha activity in the effluent increases (5 to 8 column displacement volumes). If no separation of transplutonium actinides is desired, the actinides are eluted with 8M HCl which leaves Fe(III), U(VI), etc., on the column to be eluted with dilute HCl. The purpose of the methanol is to eliminate the radiolytic destruction of HCl and to markedly reduce gassing.<sup>(111)</sup> This method has also been used at Karlsruhe.<sup>(111,112)</sup> A similar method has been used for the purification of <sup>241</sup>Am.<sup>(113)</sup> Because the poor absorption kinetics necessitate low flow rates, elevated temperature operation, and fine mesh resin, the use of extremely fine mesh resin with very high pressure feed has been successfully tested.<sup>(114)</sup>

This method of separation of Am and Cm from lanthanide fission products possesses the extremely severe disadvantages of being very corrosive to process equipment and of generating a large amount of very corrosive high salt waste. The severity of these problems is such as to probably make its use for the present purpose impractical.

- Thiocyanate Anion Exchange -- A group separation between trivalent actinides and lanthanides is also possible by anion exchange in thiocyanate solution.<sup>(115-117)</sup> This technique has been applied to macro-scale separation and purification of Am.<sup>(118,119)</sup> The method consists of loading the Am plus lanthanides from 5-8M NH<sub>4</sub>SCN feed (prepared by elution of Am, etc.

from cation exchange resin), washing with 5-8M  $\text{NH}_4\text{SCN}$  until all lanthanides are removed and eluting Am with dilute HCl. Since lanthanides load onto the resin, the resin-to-Am ratio needed will depend on the lanthanide-to-Am ratio. For a lanthanide-to-Am ratio of about 300 to 1, about 20 ml of resin per gram of lanthanide is required for good separation.<sup>(118)</sup> No studies of the anion exchange kinetics have been made, but it has been noted that low flow rates are necessary (at least with 50-100 or 100-200 mesh X-8 or X-10 resin).<sup>(119)</sup>

A very serious disadvantage of this method is that thiocyanate is not very stable toward radiolytic decomposition. It will form free sulfur. The instability is so severe that it has not proven possible to purify  $^{244}\text{Cm}$  by this route.<sup>(119)</sup> Because of this, it appears doubtful that the method would be usable for the current application even with ten-year-cooled material.

#### B.2.2 Cation Exchange

Cation exchange absorption of metal ions does not exhibit the very high selectivity often found for anion exchange processes. Cation exchange selectivity is based to a large extent on ionic charge and thus separations of, for example, monovalent metals from trivalent metals are feasible. Separation of individual ions of similar charge is normally carried out on cation exchange resins by using complexing agents having different tendency to complex the metal ions being separated and using the resin simply as a holding or retarding agent for the metal ions.

Since the lanthanides represent about one-third of the total mass of fission products, a separation of Am and Cm from the lanthanides appears desirable. Cation exchange processes for separation of adjacent lanthanides and trivalent actinides are well developed for both analytical separations and process-scale separations. All of these methods consist of the absorption of the metal ions on a cation exchange resin followed by elution down a length of resin bed by a complexing agent. The separation is achieved because of differences in the strength of the complexes formed with the different metal ions. Complexing agents which have been used include citrate, lactate, alpha-hydroxybutyrate, glycollate, polyamino carboxylic acids, and others. Among the more desirable of the eluting agents because of the high separation factors obtained are the various polyamino carboxylic acids. In

particular, diethylenetriamine-pentaacetic acid, (DTPA), shows good promise for the separation of Am and Cm from fission product rare earths.<sup>(120)</sup> Since both separation efficiency and reagent costs vary, other polyamino carboxylic acids should, of course, be considered. For analytical separations (tracer levels) the pH of the complexing elutriant is adjusted such that the various metals are separated into widely-spaced relatively-narrow bands upon elution down the resin column. For separation of very small macro amounts, this technique is also feasible, but for multigram, and particularly for the multi-kilogram separations necessary here, the use of a retaining ion to compress and hold the bands adjacent to one another is mandatory to avoid prohibitive resin inventory.

Cation exchange separation and purification of Am and Cm from lanthanide fission products using DTPA has been done on a multigram scale.<sup>(120)</sup> In the DTPA elution sequence using  $Zn^{2+}$  as a retaining ion, Am and Cm elute between Gd and the Zn retaining ion. Separation from the lanthanides heavier than Gd is poor, but these lanthanides are present in fission products only in very small amounts. The ratio of Am plus Cm to lanthanides above Gd is about 55. On the other hand, the ratio of Am + Cm to total lanthanides is about 0.016. Even Gd is expected to be present only to an extent about equal to Am plus Cm so that, depending upon the planned disposition of the Am and Cm, it might be possible to split the elution fractions in such manner as to leave the Am-Cm fraction contaminated with some Gd to minimize the actinide contamination of lanthanide fractions. In fact, if Sm removal is also considered necessary, two fractions might be collected. One would be relatively pure Am-Cm and the other could be Sm plus Eu and Gd (which constitute only about 30 percent of the mass of the Sm). This fraction would contain only traces of Am-Cm. The lighter lanthanides should be extremely free of Am-Cm.

Advantages of cation exchange separation of actinides and lanthanides in this manner include lack of corrosion problems and lack of addition of significant amounts of permanent components (metallic salts) to the waste. It might prove desirable and should be feasible to recycle the retaining ion if a metal such as  $Zn^{2+}$  is used as the retaining agent. Problems with

the method are principally those caused by radiolytic decomposition of the resin and of the organic complexant. The chief problem caused by the latter effect is gassing in the resin bed. This problem has been handled by periodic bed degassing and it has been suggested<sup>(120)</sup> that operation at moderately high pressure (150-200 psi) would alleviate this problem. It appears extremely desirable that ten years be allowed to provide for decay of  $^{144}\text{Ce}$ .

This process and similar processes have been used very successfully for purification of  $^{90}\text{Sr}$ ,  $^{147}\text{Pm}$ ,  $^{241}\text{Am}$ - $^{243}\text{Am}$  mixture, and  $^{244}\text{Cm}$ .<sup>(120,121)</sup> The process is operated at elevated temperature to improve kinetics and decrease separations times to minimize radiation damage. Even higher processing rates have been achieved by the use of extremely fine resin and very high pressure,<sup>(122,123)</sup> but such conditions find greatest application to the processing of the much more active transcurium isotopes and would probably not be economically justifiable for this application. It has also been reported<sup>(124)</sup> that addition of lactic acid markedly improves the separation rates which can be achieved with EDTA elution. Such an effect might also occur with DTPA.

Chromatographic cation exchange separation of lanthanides and trivalent actinides has normally been applied to a lanthanide-actinide concentrate which has already been separated from other fission products by another process such as solvent extraction. It is quite possible that these other steps might be eliminated and the waste, diluted with water to proper total ionic strength (probably 0.5-2.0M), could be loaded directly onto cation exchange resin. The more highly charged cations would be expected to load most strongly. These include the lanthanides,  $\text{Am}^{3+}$ ,  $\text{Cm}^{3+}$ , and, if a proper reducing agent is used,  $\text{Np}^{4+}$  and  $\text{Pu}^{3+}$ . Other ions expected to load include  $\text{Fe}^{3+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Ba}^{2+}$ . The monovalent cations,  $\text{Na}^+$ ,  $\text{Cs}^+$ , etc., and anionic fission products Tc, I, etc., would either load weakly or not at all. They could be easily eluted by dilute  $\text{HNO}_3$ . Some  $\text{Sr}^{2+}$  and  $\text{Ba}^{2+}$  might also be removed by this technique, but since they are among the more strongly absorbed divalent ions,<sup>(125)</sup> it might not be possible to completely remove them from the resin by this method without removal of some trivalent actinides.

During DTPA elution,  $\text{Fe}^{3+}$  is expected to pass through the  $\text{Zn}^{2+}$  retaining-ion bed and thus to be rapidly removed.<sup>(120)</sup> Neptunium<sup>4+</sup> is also expected to pass through the retaining bed, and if an oxidant is added to convert  $\text{Pu}^{3+}$  to  $\text{Pu}^{4+}$ , the Pu should also pass through the  $\text{Zn}^{2+}$  bed.<sup>(120)</sup> A fraction containing principally Fe, Np, and Pu would thus be **obtained**. Either solvent extraction or nitrate anion exchange would readily separate the Pu and Np from Fe. This should leave only trivalent actinides and lanthanides and Sr and Ba on the column. During chromatographic DTPA elution, the Sr and Ba should not elute as readily as the lanthanides, and thus should be well separated from the Am and Cm which elute more readily than the lanthanides.

The behavior of some other fission products in such a cation system is not known at this time. There is some reason to believe that Ru, Zr, and Nb might load to some extent.<sup>(126)</sup> A method of milligram-scale cation exchange purification of  $^{242}\text{Cm}$  has been developed;<sup>(126)</sup> in this process Ru is removed from the resin by 0.5M  $\text{H}_2\text{SO}_4$  elution followed by 0.5% oxalic acid elution of Zr, Nb, and Pu(IV). Trivalent lanthanides and actinides are left on the resin. They can be separated chromatographically by a complexant. The fate of Ru, Zr, and Nb in DTPA elution is not known and it is possible that a separate initial step such as just described might be required to remove them. It is also possible that if sufficient Sr cannot be removed before DTPA elution, it might be desirable to add a small amount of natural Y to dilute the very narrow and highly active band of  $^{90}\text{Y}$  that would be expected to form. One other possible complication that might occur in such a process is that there may be some precipitation of lanthanide or other (Zr?) phosphates during dilution to lower feed acidity prior to loading. (This problem might, of course, occur with other processes which also require decrease in the waste acidity.)

The feasibility of such direct cation exchange chromatography of the waste is not proven. The possibility looks sufficiently promising and has sufficient advantages if feasible, though, that it definitely merits the experimental work required to test its feasibility.

### B.2.3 Inorganic Ion Exchangers

These exchangers, which are available as both natural mineral and synthetic mineral exchangers, do not generally perform well in strongly acid (pH < 1) solutions. Also, their selectivities are such that applications to the partitioning of wastes are not apparent. Their chief use has been in removing a rather wide variety of isotopes from very large volumes of low- or intermediate-level wastes of low total ionic strength and in the separation of Cs from Na in alkaline solutions containing few other fission products. There is some possibility that they might find some use in a fractionation operation to remove activity (such as  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , etc.) from peripheral low-level waste streams which might be generated (such as steam condensates, etc.). It should be noted that, on a tracer scale, the separation of individual trivalent lanthanides and actinides has been accomplished by chromatographic elution with concentrated  $\text{LiNO}_3$  from a zirconium phosphate exchanger.<sup>(127)</sup> The method does not appear to be desirable for process-scale separation.

### B.2.4 Chelating Ion Exchangers

Chelating or complexing ion exchange resins have been prepared which show very high affinities for metals which tend to complex readily. They are very useful, for example, in the separation of transition metals such as Cu, Fe, Co, Ni, etc., from solutions containing very large amounts of alkali and alkaline earth salts such as seawater. There is some possibility that they might be useful for the removal of Ni isotopes if such removal is required although there is no record of their use for this purpose even on an analytical scale. Unfortunately, they can be expected to absorb also some other transition metal fission products strongly. Since they, in common with other cation exchange resins, exhibit high distribution coefficients for highly charged cations, they will show little, if any, selectivity for Ni over trivalent lanthanides.<sup>(128)</sup> Other problems with their use are that they are generally useful only at moderately high pH (>4) and the exchange kinetics are often very poor.<sup>(129)</sup>

### B.2.5 Resin Stability

Organic ion exchange resins based on cross-linked polystyrene are relatively stable to radiation damage. Because of the very high radiation levels of the wastes under consideration, though, cooling of the wastes for a period of ten years before ion exchange processing is extremely desirable. Ion exchange processes will all generate degraded and contaminated resin. Since the resins are principally organic, processes for their destruction such as incineration or radiolytic decomposition in fresh waste solution may be developed which do not add appreciably permanent components to the waste. A process such as total radiolytic degradation in fresh waste may add some ammonium ion in the case of anion resins and can be expected to add sulfate in the case of cation resins. It may not be possible to completely decontaminate inorganic ion exchange resins. Hence, their use will add some volume to the waste.

### B.2.6 Summary of Ion Exchange Review

Information reviewed in this study indicates that ion exchange technology that can meet partitioning or fractionation needs is available. Some experience has been obtained with each of the elements that might have to be isolated.

Process problems rather than separations effectiveness are most likely to restrict the practical use of ion exchange for partitioning or fractionation. The major problem seems to be the fact that lanthanides would be extracted with Am and Cm. Since the lanthanides are a large fraction of the total fission product mass, secondary processes would be required to separate the Am and Cm from the lanthanides in the bulk waste.

Other potential process problems include corrosion, addition of extra components and volumes to the waste, gassing of the resin bed, handling and disposal of contaminated waste resin, solids formation, short resin bed life, and a need to avoid high radiation levels. Storage of waste for up to ten years prior to partitioning appears mandatory if problems from high radiation levels are to be avoided.

Many of the ion exchange techniques have not been demonstrated at a scale corresponding to process operations. Extensive scale-up development would probably be necessary. Also, it can be anticipated that highly precise process control would be required in practice.

### B.3 Sorption Processes

Absorption or adsorption processes other than ion exchange in general have the same disadvantages as inorganic ion exchange. The selectivities of such absorbents or adsorbents are sometimes fairly high but their capacities are generally low and they tend to be better suited to the removal of trace constituents from low ionic strength solutions than to partitioning of macro components from strongly electrolytic solutions (which is the situation for partitioning). A possible application might be the use of a solid absorbent such as activated carbon to remove iodine from either a solution or a gas stream after volatilization of iodine.

#### B.3.1 Precipitation Methods

There are undoubtedly a rather large number of precipitation methods that could be devised for partitioning of radioactive wastes. Considerable research during the Manhattan Project and for some time later was devoted to precipitation methods for process-scale as well as analytical and research-scale separations. To a very large extent these methods have been replaced on the process-scale by solvent extraction and ion exchange methods. There are rather fundamental reasons why this is so for large-scale processing, but not necessarily so for analytical and research-scale. The principal reasons are that recovery of the desired product is improved and waste volumes generated are smaller with extraction.

There are basically two ways in which separations by precipitation can be done. The first is direct precipitation of a compound of the desired product and the second is carrier precipitation. The first has the disadvantage of generally having relatively low recoveries. It does not appear applicable to the high degree of removal of specific elements required in the current partitioning problem. The disadvantage of carrier precipitation, which is capable of removing desired elements to a very high degree of

decontamination, is that the desired material ends up diluted with a large amount of carrier precipitate. Although other steps can remove the desired element from the carrier, it is usually not easy to recycle such materials and they end up as contaminated wastes. As such they must also be stored. The greater waste volumes that these methods produce and the greater difficulty of recycling are major reasons that they have been replaced by solvent extraction and ion exchange methods in nuclear fuels processing.

Precipitation methods are particularly useful in removing moderately low levels of activity from large volumes of solutions where the decontaminated solutions can be directly discharged to the environment. It must be remembered, though, that in the present partitioning problem both the long-lived and shorter-lived fractions will be high-level wastes and appreciable addition to the volumes of either is undesirable. For this reason, it does not appear that precipitation methods would be competitive with solvent extraction and ion exchange methods wherein recycle of the solvent or resin is easily accomplished and high removal efficiency is also possible.

#### B.4 Other Methods

Virtually all known separations methods have been proposed and examined for the separation and/or purification of nuclear materials. Most have been considered for radioactive wastes. The methods include techniques such as: volatility, biological, flotation and electroflotation, molecular sieve filtration of metal complexes, dialysis, electrophoresis, and other electrochemical and pyrochemical methods.

All of these methods are deficient in one or more ways when considered for the present problem, although it is possible that some may have application to final separation of specific nuclides. Deficiencies for these methods (in comparison with solvent extraction and ion exchange) were not evaluated in detail during the course of this study.

## V. ANALYTICAL MEASUREMENTS

In practice, analytical measurements will be needed to confirm that decontamination goals required of the partitioning or fractionation process have actually been achieved. Measurements of residual concentrations of the hazardous nuclides in the bulk waste are most crucial; the partitioning operations will have accomplished nothing if the absence of long-term hazard for the bulk waste cannot be verified.

The fact that hazardous residuals in the bulk waste are most significant means that the most difficult measurements are most important. Low-level concentrations of  $\alpha$ -emitting isotopes will have to be detected and measured with high accuracy in a strong  $\beta$ - $\gamma$  field. Moreover, these measurements should be made on-line (during partitioning operations) to avoid possible need for post-operations holdup (to make measurements) and recycle of out-of-specifications waste.

At present, there are no effective methods to make on-line process measurements of the type required. A system of sensors and related readout and process control equipment will have to be developed. Also, development work will be required for laboratory measurements to be made on samples removed from process streams. Development of such methods is a necessary precursor to development of an in-line process measurement system and development of the partitioning process itself.

In brief, the state of the art for analytical measurements may not be equal to the requirements expected for partitioning depending on separations requirements. Concepts for measurements are available, however, and problem areas have been identified.

### A. Measurements Procedure Problems

A logistical support system will be required for in-line and laboratory measurements. Since development of in-line process measurement systems will be a result of development of laboratory methods, the present concern is the laboratory system. Solutions to the laboratory problems will be directly applicable to the partitioning process and its support facilities.

The first concern is the problem of getting samples to the laboratory and prepared for analysis. The radioactivity levels of the constituents to be measured are extremely low as compared to the total activity of the waste (which is estimated to be 825 Ci/l). This high level of total radioactivity places a restriction on the sample size which can be conveniently transported to the analytical facility. Also, analytical pretreatment and separation steps would have to be carried out in a shielded facility. This requirement may reduce the flexibility of the methods to be used.

In addition to the general problem of separation and measurement of the isotopes of concern, the analytical chemist must develop effective methods for sampling and treating the solid phase present in the wastes to ensure the validity of the samples and to convert the solids into chemical forms which are compatible with the proposed measurement procedure.

This need for concern about suspended solids in the waste repeats and duplicates the concern discussed in Section III. In other words, the solids are a potential problem not only for the partitioning operation but also for the analytical measurements associated with that operation. If solids are present and contain significant quantities of the nuclides of concern, they can have a major adverse effect on analytical accuracy.

One obvious potential problem is lack of homogeneity and reproducibility. Another is that solids can affect the reliability of pretreatment steps. The greatest concern, however, is that solids would be present in the waste and not be picked up in the sample or measured in the analytical sequence. The actual concentration of toxic isotopes in the waste could then be much higher than the measurements indicate. Alternatively, a sample with an unusually high solids concentration could indicate a high activity level not actually present.

For these reasons, it is imperative that any solids present be properly accounted for in the sampling and analytical procedures. Ideally, of course, solids will not be present. But the analytical procedure must confirm this and deal with any that are present.

## B. Measurement Methods

In spite of the difficulties envisioned for the analyses of the long-lived isotopes, a number of methods have been identified which potentially can be developed to achieve the requirements of the partition program.

### B.1 Actinide Elements

The most promising approach to the analysis of Np, Pu, Am and Cm is separation into individual elements followed by conventional  $\alpha$ -energy analysis. To apply  $\alpha$ -counting techniques, a reasonably good separation of each of the elements is required, but analytical ion exchange procedures are already developed for this.<sup>(130)</sup> A more difficult problem is the isolation of the actinides as a group from the bulk of the constituents in the wastes. A number of effective and selective carrier precipitation and solvent extraction methods have been identified which, with further development, appear to be feasible for this bulk separation. For example, carrier precipitation on lanthanum fluoride or oxalate effectively scavenges the trivalent actinides as a group even from very dilute solutions.<sup>(131)</sup>

Alternate methods to the  $\alpha$ -counting techniques for measurement of the actinides include  $\alpha$ -track counting and isotopic dilution mass spectrometry. The  $\alpha$ -track counting may possibly present a method for measurement without separation, but it suffers the drawback of not being specific,<sup>(132)</sup> i.e., it does not distinguish between the different alpha-emitting elements. Isotopic dilution-mass spectrometry is extremely sensitive, but requires a separation of the elements and requires standards for each element with isotopic abundances considerably different than those encountered in the sample.<sup>(133)</sup> At this time such a standard is available only for plutonium.

### B.2 Samarium

Mass spectrometry-isotopic dilution is ideally suited to the measurement of samarium.<sup>(134)</sup> This technique is extremely sensitive for this application. Isotopic standards are available, and  $^{151}\text{Sm}$  can be measured directly. A separation from the adjacent rare earths is required, but ion exchange methods currently in use can achieve the required degree of purity.

### B.3. Technetium

The analysis of technetium at the 0.01 ppm level by  $\beta$ -counting techniques can be achieved only if a decontamination factor of about  $10^{10}$  from other  $\beta$ -emitters can be attained. This does not appear to be feasible. Electroanalytic techniques such as polarography<sup>(135)</sup> show some promise but will require the isolation of technetium from the bulk of the radioactivity. Solvent extraction<sup>(136,137)</sup> and anion exchange purification procedures are known but may need additional development.

### B.4 Iodine

The measurement of iodine-129 can be achieved by neutron activation analysis<sup>(138)</sup> but will require a good separation from other radioactive components of the waste. Also, electroanalytical techniques can be used and will require less of a separation from other components in the waste.

### B.5 Tin

At this time, no feasible methods have been identified for measurement of tin when present at low levels in a highly radioactive waste.

### B.6 Nickel

The radioactive isotopes of nickel which are expected to be present in the waste are  $^{59}\text{Ni}$  and  $^{63}\text{Ni}$ . The principal mode of decay is electron capture for  $^{59}\text{Ni}$  and very low-energy beta emission for  $^{63}\text{Ni}$ ; both are therefore very difficult to measure by counting techniques even if very good separation from other radioactivities is obtained. However, nonradioactive nickel is a major component of the waste (as a result of corrosion of stainless steel process equipment), and the determination of nickel decontamination factors by measurement of total nickel may not be a serious problem. Conventional techniques such as atomic absorption photometry, calorimetry, or polarography after separation may suffice.

## C. Summary of Analytical Measurements Review

The problems involved in developing adequate analytical capability are in many ways precisely the problems involved in developing the partitioning

process itself. Development of these procedures will involve testing and verification of separation techniques that may translate directly to the process itself. For this reason, development of analytical capability is considered to be a necessary precursor to partitioning process development.

Suspended solids are potentially a major problem. Sampling and analytical procedures must confirm the existence and radioactivity content of any that are present. Assurance that results are reliable must be provided.

Because of interference from high total radioactivity in the waste, the isotopes of concern must be isolated. This is not a major restriction; the measurement methods are very effective if the separation is performed.

Measurement methods are available for the actinides, which are expected to be the elements of most concern. The major developmental need is associated with the separation process to isolate the actinides for measurement.

## VI. MODIFICATION OF REPROCESSING OPERATIONS

The partitioning method concepts discussed in Section IV can, in principle, be applied to any process stream containing the isotopes to be removed. One approach would be to modify the reprocessing operations to produce the required partitioned waste streams. A separate evaluation of this approach to partitioning was made. It was concluded that it would be impractical to attempt to obtain partitioning of all of the actinide elements from the bulk waste in existing or near future Purex process type fuel reprocessing plants. The trivalent actinide elements are intentionally routed to the first cycle waste along with the lanthanides and other fission products. Major changes in current Purex processes flowsheets and additions of in-plant equipment would be required to achieve in plant separation of the trivalent actinides from this stream.

Potential does exist through process modification, improved process control and modification of columns to improve U, Pu and perhaps Np recovery, i.e., improve removal of them from the short-lived waste fraction. The potential for improved recovery, particularly Pu, is questionable until more

is known about the presence of colloidal solids and TBP degradation products in the process streams. Adequate recovery might be achieved if the required DF from short-lived waste is not too great -- perhaps a DF of 100 or less over what is now achieved.

Coupling such a modified Purex process with an adjunct facility to remove the trivalent actinides from the high-level waste stream is an attractive possibility for achieving adequate separation of all of the actinide elements and evaluation of the combination should be a part of the R&D program. G. Koch, et al.<sup>(139)</sup> are studying a process at Karlsruhe for the removal of Am and Cm from high-level waste. The process being developed is a recovery process and may not provide the degree of separation of actinides from lanthanides and other fission products (short-lived fraction) needed for waste partition. However, consideration of the Karlsruhe process and similar processes for coupling with a Purex plant operated for high U, Pu and Np recovery should be part of the R&D program.

## VII. INTERPRETATION OF RESULTS

The results of this review can be interpreted to indicate conceptual flowsheets for implementation of partitioning processes and the key decision points involved in evaluating alternatives for a partitioning process.

### A. Partitioning Flowsheets

Figures 2 and 3 show conceptual flowsheets for partitioning by solvent extraction and ion exchange, respectively. These flowsheets do not show details but reflect the basic process steps indicated in Section IV to be necessary. Solvents used in each of the extraction operations (Figure 2) would not necessarily be the same; similarly, elutants, etc., shown in Figure 3 would not be the same for each of the ion exchange operations. The discussion in Section IV enumerates and describes the various options that are available for each of the process streams or agents.

Comparison of Figures 2 and 3 shows that they are strikingly similar. On an overall basis, the same types and number of process steps would be required for solvent extraction and ion exchange. In practice, however, there would be significant differences in detail (cf. Section IV).

A process of the type shown in Figures 2 and 3 has been proposed and partially developed by researchers at Karlsruhe.<sup>(145)</sup> This process has been tested in the laboratory with synthetic waste and found to give TRU DF's on the order of  $10^2$ . If similar performance can be obtained in practice, this process may therefore be able to meet the requirements cited in Section II.

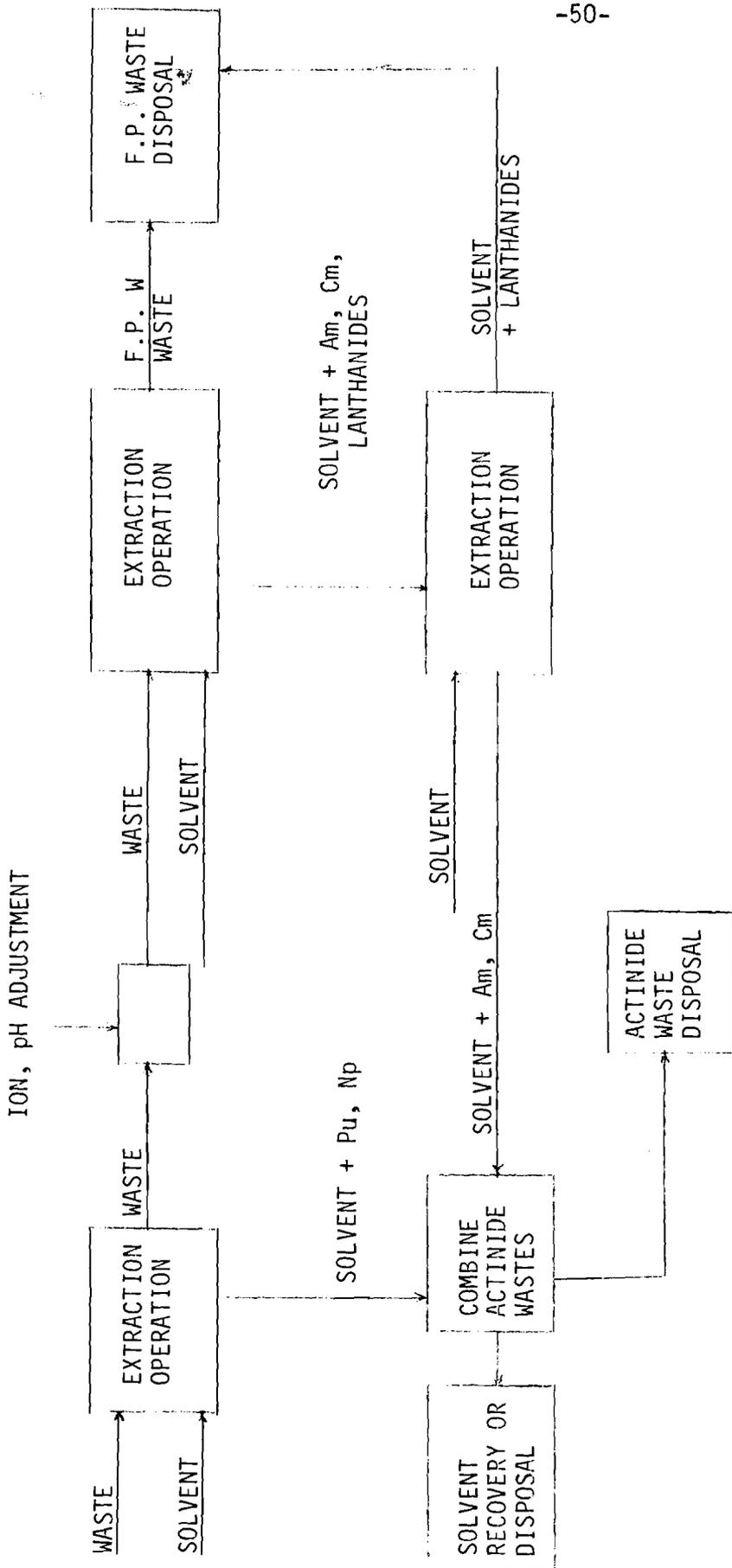


FIGURE 2. CONCEPTUAL FLOWSHEET FOR PARTITIONING BY SOLVENT EXTRACTION

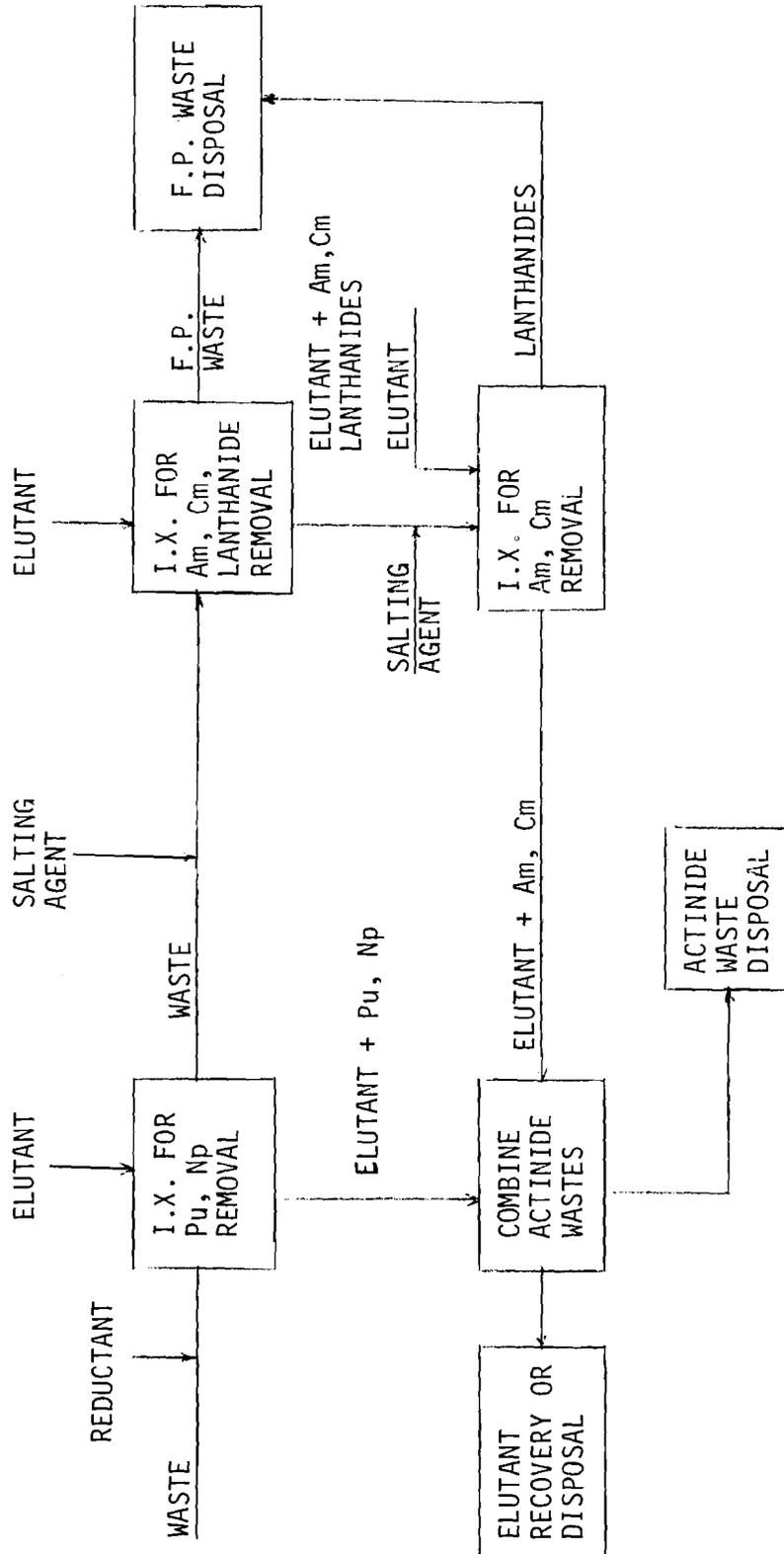


FIGURE 3. CONCEPTUAL FLOWSHEET FOR PARTITIONING BY ION EXCHANGE

## B. Partitioning Process Evaluation Logic

As indicated by prior discussion, evaluation of partitioning operation alternatives is only one part of the total problem of defining and selecting a complete process. The preferred process will be selected by consideration of factors such as the effect of suspended solids, process fluid characteristics and consumption, total waste volume and characteristics (after partitioning), and compatibility of the various operations involved in the process.

The total spectrum of problem elements and decision points is therefore quite large, as shown in Figure 4. In this context, the choice between partitioning operations (e.g., Figures 2 and 3) represents a choice for only the block labelled "Partition Operations" in Figure 4. This choice must be coupled to, and reflect, all the other decision points shown in Figure 4.

Figure 4 reflects and relates all of the problem elements previously discussed. The path through the logic diagram (i.e., the choice of exit from each decision point) will be determined by application of appropriate criteria at each point. For example, the key criteria for the decision on storage of waste prior to partitioning are process tolerance for the high radiation levels and chemistry that are characteristic of fresh waste. The criteria for the decision on solids removal are actinide content of the solids and process tolerance of their presence. The information needed to apply the criteria will be obtained from past data and experience or, when the needed information is lacking, from future R&D.

Figure 4 can serve as the basis for formulation of the R&D program for waste partitioning. It defines and structures the basic problem elements for the program. By adding to it the criteria and criteria-supporting data needs, the total spectrum of information needed to define and select a partitioning process will be identified. This spectrum of information needs can then be compared to existing data and, as a result, the R&D program needs will be defined.

To place partitioning in its proper waste management context, the problem elements shown in Figure 4 must also be coupled to the requirements and alternatives for disposal of the waste fractions that would be produced. For

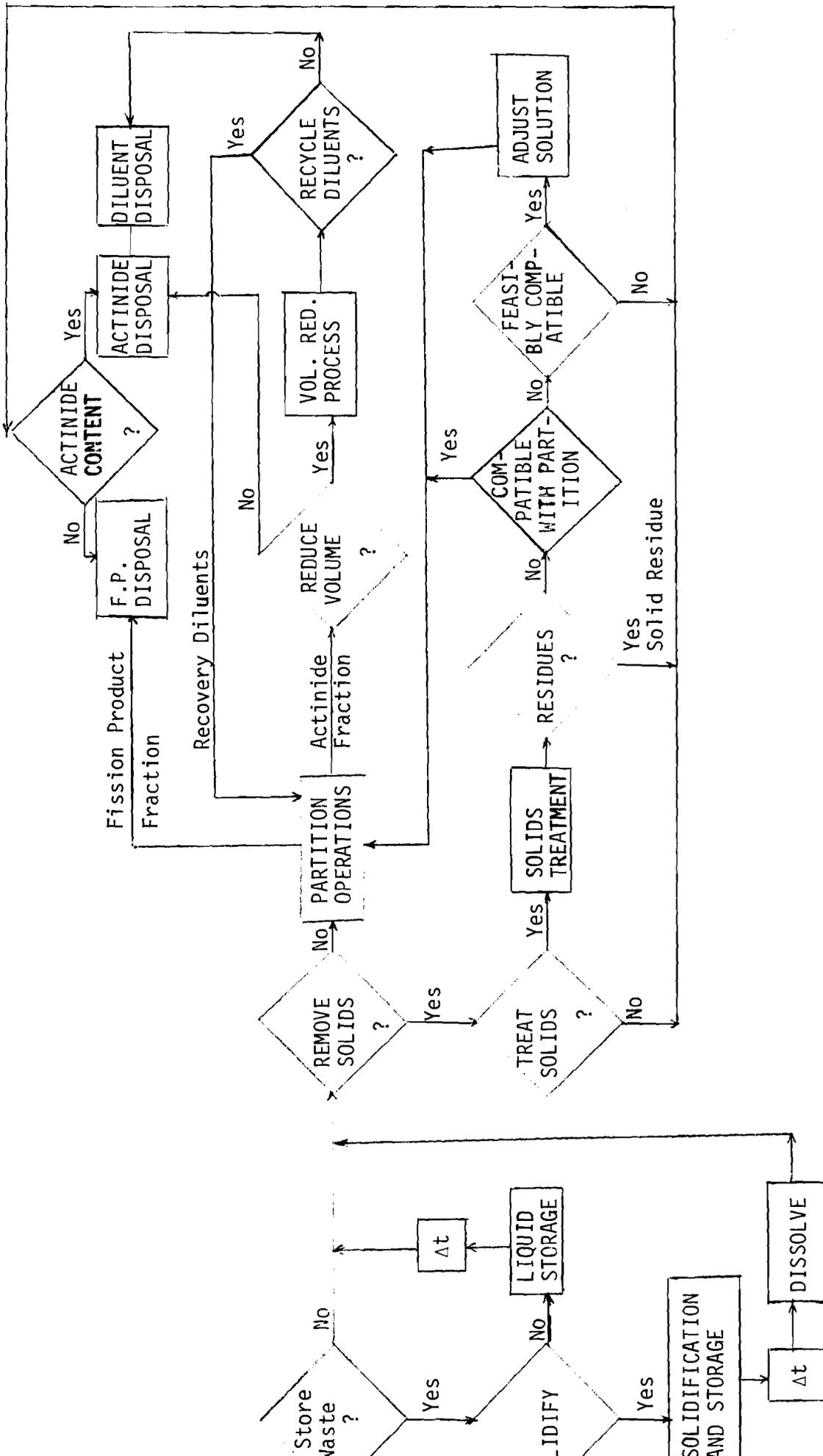


FIGURE 4. PARTITIONING PROCESS EVALUATION LOGIC

example, partitioning is expected not to change the characteristics of the fission product fraction (e.g., volume, etc.) except to eliminate the long-term risk to man. Compatibility with current concepts for disposition of fission product waste is therefore expected. But compatibility of the actinide fraction with concepts for disposal (e.g., transmutation, space) may require special action as part of the partitioning process. For example, the mass and volume of the actinides themselves will be quite small; they may be produced, however, as constituents of a dilute solution. Effective methods of volume reduction would then be required.

#### VIII. SUMMARY OF PROBLEM AREAS

This review has identified several major problem areas that would be expected to be part of an R&D program on waste partitioning. These problem areas are implicitly defined by Figure 4. For convenience, however, they are listed here in summary form.

##### 1. Waste Storage Prior to Partitioning

- necessity for storage
- acceptable storage methods
  - intact spent fuel
  - liquid
  - solid
- effect of storage on suspended solids
- time period for storage

##### 2. Suspended Solids in Waste

- sources of solids
- actinide content of solids
- effect of solids on processing
- solids formation during processing
- method of solids removal if needed
- need for solids treatment
- method of solids treatment if needed

- method of solids disposal
  - compatibility of treated solid fraction with other wastes
3. Solvent Extraction Partitioning
- selection of solvents
  - effectiveness of separation
  - compatibility of interacting streams
4. Ion Exchange Partitioning
- selection of ion exchange resins
  - selection of salting agents and elutants
  - effectiveness of separation
  - compatibility of interacting streams
5. Partitioning Process Implementation (Solvent Extraction or Ion Exchange)
- design details and process conditions
  - corrosion
  - process stability
  - radiation damage
  - interference from suspended solids
  - process measurements and control
6. Repro-Partitioning
- economic impacts
  - implementation options
  - feasibility for fresh waste
  - interference from suspended solids

7. Analytical Measurements
  - logistics of sample handling
  - sample method and validation
  - sample pretreatment and separations
  - effects of suspended solids
  - in-line process measurements
8. Partitioning Process Effluent Waste Streams
  - volume of waste streams
  - waste stream characteristics (composition, radioactivity, etc.)
  - recovery of processing agents
  - compatibility with disposal requirements
9. Comparative Evaluations
  - repro-partitioning alternatives
  - solvent extraction versus ion exchange for adjunct partitioning
  - solvent extraction and ion exchange combinations
  - adjunct versus repro-partitioning
  - criteria
    - economics
    - effects on waste disposal (volumes, hazards, etc.)
    - effects on hazard to man (near- versus long-term, etc.)

## IX. PARTITIONING COSTS

The operating costs to separate high-level waste into a long-lived and a short-lived fraction will, of course, depend on the degree of separation (DF's) required, the number of elements which must be removed from the short-lived fraction and the required purity of the long-lived fraction. A Delphi-type procedure was used to obtain an estimate of the cost to produce a short-lived fraction which will decay to negligible radioactive toxicity in about 1,000 years, i.e., removing the long-lived elements to high DF's. Several people knowledgeable in the costs of fuel reprocessing were asked to estimate the factor by which fuel reprocessing costs would be increased by the addition of facilities to accomplish this separation. The estimates ranged from a factor 1.25 to a factor of 4 with a mean factor of 2 or about \$35,000 per metric tonne of fuel.

A series of cost estimates were made on separating 99% (DF=100) of the actinide elements only from high-level waste. This degree of separation is similar to that achieved in a process developed at Karlsruhe for removing Am and Cm from waste.<sup>(145)</sup> This process was considered in making the following operating cost estimates.

	<u>Cost/MT Fuel, \$</u>
Actinides plus 1% of the Fission Products	10,000
Actinides less U + 1% of the Fission Products	15,000
Actinides less U + 0.1% of the Fission Products	20,000

## X. OUTLINE OF R&D PROGRAM

Data are needed on what can be accomplished toward long-lived isotope removal and at what cost to assess the technical and economic feasibility of the various approaches to managing the long-lived fraction as well as the overall economic impact on the nuclear fuel cycle. Hence, R&D work on partitioning (and fractionation) should not be delayed awaiting completion of the alternative disposal studies.

The following summary of waste separation R&D requirements is based on the assumption that waste fractionation will not be required and that removal of actinide elements (partitioning) from the short-lived fraction to less than 1% ( $DF \geq 100$ ) of their concentration in fuel reprocessing plant waste will be required. If further studies of risk analyses indicate waste fractionation or very high actinide DF's are required, the R&D program must be modified accordingly.

It has been emphasized during these studies that solids in waste constitute a major problem in waste partitioning and that little is known about the amount and composition of such solids. A program to obtain and characterize waste comparable to those expected from fuel reprocessing plants is needed. Resolution of problems of adequate solid-liquid separation, of whether or not treatment of the solids to remove actinides is required, and definition of processes for testing the solids would be part of this program.

Laboratory-scale studies are required to test conceptual flowsheets for attaining the required actinide element partitioning. Ideally these should be done with processing plant waste or process streams. However, these are not readily available and work with simulated materials should be done initially to define basic separations parameters; resolution of problems posed by plant derived waste would be done as it becomes available.

As conceptual flowsheets are tested and processes are developed, capital and operating cost estimates pertinent to the processes are needed both to guide the selection of a process or processes for further study and to provide cost input to other facets of waste management studies.

Pilot plant scale testing of the most promising flowsheets will be needed. This will entail facility design, construction or modification of a facility and operation of the facility to demonstrate the flowsheets, resolve problems posed by plant scale operation and provide more reliable cost data.

Development of analytical techniques should parallel flowsheet development studies. Specific analytical requirements will be defined in part by the flowsheets devised. These developments should be scheduled to permit testing of in-line analytical techniques during pilot plant testing of flowsheets.

An approximate schedule for the needed R&D program is shown in Figure 5. Approximate costs for R&D as a function of time are shown in Figure 6.

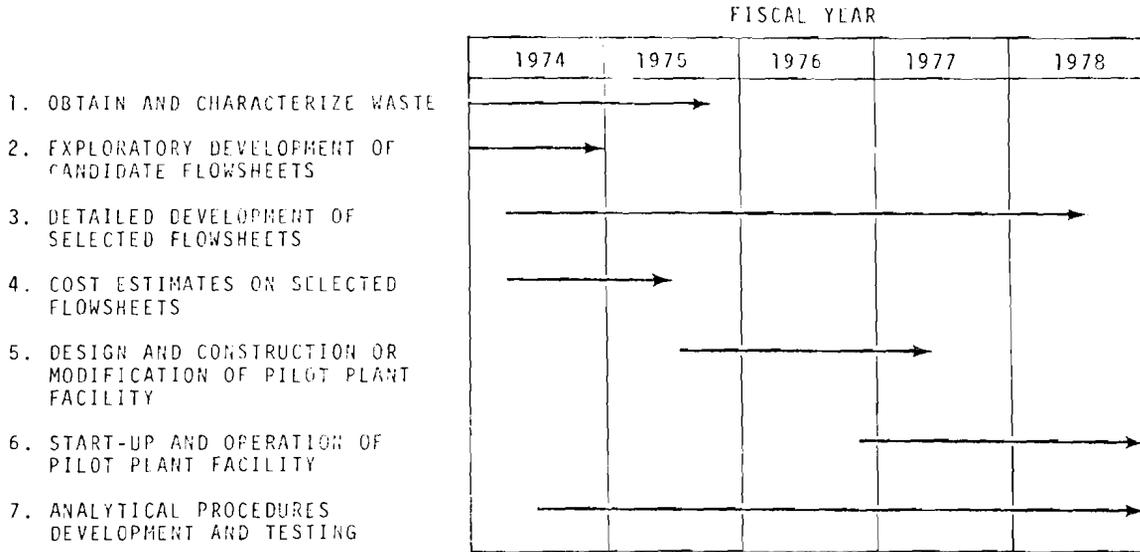


FIGURE 5. SCHEDULE FOR RESEARCH AND DEVELOPMENT

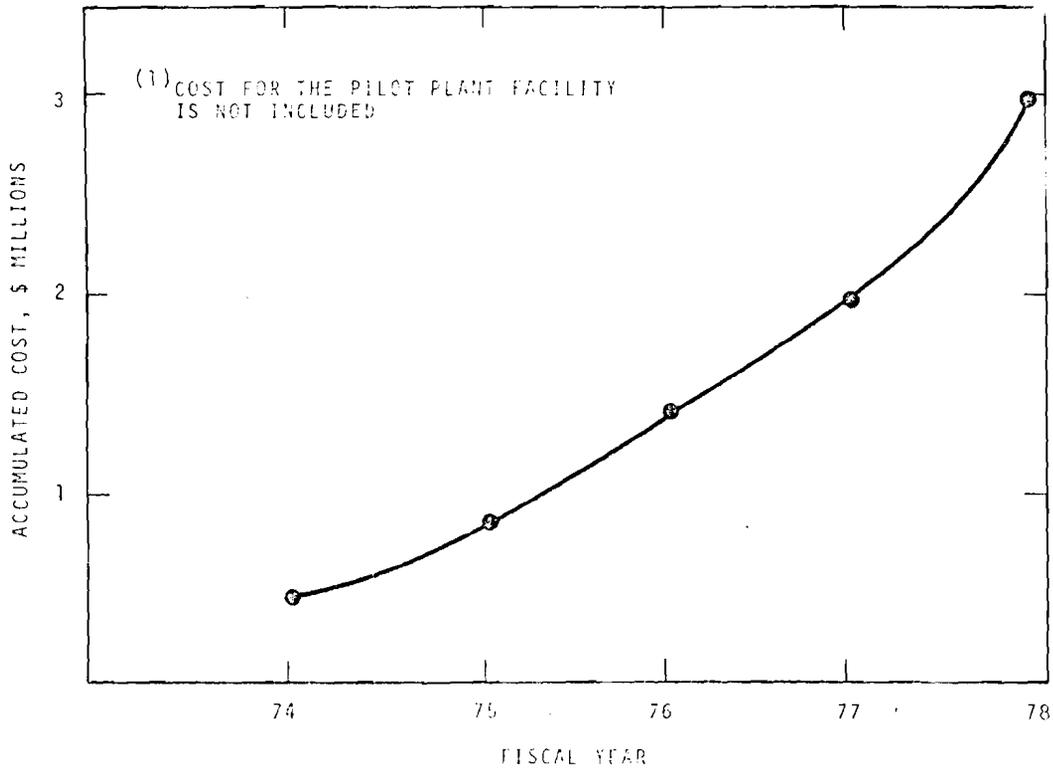


FIGURE 6. COST FOR R&D PROGRAM(1)

XI. REFERENCES

1. K. L. Rhode and J. A. Buckham, Effect of Irradiation on the Dissolution Characteristics of Important Fuel and Cladding Materials, IAEA Panel on Reprocessing of Highly Irradiated Fuels, Vienna, Austria, May 27-30, 1969.
2. J. H. Goode, Hot-Cell Dissolution of Highly Irradiated 20% PuO<sub>2</sub>-80% UO<sub>2</sub> Fast Reactor Fuel Specimens, ORNL-3754, October 1966.
3. W. Baehr and T. Dippel, On the Dissolution of Breeder Fuels Containing PuO<sub>2</sub> in Nitric Acid for Aqueous Reprocessing by the Purex Method, EURFNR-471, Karlsruhe, July 1967.
4. R. E. Lerch, Dissolution of Unirradiated Mechanically Blended, Sol Gel, and Coprecipitated Mixed Oxide Fuel, HEDL-TME-72-67, June 1972.
5. Aqueous Processing of LMFBR Fuels-Technical Assessment and Experimental Program Definition, ORNL-4436, June 1970.
6. J. M. Cleveland, The Chemistry of Plutonium, Gordon and Breach Science Publishers, New York, 1970.
7. J. H. Goode and V. C. A. Vaughen, Fuel Reprocessing Tests with Short-Cooled LMFBR-Type Fuel Rods, ORNL, Presented at the ANS Annual Meeting, Las Vegas, Nevada, June 18-22, 1972.
8. A. L. Uriarte, R. H. Rainey, Dissolution of High-Density UO<sub>2</sub>, PuO<sub>2</sub>, and UO<sub>2</sub>-PuO<sub>2</sub> Pellets in Inorganic Acids, ORNL-3695, April 1965.
9. W. Baehr and T. Dippel, On the Dissolution of PuO<sub>2</sub>-Containing Breeder Fuels in Nitric Acid for Aqueous Reprocessing by the Purex Method, Karlsruhe Report, KFK-673, EUR-3704d, 1967.
10. Sodium Cooled Reactors Fast Ceramic Reactor Development Program, Nineteenth Quarterly Report, May-July 1966, GEAP-5198, September 1966.
11. Sodium Cooled Reactors Fast Ceramic Reactor Development Program, Twenty-Second Quarterly Report, February-April 1967, GEAP-5491, May 1967.

12. C. D. Watson, et al., A Study of the Reprocessing of Spent Fast Test Reactor Fuel (and Other LMFBR Fuels) in the Nuclear Fuel Services Plant, ORNL-TM-2906.
13. ORNL-4272, Chemical Technology Division Annual Progress Report for Period Ending May 31, 1968.
14. W. W. Schulz, Aqueous Decladding and Dissolution of Plutonium Recycle Test Reactor Fuels, Part 2: PuO<sub>2</sub>-UO<sub>2</sub> Fuels, BNWL-204 PT2, November 1966.
15. W. W. Schulz, Nitric Acid Dissolution of PRTR PuO<sub>2</sub>-UO<sub>2</sub> Fuels, BNWL-CC-1103, February 1, 1967.
16. J. R. Divine, Decontamination of Plutonia Contaminated Thermal Reactor Systems, BNWL-SA-4361, June 1972.
17. G. E. Neibaur and R. D. Weed, Decontamination of the Irradiated Rupture Prototype with Peroxide-Carbonate and APACE, HW-63346, January 13, 1960.
18. J. A. Ayres, A. P. Larrick, et al., Decontamination Studies - Battelle-Northwest Laboratories, December 1964 to August 1965, BNWL-CC-173, July 1965.
19. R. D. Weed, Plutonium Dissolution Program, HW-81030, February 1964.
20. W. S. Gilman, A Review of the Dissolution of Plutonium Dioxide, MLM-1264, September 1965.
21. W. S. Gilman, A Review of the Dissolution of Plutonium Dioxide, Part II, MLM-1513, August 1968.
22. G. W. C. Milner, D. Crossley, "The Rapid Dissolution of Plutonium Dioxide by a Sodium Peroxide-Sodium Hydroxide Fusion, Followed by Determination of the Plutonium Content by Controlled-Potential Coulometry," Analyst, 93, pp. 429-432, July 1968.
23. L. M. Angeletti and W. J. Bartscher, "Dissolution of High-Fired Plutonium Oxide for the Determination of Plutonium," Anal. Chim. Acta, pp. 238-241, 1972.
24. C. E. Stevenson and D. M. Paige, "Aqueous Processing," Reactor and Fuel Processing Technology, Vol. 11, No. 2, Spring 1968.

25. ORNL-4272, Chemical Technology Division Annual Progress Report, pp. 43-46, May 1968.
26. ORNL-4422, Chemical Technology Division Annual Progress Report, pp. 71-74, May 1969.
27. J. Mamelle, "Experience in the Reprocessing of Irradiated Fuels in France," Nuclear Engineering International, pp. 709-710, September 1972.
28. V. B. Shevchenko, et al., Aqueous Processing of Power Reactor Fuels, A/Conf.49/P-435, June 1971.
29. Chemical Technology Branch Annual Report - Fiscal Year, 1969, IN-1314.
30. R. N. Henry and G. F. Offutt, Zirconium Fuel Reprocessing Campaign of 1970, IN-1471, April 1971.
31. B. E. Paige, K. L. Rohde, and B. J. Newby, Emulsion Control in Liquid-Suspension Extraction, U. S. Patent 3, 154, 376, October 1964.
32. H. J. Groh, Removal of Silica from Solutions of Nuclear Fuels, DP-293, June 1958.
33. B. C. Musgrave, et al., Clarification of Electrolytic Dissolver Solution Using a Hydrocyclone, IN-1276, April 1969.
34. P. A. Haas, et al., "Midget Hydroclones Remove Micron Particles," Chem. Eng. Progr., 53(4), p. 203, 1957.
35. H. C. Rathvon, Private Communication with L. L. Burger, 1972.
36. R. E. Lerch, Private Communication with F. P. Roberts, 1972.
37. ORNL-TM-3127, No. 18, LMFBR Fuel Cycle Studies Progress Report for August 1970.
38. ORNL-TM-3571, No. 30, LMFBR Fuel Cycle Studies Progress Report for August 1971.
39. B. C. Musgrave, et al., Chemical Development for EBR-II Fuel Progress 1967-69, IN-1285, April 1970.
40. D. E. Ferguson, C. R. Cooley, E. B. Sheldon, and D. S. Webster, "Recovery of LMFBR Fuels: Development of Techniques," Proc. Geneva Conf. on Peaceful Uses of Atomic Energy, Geneva, A/Conf. 49/P-64, September 1971.
41. ORNL-TM-3095, No. 17, LMFBR Fuel Cycle Studies Progress Report for July, 1970.

42. ORNL-4451, Siting of Fuel Reprocessing Plants and Waste Management Facilities, 1970.
43. J. P. Nickols, et al., Projections of Fuel Reprocessing Requirements and High-Level Wastes from the U. S. Nuclear Power Industry, ORNL-TM-3965, September 1972.
44. Reactor Handbook, Vol. II, Fuel Reprocessing - Section B, Aqueous Separation Processes, S. M. Stoller, R. B. Richards, Editors, Interscience, New York, 1961.
45. ORNL-4794, ORNL Chem. Tech. Division, Annual Progress Report, March 1972.
46. F. P. Roberts, L. A. Bray, Solvent Extraction of Transplutonium Elements from Redox Shippingport Waste, BNWL-CC-956, December 1966.
47. D. A. Orth, et al., "Isolation of Transplutonium Elements," Proceedings International Solvent Extraction Conference, The Hague, Soc. of Chem. Ind., p. 534, 1971.
48. J. C. Sheppard, The Distribution of Am<sup>3+</sup> Between Xylene-DBBP Solutions and Nitrate Solutions, HW-81166, March 1964.
49. R. S. Kingsley, Solvent Extraction Recovery of Americium with Dibutylbutylphosphonate, RL-SEP-518, June 1965.
50. L. E. Bruns, Proposed Curium-244 Program, Final Processing and Fuel Fabrication, pp. 250-445, December 1966.
51. G. L. Richardson, Americium Recovery by DBBP Solvent Extraction Pilot Plant Demonstration, BNWL-CC-1503, February 1968.
52. R. D. Baybarz, Separation of Transplutonium Elements by Phosphonate Extraction, ORNL-3273, August 1962.
53. D. F. Peppard, "Liquid-Liquid Extraction of Metal Ions," Advances in Inorganic Chemistry and Radiochemistry, Vol. 7, H. J. Emelius and A. G. Sharp, Editors, Academic Press, 1965.
54. L. L. Burger, "Neutral Organophosphorus Compounds as Extractants," Nucl. Sci. Eng., 16, p. 428, 1963.
55. K. Watanabe, "The Extraction of Curium and Americium by Tri-n-Octyl Phosphine Oxide," J. Nucl. Sci. Technical, Tokyo 1, p. 75, 1964.

56. J. Goffart, B. Duyckaerts, "L'Extraction des Lanthanides et des Actinides par les Oxydes D'Alkylphosphine," Anal. Chim. Acta, 46, p. 91, 1969.
57. Japan Atomic Energy Research Institute, Data of Inorganic Solvent Extraction, JAERI 1047, 1963.
58. T. H. Siddall, "Organophosphorus Compounds Other Than TBP for Processing Irradiated Fuels and By-Products," Symposium on Aqueous Reprocessing Chemistry for Irradiated Fuels, Brussels, 1963.
59. T. H. Siddall, "Bidentate Organophosphorus Compounds as Extractants--Part I," J. Inorg. Nucl. Chem., Vol. 25, p. 883, 1963. Also, "Bidentate Organophosphorus Compounds as Extractants--Part II," J. Inorg. Nucl. Chem., Vol. 26, p. 1991, 1964.
60. D. F. Peppard, et al., J. Inorg. Nucl. Chem., 4, p. 334, 1957.
61. D. F. Peppard, G. W. Mason, W. J. Driscoll, J. Inorg. Nucl. Chem., 12, 1959.
62. L. A. Bray, Solvent Extraction Process for Recovery of Strontium, Rare Earths, and Cesium from Radioactive Waste Solutions, HW-SA-2982, Northwest Regional ACS Meeting, Bellingham, Washington, 1963.
63. W. W. Schulz, Solvent Extraction of Strontium, Cerium, and Rare Earths with D2EHPA, Part 2, Laboratory Studies, HW-79762, Part 1, February 1964.
64. G. L. Richardson, Solvent Extraction of Strontium, Cerium, and Rare Earths with D2EHPA, Part 2, Pilot Plant Studies, HW-79762, Part 2, February 1964.
65. O. B. Michelsen and M. Smutz, "Extraction of Some Rare Earth Elements with Di(2-ethylhexyl)Phosphoric Acid at High Acidities," Proc. Int. Solv. Extraction Symposium, ISE7-71, p. 939, The Hague, 1971.
66. V. E. Shaw and D. J. Bauer, U. S. Bureau of Mines Report 7691, 1964.
67. I. N. Qureshi, L. T. McClendon, and P. D. LaFleur, Radiochemica Acta, 12, p.107, 1969.
68. B. Weaver, F. A. Kappelman, "Preferential Extraction of Lanthanides or Trivalent Actinides by Monoacidic Organophosphonates from Carboxylic Acids and from Mixtures of Carboxylic and Aminopolyacetic Acids," Energ. Nucl. Chem., 30, p. 263, 1968.
69. B. Weaver, F. A. Kappelman, Talspeak: A New Method of Separating Americium and Curium from the Lanthanides by Extraction from an Aqueous Solution of an Aminopolyacetic Acid Complex with a Monoacidic Phosphate or Phosphonate, ORNL-3559, August 1964.

70. Z. Kolarik, et al., Separation of Americium and Curium from Highly Radioactive Waste Solutions. Part I: Laboratory Batch Studies, KFK-1553, February 1972.
71. B. Weaver and R. R. Shoun, "Comparison of Some Monoacidic Organophosphorus Esters as Lanthanide-Actinide Extractors and Separators," J. Inorg. Nucl. Chem., 33, p. 1909, 1971.
72. J. C. Sheppard, The Extraction of Neptunium(IV) and Plutonium(IV) from Nitric Acid Solutions with Tri-n-octylamine, HW-51958, 1957.
73. M. Zifferero, "Proposed Flowsheets for Amine Systems," Symposium on Aqueous Reprocessing Chemistry for Irradiated Fuels, Brussels, 1963.
74. R. E. Leuze, R. D. Baybarz, and B. Weaver, "Application of Amine and Phosphonate Extractants to Transplutonium Element Production," Nucl. Sci. Eng., 17, p. 252, 1963.
75. F. L. Moore, "New Approach to Separation of Trivalent Actinide Elements from Lanthanide Elements," Anal. Chem., 36, p. 2158, 1964.
76. G. Kock, Recovery of By-Product Actinides from Power Reactor Fuels, KFK-976, May 1969.
77. G. E. Boyd and O. U. Larson, J. Phys. Chem., 64, p. 988, 1960.
78. D. Dyrssen, D. H. Liem, Acta. Chem. Scand., 14, p. 1100, 1960.
79. T. V. Healy, J. Inorg. Nucl. Chem., 19, p. 328, 1961.
80. M. W. Davis, Jr., J. W. Holt, R. A. Tournier, "Actinide-Lanthanide Separation in the System Kerosene - Tri-n-butylphosphate-thenoyl-trifluoroacetone," Proc. Int. Solv. Extraction Symposium, ISEC 71, p. 974, The Hague, 1971.
81. A. F. Rupp, A Radioisotope-Oriented View of Nuclear Waste Management, ORNL-4776, May 1972.
82. F. W. Tober, Proc. Second Intern. Conf. Peaceful Uses of Atomic Energy, Geneva, 1958, 17, p. 574, 1958.
83. M. D. Snyder, Recovery of Neptunium from Purex Waste by Anion Exchange, DP-742, November 1962, (Classified)
84. H. H. Van Tuyl, Recovery of Plutonium and Neptunium from Purex IWW by Anion Exchange, HW-61145, July 1959.
85. J. L. Ryan, Concentration and Final Purification of Neptunium by Anion Exchange, HW-59193 REN, February 1959.

86. J. L. Ryan and E. J. Wheelwright, The Recovery, Purification, and Concentration of Plutonium by Anion Exchange in Nitric Acid, HW-55893, January 1959.
87. W. Kraak and W. A. van der Heijden, J. Inorg. Nucl. Chem., 28, p. 221, 1961.
88. Y. Marcus and F. Nelson, J. Phys. Chem., 62, p. 77, 1959.
89. S. Adar, R. K. Sjoblom, R. F. Barnes, and P. R. Fields, J. Inorg. Nucl. Chem., 25, p. 1457, 1963.
90. Y. Marcus and M. Givon, J. Phys. Chem., 68, p. 2230, 1964.
91. J. Danon, J. Inorg. Nucl. Chem., 7, p. 422, 1958.
92. Y. Marcus, M. Givon, and G. R. Choppin, J. Inorg. Nucl. Chem., 25, p. 1465, 1963.
93. Y. Marcus and I. Abrahamer, J. Inorg. Nucl. Chem., 22, p. 141, 1961.
94. M. H. Lloyd, Nucl. Sci. Eng., 17, p. 452, 1963.
95. R. E. Brooksbank and W. T. McDuffee, Recovery of Plutonium and Other Transuranium Elements from Irradiated Plutonium Aluminum Alloy by Ion Exchange Methods, ORNL-3566, 1964.
96. J. Hines, M. A. Wahlgren, and F. Lawless, Proceedings of the Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology Held at Gatlinburg, Tennessee, October 9-11, 1962, TID-7655, p. 247, 1962.
97. V. A. Bochkarev and E. N. Voedvin, Radiokhimiya, 7, p. 461, 1965.
98. D. C. Stewart, C. A. A. Bloomquist, and J. P. Faris, Nitric Acid Organic Solvent Mixtures for Separation of Plus-Three Actinides of Anion Resins. I. Survey of Solvents, ANL-6999, 1965.
99. R. J. Morrow, Talanta, 13, p. 1265, 1966.
100. J. P. Faris and R. F. Buchanan, Anion Exchange Characteristics of the Elements in Nitric Acid and Nitrate Solutions and Application in Trace Element Analysis, ANL-6811, 1964. Also Anal. Chem., 36, p. 1157, 1964.
101. F. P. Roberts, F. M. Smith, and E. J. Wheelwright, Recovery of Technetium-99 from Hanford Waste, HW-SA-2581, May 1963.
102. D. I. Ryabchikov and A. A. Pozdnyakov, Doki, Akad. Nauk SSSR, 161, p. 869, 1965.

103. J. V. Panesko, Process for Recovery of Rhodium, Palladium and Technetium from Aged Reprocessing Wastes at Hanford, ARH-733, August 1968, and Recovery of Rhodium, Palladium and Technetium on Strongly Basic Anion Exchange Resin, ARH-1279, July 1969.
104. G. H. Higgins and W. T. Crane, Proc. 2nd Int. Conf. of the Peaceful Uses of Atomic Energy, Geneva, 1958, 17, p. 245, 1958.
105. G. H. Higgins, Radiochemistry of Transuranium Elements, NAS-NS-3031, 1960.
106. E. K. Hulet, R. T. Gutmacher, and M. S. Coops, J. Inorg. Nucl. Chem., 17, p. 350, 1961.
107. M. H. Lloyd and R. E. Leuze, Nucl. Sci. Eng., 11, p. 274, 1961.
108. R. D. Baybarz and P. B. Orr, Final Purification of the Heavy Actinides from the First Four Campaigns of the TRU Program, ORNL-TM-2083, 1967.
109. R. E. Leuze and M. H. Lloyd, Progress in Nuclear Energy, Series III, Process Chemistry, 4, p. 549, 1970.
110. W. D. Burch, J. E. Bigelow, and L. J. King, Transuranium Processing Plant Semiannual Report of Production, Status, and Plans for Period Ending June 30, 1968, ORNL-4376, 1969.
111. R. D. Baybarz, J. Inorg. Nucl. Chem., 27, p. 725, 1965.
112. W. Mueller, F. Maino, and J. Cl. Toussant, Isolation of Americium and Curium from Irradiated  $^{241}\text{Am}$  Targets, ERU-4232, 1968.
113. R. S. Kingsley, Multi-Column Ion Exchange Purification-Concentration Process for Am, RL-SEP-729(REV), 1965.
114. ORNL-4422, Chemical Technology Division Annual Progress Report for Period Ending May 31, 1969, p. 170, 1969.
115. S. G. Thompson, B. G. Harvey, G. R. Choppin, and G. T. Seaborg, J. Amer. Chem. Soc., 76, p. 6229, 1954.
116. J. P. Surls, Jr., and G. R. Choppin, J. Inorg. Nucl. Chem., 4, p. 62, 1957.
117. J. S. Coleman, L. B. Asprey, and R. C. Chisholm, J. Inorg. Nucl. Chem., 31, p. 1167, 1969.
118. J. S. Coleman, R. A. Penneman, T. K. Keenan, L. E. Lamar, D. E. Armstrong, and L. B. Asprey, J. Inorg. Nucl. Chem., 3, p. 327, 1956.

119. T. K. Keenan, J. Inorg. Nucl. Chem., 20, p. 185, 1961.
120. E. J. Wheelwright and F. P. Roberts, The Use of Alternating DTPA and NTA Cation-Exchange Flowsheets for the Simultaneous Recovery and Purification of Pm, Am, and Cm, BNWL-1072, July 1969.
121. E. J. Wheelwright, Ion Exchange: A Generic Nuclear Industry Process for the Recovery and Final Purification of Am, Cm, Pm, Sr, Pu, Np, Cs, Tc, Rh, and Pd, BNWL-SA-1945, October 1968.
122. S. R. Buxton and D. O. Campbell, Application of High Pressure Ion Exchange Column to the Separation of Actinides and Lanthanides, ORNL-TM-1876, May 1967.
123. W. H. Hale and J. T. Lowe, Inorg. Nucl. Chem. Lett., 5, p. 363, 1969.
124. E. Bruecher and P. Szarvas, Acta. Chim. Acad. Sci. Hung., 52, p. 31, 1967.
125. O. D. Bonner and L. L. Smith, J. Phys. Chem., 61, p. 326, 1957.
126. G. Hoehlin, H. J. Born, and W. Weinlaender, Radiochim. Acta., 10, p. 85, 1968.
127. A. M. Trofimov, G. N. Kovalev, V. G. Pitalev, Radiokhimiya, 9, p. 409, 1967.
128. R. Christell, S. Forberg, and T. W. Westermark, J. Inorg. Nucl. Chem., 19, p. 187, 1961.
129. F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962.
130. Olaf Samuelson, Ion Exchange in Analytical Chemistry, John Wiley & Sons, New York, 1963.
131. G. H. Coleman, The Radiochemistry of Plutonium, National Academy of Sciences, NAS-NS-3058, 1965.
132. R. L. Fleischer, H. Walter, S. C. Farman, P. B. Price, and R. M. Walker, "Particle Track Etching," Science, 178, pp. 255-263, October 1972.
133. M. H. Goheen, Private Communication.
134. C. R. Lagergren, Private Communication.
135. D. L. Love and A. E. Greendale, "Polarographic Determination of Technetium and Ruthenium Radionuclides in Fission Products," Anal. Chem., 32, pp. 780-786, 1960.

136. S. J. Remshaw and G. F. Malling, "Solvent Extraction of Technetium and Rhenium with Pyredine or Methyl-Substituted Pyredine from Alkaline Media," Anal. Chem., 33, pp. 751-754, 1961.
137. R. E. Foster, W. J. Maeck and J. E. Rein, "Liquid-Liquid Extraction of Technetium as Tetrapropylammonium Salt," Anal. Chem., 39, pp. 563-566, 1967.
138. L. A. Rancitelli, Private Communication.
139. G. Koch, et al., Recovery of Transplutonium Elements from Fuel Reprocessing High-Level Waste Solutions, Report No. KFK-1651, November 1972.
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