OC - 1131

ORNL-5012

**Feasibility Studies of the Partitioning of
Commercial High-Level Wastes Generated
in Spent Nuclear Fuel Reprocessing:
Annual Progress Report for FY-1974**

W D Bond R E Leuze

BLANK PAGE

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
Price: Printed Copy \$5.45; Microfiche \$2.25

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

ORNL-5012
UC-70 - Waste Management

Contract No. W-7405-eng-26

CHEMICAL TECHNOLOGY DIVISION

**FEASIBILITY STUDIES OF THE PARTITIONING OF COMMERCIAL HIGH-LEVEL
WASTES GENERATED IN SPENT NUCLEAR FUEL REPROCESSING:
ANNUAL PROGRESS REPORT FOR FY-1974**

W. D. Bond and R. E. Leuze

Contributions by:

J. O. Blomeke
D. O. Campbell
H. C. Claiborne
F. A. Kappelmann
F. G. Kitts
L. E. Morse
B. Weaver

JANUARY 1975

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

DISTRIBUTION OF THIS DOCUMENT UNLIMITED

CONTENTS

	<u>Page</u>
Abstract	1
1. Introduction	1
2. Benefits of Removing Long-Lived Radioisotope Hazards from High-Level Wastes	7
3. Calculation of the Required Actinide Removal	9
3.1 Basis of Calculations	9
3.2 Degree of Actinide Removal Required	11
4. Current Processes for Recovering Actinides	16
4.1 Processes for Uranium, Neptunium, and Plutonium Recovery.	16
4.1.1 Uranium and plutonium	17
4.1.2 Neptunium	20
4.2 Processes for Americium and Curium Recovery	22
4.2.1 Separation of americium and curium from lanthanide fission products	23
4.2.2 Preparation of suitable trivalent actinide-lanthanide feed solutions from high-level wastes	26
5. Conceptual Processes for Removing Actinides from High-Level Wastes	35
5.1 Processing Sequence	35
5.2 Recovery of Uranium, Neptunium, and Plutonium by the Purex Process in the Fuel Reprocessing Plant	37
5.3 Additional Recovery of Uranium, Neptunium, and Plutonium by Exhaustive Extraction	38
5.4 Interim Storage of High-Level Wastes	38
5.5 Removal of Inextractable and Daughter Plutonium	40
5.6 Removal of Americium and Curium	41
5.7 Recycle of Waste Streams Generated in the Processing	42
6. Major Problems to Be Solved	43
6.1 Undissolved Residues of Fuel and Solids Generated in the Processing	43
6.2 Inextractable Plutonium	45
6.3 Development of an Americium-Curium Removal Process	45

BLANK PAGE

	<u>Page</u>
6.4 Alternative Reductants for Uranium, Neptunium, and Plutonium Partitioning	46
6.5 Control of Neptunium Valence in Coextraction	48
6.6 Recycle of Waste Streams	49
7. Laboratory Studies on Process Development	51
7.1 Removal of Americium and Curium from High-Level Wastes . .	51
7.1.1 Solvent extraction process methods	52
7.1.2 Ion exchange process methods	59
7.2 Neptunium Recovery	63
7.2.1 Purex process and nomenclature used	63
7.2.2 Coextraction of neptunium, uranium, and plutonium (HA column)	63
7.2.3 Partitioning step (column HB)	66
7.2.4 First uranium purification cycle	71
7.2.5 U(IV)-H ₂ H ₄ as a reductant for neptunium	71
8. Conceptual Flowsheet Studies on Recycle in the Purex Process. .	75
9. Summary	82
10. Appendixes	85
10.1 Appendix A: Hazard Index Values for the Major Components of Unprocessed Spent Fuels from the Principal Reactor Types	85
10.2 Appendix B: Calculation of the Hazard Indexes of Uranium Minerals	91
10.3 Appendix C: Relative Contributions of the Major Components of High-Level Waste from Conventional Reprocessing of Uranium-plutonium Fuels and from Assumed Secondary Processing of the Waste	93
10.4 Appendix D: Relative Contribution of Each Long-Lived Fission Product to the Total Hazard Index of Fission Products in High-Level Wastes	97
10.5 Appendix E: Preparation of Synthetic Waste Solutions . .	99
11. References	103

FEASIBILITY STUDIES OF THE PARTITIONING OF COMMERCIAL HIGH-LEVEL
WASTES GENERATED IN SPENT NUCLEAR FUEL REPROCESSING:
ANNUAL PROGRESS REPORT FOR FY-1974

W. D. Bond and R. E. Leuze

ABSTRACT

The feasibility of removing long-lived actinides from high-level waste has been evaluated on a preliminary basis. Results indicate that it may be possible to remove actinides to a sufficiently low level to decrease the potential hazard of high-level waste at 1000 years to a value comparable to that of naturally occurring uranium minerals. The feasibility study was directed primarily at high-level waste generated by the commercial reprocessing of LWR fuel. Although certain separations processes have the potential for the necessary actinide removals (up to 10^4 on a spent-fuel basis), they have not been applied to the particular problem of separations from waste solutions. A research and development program of considerable depth is required to determine whether these separations processes can be successfully modified and adapted to achieve the necessary separations and, in turn, be integrated into a functional waste processing facility at the expected levels of radioactivity. Data obtained in studies carried out thus far indicate that the most promising concept for achieving the desired removals of actinides will require improved recovery of actinides in conventional reprocessing of fuels as well as secondary processing of the waste. Potential processes for the necessary actinide removals were studied, and several problems that must be solved to develop satisfactory process flowsheets were identified. Present laboratory studies are designed to pinpoint the advantages of various promising potential processes and to resolve some of the difficult chemical problems.

1. INTRODUCTION

The Waste Partitioning Program was initiated in FY-1974 by the U.S. Atomic Energy Commission (USAEC). The objective of this program is to determine the technical and economic feasibility of removing the potentially hazardous very long-lived (>1000 years) radionuclides (primarily actinide isotopes) from high-level wastes generated in the commercial reprocessing

of spent nuclear reactor fuels. Because of the long-lived and potentially hazardous radionuclides present in high-level wastes from the present-day reprocessing of nuclear fuels, prudence dictates that these wastes be managed for a million years or longer in a manner whereby they are restrained from entering the environment. Although this waste management alternative is a viable one, it depends on predicting the stabilities of certain geological formations with sufficient confidence to permit their selection as storage sites for the wastes.

Removal of the long-lived (actinides) radionuclides is a potential means not only for making wastes more acceptable in terms of long-term hazards, but also of alleviating storage requirements.

Several of the waste management alternatives being studied by the USAEC depend on separating and solidifying one stream containing fission products with an acceptably low content of long-lived radionuclides and producing a second scrapure, concentrated stream containing the long-lived radionuclides.¹ The latter stream might possibly be eliminated by transmutation,¹⁻³ while the actinide-depleted, solidified fission product stream might be disposed of in geological formations reliably predicted to be stable for thousands of years. [While there is considerable confidence in predicted stabilities of geological formations for thousands of years, there is less confidence in such predictions for the period of a million years or more required for managed storage of fission products containing the long-lived (actinide) radionuclides.]

The present study provides a part of the necessary technological basis for evaluating the waste management alternatives currently under study by the USAEC. Initially, the emphasis will be directed primarily at the wastes from the reprocessing of LWR fuel because this is the only reactor fuel expected to be processed commercially during the next decade. However, some attention will be given to LMFBR and HTGR fuels, during the development of reprocessing concepts, to make certain that methods for reprocessing these fuels are compatible with processes for removing the long-lived radionuclides.

Spent LWR fuels contain several very long-lived radionuclides — both actinides and fission products — which are discharged to wastes in conventional reprocessing. The actinides are the major contributors to the potential long-term hazard, representing greater than 99% of that for 1000-year-decayed waste.² The actinides of concern are uranium, neptunium, plutonium, americium, and curium. The long-lived fission products of concern are ⁹⁹Tc, ⁹³Zr-⁹³Nb, ¹³⁵Cs, and ¹²⁹I. Removal of the actinides and ¹²⁹I to the desired degree would reduce the potential hazard posed by canned high-level waste after 1000 years to values comparable to those of naturally occurring uranium minerals.^{2,4}

Commercial reprocessing of spent LWR fuel is carried out for the purpose of recovering the economic values in the fuel. Uranium and plutonium recoveries of up to 99.5% are attained in conventional reprocessing. In some cases, 90 to 95% of the neptunium has been recovered for special uses, although it has no fissile value in commercial industry. The high-level waste does not contain all of the unrecovered uranium, plutonium, and neptunium. Significant amounts are also found in intermediate- or low-level wastes such as those generated in secondary purification cycles and in wastes accumulated from the purification of spent solvents. Sometimes these are concentrated and combined with the high-level wastes. Americium and curium are not normally recovered and thus are present in the high-level waste. The volatile fission products, which include iodine, tritium, and the rare gases, are removed during reprocessing and are managed as separate wastes.

Our initial studies on the partitioning of high-level wastes showed the program needed to be greatly expanded in scope. Secondary processing of the wastes from conventional reprocessing is not the most efficient way to accomplish the desired levels of actinide removal. In addition to secondary processing of the high-level waste, the program should also include improved methods of reprocessing spent fuels. Significant advantages are possible by modifications of present-day reprocessing methods. First, losses of fissile and fertile values to the high-level waste can be reduced; in addition, neptunium can be removed by the Purex process, which

is already employed in the reprocessing plant. Second, there are potential methods to eliminate or recycle the miscellaneous low- and intermediate-level wastes generated in the reprocessing plant which also contain long-lived radionuclides (primarily actinides). These miscellaneous actinide-bearing wastes presently require relatively large-area sites for disposal or storage. We have therefore expanded the original concept to include both improved methods for spent fuel reprocessing and secondary processing of the high-level waste.

Preliminary calculations indicate that the potential long-term waste hazard level achieved by removing 99.9% of the uranium, americium, curium, and ^{129}I , 99.99% of the plutonium, and 95% of the neptunium from LWR fuels that utilize plutonium recycle and have been irradiated to 33,000 Mwd/metric ton is comparable to that from naturally occurring uranium deposits. This means that the total losses in all wastes (high-, intermediate-, and low-level) must not exceed 0.01% of the plutonium, 0.1% of the uranium, americium, curium, or iodine, and 5% of the neptunium. Attaining these recoveries of actinides will require that the recoveries of uranium, neptunium, and plutonium be substantially increased over those achieved in conventional reprocessing; in addition, americium and curium will have to be removed from the high-level waste. Considerable improvements and advances in process methods and technology will be required to attain the desired actinide removal. It must also be remembered that any waste stream whose composition exceeds the maximum permissible concentrations for unrestricted release to the environment (10 CFR 20^{*}) must be recycled to some appropriate step in the processing or combined with the high-level waste for disposal. Processes employed to effect the necessary removals of the long-lived constituents must not utilize chemical reagents that greatly increase the volume of the solidified high-level waste.

Determination of the technical and economical feasibility of significantly reducing the potential long-term hazards and storage requirements of commercial wastes is a major undertaking. It appears that the program

^{*}Title 10 Energy, Code of Federal Regulations, Part 20.

required is of the same order of magnitude as the original program to develop today's commercial reprocessing methods. Ultimately, it will be necessary to operate a full-activity-level pilot plant (or demonstration plant) that satisfactorily treats all waste streams from a nuclear fuel reprocessing facility to confirm the feasibility of separating the long-lived radionuclides, demonstrate the required operational and recycle techniques, and provide operating and capital cost data. This feasibility study can be divided into eight problem areas, which are listed below in the order in which the work should proceed; however, work in the different tasks will often be carried out concurrently, and thus provide mutually beneficial information that will help to regulate and to determine the program details.

- (1) Determine the benefits of removing long-lived radionuclides and, from this, infer the amounts to be removed.
- (2) Develop an overall process concept that is compatible with nuclear fuel reprocessing methods and with ultimate disposal methods for the wastes.
- (3) Devise flowsheets that will accomplish the required removals but will not generate low- or intermediate-level wastes of potential long-term hazard or greatly increase the volume of high-level waste. In such flowsheets, the exit streams would either meet the limits as defined by 10 CFR 20, be combined directly with the high-level waste, or be recycled to the process.
- (4) Demonstrate each process of the overall flowsheet in laboratory-scale tests with synthetic feed.
- (5) Carry out small-scale hot-cell tests and demonstrate, at full activity levels, the steps of those processes that may be affected by irradiation.
- (6) Perform engineering-scale investigations of new equipment or process concepts which require scale-up information. The purposes of this task are to examine the overall problem of

waste partitioning plant design and to relate any individual problems in waste partitioning to the overall concept. Such investigations will provide design information for a "hot" pilot plant. This work is necessary in order to find and eliminate any equipment- or process-related difficulties that were not predicted on the basis of smaller-scale development work.

- (7) Operate a full-activity-level pilot plant or demonstration plant.
- (8) On a technical and economic basis, evaluate the entire concept for reducing the long-term hazard of wastes. This task will remain active throughout the duration of the program. Judgments should be made at each stage of the program to determine whether problems arise that make the concept infeasible. If the program proceeds through a full-activity demonstration, it will be necessary to prepare a final summary report dealing with all technical and economical aspects of the demonstration concept.

A previous study³ of waste partitioning included actinide removal from high-level waste and a general survey of possible methods for removing the actinides from fission products. Some of the main conclusions reached in that study were:

- (1) The separation factors for removal of actinides from high-level waste can range from as low as 10 to as much as 10^6 to 10^8 , depending on the assumptions and conditions of the specific case. Most likely, they will be somewhere in the middle of the range, probably between 100 and 10,000.
- (2) Adequate basic separations technology exists for developing separations processes which give separation factors of up to 10^4 , but it has not been applied to the particular problem of waste partitioning.

(3) Solvent extraction and ion exchange processes hold the best promise of achieving the required separation factors.

(4) Solids present in liquid high-level radioactive waste will complicate separations process development.

Acknowledgments. The authors express their sincere appreciation to R. G. Wymer for technical advice throughout the course of this study and for editorial suggestions during the preparation of this report. Special thanks are also due Martha G. Stewart for editing and to Jane Posey for typing this report. Significant portions of the experimental work reported in this study were capably performed by R. L. Hickey and D. L. Davis.

2. BENEFITS OF REMOVING LONG-LIVED RADIOISOTOPE HAZARDS FROM HIGH-LEVEL WASTES

If it were possible to divide wastes into a series of fractions strictly according to the half-lives of the radioactive components, the various waste fractions could then be released to the environment one by one after suitable storage times. Thus, the fraction containing only stable isotopes could be released immediately, the fraction containing isotopes with very short lives could be released after only a few years, and so on. On first consideration, this seems to be a particularly attractive concept for managing high-level waste from commercial reprocessing of nuclear fuel, since there are only a few fission products and actinide elements that have very long lives. About 60 wt % of the fission products will decay essentially to stable daughters in 100 years. After 1000 years, the only radioactive hazards remaining will stem from a few fission products (e.g., ^{129}I , ^{93}Zr , ^{99}Tc , and several others of lesser importance) and the actinides.

The difficulty with this approach to waste management is that large separation factors are required. Long-lived isotopes remaining in the fractions of stable (or short-lived) isotopes cannot exceed the maximum permissible levels for uncontrolled release (as stipulated in 10 CFR 20). This requires decontamination factors (DFs) up to 10^{11} for release at 10 years, up to 10^{10} for release at 100 years, and up to 10^7 for release at

1000 years. All of these factors are greatly beyond the range of present-day technology, and it seems highly improbable that such separations can be attained on a practical basis. However, as has already been intimated, advantages may be realized by separations which, although of somewhat poorer quality, may be technically feasible.

In our initial attempt to investigate this possibility, it was assumed that 99.9% of the iodine (which, of course, includes 99.9% of the isotope ^{129}I) would be removed in head-end processing and thus would not report to the high-level waste, and that removal of actinides from the high-level waste should be sufficient to decrease their hazard value at 1000 years to a hazard comparable to that of the long-lived fission products. With these actinide removals, the resultant high-level waste at 1000 years would have a hazard comparable with that of naturally existing ore bodies (one-twentieth of the hazard from high-grade pitchblende and ~50 times the hazard from uranium ores in the western United States). If it becomes necessary or desirable to decrease the hazard even further, significant amounts of the long-lived fission products, as well as additional amounts of the actinides, will have to be removed. For the initial investigation, we will consider removing the actinides to only moderately low levels (i.e., to levels posing hazards comparable to the hazards from long-lived fission products). The most demanding removals are required for LWR reactor fuel with plutonium recycle. For fuel irradiated to 33,000 MWd/metric ton, these removals amount to 99.9% of the uranium, 95% of the neptunium, 99.99% of the plutonium, and 99.9% of the americium-curium.

Radioactive wastes from present-day reprocessing of nuclear fuel will remain hazardous for over a million years; however, removing the long-lived radioisotopes as described above will greatly decrease the hazard for times beyond 1000 years. The actinide-depleted, solidified fission products might be safely disposed of in geological formations reliably predicted to be stable for thousands of years. The recovered actinides might be eliminated by transmutation.

3. CALCULATION OF THE REQUIRED ACTINIDE REMOVAL

Calculations were carried out to determine the degree of actinide removal, together with removal of 99.9% of the iodine, that would be required from spent fuels to reduce the actinides to levels where their contribution to the hazard index^{*} of 1000-year-decayed waste would be comparable to that of the remaining long-lived fission products. When the actinides and ¹²⁹I have been reduced to this extent, the hazard index of high-level waste after 1000 years of decay will be in the range of calculated hazard index values for uranium minerals; it will be only about 5% of the value for pitchblende. The calculations showed that wastes from the reprocessing of uranium-plutonium fuels will require removal of uranium, neptunium, plutonium, americium, and curium; wastes from thorium-uranium fuels will also require removal of thorium and protactinium.

It is likely that the calculations of actinide removal presented here will eventually have to take into account the possibility of breach of containment and be extended to include an environmental pathway analysis in which the physical and chemical forms of the wastes and radionuclide content are evaluated with respect to potential modes for solubilization and to mechanisms of transport in environmental media. However, the calculations based on comparative hazard index values are entirely satisfactory for the initial work on the evaluation of the technical feasibility of actinide removal.

3.1 Basis of Calculations

The details of the calculational method and the basis on which the calculations of the required actinide removals were made have been reported

* The hazard index is defined as the volume of water required to dilute a unit volume of a radionuclide mixture to the levels defined in the Code of Federal Regulations (10 CFR, Part 20) as the maximum permissible concentration for unrestricted use of water. The hazard index provides only an approximate comparison of radiological risks since it does not allow for accumulation or reconcentration of a nuclide in environmental media, or for the total impact of a number of nuclides. For limited comparisons, it is an acceptable alternative to dose calculations if used with caution.

previously.² Therefore, only the basis of the calculations need be presented here to provide an understanding of the percentage removal requirements of the actinides from high-level wastes.

The effect of the degree of removal of actinides on the radiological toxicity was estimated by calculating the hazard index value as a function of time for the mixture of fission products and actinides that remained in the high-level wastes after assumed percentages of initial actinide removal. The bases on which these calculations were made were as follows:

- (1) The total quantities of actinides not recovered in the processing of 1 metric ton of spent LWR, LMFBR, and HTGR fuels were assumed to be present in 2, 3, and 6 ft³, respectively, of solidified high-level fission product waste.
- (2) All of the rare gases, 100% of the tritium, and 99.9% of the iodine were assumed to be removed as separate wastes in the fuel reprocessing and hence were not present in the high-level fraction. The total quantities of all other fission products were assumed to be present in this fraction. None of the activation products produced in the fuel cladding was assumed to report to the high-level waste.
- (3) Fuels from a 1000-MW(e) LWR of the pressurized water type (PWR), a 1100-MW(e) LMFBR of the General Electric Follow-On (GEFO) design, and a 1160-MW(e) reference design HTGR were used as the representative classes of fuels in a commercial industry. Two classes were considered for the LWR: PWR-U, in which there is no recycle of the plutonium; and PWR-Pu, in which the plutonium is recycled. It was assumed that waste from PWR-Pu was blended (one-third PWR-Pu - two-thirds PWR-U).

- (4) The average exposures of the LWR, LMFBR, and HTGR fuels were assumed to be 33,000, 41,200, and 94,300 MWd/metric ton, respectively. The fission product and actinide contents of the spent fuels were calculated by use of the ORIGEN⁵ code.
- (5) Radiation control guide (RCG) values were not listed for all of the nuclides in 10 CFR 20. Therefore, the RCG values calculated by LaVerne⁶ were used for any unlisted nuclides. Appendix A of this report gives the hazard index values that were used to calculate the degree of removal of actinides for PWR-U, PWR-Pu, LMFBR, and HTGR fuels.
- (6) Hazard index values of 1×10^8 and 1×10^5 were used for pitchblende and domestic ores, respectively. These values reflect the range of uranium concentration found in economic ore deposits (see Appendix B). On a hazard index basis, pitchblende represents the upper limit of toxicity of radioactive minerals.

3.2 Degree of Actinide Removal Required

Figure 1 shows the effect of the removal of actinides from high-level wastes. The hazard index of high-level waste generated by conventional reprocessing of spent fuel from a typical LWR (no plutonium is recycled) is compared with that of the same waste after additional removal of actinides by secondary treatment. It was assumed that 99.9% of iodine and 99.5% of uranium and plutonium had been removed in conventional reprocessing, whereas 99.95% of the plutonium, 99.9% of the uranium, americium, curium, and iodine, and 95% of the neptunium had been removed in combined conventional and secondary processing. The hazard indexes associated with pitchblende (70% uranium content) and with uranium ore containing 0.2% uranium (high-grade domestic ore that occurs in the Colorado Plateau) are included for reference purposes. As seen, the hazard index of wastes

ORNL DWG 74-10105R1

Fig. 1. Effect of age and method of treatment on the hazard index of high-level wastes from LWRs.

generated by conventional reprocessing decreases rapidly over the first 1000 years (due mainly to decay of ^{90}Sr and ^{137}Cs) but remains almost as great as pitchblende for more than a million years. However, the hazard index for waste produced by secondary treatment falls well within the range of naturally occurring radioactive materials after only about 1000 years, a time span for which the effects of geologic, climatic, and other natural phenomena can be reliably predicted.

One method for disposing of the separated actinides and ^{129}I would be to recycle them with fresh fuel to power reactors. Previous calculations² show that even after sustained recycle of these materials (which would tend to build up the levels of the actinides), the hazard index of the waste would still lie within the range of naturally occurring radioactive minerals although it is 20 to 30% higher than without recycle.

Table 1 gives the percentage removal of each actinide element for different reactor fuels that would be required to reduce the hazard index of wastes after 1000 years of storage to about 5% of pitchblende. Each fuel type requires removal of uranium, plutonium, neptunium, and americium and curium; in addition, HTGR fuel requires removal of thorium and protactinium. If it is assumed that conventional reprocessing removed 99.5% of the uranium and plutonium from all fuel types, plus 99.5% of the thorium from HTGR fuel, the secondary treatment of waste to achieve the overall removal of actinides shown in Table 1 reduces the hazard index of 1000-year-old wastes from conventional reprocessing by factors of 60, 400, 240, and 270 for PWR-U, PWR-Pu, LMFBR, and HTGR fuels, respectively.

Evaluation of the technical feasibility of actinide removal processes for LWR fuels will be based on the removals required for PWR-Pu fuel, which are equal to or greater than removals required for PWR-U fuels. To attain the required removal of actinides from spent PWR-Pu fuels, minimum additional removal factors from high-level waste of 5, 20, 50, 1000, and 1000 are needed for uranium, neptunium, plutonium, americium, and curium.

Figure 2 shows the relative contribution of individual actinides and fission products in PWR-Pu waste after removal of 99.99% of the plutonium,

Table 1. Percentage removals from spent fuels required to reduce the hazard index of aged wastes to approximately 5% of that of pitchblende^a

Actinide	PWR-U	PWR-Pu	LMFBR	HTGR
Th				95.5
Pa				95.0
U	99.9	99.9	99.9	99.99
Np	95.0	95.0	70.0	95.0
Pu	99.95	99.99	99.99	99.9
Am & Cm	99.9	99.9	99.9	95.0

^aMineral containing 70% uranium.

99.9% of the uranium, americium, curium, and iodine, and 95% of the neptunium. The contributions of americium, plutonium, and ⁹⁹Tc to the hazard index of the PWR-Pu waste at 1000 years are about equal, and these radionuclides constitute about 80% of the calculated hazard index of the waste. The relative contributions of actinides and long-lived fission products of PWR-Pu wastes are similar to LMFBR and PWR-U wastes having the actinide removals shown in Table 1 (see Appendixes C and D). On a calculated hazard index basis, further removal of actinides from PWR-Pu waste would not be warranted unless one also removed the ⁹⁹Tc. However, biological pathway analysis will be needed before final judgment can be made concerning the desirability of additional actinide removal without a commensurate removal of long-lived fission products.

Fig. 2. High-level waste from the reprocessing of spent Pu recycle LWR fuel irradiated to a burnup of 33,000 MWD/ton.

Assumed removals: Mg , 95%;
 ^{129}I , U , Am , Cm , 99.9%;
 Pu , 99.99%.

4. CURRENT PROCESSES FOR RECOVERING ACTINIDES

The recovery processes that are reviewed here are mainly those which have been utilized on the largest scale of plant operations or that have the greatest potential for recycle of process wastes and chemicals. The extensive literature relative to separation of actinides from fission products was surveyed in a previous study.³ In cases where no clear potential advantages could be established for processes not yet sufficiently developed for large-scale application, it appeared that increasing the recovery of actinides to the desired level by improvements and modifications to processes currently employed in fuel reprocessing and in transplutonium-element production programs was the most desirable approach. These processes were developed originally to provide recovery of actinides for their economic value; therefore, relatively little effort was made during their development to achieve a more quantitative recovery by additional recovery cycles and by optional recycle of waste streams. Processes presently used in commercial fuel reprocessing plants may give uranium and plutonium recoveries of up to 99.5%. From 90 to 99% of the neptunium and americium-curium are normally recovered in special processing which is carried out to recover actinides for research purposes and certain specific uses.

4.1 Processes for Uranium, Neptunium, and Plutonium Recovery

Uranium, neptunium, and plutonium are normally recovered from nitric acid solutions of actinides and fission products or of spent fuels by the Purex process. In this process the three actinides are extracted into tributyl phosphate (TBP), leaving the fission products in the aqueous phase. Separation of the three actinides from each other after coextraction by TBP is then accomplished by partitioning in subsequent solvent extraction cycles or in anion exchange cycles. At present, it does not appear that there is any obvious advantage in considering any extractant other than TBP for the primary recovery of uranium, neptunium, and plutonium from solutions of fission products. Although various other solvents have been the subject of

considerable research during the past 25 years, none has proved to be superior to TBP for recovering uranium, neptunium, and plutonium from solutions of actinides and fission products.⁷

4.1.1 Uranium and plutonium

The only commercial operating experience with the recovery of uranium and plutonium in large-scale processing of LWR fuels has been at the West Valley Facility of Nuclear Fuel Services, Inc. (NFS), which uses the Purex process. Two new reprocessing plants, General Electric's Midwest Fuel Recovery Plant (MFRP) at Morris, Illinois, and the Allied-General Barnwell Nuclear Fuel Plant (BNFP) at Barnwell, South Carolina, were also designed to use a Purex flowsheet for the primary recovery of uranium and plutonium. The Purex process flowsheet used as a design basis for MFRP includes the routine recovery of neptunium and plutonium. At the NFS plant and at BNFP, the Purex process flowsheet calls for the discharge of neptunium to the aqueous, high-level fission product waste stream. (If desired, the neptunium-bearing waste may later be recovered by batch processing using the Purex process.) Recently, it has been announced that the future operation of the MFRP is uncertain, primarily because of the inoperability of certain equipment and processes related to conversion of the purified uranium to UF_6 .

Figure 3 shows a schematic Purex flowsheet which typifies that used by the NFS plant. The NFS plant is presently shut down for modifications and additions which will increase its capacity and waste handling capability. Uranium and plutonium recoveries of about 98.5% were achieved in the NFS plant during average operation. The high-level aqueous waste generated in this plant contains greater than 99.9% of the nonvolatile fission products as well as a large fraction of the unrecovered uranium and plutonium. In addition, it contains essentially all of the neptunium and transplutonium elements. Aqueous wastes generated in the uranium and plutonium purification cycles that utilize TBP extraction are concentrated by evaporation, and the nitric acid values are recovered (see Fig. 4). The concentrated, purification-cycle wastes are combined with the similarly concentrated

ORNL DWG. 74-2002 R1

Fig. 3. Outline of conventional processing using a Purex process.

Fig. 4. Recovery of uranium and plutonium by the Purex process in the Nuclear Fuel Services plant. (Uranium and plutonium percentages are typical values.)

high-level waste from the first-cycle solvent extraction. Recycling the concentrated aqueous wastes from the uranium and plutonium purification cycles to the feed to the first-cycle solvent extraction would avoid the losses from these cycles. With recycle, the uranium and plutonium losses to the concentrated high-level waste would be expected to be about 0.2% and 0.5%, respectively, rather than the corresponding 0.4% and 1% expected with no recycle. The losses listed for the waste streams shown in Fig. 4 are based upon the plant input and were estimated from processing campaign experience in which Yankee Atomic fuel having irradiation exposures of 8500 to 16,500 Mwd/metric ton was processed.⁸ Uranium and plutonium losses to the alkaline waste from solvent purification by caustic scrubbing were 0.5% and 0.3%, respectively. Processes for removing the actinides from the alkaline wastes or new methods for purification of the solvent will have to be developed if the overall recoveries from spent fuels shown in Table 1 are to be achieved. Fuel exposures in LWRs are expected to be about 33,000 Mwd/metric ton, and even greater losses to the alkaline waste may possibly occur when solvent purification is effected by caustic scrubbing.

During the operational period of the NFS plant, there was no economic incentive to recover the neptunium from commercial fuels. Therefore, flow-sheet conditions were chosen so that neptunium was rejected to the high-level wastes. About two-thirds was rejected directly in the first-cycle solvent extraction, about one-third in the two plutonium purification cycles, and about 1% in the two uranium purification cycles.

4.1.2 Neptunium

Various neptunium recovery methods based on solvent extraction from nitric acid solutions of nuclear fuel have been developed; however, only those methods in which the Purex process plays the major role have found applicability in large-scale processing.⁹ Considerable experience exists for recovering neptunium via the Purex process in programs involving the production of ²³⁸Pu at Hanford and at Savannah River. Generally, 90 to 99% recovery of the neptunium has been achieved, depending on the processing rate required. The lower recoveries were obtained at high processing rates

and were apparently caused by the slowness of the kinetic processes for neptunium valence adjustment relative to the processing rate required in the production campaigns.

Two basically different approaches have been used for recovering neptunium by the Purex process:

- (1) Coextraction of neptunium with uranium and plutonium in the first extraction cycle, and separation from these other elements in subsequent cycles.
- (2) Rejection of neptunium as Np(V) to the high-level aqueous waste in the first extraction cycle, and recovery from the waste by ion exchange or solvent extraction methods.

The first approach is clearly the most advantageous for use in a Purex plant where commercial fuels are processed. The radiation damage is reduced because most of the fission products come in contact with solvent only in the initial extraction column, fewer process steps are required, and less additional equipment is needed. Therefore, only this approach is discussed here.

Coextraction of uranium, neptunium, and plutonium is effected in the first cycle of the Purex process by adjusting the valence of the neptunium to Np(VI) by nitrous acid-catalyzed oxidation of Np(V) with nitric acid. Neptunium can then be separated from uranium and plutonium in subsequent Purex extraction cycles or by anion exchange cycles. When the three actinides are coextracted, it appears that their separation in additional Purex extraction cycles (as is done at Hanford) is more advantageous than costripping followed by separation by anion exchange (as is planned at MFRP). Since these extra cycles of the solvent extraction are similar to the main Purex cycle, recycle of waste streams and process chemicals is simplified. A reducing agent is required, regardless of whether the three actinides are partitioned by solvent extraction or by anion exchange.

In the recovery and subsequent separation of uranium, neptunium, and plutonium by Purex processing at Hanford, the three actinides are co-extracted as U(VI), Np(VI), and Pu(IV) from 2 to 3 M HNO_3 solutions; the plutonium is then stripped from the TBP by an aqueous ferrous sulfamate solution which reduces Pu(IV) to Pu(III), leaving the U(VI) and Np(IV) in the organic phase. The uranium and neptunium are subsequently separated in the second uranium purification cycle, where Np(IV) is partitioned to the aqueous raffinate by keeping the organic phase highly saturated with uranium. Some of the important variables in the recovery of neptunium in the Hanford pulsed coextraction column are:

- (1) nitrous acid and nitric acid concentrations at all points along the column profile,
- (2) column temperature,
- (3) pulse frequency and amplitude,
- (4) processing rate, and
- (5) degree of uranium saturation of the organic phase.

4.2 Processes for Americium and Curium Recovery

Considerable experience exists relative to the recovery of americium and curium in connection with transplutonium-element production programs at Oak Ridge National Laboratory and the Savannah River Laboratory. Typically, recoveries have been 90 to 99% from specially irradiated targets. The separation methods have consisted of combinations of solvent extraction, ion exchange, and precipitation steps.

Several different processes have been utilized in the sequence of separations required for recovering the transplutonium elements. However, separation of the transplutonium elements from the chemically similar lanthanide elements has most often been effected by the *Tramex* process,^{10,11} which is based on extraction of the transplutonium elements from concentrated LiCl solutions. Of course, processing equipment that comes into contact with such solutions, which are very corrosive, must be constructed of special and expensive materials; consequently, LiCl-based processes are

not presently considered to be practical for removing americium and curium from commercial high-level wastes. Thus, the only process that has been used to any great extent for the recovery of americium and curium in multi-gram amounts on a plant scale is unsuitable for improvement and adaptation to the removal of these actinides from high-level wastes.

Two processes that have been developed as possible alternatives to the Tramex process appear to have the potential necessary for providing a high degree of removal of americium and curium from lanthanide fission products. One is a cation exchange chromatography (CEC) process;¹²⁻¹⁴ the other is a solvent extraction process, Talspeak.^{* 15,16} However, neither of these processes has been demonstrated at radioactivity levels comparable to those encountered in the Tramex process. Also, each requires an actinide-lanthanide feed solution that is essentially free of the other fission products. A considerable amount of development work will be needed to determine whether these processes are feasible for use in recovering americium and curium from high-level wastes and whether methods for preparing suitable feed solutions for these processes can be worked out. If not, a wholly new approach must be developed.

4.2.1 Separation of americium and curium from lanthanide fission products

The available processes that appear to have the greatest potential for use in the separation of americium and curium from the lanthanide fission products are CEC¹²⁻¹⁴ and Talspeak.^{15,16} Other methods currently employed for trivalent actinide-lanthanide separations were judged to be unsuitable primarily on the basis of the types and/or amounts of chemical reagents used in the processing.

Cation exchange chromatography (CEC). Processes based on CEC have been successfully applied to multigram separations of americium and curium from fission product lanthanides both at Hanford and at Savannah River.¹²⁻¹⁴ Existing flowsheets for these processes require a feed that contains only

* Acronym for trivalent actinide-lanthanide separation by phosphorus reagent extraction from aqueous (k)omplexes.

minor amounts of other fission products and inert materials, other than sodium. With this type of feed, resin columns can be loaded to near-theoretical exchange capacity without causing breakthrough of actinides and lanthanides when solution with acidities as high as 1 N are used.¹⁴ Organic reducing agents, such as formic acid, are used to adjust the acidity of the solution by chemical reaction with the excess nitric acid. After the actinides and lanthanides have been sorbed on a loading column, chromatographic separation is effected by band displacement through a series of ion exchange columns with an eluent containing a chelating agent, usually sodium diethylenetriaminepentaacetate (Na_5DTPA) (Fig. 5). Zinc is employed as a barrier ion so that the developing bands remain "sharp" for the individual elements throughout the many band displacement volumes that are required for separation and purification. "End-cutting" of products is simplified by effecting band displacement through a series of successively smaller-diameter columns. This resin configuration minimizes the losses due to end-cutting and, in turn, the quantity of material that must be reworked and recycled. Because of the large quantity of zinc that is needed for providing the barrier ion, zinc will need to be recycled. Also, significant amounts of contaminated waste resin will be produced because of mechanical, chemical, and radiation damage to the resin particles. Recycle of the complexing agent, DTPA, would be desirable; however, an alternative is to convert it to a noncontaminated gaseous chemical waste. Solutions to these recycle problems and to disposal of waste resin and DTPA will require further study of both a conceptual and an experimental nature.

The CEC process has been developed at Savannah River¹⁴ for a capacity of about 20 moles of rare earths and actinides, although not at full activity levels. This is about one fourth the capacity necessary for the americium, curium, and rare earths in 1 metric ton of LWR fuel.

Talspeak process. The Talspeak process is based on the preferential extraction of lanthanides from trivalent actinides by di(2-ethylhexyl)phosphoric acid (HDEHP) from a carboxylic acid solution containing Na_5DTPA .

Fig. 5. Schematic flowsheet of cation exchange chromatographic process for recovery of americium and curium.

A conceptual flowsheet for a Talspeak process is shown in Fig. 6. According to this flowsheet, the lanthanides are separated from the actinides by extraction from a 1 M lactic acid solution of these elements with 0.5 M HDEHP in diisopropylbenzene diluent and then scrubbing the organic phase with a solution containing lactic acid and Na_5DTPA . The pH of the aqueous phase is maintained at 2.5 to 3.0. The americium and curium may be recovered as oxalates by precipitation from the aqueous phase or as a nitrate solution by an additional cycle of solvent extraction with HDEHP as the extractant. Extractions from 1 M solutions of a number of carboxylic acids (formic, acetic, propionic, and malonic acids) have also been shown to be effective.^{15,16} The choice of carboxylic acid depends on the particular application.

The development of the Talspeak process has been confined, for the most part, to tracer-level laboratory studies. Limited studies have been carried out at Karlsruhe relative to removal of americium and curium from waste solutions.¹⁷ In view of this, considerable development work will be required to determine whether the Talspeak process is feasible for use in the recovery of americium and curium from high-level wastes. Acceptable methods would have to be developed for the preparation of a suitable lanthanide-actinide feed for the process; in addition, an improvement in the extraction kinetics would be desirable. The process chemicals, other than sodium, are organics and have the potential for being eliminated from the final calcined high-level wastes by volatilization or combustion methods; however, acceptable disposal methods would have to be developed. Improved methods for purifying the HDEHP solvent used in the process are also needed. Commercially available HDEHP contains moderate amounts of impurities which are detrimental in the processing and must be removed. A practical method for this purification is needed.

4.2.2 Preparation of suitable trivalent actinide-lanthanide feed solutions from high-level wastes

As discussed previously, all processes presently used for separating trivalent actinides from lanthanides require feed solutions that are essentially free of certain fission products. These fission products would

Fig. 6. Conceptual flowsheet for recovery of americium and curium by a Talspeak process.

precipitate via hydrolysis in the low-acidity solutions employed in the subsequent processing. Also, the presence of phosphate ion in the high-level wastes from Purex processing could cause actinides and lanthanides to precipitate at low acidities.

Feed solutions are generally prepared by removing the actinide-lanthanide fraction from the other fission products or chemicals present from the previous processing. Currently employed methods of feed preparation have not been developed to a sufficient extent to give the recoveries required for americium and curium from high-level waste. It is possible that the methods presently being used in transplutonium-element production programs could be modified to give the required recoveries. However, most of these methods require large quantities of nonvolatile chemicals which, because they cannot be recycled, would increase the final volume of high-level fission product waste by prohibitive amounts. The methods that appear to have the greatest potential for preparing satisfactory feed solutions from high-level wastes are:

- (1) TBP extraction of lanthanides and actinides from solutions salted by aluminum nitrate,
- (2) ion exchange separation of the lanthanide-actinide fraction,
- (3) specific extractants for trivalent actinides and lanthanides from acidic solution, and
- (4) removal of easily hydrolyzable fission-product elements by solvent extraction (selective fission-product removal).

Perhaps some combination of these methods may be superior to any one of them.

TBP extraction of lanthanides and actinides. The extraction of trivalent actinides and lanthanides by TBP from fission product solutions salted with aluminum nitrate has been utilized in transplutonium-element programs.^{11,18-20} This process is operated batchwise, with the acidity being adjusted between successive extractions. Since low-acidity solutions (0.1 to 0.35 M) are required, precipitation occurs if too much acid is extracted by the TBP or is destroyed by radiolysis in the processing.

Americium and curium recoveries of 95 to 99% are usually achieved by two batch extractions. To be useful in waste partitioning, this process would have to be modified to attain the desired recoveries and to allow the salting agent to be recycled. The low acidity required for extractability of the actinides and lanthanides in TBP presents difficult control problems relative to product losses by hydrolysis and precipitation reactions both in the extraction process and in preparation of the aqueous feed for the process.

A flowsheet for the recovery of greater than 99.5% of the lanthanides and actinides by means of a continuous countercurrent extraction with TBP in mixer-settlers has been demonstrated at Savannah River, although not at full activity levels.¹⁹ This flowsheet is also potentially applicable to the separation of actinides plus heavy lanthanides from the lighter lanthanides. As shown in Fig. 7, the first step in the process involves co-extracting the lanthanides and trivalent actinides into acidified TBP, along with any other actinides and most of the ruthenium and zirconium, from a feed solution highly salted with aluminum nitrate (2 M). The trivalent actinides and lanthanides are then selectively stripped into dilute nitric acid, leaving zirconium, ruthenium, and any actinides at higher valence states [e.g., U(VI), Pu(IV)] in the spent solvent. Material balances for this flowsheet were based on high-level waste from the reprocessing of 1 metric ton of LWR fuel irradiated to a burnup of 33,000 MW/metric ton. It was assumed that 5000 liters of high-level waste was concentrated into a highly salted feed volume of 2000 liters. This assumption may be optimistic. The amount of nitrate salts needed for processing this volume of waste is about 2 metric tons - a prohibitively large quantity. The flowsheet given here (Fig. 7) typifies the disadvantage of separations based on high metal salt strength, regardless of whether they are accomplished by solvent extraction or ion exchange.

The feed solution to this process is prepared by steam-stripping the high-activity waste from a Purex plant to reduce the nitric acid concentration, and is finally adjusted to 0.4 M in HNO_3 and 2 M in $\text{Al}(\text{NO}_3)_3$.¹⁸

ORNL Dwg 74-7500

Fig. 7. Conceptual flowsheet for removal of lanthanides and tri-valent actinides from high-level waste by extraction with TBP from nitrate-salted solutions.

Final adjustment of aluminum nitrate solutions to low acidities has been accomplished by digestion of the solution at 140°C.²¹ The method used for feed adjustment also would require development work to adapt it to the large-scale continuous operation. Because of the high radiation exposure and the fission product content of commercial fuels, the stability of the $\text{Al}(\text{NO}_3)_3\text{-HNO}_3$ solution toward precipitation would require study in terms of specific fission-product concentrations and acidity.

Ion exchange separation of the trivalent actinide-lanthanide fraction.

During the past two decades or so, ion exchange separation has been employed as a general laboratory and analytical method for achieving group separations of elements according to their valence. This method appears to have the potential for isolating a trivalent-element fraction from high-level waste solutions. Ion exchange separations have not found wide applicability in large-scale processing where high-level radiation is involved because of radiation damage to the resins. However, if the waste solutions are allowed to decay for a suitable period of time (perhaps 5 years) prior to processing, ion exchange may prove to be satisfactory for separation of a lanthanide-actinide fraction. Ion exchange also offers the potential for removing residual plutonium, uranium, and neptunium, which could perhaps be accomplished at the same time that the trivalent actinide-lanthanide fraction is separated.

A number of ion exchange methods have been employed for various fission product separations. For example, a laboratory-scale cation exchange process has been developed for separating lanthanides and actinides from other fission products.²² However, none of the methods was aimed at the large-scale separation of trivalent actinides and lanthanides from the other fission products. Ion exchange would offer an advantage over currently employed methods in that moderately high acidities, 1 to 2 M , could probably be employed in the feed, thereby avoiding the generation of solids by hydrolysis and precipitation. Also, it would be expected that a significant portion of the nitric acid that is used as an eluent could be recycled. It is likely that the remainder of the necessary elution steps could be carried out with organic complexing agents which could be

principally converted to gaseous chemical wastes and thus would not increase the volume of the final calcined high-level waste. The desirable features of such an ion exchange process are sufficient to justify experimental work to determine its feasibility.

Specific extractants for trivalent actinides and lanthanides from acidic solutions. It would be highly desirable to find an extractant which would selectively remove the trivalent actinides and lanthanides from nitric acid solutions of high-level wastes without the use of metal nitrate salting and which could be stripped to produce a moderately concentrated product. It would be preferable if the extraction could be made at waste solution acidities of 2 M or greater, where the stability of solutions with regard to hydrolysis of certain metal ion constituents is a minimal problem. A search was conducted for such an extractant during the process development work associated with transplutonium-element production programs. However, all the solvents that possessed this capability were found to suffer various other disadvantages, and no major attempt was made to overcome these disadvantages through appropriate development studies. Extractants which removed the actinide-lanthanides from low-acidity or highly salted solutions were acceptable in the transplutonium-element program because (1) the transplutonium elements are much more concentrated in the specially irradiated targets to be processed than in power reactor fuels, and (2) the required degree of recovery is considerably lower than that required for waste partitioning. Since the concentrations of americium and curium in the high-level waste solutions are quite low, a solvent extraction process which would yield a highly concentrated product of actinides and lanthanides, even without a high degree of decontamination from other fission products, would offer a considerable advantage. The potential usefulness of such a process is sufficient to justify a reexamination of extractants.

Many extractants have been studied with regard to their capability for extracting trivalent actinides and lanthanides from acid solutions.^{3,23} However, any extractant which provides high extraction coefficients from solutions of moderately high acidity is apt to make stripping of the

extracted americium and curium difficult. In such cases, the extracted species are so strongly complexed by the extractant that they can only be effectively stripped into an aqueous phase through the use of complexing agents which form stronger complexes with the metal ions in the aqueous phase than does the extractant in the organic phase. If reagents with suitable characteristics cannot be found, the metal ions must be stripped by destruction of the extractant via certain chemical reactions such as hydrolysis or displacement with a more extractable ion. Another disadvantage of such extractants is that they also extract the higher-valent fission products, which must be subsequently separated from the lanthanides and actinides or be removed prior to extraction of the trivalent elements. These undesirable features could possibly be circumvented through appropriate process chemistry and flowsheet development work. A process which uses the extractant di(2-ethylhexyl)pyrophosphoric acid (DOPP), in which stripping is accomplished by hydrolysis of the DOPP, has been reported for the recovery of actinides from kilogram quantities of rock samples from underground nuclear explosions.²⁴ Extraction was effected from a 2 M HF--3 M HCl solution.

Although many extractants have been employed in the laboratory for extracting transplutonium elements from unsalted, acidic solutions, only one has found application on a significant scale. Di(2-ethylhexyl)phosphoric acid (HDEHP) can be used to extract trivalent actinides and lanthanides at low acidities (0.1 to 0.3 M), and the extracted species can then be stripped with 2 M acid. This extractant forms the basis for the Dapex²⁵ and Cleanex²⁶ processes. The Transuranium Processing Facility (TRU) at ORNL currently employs the Cleanex process, in which the lanthanides and actinides are coextracted from 0.1 M HNO₃ into HDEHP and then stripped into 2 M HCl. The primary purpose of the use of this process is to prepare a chloride-based feed solution for subsequent separations of actinides and lanthanides. However, significant decontamination from other fission product elements and corrosion products is also obtained. Since this extraction process must be employed with low-acidity solutions, feed preparations must be carefully carried out. Solution acidity is adjusted by a

combination of neutralization of the acid with sodium hydroxide and dilution. This procedure yields small amounts of a precipitate which can be accommodated in the batch extraction with HDEHP. It is not known whether this precipitate contains small amounts of actinides.

In addition to the trivalent actinides and lanthanides, HDEHP also extracts many higher-valent elements at low acidities. However, since the extraction coefficients for the higher-valent ions are also high at higher acidities, selective stripping of the trivalent actinides and actinides might be carried out after coextraction; another possible approach would be to remove the higher-valent ions by extraction into HDEHP from 6 M acid prior to the extraction of trivalent elements at low acidity. At TRU, plutonium and other fission products (zirconium, molybdenum, niobium) are removed in this manner by the Pubex process²⁶ before the Cleanex process is used to extract the actinide-lanthanide fraction.

Selective fission product removal. The problems associated with recovery processes which require low-acidity solutions are largely a result of the presence of certain hydrolyzable fission products. Removal of these fission products would avoid potential losses to precipitates and would also permit a more-concentrated feed solution to be prepared. Fission products with valences greater than 3 also complicate the recovery of a trivalent actinide-lanthanide fraction from high-acidity solutions since they are coextracted in solvent extraction processes or are sorbed on cation exchange resins ahead of the trivalent fractions. It may be advantageous to remove certain of these fission products prior to the preparation of an actinide-lanthanide feed solution for final isolation of americium and curium. It would be preferable, of course, that any selected fission product removal and the separation of a relatively pure actinide-lanthanide fraction be accomplished in the same process. However, this may not be practical or possible.

The fission products that usually present problems in americium and curium recovery processes are zirconium, molybdenum, and noble metals. Of course, others may also cause difficulties at the concentrations present

in higher-burnup fuels. In some instances, removal of the fission product(s) may be required either to avoid troublesome precipitates or simply to allow the preparation of a more-concentrated feed solution of lanthanides and actinides.

Processes for selected fission-product removal should only be developed as circumstances dictate. Extractants are available for removing some of the troublesome fission products. For example, HDEHP extracts zirconium, molybdenum, and niobium from 6 M HNO_3 , as described in the previous section. On the other hand, a significant problem to be resolved with the use of HDEHP is finding a practical method for stripping the fission products so that the solvent can be recycled.

Certain fission products such as zirconium and molybdenum are effectively extracted by TBP along with the lanthanides and actinides from 12-16 M HNO_3 , and it may be possible to effectively partition the extracted materials by selective stripping techniques. Although ion exchange techniques are also potentially attractive for the removal of various fission products, they appear to be more applicable to the separation of a lanthanide-actinide fraction from the remainder of the fission products as previously discussed.

5. CONCEPTUAL PROCESSES FOR REMOVING ACTINIDES FROM HIGH-LEVEL WASTES

Investigation thus far indicates that the removal of actinides can best be accomplished by improved recovery of actinides in conventional fuel reprocessing plus secondary treatment of the high-level wastes. Both the conceptual processing sequence for removing the actinides and the processes for their removal are presently being studied.

5.1 Processing Sequence

The present version of the processing sequence for removing actinides during LWR fuel reprocessing is illustrated in Fig. 8. According to this concept, neptunium would be recovered along with the economic values of

ORNL DWG 74-3054R

Fig. 8. Conceptual processing sequence for the removal of actinides from LWR reactor fuel.

uranium and plutonium in the primary Purex plant. If technically feasible, essentially complete removal of the reactor-bred plutonium, uranium, and neptunium would be accomplished by means of additional extraction stages or an additional cycle of the Purex process. Next, the high-level wastes would be stored for a certain period (up to several years) in order to reduce the radiation damage to reagents in subsequent processing. In the next step, as presently visualized, any inextractable plutonium remaining from the exhaustive extraction step and the plutonium daughter from curium decay would be removed. The americium and curium would be isolated following the final removal of plutonium.

5.2 Recovery of Uranium, Neptunium, and Plutonium by the Purex Process in the Fuel Reprocessing Plant

It is expected that a neptunium recovery of 95 to 99% can be obtained in the fuel reprocessing plant, along with an improvement in the usual uranium and plutonium recoveries. Insoluble residues from fuel dissolution would be separated and processed in a secondary dissolver. Additional improved recovery of uranium and plutonium would be obtained by recycle of the aqueous waste stream from the uranium, neptunium, and plutonium purification cycles. It appears that recycle of the aqueous waste streams from the purification cycles would increase recoveries of uranium and plutonium to as much as 99.8% and 99.5%, respectively. Recoveries obtained in the coextraction of uranium and plutonium in the first extraction column at NFS have been as high as 99.97% uranium and 99.7% plutonium during some operational periods in the Yankee fuel campaigns,⁸ indicating that the Purex process has at least this potential.

Considerable development work will be required in order to achieve the desired recovery of neptunium and the improved recovery of uranium and plutonium. For instance, methods for maintaining the neptunium valence during extraction require further study. Also, an alternative reductant for ferrous sulfamate, which is used in partitioning uranium, neptunium, and plutonium, will have to be developed in order to accomplish the necessary recycle for improved recovery and to eliminate sulfate ion, which interferes with the subsequent processing of the wastes.

5.3 Additional Recovery of Uranium, Neptunium, and Plutonium by Exhaustive Extraction

Essentially complete removal of uranium and neptunium is expected to be accomplished in the additional stages of Purex extraction. It is not possible to estimate what fraction of the residual plutonium will be removed since neither the amount nor the nature of the inextractable plutonium is known. The small quantity of actinides removed by the exhaustive extraction will be recycled to the primary Purex extraction to avoid the necessity for extra purification cycles for fission-product decontamination. Also, it is expected that a high decontamination from fission products will not be necessary during the exhaustive extraction since the recycled actinides are coextracted under conditions where good fission-product decontamination is achieved.

5.4 Interim Storage of High-Level Wastes

Fission product yttrium and rare earths are associated with americium and curium throughout most of the processing; therefore, radiation damage to chemical reagents, resins, and solvents will be quite high unless the waste is allowed to decay for a suitable time prior to processing. The bulk of the activity in the rare-earth fission products is primarily due to cerium and its daughter praseodymium, and to yttrium (Fig. 9). The only other rare earths of radiation significance are europium and promethium. The thermal power of 1-year-decayed yttrium and rare earths is reduced by factors of about 3, 6, and 9 at total decay times of 3, 5, and 10 years, respectively. In 10-year-decayed waste, essentially all of the radiation associated with rare-earth fission products (97%) is actually due to yttrium. Taking these facts into consideration, storage times of 10 years or greater would give considerable advantage in the processing. However, current USAEC regulations require that the wastes be solidified within 5 years and that the solid wastes be assigned to the USAEC for management within 10 years. It would be desirable to recover the americium and curium before the wastes are solidified to avoid the necessity for redissolution. Materials such as Al_2O_3 , which may be added to stabilize the wastes and make them difficultly soluble, will complicate processing.

Fig. 9. Thermal power of high-level waste from the conventional reprocessing of LWR fuels.

Developmental work will proceed with the assumption that americium and curium will be recovered after the 5-year maximum permissible period for storage of liquid high-level waste. The effect of processing at shorter times will also be investigated.

Storage of the waste also presents significant disadvantages. For example, large inventories of liquid will be accumulated, solids will form during storage, and plutonium that grows back into the waste from curium decay will again require removal. About 9 g of plutonium (primarily ^{240}Pu) would "grow into" the waste from each metric ton of fuel by decay of curium during the 5-year storage period. Since plutonium will definitely have to be removed after the storage period, it is not certain at this time whether there is any advantage in attempting to obtain complete plutonium removal prior to storage. An all-ion-exchange process has the potential for recovering the plutonium, along with americium and curium and perhaps also the neptunium and uranium. However, it seems advantageous to recover the required amount of uranium and neptunium by extra Purex stages since that process is already employed and has the potential for the necessary degree of recovery. Although additional plutonium will also be extracted in these extra stages, it is doubtful that complete extraction will be obtained because of the presence of inextractable forms of plutonium.

5.5 Removal of Inextractable and Daughter Plutonium

The type of processing required for this step cannot be determined until the nature of the plutonium in the aged wastes is determined. It will probably involve a chemical treatment to convert soluble but inextractable plutonium (colloids or complexes) to extractable species and a solids removal step to remove actinide-bearing solids for subsequent treatment. If feasible, these solids will be dissolved in nitric acid or leached free of actinides by nitric acid and the solution recycled to the Purex process. However, if this is not feasible, the solids might be processed in a special manner by the use of nitric-hydrofluoric acid mixtures or molten salts. Any solubilized, but inextractable, forms

of plutonium such as plutonium polymer or complex ions which may exist will present a difficult problem and will require developmental work so that the inextractable forms may be identified and the necessary methods for rendering them extractable can be developed.

5.6 Removal of Americium and Curium

The americium and curium will be recovered following final removal of the plutonium. The specific process that will be used for recovery cannot yet be designated and must be developed. Existing processes for the removal of americium and curium from fission products are deficient from several points of view; although several of them are potentially promising for use as the final removal step in which the americium and curium are to be separated from the lanthanide fission products, methods for preparing a satisfactory feed solution will have to be developed. Conventional processes for separating americium, curium, and lanthanide from gross fission products utilize high concentrations of metal salts; thus it will be necessary to devise methods for eliminating these salts from the final fission product waste or to develop a completely different process as an alternative.

Two processes that are currently being evaluated for the final removal of americium and curium from the lanthanides are CEC,¹²⁻¹⁴ in which separation is accomplished by chromatographic elution from cation exchange resin; and Talspeak,^{15,16} in which removal is effected by solvent extraction from carboxylic acid solutions. Methods that are being evaluated for the preparation of suitable actinide-lanthanide feed solutions for these processes include:

- (1) ion exchange,
- (2) TBP extraction of lanthanides and actinides from solutions salted with aluminum nitrate, and
- (3) solvent extraction from acid solutions of fission products.

All of these methods were previously discussed (see Sect. 4) in light of their potential for recovery and specific problems associated with their use in high-level waste processing. Each method presents difficult

problems relative to prevention of losses of actinides by hydrolysis and precipitation and in the handling of the waste streams generated by the americium and curium processing. Prevention of the formation of solids in the americium and curium processing will be difficult, and the problems associated with separating and processing solids may again be encountered. As development studies proceed, it may be possible to combine the separated solids from all sources in the overall processing of the high-level waste, and to recover any actinides from the combined solids. A sufficient amount of experimental data regarding the nature of the generated solids will have to be obtained before such a concept can be evaluated with respect to the overall processing requirements in removing actinides from wastes.

5.7 Recycle of Waste Streams Generated in the Processing

Satisfactory recycle of process chemicals and liquids appears to be feasible in conceptual processes in which improved recovery of uranium, plutonium, and neptunium is achieved by modifications and additions to the Purex process. The feasibility of recycling waste streams generated during the recovery of americium and curium has not been determined, and development of the necessary methods will require a substantial research and development effort. The ability to satisfactorily handle the waste streams from processes designed to remove inextractable and daughter plutonium after waste storage is unknown and must await development of the processing that will be employed to effect plutonium removal.

Conceptual flowsheets for the recycle of aqueous waste streams from the Purex process were evaluated in some detail with regard to the main-line processing and exhaustive extraction (see Sect. 8). Solutions to specific problems associated with the solvent purification and recycle were not included in the flowsheets and require further analysis.

6. MAJOR PROBLEMS TO BE SOLVED

Several difficult chemical problems will have to be solved before the technical feasibility of actinide removal can be determined. In addition to the undissolved residues in fuel dissolution, these problems largely stem from chemical changes that occur in solutions of actinides and fission products during conventional and additional processing and during the recycle of generated waste streams. Major problems that have been identified include the following:

- (1) elimination of actinide losses to undissolved residues of fuel and to solids generated in the processing,
- (2) identification and recovery of inextractable forms of plutonium,
- (3) development of an americium-curium removal process,
- (4) development of alternative reductants of uranium, neptunium, and plutonium partitioning,
- (5) control of neptunium valence during extraction,
- (6) satisfactory recycle and management of waste streams generated by the processing.

To a large extent, these problems are interrelated.

6.1 Undissolved Residues of Fuel and Solids Generated in the Processing

Attainment of a high degree of recovery of actinides from spent fuels by chemical reprocessing, and hence their elimination from the high-level waste, will require that losses caused by undissolved residues of spent fuel and solids generated in subsequent separations processes be avoided or reduced to very small levels. Losses that have been experienced in reprocessing plants with metal-clad oxide fuels have not been adequately reported, and little information is available from the literature. Solids have been a problem not only because they represent a loss of fissile material, but also because they often cause operational difficulties. In a previous study,³ the literature was surveyed with regard to the

nature of the solids to be expected from fuel dissolution and, in a broad sense, this survey helped to identify difficulties that can be expected as a result of these solids.

Results of experimental studies have shown that the insoluble residues from the dissolution of various fuel elements consist primarily of undissolved core materials and some insoluble cladding oxides, and that the quantity of insolubles increases as the burnup of the fuel increases. Leaching the residues with nitric acid that contains catalytic amounts of fluoride ion has been shown to be effective in reducing the losses of plutonium to these residues. Insoluble residues that have been identified from the dissolution of $\text{PuO}_2\text{-UO}_2$ fuels predominantly contain molybdenum, zirconium, niobium, ruthenium, rhodium, and palladium. Losses of plutonium to these residues have been reduced to a few hundredths of a percent in small-scale leaching tests on irradiated fuel pellets after secondary treatment of these solids with 8 M HNO_3 --0.05 M HF.^{27,28}

In large-scale processing, undissolved fuel fines and insoluble residues emerge with the exiting liquid from the dissolver. These materials are suspended via agitation of the solution by the nitric oxide gases generated in dissolution and by the flowing liquid. Separation of these solids may be difficult.

Even if the actinides are successfully removed from the fuel dissolution residue, solids may again be generated in subsequent processing or during storage of the high-level wastes. In the past, solids may have been generated simply because of aging that occurs while the processing is being carried out. Some of the fission products are hydrolyzed, precipitating slowly and somewhat irreproducibly.

A considerable amount of definitive work will be needed to identify the solids, the conditions by which they are generated, and the actinide losses associated with them. In cases where the formation of solids cannot be prevented, methods for handling these solids and for recovering any actinide values associated with them will have to be developed. It is expected that a large fraction of the definitive work can be accomplished

with synthetically prepared waste solutions and wastes prepared from the dissolution of small irradiated fuel specimens.

6.2 Inextractable Plutonium

In the past, the complete recovery of plutonium has been inhibited by the presence of inextractable forms. These consist of fuel dissolution residues and of forms generated during processing, not yet identified, which may include colloids, precipitates, sorbed species, and complex ions. Data reported by workers at Karlsruhe²⁹ indicate that plutonium becomes inextractable after repeated Purex extraction cycles when concentrations of 0.8 ± 0.4 mg/ml are reached. This amount of inextractable plutonium calculates to be 4 ± 2 g per metric ton of LWR fuel processed or about 0.05% of the plutonium in spent LWR fuel, assuming that 5000 liters of unconcentrated high-level waste is produced per ton of fuel processed.

Developmental work will be required to identify the inextractable forms of plutonium and the mechanisms by which they are produced. Process conditions which favor the formation of colloidal or polymeric plutonium must be avoided since such material, once formed and aged, does not readily redissolve in nitric acid. Steps where polymer is likely to be produced include stripping of plutonium from TBP with low-acidity solutions (<0.2 M) or "localized dilutions" where low-acidity condensate is allowed to drip into plutonium solutions during concentration via evaporation.

6.3 Development of an Americium-Curium Removal Process

The development of a satisfactory process for the removal of americium and curium is probably the most formidable task in the fractionation of high-level waste. Attainment of the necessary recoveries at the low-acidity conditions that are dictated by the separations processes will require either drastic modifications of present processes or an entirely new approach. Also, the types and amounts of process reagents that are used must be closely scrutinized with regard to their amenability to recycle and minimizing the final volume of high-level waste.

Some of the processes that are available for the final isolation of americium and curium from the chemically similar lanthanide fission products appear to have the required potential. However, the feed to the process must be essentially free of the other fission products. Existing processing methods for the recovery of americium and curium from solutions of fission products will not meet the overall requirements of waste fractionation. The available processes and their limitations were previously discussed in Sect. 4.2.

6.4 Alternative Reductants for Uranium, Neptunium, and Plutonium Partitioning

Ferrous sulfamate, $\text{Fe}(\text{NH}_2\text{SO}_3)_2$, is used in the Purex process for reducing Pu(IV) to Pu(III) in the partitioning of plutonium from uranium and neptunium and in the subsequent purification cycles of these actinides. This reductant introduces iron and sulfate, both of which interfere with recycle of the aqueous wastes from subsequent purification cycles and ultimately appear in the high-level waste. Although the iron is not necessarily objectionable, the sulfate forms complex ions with plutonium which interfere with plutonium recovery in subsequent cycles of TBP extraction or ion exchange and also increase corrosion in stainless steel equipment. The difficulties caused by ferrous sulfamate are magnified as the plutonium content of reactor fuels is increased and more reductant is required. The problem of reductants is recognized in the reprocessing of LMFBR fuels, and alternative reductants are also under study in that program.^{7,30} This problem is even more acute in waste fractionation because chemicals which prevent the extractability of the residual plutonium or other actinides from the high-level waste cannot be introduced into the primary Purex plant. Such reductants would seriously retard, if not prevent, significant improvements of plutonium recovery in the Purex plant and in recycle of the concentrated aqueous wastes from the purification cycles (see Fig. 4, Sect. 4.1.1).

Chemical reductants that appear to be the most promising in the partition cycle are U(IV) or ferrous nitrate solutions that are stabilized by hydrazine.^{7,30} Electrolytic reduction may be an even more desirable

alternative. In the BFNP, plutonium will be electrolytically reduced in the mixed phase in the solvent extraction equipment.³¹ Studies of potential electrolytic processes have been initiated at ANL³² and Karlsruhe.³³ Hydroxylamine nitrate (HAN) has been substituted for ferrous sulfamate in the second plutonium cycle where plutonium is stripped under conditions of low acidity. However, HAN is ineffective in the partitioning cycle where the aqueous-phase acidities are much higher because of the slowness of reduction. Ferrous nitrate is needed in moderate concentrations to catalyze the reduction of Pu(IV) by HAN and has been reported to be sufficiently rapid to be effective in the partitioning of plutonium.³⁴

A series of tests was made in the Hanford Purex Plant to compare the performance of several chemical reductants with that of ferrous sulfamate.³⁵ Uranium(IV)-hydrazine and ferrous nitrate--hydrazine were found to be effective reductants in the partitioning cycle. Ferrous nitrate--hydrazine was also successfully substituted in the second uranium cycle and in the second neptunium cycle. HAN was demonstrated as an acceptable reductant in both the second plutonium cycle³⁶ and the second uranium cycle. Uranium(IV) nitrate has been demonstrated as an effective reductant in plants at several European installations.³⁷

Difficulties have been encountered in some of the operations with these alternative reductants. Most of the difficulties were reportedly associated with controlling the concentration profiles of reductant or hydrazine in the extraction columns that are necessary for successful operation, and with maintaining stability of U(IV) nitrate solutions. Although further developmental work is needed before a practical operating process can be realized with these alternative reductants, their general feasibility has been adequately demonstrated. Electrolytic reduction processes will also require further study. It would be of considerable advantage to generate a chemical reductant such as U(IV) or Fe(II) in situ if this could be accomplished without producing other undesirable electrode reactions.

It is necessary that the behavior of any alternative reductant be satisfactory in regard to the reduction of Np(VI) in the Purex process,

since reductants that reduce Pu(IV) also reduce Np(VI). In the partitioning of plutonium from neptunium and uranium, it is necessary that neptunium be reduced completely to Np(IV) so that it remains in the TBP phase with the uranium. In this step, the reduction rate must be sufficiently rapid to prevent Np(V) from being discharged with the partitioned plutonium. Ferrous ion and U(IV) ion appear to be satisfactory for preventing neptunium from entering the plutonium stream, but experimental work is needed to determine the choice of conditions.

6.5 Control of Neptunium Valence in Coextraction

In the coextraction of neptunium, uranium, and plutonium from nitric acid solutions of spent fuel by the Purex process, the neptunium is extracted as Np(VI). Neptunium is maintained in the hexavalent state by means of the nitrous acid-catalyzed oxidation of Np(V) by nitric acid. The chemical equilibrium between Np(V), which is inextractable in TBP, and Np(VI), the preferred extractable state, is given by the equation

The hexavalent state is favored by high acidity and low HNO_2 concentration. However, catalytic amounts of HNO_2 ($>5 \times 10^{-5} \text{ M}$) are required to obtain practical oxidation rates. The oxidation rate is increased by increasing the temperature and the nitric acid concentration. There is a limit, however, of the extent to which nitric acid concentration can be increased without seriously affecting fission product decontamination factors. In practice, satisfactory rates of oxidation of Np(V) during extraction are obtained at concentrations of 2 to 3 M HNO_3 and 10^{-4} to 10^{-3} M HNO_2 and at an extraction temperature of 45°C . The required nitrous acid is generated by adding sodium nitrite to the acidic system.

One of the major difficulties in obtaining good recoveries of neptunium involves maintaining the necessary nitrous acid concentration profile throughout the many stages of countercurrent extraction.⁹ This difficulty is caused by two factors. First, nitrous acid is highly extractable by TBP and control of the HNO_2 concentration in the aqueous

phase requires additions that offset the losses by TBP extraction. Second, nitrous acid is required in feed preparation to ensure that any Pu(VI) is reduced to Pu(IV) so that plutonium is in its most extractable state. This further complicates the neptunium valence adjustment process, since the amount of nitrous acid necessary to reduce the plutonium is highly variable. The amount of Pu(VI) formed during dissolution increases with boiling time and ferric ion content of the solution, ranging typically from 10 to 50% of the total plutonium.⁷ The amount of Pu(VI) will also be related to the plutonium content of the fuel and the radiation density of the fuel solution. It is probable that the amount of Np(VI) formed during dissolution is also variable. Suitable methods will have to be developed for adjusting the plutonium valence in the feed and still maintaining the nitrous acid concentration required for neptunium extraction. Overall, a significant amount of development work will be needed to demonstrate the capability for maintaining control of the feed composition and extraction column concentration profile necessary to routinely achieve a high recovery of neptunium at the required processing rate.

Because of the large quantity of sodium nitrite required to adjust plutonium valence in concentrated plutonium solutions and its ultimate contribution to the high-level waste, alternative reagents are currently being evaluated in the LMFBR program. Bubbling NO or NO₂ gas through dissolver solutions and electrolytic reduction are being considered as attractive possibilities. Either of these methods is probably compatible with subsequent adjustment of conditions for neptunium extraction.

6.6 Recycle of Waste Streams

The development of acceptable concepts and methods for the recycle of waste streams generated by the processes used for removing actinides from high-level waste will require a major effort. The americium and curium removal processes will present the greatest difficulties with recycle because of the nature and amounts of reagents that are required (see Sect. 4.2). The processing of the high-level waste must be carried out in a manner such that any generated waste streams which do not meet

10 CFR 20 regulations are recycled or are amenable to concentration and combination with the high-level waste. All recycle concepts will require evaluation with regard to the potential for buildup of impurities in sustained operations that are detrimental to certain process steps.

It appears that recycle methods can be developed for the various Purex process steps in the conceptual sequence of actinide removal. The nitric acid can be recovered by distillation, and the actinides from the purification waste stream can be recycled if acceptable reductants are used in the partitioning of uranium, neptunium, and plutonium (see above and Sect. 8). Methods for satisfactory recycle of the solvent can probably also be developed so that waste streams from the purification can be recycled to the Purex process.

Studies will have to be carried out to determine the extent of recycle and treatment of waste streams expected from the candidate processes for americium and curium recovery. The results obtained in these studies will be a governing factor in selecting the ultimate process for americium and curium removal. Any chemicals required in the removal processes will have to be carefully evaluated as to satisfactory methods for their removal as chemical wastes or for recycle. Process chemicals which can be recycled via purification by distillation or which can be converted to volatile, noncontaminated wastes by chemical reaction or combustion methods would appear to be the most desirable. Spent ion exchange resins, organic complexing agents, volatile mineral acids, and badly deteriorated solvents can potentially be handled in this manner.

Methods which employ large quantities of relatively nonvolatile metal nitrate salting agents cannot be ruled out at this time. It may be possible to develop methods for satisfactory recycle of these materials by crystallization of the salts, or for reducing the amounts required to acceptable levels for combination with the high-level waste.

7. LABORATORY STUDIES ON PROCESS DEVELOPMENT

Experimental studies have been initiated relative to the tentative conceptual flowsheet (see Fig. 8, Sect. 5.1) for removing actinides from high-level waste, and to major problems that must be solved to employ this flowsheet. Thus far, synthetic waste solutions have been used in these studies (see Appendix E). Scoping studies are being carried out for removal of americium and curium from high-level wastes by solvent extraction and by ion exchange. Although no experimental work has been performed to date, calculations of the approximate conditions for neptunium recovery by the Purex process have been made from published data. These calculations were performed preparatory to laboratory experiments in which conditions for coextraction of uranium, neptunium, and plutonium and their subsequent partitioning will be investigated.

7.1 Removal of Americium and Curium from High-Level Wastes

Several process methods have been used to recover americium and curium from fission product wastes; however, these methods are not directly applicable to waste fractionation. Recoveries of only 90 to 99% are achieved, and the large amounts of chemical reagents required greatly complicate the treatment and disposal of the wastes. In most of the methods, the rare-earth fission products (which constitute about one-third of the fission products by mass) are recovered along with americium and curium; therefore, an additional process step is required to remove the americium and curium from the rare earths. Moreover, the processing experience on the separation of americium and curium from lanthanides has been obtained, for the most part, with specially irradiated targets where the mole ratio of rare earths to trivalent actinides is about 20, whereas in typical LWR fuels the ratio is about 100.

Both solvent extraction and ion exchange techniques are being investigated for removal of americium and curium from high-level wastes. A sufficient number of experiments will be carried out to permit a judicious selection of the processes necessary for removal of americium, curium, and

rare earths from the waste and for their subsequent separation. Involved in this choice is the preparation of detailed flowsheets which include recycle or any special treatment required for each waste stream generated in the processing.

7.1.1 Solvent extraction process methods

Solvent extraction is being considered for use in removing trivalent actinides and rare earths from the high-level waste and for the subsequent separation of the two groups of elements. Separation of americium-curium and the rare earths from waste solutions has been studied with TBP and HDEHP as extractants. Also, the Talspeak process has been investigated for its potential applicability to this separation. Results of experimental studies made to date have revealed a number of problems that must be solved before these separations methods can be satisfactorily employed in waste processing. A tentative conceptual process based entirely on solvent extraction has been proposed, and the areas requiring further work have been defined.

Extraction of americium, curium, and rare earths from waste solutions.

Two extraction methods were tested for their potential applicability in preparing acceptable feed solutions of actinides and lanthanides from synthetic waste solutions. The literature data indicate that separations based on TBP or HDEHP as extractants might be feasible.

TBP is a moderately strong extractant of trivalent elements from high concentrations of nitric acid. Data in the literature³⁸ confirmed and extended in our experimental work indicate that americium and curium can be satisfactorily extracted into undiluted TBP from 16 M HNO_3 in ten or more equal-volume extraction stages and can then be stripped into a more dilute nitric acid solution. However, thus far we have been unable to obtain an americium--curium--rare-earth product that is free of fission product molybdenum. (Molybdenum would probably cause the formation of precipitates in the subsequent separation of americium and curium from the rare earths.) When 12 M HNO_3 was used as the stripping agent, zirconium

remained in the TBP but molybdenum was stripped along with the trivalent elements. Although all stripping conditions were not explored, it does not appear that a TBP process with nitric acid as the only salting agent has the capability for removing both zirconium and molybdenum from the trivalent actinides and rare earths.

It is possible that such a process could be used in conjunction with some other process for molybdenum removal; however, this would not be desirable if a satisfactory single-step method could be developed. Also, solvent extraction processes that employ modified TBP and high acid concentrations present many difficulties in practical operations. Phase separations are very slow because of the small density difference between phases and of the high viscosity of the undiluted TBP. In addition, the solubility of TBP in nitric acid is somewhat high for a large-scale solvent extraction process, and significant losses of TBP by hydrolysis would be expected to occur at the high acidities employed.

As predicted from the literature, zirconium and molybdenum are readily extracted into HDEHP from waste solutions. For example, they are extracted into 1 M HDEHP in diethylbenzene (DEB) from 6 M HNO_3 with only a few stages of extraction. An aqueous solution containing the trivalent actinides, rare earths, and other fission products is obtained. This solution may be suitable for the preparation of low-acidity feeds necessary for the final removal of the americium and curium, but this remains to be demonstrated. Other major difficulties to be overcome in the use of HDEHP involve the purification and recycling of this extractant, as previously discussed in Sect. 4.2.

Separation of americium and curium from the rare earths. Talspeak is the only solvent extraction process that is currently being studied in the laboratory for the separation of americium and curium from the rare-earth fission products. In this process, the separation of trivalent actinides and rare earths is accomplished by coextracting the two groups of elements into HDEHP from a carboxylic acid solution and then partitioning the trivalent actinides into an aqueous phase by stripping the HDEHP extractant with an aqueous, carboxylic acid solution containing the complexing agent

DTPA (see Fig. 6, Sect. 4.2.1). The trivalent elements are strongly extracted into HDEHP from various carboxylic acid solutions. (Formic, acetic, propionic, malonic, and lactic acids have been shown to be effective.^{15,16}) Formic acid appears to be an attractive extraction medium for the development of a satisfactory process for preparing a carboxylic acid feed solution for the Talspeak process. Formic acid has often been used for the chemical destruction of nitric acid and nitrate ion in the preparation of feed solutions for solvent extraction, and a considerable amount of research has been carried out to delineate the chemical reactions involved. Kolarik and co-workers¹⁷ at Karlsruhe have used this method to prepare carboxylic acid feed solutions for Talspeak, and their results indicate that it may be possible to adapt the process for the present application.

We have initiated laboratory studies of several of the problem areas associated with the application of the Talspeak process for final removal of americium and curium in the waste processing. One of these is the conversion of nitric acid solutions of trivalent actinides and rare earths to formic acid media by chemically reacting a nitric acid solution of the nitrate salts with formic acid. In addition, distribution coefficient data are being obtained for the extraction from formic acid. Considerable attention is also being given to problems associated with the Talspeak partitioning cycle and to the purification of HDEHP.

Although considerable research has been done on the destruction of nitric acid by formic acid, much work still needs to be carried out relative to scale-up. In this destruction method, the reaction of formic acid with nitric acid is usually carried out at or near boiling temperature and is effected batchwise. The stoichiometry of the reaction varies with the nitric acid concentration. For example, Healy³⁹ reported that one mole of formic acid decomposes two moles of 6 M HNO_3 , but only about two-thirds mole of 1 M HNO_3 . However, our experience in batch tests indicates that about two moles of formic acid are required to destroy only one mole of nitric acid at an initial concentration of 6 M. The reaction rate decreases as the concentrations of the reactants decrease. A considerable amount of

work will be required to establish the best method for effecting this chemical reaction and controlling the exothermic reaction. Detailed studies are yet to be carried out concerning the effect of mixing and boilup rate, skin temperature effects at heated vessel walls, and recycle of volatilized but unreacted formic and nitric acids and of the NO_x gases evolved by the chemical reaction.

Distribution coefficients for the extraction of americium into 0.6 M HDEHP in DEB from 0.5 to 2.0 M formic acid solutions were found to be >100 . Scrubbing of the extract phase with dilute formic acid is necessary to free the extracted americium, curium, and rare earths from all other elements.

Considerable attention is being given to problems directly associated with the Talspeak partitioning cycle. In earlier work,^{15,16} it was observed that extraction, especially for the heavier elements, was slow when the standard partitioning solution was 1 M lactic acid--0.05 M Na_5DTPA . Hence improvements in the extraction kinetics were desirable. Although increasing the lactic acid concentration to 4 M improved the extraction rates, this high concentration is undesirable. Substitution of glycolic acid for lactic acid was found to give satisfactory extraction rates and also to increase the distribution coefficients. Increasing the extraction temperature from 25°C to 50°C decreased the equilibrium extraction time by a factor of about 2. Also, this temperature reduced the distribution coefficients (organic/aqueous) by about a factor of 2, which decreases the volume of stripping solution required by about one-half. A maximum equilibrium time of 100 sec was observed for extraction from 1 M glycolic acid--0.05 M Na_5DTPA at 50°C, which should be adequate for a continuous partitioning process carried out in mixer-settlers. Although specific distribution coefficients cannot be determined for the partitioning cycle until optimum conditions are determined, experiments have shown that it is possible to obtain good separation factors by extracting from 1 M glycolic acid--0.05 M Na_5DTPA . A separation factor of about 50 was obtained between americium and neodymium, which is the least-extractable rare earth.

The optimum concentration of HDEHP in DEB is determined by the distribution coefficients of the two groups of elements and the solubilities of rare earths in the extractant. The solubility of europium in 0.6 M HDEHP-DEB is about 0.03 M at 25°C; the solubilities of lighter rare earths are even less. All the solubilities are somewhat higher at 50°C. Substituting another hydrocarbon diluent does not increase the solubility. The volume of extractant required will be determined largely by the solubilities of the trivalent actinides and rare earths in the extractant.

Impurities present in commercial-grade HDEHP decrease the separation of americium and curium from the rare earths. Most of this effect is attributable to mono(2-ethylhexyl)phosphoric acid (H_2EHP). Tests indicate that only 1% H_2EHP in HDEHP will decrease the americium-europium separation factor from about 100 to about 40. A further decrease is caused by the presence of small amounts of polyphosphates and pyrophosphates. Our studies have shown that pretreatment of HDEHP with glycolate-DTPA solutions removes the H_2EHP and possibly other impurities, and a method for purification of HDEHP based on this observation is now under development. Commercial-grade HDEHP seldom has a guaranteed purity of greater than 90%, although it is usually much higher. It may be possible to improve the complex and expensive methods of purification that have been employed previously.

Tentative conceptual process for americium-curium removal based on solvent extraction. A tentative conceptual process sequence based on our very preliminary laboratory investigations has been proposed for the removal of americium and curium. The brief outline of the sequence presented here serves to point out the multitude of problems remaining to be solved. For example, the process uses only one extractant, HDEHP, and assumes prior removal of uranium, neptunium, and plutonium. In addition, the proposed sequence involves steps in which solids are removed, and thus far no work has been carried out to determine the losses of americium and curium to these solids or the methods by which these solids would be handled. The steps in the tentative process are as follows:

- (1) Evaporate the 2 M HNO_3 solution of waste to an HNO_3 concentration of 6 M.
- (2) Cool the concentrated waste solution, and separate the solids. The final, complete processing will have to include treatment or recycle of these solids. The first objective in our experimental work was to test solvent extraction concepts on nitric acid solutions of americium, curium, and rare earths which also contained the soluble fission products and saturation amounts of the insoluble fission products.
- (3) Remove zirconium and molybdenum by multistage, counter-current extraction into 0.6 M HDEHP. This extraction must include scrubbing stages with 6 M HNO_3 to prevent unacceptable losses of americium and curium. Any residual Pu(IV), Pu(VI), Np(IV), and U(VI) in the solution would be quantitatively extracted here. This extraction could perhaps serve as a satisfactory alternative to the exhaustive extraction (see Fig. 8, Sect. 5.1) if suitable stripping and partitioning methods could be developed.
- (4) Treat the aqueous solution with excess formic acid to destroy all of the nitrate and to produce a feed solution that is 1 M in formic acid. In the laboratory, this chemical reaction is carried out at about 100°C in a batch process in which the nitrate waste solution is added gradually to a HCOOH solution. About two moles of HCOOH are used per mole of HNO_3 .
- (5) Cool and separate the relatively small volume of solids, which appear to be chiefly silver, rhodium, and palladium.
- (6) Extract the americium, curium, and rare earths into 0.6 M HDEHP (Talspeak extraction) from the formic acid solution. In this step, the trivalent actinides and rare earths are separated from essentially all of the other remaining fission products. Several countercurrent stages of

extraction, followed by several stages of scrubbing the extract phase with 1 M HCOOH , are required to achieve the necessary (>99.9%) recovery.

- (7) Separate the americium and curium from the rare earths by stripping the extractant phase with an aqueous 1 M glycolic acid—0.05 M Na_5DTPA solution (Talspeak partitioning).
- (8) Recover the americium and curium from the aqueous solution. Potential methods appear to be direct oxalate precipitation, or concentration by cation exchange or HDEHP extraction and subsequent precipitation as oxalates. No laboratory studies of this step have been carried out.
- (9) Purify the solvent for recycle. No method has been devised for removing zirconium and molybdenum (step 3). Present methods are unacceptable. Studies will have to be made to determine whether there are any technically feasible methods that are practical.
- (10) Treatment of aqueous waste streams. It may be possible to chemically treat the high-level waste stream so that the organic acids and complexes are destroyed. However, a number of difficulties (e.g., foaming) may be associated with this step, and laboratory work will be required to identify specific problems and their magnitude.

It must be emphasized that this outline is only tentative. For example, it is possible that an ion exchange process (see Sect. 7.1.2) would be more effective for preparing a feed solution of actinides and rare earths for the Talspeak process. Also, much more work remains before a flowsheet with quantitative specifications can be developed. Additional difficulties may be encountered in the future. In one instance, a synthetic waste solution could not be extracted with HDEHP without producing unbreakable emulsions, apparently due to a particular batch of zirconyl nitrate (of dubious quality) that was used in preparing the waste solution. Of course,

it is impossible to predict whether an actual waste solution will behave in the same way. Further, the effects of corrosion products and other chemicals that might be present in waste have not yet been investigated. Phosphate present as the result of degradation of the TBP in the previous processing and any fluoride present as the result of its use in fuel dissolution will also tend to cause precipitates in the processing. Therefore, methods must be devised for their removal as a part of the developmental studies.

7.1.2 Ion exchange process methods

Experimental studies are being carried out with synthetic waste solutions to evaluate a cation exchange process for selectively removing the trivalent elements (rare earths and actinides). In this process, the actinides and rare earths, along with certain other fission products in the waste solution, are sorbed on cation exchange resin. Selected reagents are then used to elute the trivalent actinides and rare earths, leaving the other fission products sorbed on the column. The eluate thus obtained would provide a satisfactory starting solution for the Talspeak process or for the CEC processes in which the trivalent actinides are separated from the rare earths.

Zirconium and the noble metals, which would interfere in the subsequent separation of americium and curium, appear to be adequately removed by cation exchange. Although this treatment may not effectively separate some other elements present in smaller amounts (alkaline earths, perhaps), a subsequent chromatographic step for separating the actinides from the lanthanides would readily yield the desired results.

Radioisotopes have been used to follow the behavior of the rare earths; also, some of the noble metals have been observed to form colored bands and solutions. However, we have not been able to determine with any precision the behavior of any of the other components since only a few analytical results are presently available for these components. In some cases, zirconium has been estimated by phosphate precipitation from concentrated nitric acid solution.

The capacity of Dowex 50-X8 resin at the point where rare earths first break through the column (about 0.01% of the feed concentration) is in the range of 7 to 10.5 resin bed volumes of synthetic waste (i.e., a solution, 2 M in HNO_3 , simulating that generated by reprocessing irradiated fuel). The higher capacities were obtained when the solution was diluted with three volumes of water. A lower apparent capacity is obtained in subsequent runs if the column is not thoroughly eluted.

At breakthrough, the quantity of rare earths loaded on the column is in the range of 0.5 to 0.8 meq/ml, increasing with the use of more dilute feed. The resin capacity is 1.8 meq/ml, and the remainder of the resin is loaded with materials which have a stronger affinity for the resin than do the rare earths. Noble metals can contribute no more than about 15 to 20% of the resin loading, whereas sufficient zirconium is present to occupy over half the total capacity.

When the synthetic waste is passed through an ion exchange column containing Dowex 50 resin, the trivalent elements, zirconium, and some of the noble metals are loaded very strongly. Although other metals such as barium and strontium may load as strongly, zirconium and the noble metals appear to present the most severe problem. Most of the palladium and rhodium are in the effluent, whereas the largest fraction of the ruthenium is held by the resin. The ruthenium may be present as more than one complex species since three colored bands (presumably all of which are ruthenium) were observed to load on the resin. Results of recent tests indicate that the noble metals may be prevented from loading if appropriate complexing agents (e.g., nitrite ion or hydroxylamine) are present in the feed. These materials, which are commonly used for valence adjustment in solvent extraction processing, may affect the valence of the noble metals. No evidence of reduction to the metallic state was observed with these materials in acidic solutions; however, hydrazine appeared to yield some metal, especially at higher pH. Hydroxylamine and nitrite form complexes with the noble metals, as indicated by a rather slow change in the color of the solutions. There was no evidence of loading on the resin (i.e., no colored bands) from feed which had

been complexed in this manner; thus, it appears that the interference from noble metals can be readily eliminated.

The addition of iron (which may be present from equipment corrosion or partial dissolution of fuel hardware) caused a significant decrease in resin capacity for the trivalent elements. With 0.1 M iron and a two- to threefold dilution of the feed, breakthrough of trivalent ions occurred after elution of about 5 to 6 resin bed volumes, compared with about 8 when iron was absent. The effect may have been somewhat greater with ferric iron than with ferrous, but the difference was not major. The product that was eluted with 3 M HNO_3 contained some iron in addition to the rare earths; however, iron could probably be eluted selectively with dilute oxalate solution prior to elution of the product, if this should become necessary.

Several colored bands were apparent in these tests. No rare-earth tracer (less than 0.01%) was detected in the effluent when the most rapidly moving band, which was yellow-colored (iron), moved off the resin bed. This band is not observed when iron is absent. The rare earths broke through when a long, light-gray band (which is always observed) reached the bottom of the column. The upper part of this band consists primarily of zirconium plus some rare earths, while the lower part is appreciably higher in rare-earth concentration. Apparently, the iron, which is at a much higher concentration than any other metal, competes with zirconium and trivalent ions such that it occupies approximately 30% of the resin and causes the front of this mixed band to reach the bottom of the column in less volume than when iron is absent.

Separation of the trivalent elements from zirconium has been accomplished in two ways. Elution of the loaded resin with dilute oxalic acid removes zirconium very rapidly without significantly affecting the rare earths. After most of the zirconium has been removed, the oxalic acid also strips noble metals, yielding a solution with an extremely intense color. Subsequently, the trivalent elements can be eluted with nitric acid or a complexing agent to yield a feed for the next separation step.

Indications of precipitation within the resin bed have been observed in some cases with oxalic acid, even though the concentrations were such that no metal oxalates were expected to precipitate. While this does not appear to preclude use of the method, a procedure which does not produce precipitates would be preferred. Results of tests with dilute nitric acid--oxalic acid solutions (0.25 to 0.1 M) were encouraging. Several other complexing agents, including malonic and maleic acids, were also investigated; however, they did not show the selectivity of oxalic acid. Materials such as ethylenediaminetetraacetic acid, which would be expected to give a separation of zirconium from rare earths, might be suitable, depending on the subsequent processing steps.

Even if zirconium is not eluted with some complexing agent prior to recovery of the trivalent elements, elution with nitric acid will yield a product containing essentially all the rare earths and only a very small fraction of the zirconium. A nitric acid concentration of 3 to 4 M probably represents the best compromise between zirconium separation and a reasonably small product volume. The only analytical results obtained to date for a separation made by this method show that the rare-earth product contained less than 10% (with a substantial margin of error) of the zirconium and much less of any other element in the waste. Such a product should provide a suitable feed for a subsequent actinide-lanthanide separation. With rare-earth tracers, the total loss to all fractions, except the product, was easily held to less than 0.1%.

All the results obtained to date indicate that a satisfactory ion exchange process for preparing feed solutions of the trivalent actinide and rare earths can be developed. Additional work remains to be done in regard to identifying ionic impurities in the actinide--rare-earth product, demonstrating that the product is satisfactory feed for the final removal process for americium and curium, selecting the best eluents, scaling-up the process, and recycling the process streams.

7.2 Neptunium Recovery

Calculations were carried out to estimate the number of stages and the conditions necessary for recovering neptunium in a Purex plant for the reprocessing of commercial LWR fuels. These calculations were made to aid in planning laboratory experiments in which methods for maintaining the necessary concentrations of nitric and nitrous acids in the coextraction of uranium, neptunium, and plutonium and of reductants in the partitioning cycles will be studied. Calculations for equilibrium conditions were made from distribution coefficient data and material balance data. The uranium, neptunium, and plutonium concentrations in the aqueous feed were assumed to be the same as those calculated for typical LWR fuels having a burnup of 33,000 Mwd/metric ton.

7.2.1 Purex process and nomenclature used

The solvent extraction process that was studied is a modification of the NFS Purex flowsheet. In this process, the uranium, neptunium, and plutonium are first separated from the bulk of the fission products, and the plutonium is then partitioned from the uranium and neptunium in an initial cycle comprised of columns designated HA, HB, and HC (see Table 2). The uranium and neptunium are further purified (from both plutonium and fission products) and are separated from each other in subsequent cycles in columns 1A, 1B, etc. The plutonium is processed further in columns designated as 2A and 2B. The process streams are identified by both the column and the type of stream. For example, designations such as 1AF, 1AS, 1AX, 1AF, and 1AW refer to the following respective streams associated with the 1A column: feed, scrub, extractant, product, and waste.

7.2.2 Coextraction of neptunium, uranium, and plutonium (HA column)

Several calculations were made to determine the approximate behavior of neptunium and other important constituents in the HA column as a function of key variables and to assess potential methods and conditions for recovering neptunium as Np(VI) . The purpose of the calculations was

Table 2. Nomenclature in Purex solvent extraction at NFS

Cycle	Column designation	Column function
High-activity, head-end, or co-decontamination	HA	Coextraction of U, Pu, and Np; fission products, Am, and Cm in aqueous waste stream (HAW).
	HE	Partition of Pu from U and Np; Pu stripped into an aqueous product stream.
	HC	Stripping of U and Np into aqueous phase.
First uranium purification	1A	Coextraction of U and Np; Pu and fission products in aqueous waste.
	1B	Partition of U and Np; Np stripped into aqueous phase.
	1C	U stripping.
Second uranium purification	1D	Uranium extraction.
	1E	Uranium stripping.
Plutonium purification	2A	Plutonium extraction; fission products in aqueous waste.
	2B	Plutonium stripping.

to provide an approximate guide to the design of laboratory experiments on methods for controlling the important process variables.

The difficulties associated with oxidizing Np(V) to Np(VI) by means of the nitrous acid-catalyzed reaction between Np(V) and nitric acid and then coextracting the Np(VI) along with the plutonium and uranium in a Purex process were discussed in Sect. 6.5. The chief difficulty to be overcome is maintaining the neptunium as Np(VI) in the aqueous phase during extraction so that the desired neptunium extraction is attained in a practical number of extraction stages at the relative high extractant loadings of uranium and plutonium. This difficulty is caused by the relatively slow oxidation rate of Np(IV) in the 2 to 3 M HNO_3 concentration range that is dictated by the overall extraction requirements of the process. Further complications arise because the nitrous acid is highly extractable by TBP and its aqueous-phase concentration should not be allowed to fall below about 10^{-5} M during the extraction of neptunium. Also, the high loading of uranium in the TBP that is necessary for high-throughput plants lowers the neptunium distribution coefficients.

Calculations were made to estimate the following parameters involved in the coextraction of neptunium, uranium, and plutonium:

- (1) The minimum number of theoretical equilibrium extraction stages necessary for coextraction of 95 to 99% of the neptunium, along with 99% of the uranium and plutonium, from 2 to 3 M HNO_3 solutions of LWR fuel, assuming that all the neptunium is initially present as Np(VI).
- (2) The magnitude of the depletion of the nitrous acid catalyst in the aqueous phase due to its extraction into TBP during countercurrent extraction of 95 to 99% of the neptunium.
- (3) The nitric acid and nitrous acid concentrations in the fuel solution that will permit sufficient oxidation during the residence time of the aqueous phase in a coextraction column operating at practical flow rates.

At an initial aqueous-phase feed plate concentration of 2.4 to 3.5 M HNO_3 , 96 to 99% of the Np(VI) is calculated to be extracted in three theoretical equilibrium stages at solvent loadings of uranium and plutonium attained by 99% extraction of these actinides (see Table 3). The nitrous acid concentration of the aqueous phase is rapidly depleted; the relative amount of depletion is about 99% after three stages. However, even if the initial 2.4 M HNO_3 --0.005 M HNO_2 concentration in the aqueous phase is maintained throughout all three stages, the time required for oxidation of the Np(V) to Np(VI) is too great to be accomplished in extraction equipment that operates at practical conditions and throughput rates. It would be more practical to effect oxidation of the Np(V) in a feed preparation step prior to solvent extraction. At a feed plate concentration of 3.5 M HNO_3 --0.005 M HNO_2 , it may be possible to accomplish the necessary oxidation and to extract 98 to 99% of the neptunium in pulsed columns of dimensions used at NPS (see Table 3). A residence time of about 22 min for the aqueous phase in the extraction section of a 10-in.-diam by 17-ft-long column was estimated at the flow conditions given in Table 4 for operation in the organic continuous mode.

An extensive amount of development work will be needed to determine the permissible range of nitric acid and nitrous acid concentrations and the method for carrying out the oxidation of neptunium. The process that is selected must accomplish the necessary recovery factors for uranium, neptunium, and plutonium and also achieve the necessary decontamination factors from fission products such as zirconium and ruthenium. Higher nitric acid concentrations improve the neptunium extraction but decrease the fission product decontamination; therefore, the effect of nitric acid concentration on overall processing requirements will require careful evaluation.

7.2.3 Partitioning step (column HB)

In this column, uranium and neptunium are separated from plutonium by maintaining reducing conditions. Tetravalent plutonium is reduced to unextractable Pu(III) , which transfers into the aqueous phase, while Np(VI)

Table 3. Recovery of neptunium: calculated equilibrium behavior of some components in a Purex extraction at 45°C

Organic phase: 30% TBP in n-dodecane
 Organic/aqueous volume ratio: 2
 Initial HNO_3 concentration: $5 \times 10^{-3} \text{ M}$

Aqueous HNO_3 feed plate concentration (<u>M</u>)	Extraction stage	Component ^a (% extracted)				Equilibrium aqueous-phase composition		$t_{1/2}$ (min) ^b
		Np	U	Pu	Zr	HNO_3 (<u>M</u>)	HNO_2 (<u>M</u> $\times 10^4$)	
2.4	1	37	88	28	9	2.0	2.0	16
	2	75	99+	99+	-	1.9	0.5	20
	3	96	99+	99+	-	1.8	0.03	21
3.5	1	68	88	88	12.0	3.0	9.0	4.1
	2	96	99+	99+	-	2.8	1.0	5.0
	3	99+	99+	99+	-	2.8	0.09	>5.0

^aInitial concentrations of neptunium, uranium, and plutonium were 0.135, 171.5, and 1.63 g/liter, respectively.

^bTime required to oxidize 50% of the Np(V) to Np(VI) at the equilibrium aqueous-phase concentrations of HNO_3 and HNO_2 indicated. At the initial concentration, the $t_{1/2}$ values for 2.4 and 3.5 M HNO_3 are 9.0 and 2.5 min, respectively.

Table 4. Calculated compositions of streams exiting the coextraction and scrubbing columns
Compositions based on three extraction and two scrubbing stages and organic-phase continuous operation

Stream	Volume (liters/hr)	HNO ₃ (M)	HNO ₂ (M)	Metal content				
				U	Pu	Np ^a		Zr
						Case A	Case B	
Organic product (HAP)	464	0.22	0.0024	83.3 g/liter	0.79 g/liter	0.045 g/liter	0.045 g/liter	1.2% ^b
Aqueous raffinate (HAW)	242	3.06	0.00011	0.02%	0.08%	1.27%	0.14%	-

^aIn Case A, 100% of the neptunium was assumed to enter the HA column as Np(V); in Case B, it was assumed to be 100% Np(VI).

^bDenotes percentage of total in that phase.

is reduced to Np(IV), which is also extractable and thus remains in the organic phase along with the U(VI). Calculations are being carried out to determine the approximate concentration of U(IV)nitrate-hydrazine that will be required for experiments in which alternative reductants for the partitioning of plutonium from uranium and plutonium will be studied.

Thus far, one calculation has been made for an amount of U(IV) reductant that was satisfactory for partitioning greater than 99% of the plutonium from greater than 99% of the uranium (Table 5). Partitioning conditions were chosen so that the nitric acid concentration in the aqueous phase was maintained between 1.5 and 1.75 M in all extraction stages. Aqueous-phase concentrations of nitric acid which exceed 2 M in any extraction stage were considered undesirable because of possible reoxidation of the Pu(III) to Pu(IV), which would lower the separation factor for uranium and plutonium.

The reduction conditions employed were not sufficient to keep all of the neptunium in the organic-phase product (HCU) with the uranium; about 86% was present in the uranium product (HCU), and about 14% in the plutonium product (HBP). Although the calculations of the neptunium separation are only approximate, they tend to give further support to the feasibility of U(IV) as a reductant for partitioning plutonium from uranium and neptunium. The U(IV) concentration was estimated on the basis of the requirements for reduction of Pu(IV) to Pu(III), but the neptunium behavior in plutonium partitioning was based on neptunium distribution coefficients that were obtained with an initial reductant concentration of 0.01 M U(IV)--0.1 M N_2H_4 . These coefficients are probably low since a higher U(IV) concentration was employed in the evaluation of the composition and contents of the product streams. However, a literature search showed that these were the only coefficient values that were applicable to our calculations, and our purpose in the neptunium calculations was to evaluate the magnitude of the neptunium recovery problem. It is believed that the calculated value for the quantity of neptunium in the uranium product is conservative. This subject, along with the process control difficulties that are expected with the use of U(IV) as a reductant in partitioning, is discussed further in Sect. 7.2.5.

Table 5. Calculated stream compositions for partition column HB

Section HBX: 6 theoretical stages
 Section HBS: 4 theoretical stages
 Temperature: ~45°C

	Stream						
	Feed (HAP)	Pu strip (HBX)	Scrub (HBS)	Diluent (HBS)	Reductant	U-Np product (HCU)	Plutonium product (HBP)
Stage ^a	6	1	10	6	7	1	10
Phase	30% TBP--NPH	Aqueous	30% TBP--NPH	30% TBP--NPH	Aqueous	30% TBP--NPH	Aqueous
Flow, liters/hr	464	74	135	141	16	740	90
HNO ₃ , <u>M</u>	0.2	1.72	0.3	-	1.0	0.195	1.56
Np, ^b %	100	-	-	-	-	86	14
Pu, ^b %	100	-	-	-	-	<0.1	99+
U(VI), %	100	-	-	-	-	>99	<0.001
U(IV), ^c <u>M</u>	-	-	-	-	0.5 ^d	0.01	0.01
N ₂ H ₄ , ^c <u>M</u>	-	0.2	-	-	0.2	-	0.2
NO ₂ ⁻ , <u>M</u>	0.0022	-	-	-	-	-	-

^aStage number where stream enters or leaves the column.

^bPercentages are based on the amounts of neptunium and plutonium in the feed stream (HAP).

^cChemical reactions in the column are not taken into account.

^dU(IV) concentration is based on requirements for the reduction of Pu(IV) to Pu(III).

7.2.4 First uranium purification cycle

Uranium and neptunium are stripped from the organic effluent of the HB column with 0.05 M HNO_3 in the HC column to yield a solution which is 0.11 M in U(VI), 0.15 M in HNO_3 , and contains 86% of the neptunium in the HB column feed plus traces of plutonium. The solution is concentrated by evaporation, and its composition is adjusted to 1.40 M U(VI)--2.0 M HNO_3 in order to prepare the aqueous feed (1AF) for the first uranium purification cycle.

Column 1A. In this column, the uranium and neptunium are again partitioned from the last traces of plutonium by maintaining reducing conditions in the column with U(IV)- N_2H_4 . The calculated stream compositions, given in Table 6, show that the aqueous raffinate should contain essentially all of the remaining plutonium (99+% of the trace amount in the feed stream to this column), less than 0.01% uranium, and about 38% of the neptunium in the feed to this column. The poor neptunium recovery is discussed in Sect. 7.2.5.

Columns 1B and 1C. In column 1B, uranium and neptunium are separated by maintaining a high U(VI) concentration (0.21 M) in the organic phase and a low acidity (0.5 M HNO_3) in the aqueous phase, so that Np(IV) is forced into the aqueous phase. The calculations show that 99+% of the neptunium in the 1AF feed will report to the neptunium product stream, as will about 0.2% of the uranium, which is readily separable in any subsequent neptunium purification cycle. In column 1C, the uranium is stripped from the organic phase with 0.05 M HNO_3 to yield a product solution that is 0.125 M in U(VI). The results of calculations for these two columns are contained in Table 7.

7.2.5 U(IV)- N_2H_4 as a reductant for neptunium

The substitution of U(IV)- N_2H_4 for $\text{Fe}(\text{NH}_2\text{SO}_3)_2$ is complicated, not only because the kinetics of neptunium reduction is slower but also because an appreciable quantity of U(IV) may be extracted under certain conditions. The neptunium distribution coefficients, D_a^0 [Np(IV)], used in the calculations

Table 6. Calculated stream compositions for column 1A

Scrub section: 4 theoretical stages
 Extraction section: 4 theoretical stages
 Temperature: ~45°C

	Stream				
	Feed (1AF)	Scrub (1AS)	Extractant (1AX)	Overhead (1AP)	Raffinate (1AW)
Stage ^a	5	1	8	1	8
Phase	Aqueous	Aqueous	30% TBP--NPH	30% TBP--NPH	Aqueous
Flow, liters/hr	98	67	335	335	165
HNO ₃ , <u>M</u>	2.0	2.0	-	0.005	2.0
Np, ^b %	100	-	-	62.5	37.5
Pu, ^b %	100	-	-	<0.1	>99
U(VI), ^b %	100	-	-	>99	<0.01
U(IV), ^c <u>M</u>	0.01	-	-	0.0021	0.0015
N ₂ H ₄ , ^c <u>M</u>	0.1	0.1	-	-	0.1

^a Stage number where stream enters or leaves column.

^b Percentages are based on the amounts of neptunium, plutonium, and uranium in the feed stream (1AF).

^c Chemical reactions in column are not taken into account.

Table 7. Calculated stream compositions for columns 1B and 1C

Extraction section: 4 theoretical stages
 Scrub section: 4 theoretical stages
 Strip column (1C): 4 theoretical stages
 Temperature: Ambient

	Stream						
	Feed (1AP)	Scrub (1BS)	Extractant (1BX)	Overhead (1BU)	Np product (1BP)	Spent organic (1CW)	U product (1CU)
Stage ^a	5	1	8	1	8	4	1
Phase	30% TBP--NPH	Aqueous	30% TBP--NPH	30% TBP--NPH	Aqueous	30% TBP--NPH	Aqueous
Flow, liters/hr	335	85	104	439	85	439	1097
U(VI), <u>M</u>	0.41	-	-	0.31	0.0038	-	0.125
HNO ₃ , <u>M</u>	0.005	0.5	-	<0.01	0.52	-	0.05
Np, ^b %	100	-	-	<0.1	99+	-	<0.1

^aStage number where stream enters or leaves column.

^bPercentages are based upon the amount of neptunium in the feed stream (1AP) to column 1B.

for columns HB and 1A were derived from results on work in which 30% TBP—NPH* loaded with varying U(VI) concentrations and containing 5×10^{-4} M Np(VI) was equilibrated for 15 min with aqueous acid solutions containing 0.01 M U(IV)—0.1 M N_2H_4 as the reductant.⁴⁰ For constant acid concentrations, the neptunium distribution coefficient was a maximum when the organic phase was about 30% saturated with uranium [~ 0.16 M in U(VI)]. The neptunium distribution coefficient increased with acidity for constant organic U(VI) loading; it also increased with increasing temperature. Similar D_a^0 data, which were obtained with $Fe(NH_2SO_3)_2$ as the reductant, showed a steady increase in neptunium distribution coefficients with decreasing U(VI) loading in the organic phase. A contributing cause for this difference (in addition to slower kinetics) may be the extractability of U(IV). As loadings decrease in the organic phase, the neptunium distribution coefficient may be expected to increase; however, in this case, the extraction of U(IV) would also increase and, since the reduction of U(V) to Np(IV) occurs in the aqueous phase, the lower aqueous U(IV) concentration might affect the reduction rate and thus result in lower D_a^0 [Np(VI)]. Although the experimental conditions appear to be a good approximation to column operation, the results calculated with these D_a^0 [Np(IV)] are probably pessimistic due to the low initial U(IV) concentration.

In the separations carried out in columns HB and 1A, the highest concentration of U(IV) in the aqueous phase occurs in the upper extraction stages, whereas the lowest U(IV) concentrations in the aqueous phase occur in the lower extraction stages. These concentration differences are the result of U(IV) extractability in the organic phase. Even though the extractability of U(IV) is reduced by maintaining the highest U(VI) concentrations of the organic phase in the upper extraction stages, it is still sufficiently high to deplete the U(IV) concentration in the lower extraction stages. Thus, Np(VI) entering the column in the organic phase is reduced rapidly to the poorly extractable Np(V), which migrates down the column where the probability of further reduction is diminished by the low aqueous U(IV) concentration. It is evident that care must be exercised to ensure that an adequate U(IV) concentration is present where it is

* NPH = normal paraffin hydrocarbon.

required in the column. The loss calculated for the 1A column is associated with the questionable values of $D^0_{36^a} [Np(IV)]$ used in the calculations. Results of a test at the Hanford plant^{36a} in which $U(IV)-N_2H_4$ was substituted for $Fe(NH_2SO_3)_2$ in the partition column showed that effective reduction of plutonium was achieved without increasing the neptunium concentration in the plutonium product. This suggests that $U(IV)-N_2H_4$, when properly used, would also be an effective reductant for neptunium.

8. CONCEPTUAL FLOWSHEET STUDIES ON RECYCLE IN THE PUREX PROCESS

Conceptual material-balance flowsheets for the recycle of nitric acid and actinide-bearing streams in a Purex process were evaluated in considerable detail with regard to main-line fuel reprocessing and exhaustive extraction. The purpose of the flowsheet studies is to aid in the visualization of plant modifications which will enable effective integration of a primary reprocessing plant with a waste processing plant (Fig. 10). The flowsheets are based largely on operating experience at NFS. Material balance flowsheets for the recycle of nitric acid and actinides are shown in Figs. 11 and 12. The material balances are based on fuel irradiated to a burnup of 33,000 MWd/metric ton. Details of the material balances throughout the many processing steps are shown in Figs. 13 and 14. The nomenclature used in designating equipment in these flowsheets is the same as that described in Sect. 7.2.1.

In order to prevent losses of uranium, neptunium, and plutonium to waste streams from the partitioning and purification processes, these streams must be recycled to the first extraction column in which all three actinides are coextracted (Figs. 11 and 12). This can be accomplished by an evaporation-distillation process in which the streams are concentrated by evaporation and further distillation (Fig. 15). The overheads from evaporation are combined with other nitrate recovery streams (including NO_x absorption) and processed through a HNO_3 recovery tower. The recovered nitric acid is then recycled to previous stages in the processing, and the actinide concentrate is recycled to the coextraction column (HA) via the dissolver.

Fig. 10. Conceptual flowsheet for solvent extraction processing of irradiated LWR fuel with waste partitioning and recycle of heavy-metal and nitric acid values.

Fig. 11. Conceptual flowsheet for solvent extraction

irradiated PWR-U fuel including waste partitioning, show recycle schemes and typical material balances for heavy acid values.

10
we

BLANK PAGE

BLANK PAGE

ORNL Dwg 74-7340

2

flowsheet for solvent extraction processing of
 including waste partitioning, showing proposed
 material balances for heavy metals and nitric

Fig. 13. Detailed nitric acid balance and uranium purification.

acid balance in neptunium partitioning

BLANK PAGE

150
30%

20
POLIM

BLANK PAGE

ice in codecontamination, plutonium

2

Fig. 15. Details of dissolvent and nitric acid recovery systems.

The necessity of recycle restricts the choice of reductants used in plutonium partitioning and possibly of other process chemicals as well. In our reference flowsheet, we have chosen $U(IV)-N_2H_4$ rather than ferrous sulfate as the reductant for plutonium. Although material balances for this reagent have not been completed, it now appears that effective recycle can be accomplished if a reductant such as $U(IV)-N_2H_4$ is suitable and if adequate fission product decontamination can be maintained when all of the nitric acid is recycled. Experimental studies will need to be carried out to determine the suitability of various alternative reduction methods for plutonium and the effect of complete nitric acid recycle on fission product decontamination. Also, it is important to know what impurities are generated by radiation damage to the solvent, since they may ultimately appear in the aqueous waste streams in significant concentrations and cause complications during prolonged recycle of the waste streams.

9. SUMMARY

The percentage removals of actinides and ^{129}I from spent fuels that will reduce the potential hazard values of commercial high-level waste at 1000 years to values comparable to uranium minerals have been determined, and the feasibility of various processes for accomplishing these removals is being studied. Removal of 99.99% of the plutonium, 99.9% of the uranium, americium, curium, and ^{129}I , and 95% of the neptunium from LWR fuel (with plutonium recycle) decreases the hazard value of high-level waste at 1000 years to about 5% of the value for pitchblende. Removal of actinides and ^{129}I from LWR fuels to this extent appears to be a desirable goal to attain before consideration of further treatment. Such a goal is necessary because the actinides are the major contributors to the potential hazard of high-level waste and removing them will require removal factors 10 to 100 times greater than those reported for actinides in processing facilities at radiation levels comparable to that from high-level waste. At the aforementioned removal percentages, ^{99}Tc and the residual plutonium and americium contribute about equally to the hazard of high-level waste from LWR fuels in which the plutonium is recycled. Further removal of the actinides does not appear to be warranted unless ^{99}Tc is also removed. Of course, other

combinations of calculated percentages of removal will also reduce the potential waste hazard to about 5% of that for pitchblende, and further refinements in the percentages may be necessary as the program progresses.

Results of studies made thus far indicate that the most promising concept for achieving the desired removals of actinides from LWR fuels includes both improved recovery of the actinides in conventional fuel reprocessing and secondary processing of the high-level waste. Conceptual flowsheet studies of separations processes that are potentially applicable to this removal concept have revealed a number of difficult problems that will have to be solved before satisfactory processes can be developed and, in turn, integrated into a functional waste processing facility at the expected levels of radioactivity. The most important of these appear to be:

- (1) Increasing the recovery of plutonium to the desired levels.
- (2) Development of a satisfactory americium and curium process.
- (3) Devising methods for avoiding actinide losses to insoluble residues from fuel dissolution and to solids that are generated in the subsequent processes.
- (4) Adequate recycling of streams generated in the processing.

It appears that the necessary removal of uranium and neptunium can probably be accomplished by modifications and additions to the currently used Purex process. Satisfactory recycle of process chemicals can probably be developed for conceptual processes in which improved recoveries of uranium, neptunium, and plutonium are achieved in a Purex process. A substantial research and development effort is needed to determine whether the recycle problems associated mainly with the secondary processing for americium and curium can be solved.

Laboratory studies of separations methods that appear most promising are under way, and results from these studies are reported. Several candidate processes of potential applicability have been reviewed, and conceptual flowsheet analyses of some of these processes are presented. A tentative processing sequence for the removal of the actinides is discussed.

10. APPENDIXES

**10.1 Appendix A: Hazard Index Values for the Major Components
of Unprocessed Spent Fuels from the
Principal Reactor Types**

BLANK PAGE

Table A-1. Contribution of each component^a to the hazard of unprocessed spent fuel from a PWR

Parent Component	Hazard ^b of each component (m ³ H ₂ O/metric ton of fuel) after decay times (years) of:					
	10 ³	10 ⁴	5 x 10 ⁴	10 ⁵	5 x 10 ⁵	10 ⁶
U	1.18 x 10 ⁵	2.27 x 10 ⁶	1.16 x 10 ⁷	1.84 x 10 ⁷	2.10 x 10 ⁷	1.61 x 10 ⁷
Np	1.17 x 10 ⁵	1.41 x 10 ⁵	3.63 x 10 ⁵	6.17 x 10 ⁵	1.38 x 10 ⁶	1.33 x 10 ⁶
Pu	3.31 x 10 ⁸	8.64 x 10 ⁷	3.23 x 10 ⁷	2.83 x 10 ⁷	1.89 x 10 ⁷	6.94 x 10 ⁶
Am	1.23 x 10 ⁷	2.51 x 10 ⁶	5.36 x 10 ⁵	2.58 x 10 ⁵	1.99 x 10 ⁵	1.41 x 10 ⁵
Cm	1.34 x 10 ⁶	6.36 x 10 ⁵	4.90 x 10 ⁵	7.23 x 10 ⁵	5.09 x 10 ⁵	1.36 x 10 ⁵
Other ^c	4.06 x 10 ²	9.16 x 10 ²	6.40 x 10 ²	4.08 x 10 ²	1.38 x 10 ¹	5.21 x 10 ⁻¹
FP	8.35 x 10 ⁴	8.03 x 10 ⁴	7.00 x 10 ⁴	6.20 x 10 ⁴	2.30 x 10 ⁴	1.04 x 10 ⁴
Total	3.45 x 10 ⁸	9.20 x 10 ⁷	4.54 x 10 ⁷	4.84 x 10 ⁷	4.20 x 10 ⁷	2.47 x 10 ⁷

^aIncludes all decay products. Assumes 99.9% removal of 129I.

^bWater required to dilute mixture to MCC value for each nuclide.

^cIncludes all other actinides and their decay products, as well as all other decay products formed prior to 150 days.

Table A-2. Contribution of each component^a to the hazard of unprocessed, blended spent fuel^b from a PWR utilizing equilibrium plutonium recycle

Parent Component	Hazard ^c of each component (m ³ H ₂ O/metric ton of fuel) after decay times (years) of:					
	10 ³	10 ⁴	5 x 10 ⁴	10 ⁵	5 x 10 ⁵	10 ⁶
U	9.91 x 10 ⁴	1.84 x 10 ⁶	9.47 x 10 ⁶	1.53 x 10 ⁷	1.87 x 10 ⁷	1.54 x 10 ⁷
Np	8.78 x 10 ⁴	1.06 x 10 ⁵	2.72 x 10 ⁵	4.62 x 10 ⁵	1.03 x 10 ⁶	9.97 x 10 ⁵
Pu	7.44 x 10 ⁸	1.49 x 10 ⁸	7.02 x 10 ⁷	7.65 x 10 ⁷	5.43 x 10 ⁷	1.94 x 10 ⁷
Am	7.68 x 10 ⁷	2.53 x 10 ⁷	5.12 x 10 ⁶	2.15 x 10 ⁶	1.17 x 10 ⁶	6.71 x 10 ⁵
Cm	2.82 x 10 ⁷	1.22 x 10 ⁷	2.76 x 10 ⁶	3.85 x 10 ⁶	2.79 x 10 ⁶	8.57 x 10 ⁵
Other ^d	3.49 x 10 ²	7.17 x 10 ²	4.97 x 10 ²	3.17 x 10 ²	1.15 x 10 ¹	9.17 x 10 ⁻¹
FP	8.42 x 10 ⁴	8.09 x 10 ⁴	7.05 x 10 ⁴	6.25 x 10 ⁴	2.32 x 10 ⁴	1.05 x 10 ⁴
Total	8.79 x 10 ⁸	1.89 x 10 ⁸	8.79 x 10 ⁷	9.83 x 10 ⁷	7.35 x 10 ⁷	3.51 x 10 ⁷

^aIncludes all decay products. Assumes 99.9% removal of ¹²⁹I.

^bBlended fuel is two-thirds PWR-U and one-third PWR-Pu.

^cWater required to dilute mixture to MCG value for each nuclide.

^dIncludes all other actinides and their decay products, as well as all other decay products formed prior to 90 days.

Table A-3. Contribution of each component^a to the hazard of unprocessed spent fuel from an LMFBR

Parent Component	Hazard ^b of each component (m ³ H ₂ O/metric ton of fuel) after decay times (years) of:						
	10 ³	10 ⁴	5 x 10 ⁴	10 ⁵	2.5 x 10 ⁵	5 x 10 ⁵	10 ⁶
U	3.19 x 10 ⁴	2.82 x 10 ⁵	1.62 x 10 ⁶	3.07 x 10 ⁶	6.47 x 10 ⁶	9.87 x 10 ⁶	1.24 x 10 ⁷
Np	5.94 x 10 ⁴	7.14 x 10 ⁴	1.84 x 10 ⁵	3.13 x 10 ⁵	5.74 x 10 ⁵	7.06 x 10 ⁵	6.74 x 10 ⁵
Pu	1.95 x 10 ⁹	7.85 x 10 ⁸	2.26 x 10 ⁸	1.34 x 10 ⁸	1.11 x 10 ⁸	7.28 x 10 ⁷	2.61 x 10 ⁷
Am	8.76 x 10 ⁷	8.06 x 10 ⁶	2.50 x 10 ⁶	2.10 x 10 ⁶	2.42 x 10 ⁶	2.08 x 10 ⁶	1.37 x 10 ⁶
Ce	1.30 x 10 ⁶	7.7 x 10 ⁵	1.44 x 10 ⁶	2.17 x 10 ⁶	2.47 x 10 ⁶	1.51 x 10 ⁶	3.91 x 10 ⁵
Other ^c	1.77 x 10 ¹	4.27 x 10 ¹	3.14 x 10 ¹	2.13 x 10 ¹	7.37	1.87	3.30 x 10 ⁻¹
FP ^d	1.19 x 10 ⁵	1.11 x 10 ⁵	9.99 x 10 ⁴	8.74 x 10 ⁴	6.13 x 10 ⁴	3.74 x 10 ⁴	2.06 x 10 ⁴
Total	2.04 x 10 ⁹	7.94 x 10 ⁸	2.32 x 10 ⁸	1.42 x 10 ⁸	1.23 x 10 ⁸	8.70 x 10 ⁷	4.10 x 10 ⁷

^aIncludes all decay products.

^bWater required to dilute a mixture to the RCG for each nuclide.

^cIncludes all other actinides and their decay products, and all decay products formed prior to 90 days.

^dAssumes prior removal of 99.9% of iodine and 100% of tritium and noble gases.

Table A-4. Contribution of each component^a to the hazard of unprocessed spent fuel from an HTGR

Parent Component	Hazard ^b of each component (m ³ H ₂ O/metric ton of fuel) after decay times (years) of:						
	10 ³	10 ⁴	5 x 10 ⁴	10 ⁵	2.5 x 10 ⁵	5 x 10 ⁵	10 ⁶
Th	3.86 x 10 ⁶	3.94 x 10 ⁶	3.59 x 10 ⁶	3.44 x 10 ⁶	3.25 x 10 ⁶	3.18 x 10 ⁶	3.17 x 10 ⁶
Pa	2.48 x 10 ⁶	2.05 x 10 ⁶	8.80 x 10 ⁵	3.07 x 10 ⁵	1.58 x 10 ⁴	1.28 x 10 ³	1.42 x 10 ²
U	1.08 x 10 ⁸	8.10 x 10 ⁸	1.80 x 10 ⁹	2.12 x 10 ⁹	1.96 x 10 ⁹	1.10 x 10 ⁹	2.65 x 10 ⁸
Np	5.40 x 10 ⁵	6.49 x 10 ⁵	1.67 x 10 ⁶	2.84 x 10 ⁶	5.21 x 10 ⁶	6.42 x 10 ⁶	6.12 x 10 ⁶
Pu	2.93 x 10 ⁷	2.41 x 10 ⁷	1.01 x 10 ⁸	1.53 x 10 ⁸	1.73 x 10 ⁸	1.06 x 10 ⁸	2.75 x 10 ⁷
Am	3.18 x 10 ⁶	1.00 x 10 ⁶	1.83 x 10 ⁵	5.45 x 10 ⁴	2.54 x 10 ⁴	2.69 x 10 ⁴	2.32 x 10 ⁴
Cm	8.91 x 10 ⁵	3.66 x 10 ⁵	3.12 x 10 ⁴	3.75 x 10 ⁴	4.34 x 10 ⁴	2.82 x 10 ⁴	9.59 x 10 ³
Other ^c	5.32 x 10 ²	1.14 x 10 ¹	4.32 x 10 ⁻²	3.08 x 10 ⁻²	4.03 x 10 ⁻²	4.29 x 10 ⁻²	3.68 x 10 ⁻²
FF ^d	2.02 x 10 ⁵	1.96 x 10 ⁵	1.76 x 10 ⁵	1.53 x 10 ⁵	1.04 x 10 ⁵	6.02 x 10 ⁴	2.92 x 10 ⁴
Total	1.61 x 10 ⁸	8.70 x 10 ⁸	2.31 x 10 ⁹	4.41 x 10 ⁹	4.56 x 10 ⁹	2.70 x 10 ⁹	6.90 x 10 ⁸

^aIncludes all decay products. Does not include the spent ²³⁵U recycle fuel.

^bWater required to dilute mixture to the RCG for each nuclide.

^cIncludes all other actinides and their decay products, and all decay products formed prior to 365 days.

^dAssumes prior removal of 99.9% of iodine and 100% of tritium and noble gases.

10.2 Appendix B: Calculation of the Hazard Indexes of Uranium Minerals

Pitchblende mineral, which occurs principally in South Africa and Canada, represents the upper limit of radiological toxicity of naturally occurring minerals on the basis of hazard index values. Carnotite ore found in deposits on the Colorado Plateau of the western United States was selected as typical of considerably lower-content uranium ores of fairly widespread occurrence. These two minerals reflect the approximate range of uranium concentrations found in all uranium minerals of economic value and major radiological significance.

The hazard index values for the ores were calculated from the following data:

- (1) The volume of water needed to dilute 1 g of natural uranium in equilibrium with its daughters to 10 CFR 20 values is 15.1 m^3 , as calculated using the ORIGEN code.

(2)	<u>Density, g/cc</u>	<u>U Content, wt %</u>
Pitchblende	9	70
Carnotite	3	0.2

The density of pitchblende minerals ranges from about 6 to about 9 g/cc, and the uranium content may vary from about 40 to 70%. Similar variations in properties can occur for carnotite minerals. Density values and uranium content values were selected to represent upper limits of toxicity for pitchblende and the relatively high-grade carnotite ore. Only one significant figure was used for the calculated hazard index because of the uncertainties regarding the mineral property values.

- (3) Hazard indexes (HI) values were calculated as follows:

$$\begin{aligned} \text{HI (pitchblende)} &= 9 \text{ g/cm}^3 \times 0.7 \times 15.1 \text{ m}^3/\text{g} \times 10^6 \text{ cm}^3/\text{m}^3 \\ &= 1 \times 10^8 \end{aligned}$$

$$\begin{aligned} \text{HI (carnotite)} &= 3 \text{ g/cm}^3 \times 0.002 \times 15.1 \text{ m}^3/\text{g} \times 10^6 \text{ cm}^3/\text{m}^3 \\ &= 1 \times 10^5 \end{aligned}$$

**10.3 Appendix C: Relative Contributions of the Major Components
of High-Level Waste from Conventional Reprocessing
of Uranium-Plutonium Fuels and from Assumed
Secondary Processing of the Waste**

Table C-1. Relative contributions of the components of high-level waste to the hazard index for wastes from uranium-plutonium fuels after conventional reprocessing

Type of Waste	Decay Time (years)	Relative contribution to total hazard of the waste ^a (%)						Hazard index of waste ^a (m ³ H ₂ O/m ³ waste)
		U	Np	Pu	Am	Cm	Fission Products	
PWR-U	10 ³	Nil ^b	0.8	11	79	9	0.5	2.74 x 10 ⁸
	10 ⁴	0.3	3	11	67	17	2	6.73 x 10 ⁸
	10 ⁵	5	33	8	14	38	3	3.34 x 10 ⁷
	10 ⁶	5	77	2	8	8	0.6	3.07 x 10 ⁷
PWR-Pu	10 ³	Nil	0.08	3	71	26	0.1	1.92 x 10 ⁸
	10 ⁴	0.02	0.3	2	65	31	0.2	6.79 x 10 ⁸
	10 ⁵	1.1	7	6	31	55	0.9	1.23 x 10 ⁸
	10 ⁶	2.8	37	4	25	32	0.4	4.79 x 10 ⁸
LMFBR	10 ³	Nil	0.06	10	89	1	0.1	1.16 x 10 ⁹
	10 ⁴	0.01	0.6	30	62	6	0.9	1.53 x 10 ⁸
	10 ⁵	0.3	6	12	39	40	2	6.30 x 10 ⁷
	10 ⁶	2	26	5	52	15	0.8	3.12 x 10 ⁷

^aIncludes all decay products. Assumes that the high-level wastes contain 0.5% of the uranium and plutonium, 0.1% of the iodine, and none of the tritium and rare gases from the spent fuel.

^bNil is defined as less than 5×10^{-3} .

Table C-2. Relative contributions of actinides and fission products to the hazard index of high-level waste from uranium-plutonium fuels after secondary processing^a

Decay time (years)	Type of waste	Percent of pitchblende hazard ^b	Percent contribution to total hazard index of the high-level waste					Fission Products
			U	Np	Pu	Am	Cm	
10 ³	PWR-U	5	0.04	2	61	5	0.5	31
	PWR-Pu	5	0.04	2	28	29	11	31
	LMFBR	5	0.01	0.7	48	22	0.3	29
10 ⁴	PWR-U	2	2	5	32	2	0.5	59
	PWR-Pu	2	1	4	11	18	9	58
	LMFBR	2	0.1	2	39	4	0.4	55
10 ⁵	PWR-U	2	15	24	11	0.2	0.6	49
	PWR-Pu	2	13	20	7	2	3	54
	LMFBR	1	2	13	11	2	2	71
10 ⁶	PWR-U	2	17	69	4	0.1	0.1	11
	PWR-Pu	1	19	62	2	1	1	13
	LMFBR	1	17	47	4	2	0.6	29

^aAfter secondary processing, the percentage removals from spent fuel elements were assumed to be as follows: PWR-U - 99.9% Np, 99.95% Pu, and 99.9% Am, Cm, and I

PWR-Pu - same as PWR-U except 99.99% of Pu was removed

LMFBR - same as PWR-Pu

^b(Hazard index of high-level waste ÷ hazard index of pitchblende) x 100. (Hazard index of pitchblende) = 1.0 x 10⁸ m³ of H₂O/m³ of mineral.

**10.4 Appendix D: Relative Contribution of Each Long-Lived Fission
Product to the Total Hazard Index of Fission Products
in High-Level Wastes**

BLANK PAGE

Table D-1. Relative contribution of each long-lived fission product to the total hazard index of fission products^a in high-level wastes from the principal types of reactor fuels

Decay time (years)	Type of waste	Contribution to total hazard index of fission products (%)							Total hazard index of fission products ^d
		⁹³ Zr	^{93m} Nb ^b	⁹⁹ Tc	¹⁰⁷ Pd	¹²⁹ I	¹³⁵ Cs	Other ^c	
10 ³	PWR-U	3	6	86	0.1	1	3	1	1.47 x 10 ⁶
	PWR-Pu	2	4	84	0.3	1	6	2	1.51 x 10 ⁶
	LMFBR	2	4	77	0.2	1	10	4	1.40 x 10 ⁶
	HTGR	4	8	83	0.02	1	3	0.3	1.18 x 10 ⁶
10 ⁴	PWR-U	3	6	86	0.1	1	3	N11	1.42 x 10 ⁶
	PWR-Pu	2	4	85	0.3	1	6	N11	1.45 x 10 ⁶
	LMFBR	2	4	80	0.3	2	13	N11	1.31 x 10 ⁶
	HTGR	4	8	83	0.02	1	13	N11	1.15 x 10 ⁶
10 ⁵	PWR-U	4	7	93	0.2	1	5	N11	1.10 x 10 ⁶
	PWR-Pu	3	5	82	0.3	2	8	N11	1.13 x 10 ⁶
	LMFBR	2	5	75	0.3	2	16	N11	1.03 x 10 ⁶
	HTGR	5	10	79	0.03	1	4	N11	9.00 x 10 ⁵
10 ⁶	PWR-U	14	29	26	1	8	22	N11	1.80 x 10 ⁵
	PWR-Pu	10	20	24	2	9	36	N11	2.93 x 10 ⁵
	LMFBR	7	13	17	1	8	54	N11	2.44 x 10 ⁵
	HTGR	18	35	22	0.1	7	18	N11	1.72 x 10 ⁵

^a

Assumes that 99.9% of the iodine was removed and no activation products from the cladding.

^b

Short-lived but in equilibrium with ⁹³Zr.

^c

Primarily ¹⁵¹Sm.

^d

m³ of H₂O/m³ of waste. At 1000 years, the hazard index value of the long-lived fission products is about 1 to 1.5% of the value for pitchblende.

10.5 Appendix E: Preparation of Synthetic Waste Solutions

Waste solutions were synthetically prepared by mixing nitric acid solutions of nitrate salts of nonradioactive isotopes of fission product elements. The quantities of fission product elements were based on the quantities of fission products that were calculated by the ORIGEN code for typical LWR fuel (no Pu recycle) irradiated to 33,000 MWd/metric ton. The fission product content of the waste was based on a fuel reprocessing time of 160 days and storage of the waste for five years after reprocessing. The fission products from 1 metric ton of this fuel were assumed to be present in 3100 liters of 2 M HNO_3 . The volume, acid concentration, and fission product content values correspond to approximately those expected for the feed solution to the coextraction column (first TBP cycle) in a Purex plant. The fission product and acid concentrations in the original Purex feed were chosen because the formation of solids and precipitates in the subsequent solvent extraction steps from which the high-level wastes is generated can be also studied.

The approach to preparing the synthetic waste solutions was to make up individual solutions of each element and then combine appropriate volumes of the solutions to obtain the desired concentrations. Some of the elements are either insoluble or only slightly soluble in nitric acid, and this complicates the preparation. In these cases, the solutions were freshly prepared prior to use, whereas solutions composed of soluble elements were prepared and stored until needed. The synthetic waste elements, their desired quantities in the synthetic waste, the starting compound, and the method used to dissolve the individual elements in nitric acid solution are given in Table E-1. The solutions containing tin and antimony are not stable with regard to precipitation and thus must be prepared immediately before combining with the other solutions.

The following procedure was used to prepare 15-liter batches of synthetic solutions containing nonradioactive forms of the fission product elements:

- (1) Add proper volumes of individual solutions of I, Br, Mo, Zr, As, Sb, Ag, Gd, and Eu to a stock solution containing the Sr, La, Sm, In, Cd, Cs, Pr, Se, Ce, Ba, Te, Nd, and Y.

- (2) Add proper volumes of Rb, Rh, Ru, Pd, and Sn solutions to the solution prepared in (1). Precipitation will occur; however, most of the solids will redissolve on stirring the solution for about 1 hr.
- (3) Filter the solution. A small quantity of gray-colored solids is separated. The composition of the solids is not precisely known at the present time; however, they appear to consist primarily of tin and antimony.

Methods for preparing synthetic waste solutions will continue to be investigated, particularly in regard to the formation of precipitates and colloids. These studies will provide valuable information concerning the conditions and concentrations favoring formation of precipitates, and the actinide content of these precipitates, if any.

Table E-1. Preparation of synthetic waste solutions

Element	Quantity (g/liter)	Compound	Remarks
Sr	0.263	$\text{Sr}(\text{NO}_3)_2$	Dissolved in water
In	0.0004	$\text{In}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	Dissolved in 1 <u>M</u> HNO_3
Cd	0.027	Metal	Dissolved in 8 <u>M</u> HNO_3
Cs	0.780	CaNO_3	Dissolved in 0.1 <u>M</u> HNO_3
Se	0.016	H_2SeO_3	Dissolved in 2 <u>M</u> HNO_3
Ba	0.536	$\text{Ba}(\text{NO}_3)_2$	Dissolved in water
Te	0.181	Metal	Dissolved in 8 <u>M</u> HNO_3
Mo	1.10	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	Dissolved in 0.5 <u>M</u> HNO_3
Sn	0.016	Metal, granul, 30 mesh	Dissolved in 4 <u>M</u> HNO_3 , no heat, no stirring
Ag	0.019	AgNO_3	Dissolved in water
Zr	1.17	$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	Dissolved in 1 <u>M</u> HNO_3
Br	0.005	NaBrO_3	Dissolved in water
I	0.086	HIO_3	Dissolved in water
As	0.00003	Metal	Dissolved in 8 <u>M</u> HNO_3
Sb	0.004	Metal	Dissolved in 8 <u>M</u> HNO_3
Pd	0.456	Metal	Dissolved in 8 <u>M</u> HNO_3 , added 3 drops HCl , boiled off chloride
Rh	0.125	Metal	Dissolved in a sealed tube containing HCl at high pressure, ^a converted to nitrate by precipitating the chloride
Rb	0.107	RbCl	Dissolved in water, precipitated chloride with AgNO_3
Ru	0.688	RuCl_3	Dissolved in 4 <u>M</u> HCl , reduced acidity by heat and dilution, precipitated chloride with AgNO_3
La	0.410	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	Dissolved in water
Y	0.151	$\text{Y}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$	Dissolved in 0.5 <u>M</u> HNO_3
Nd	1.32	$\text{Nd}_2(\text{CO}_3)_3$	Dissolved in 2.0 <u>M</u> HNO_3
Pr	0.386	$\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	Dissolved in 1 <u>M</u> HNO_3

Table E-1. (continued)

Element	Quantity (g/liter)	Compound	Remarks
Ce	0.796	$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	Dissolved in 1 <u>M</u> HNO_3
Sm	0.286	Sm_2O_3	Dissolved in 12 <u>M</u> HNO_3 , evaporated to near dryness, added water
Gd	0.038	Gd_2O_3	Dissolved in 12 <u>M</u> HNO_3 , evaporated to near dryness, added water
Eu	0.055	Eu_2O_3	Dissolved in 12 <u>M</u> HNO_3 , evaporated to near dryness, added water
Tb ^b	0.0006		
Dy ^b	0.0004		
Ho ^b	0.00003		
Er ^b	0.00001		
Ge	0.00012	Omitted	
Nb	0.000008	Omitted	
Tc	0.271	Omitted	
Pm	0.009	Omitted	

^a Rhodium metal was dissolved by personnel in the ORNL Analytical Division.

^b Rare-earth elements were not used.

11. REFERENCES

1. High-Level Radioactive Waste Management Alternatives, WASH-1297, U. S. Atomic Energy Commission (May 1974).
2. H. C. Claiborne, Neutron-Induced Transmutation of High-Level Radioactive Wastes, ORNL-TM-3964 (December 1972).
3. J. W. Bartlett, L. A. Bray, L. L. Burger, R. E. Burns, and J. L. Ryan, Feasibility Evaluation and R&D Program Plan for Transuranic Partitioning of High-Level Fuel Reprocessing Wastes, BNWL-1776, Battelle Northwest Laboratory (November 1973).
4. J. O. Blomeke, J. P. Nichols, and W. C. McClain, "Managing Radioactive Wastes," Physics Today 26(8), 36-42 (1973).
5. M. J. Bell, ORIGEN - The ORNL Isotope Generation and Depletion Code, ORNL-4628 (May 1973).
6. M. E. LaVerne, Appendix I of Ref. 2.
7. Aqueous Processing of LMFBR Fuels - Technical Assessment and Experimental Program Definition (compiled and edited by the Staff of the Chemical Technology Division), ORNL-4436 (June 1970).
8. Reprocessing of Yankee Reactor Fuel at Nuclear Fuel Services, Inc., West Valley Facility (prepared by Fuels Reprocessing Branch, USAEC, Savannah River Operations Office), SRO-124 (Oct. 21, 1968).
9. W. W. Schultz and G. E. Benedict, Neptunium-237 Production and Recovery, AEC, Critical Review Series, U.S.A.E.C. Office of Information Services (1972).
10. R. E. Leuze and M. H. Lloyd, "Processing Methods for the Recovery of Transplutonium Elements," in Process Chemistry, Vol. 4, Pergamon, New York, 1969.
11. R. G. Baxter, Actinide Properties and Methods of Production, DP-1269, E. I. du Pont de Nemours and Co. (December 1972).
12. E. J. Wheelwright and F. P. Roberts, The Use of Alternating DTPA and NTA Cation-Exchange Flowsheets for the Simultaneous Recovery of and Purification of Pu, Am, and Cm, BNWL-1072, Battelle Northwest Laboratory (July 1968).
13. S. J. Beard and R. L. Moore, "Large Scale Recovery and Purification of Fission Products," in Process Chemistry, Vol. 4, Pergamon, New York, 1969.

14. J. A. Kelley, Ion Exchange Process for Separating Americium and Curium from Irradiated Plutonium, DP-1308, E. I. du Pont de Nemours and Co. (November 1972).
15. B. Weaver and F. A. Kappelmann, "Preferential Extraction of Lanthanides or Trivalent Actinides by Monoacidic Organophosphonates from Carboxylic Acids and from Carboxylic and Aminopolyacetic Acids," J. Inorg. Nucl. Chem. 30, 263-72 (1968).
16. B. Weaver and F. A. Kappelmann, Talspeak: A New Method of Separating Americium and Curium from Lanthanides by Extraction from an Aqueous Solution of Aminopolyacetic Acid Complex with a Monoacidic Phosphate or Phosphonate, ORNL-3559 (August 1964).
17. Z. Kolarik, G. Koch, H. H. Kuesel, and J. Fritsch, Separation of Americium and Curium from Highly Radioactive Waste Solution, KFK-1553 (1972).
18. H. E. Henry, Isolating Americium and Curium from $\text{Al}(\text{NO}_3)_3\text{-NaNO}_3\text{-HNO}_3$ Solutions by Batch Extraction with Tributyl Phosphate, DP-972, E. I. du Pont de Nemours and Co. (August 1965).
19. D. A. Orth, J. M. McKibben, W. E. Prout, and W. C. Scotten, "Isolation of Transplutonium Elements," pp. 534-55 in Proceedings of the International Solvent Extraction Conference, The Hague, Soc. of Chem. Ind. (1971).
20. M. C. Thompson, Distribution of Selected Lanthanides and Actinides Between 30% TBP in n-Paraffin and Various Metal Nitrate Solutions, DP-1336, E. I. du Pont de Nemours and Co. (November 1973).
21. M. H. Lloyd, "An Anion Exchange Process for Americium-Curium Recovery from Plutonium Process Waste," Nucl. Sci. Eng. 17, 452-56 (1963).
22. G. Hoehlin, H. J. Born, and W. Weinlander, "The Isolation of ^{242}Cm from Neutron-Irradiated ^{241}Am ," Radiochim. Acta 10, 85-91 (1968).
23. B. Weaver, "Solvent Extraction in the Separation of Rare Earths and Trivalent Actinides," pp. 189-277 in Ion Exchange and Solvent Extraction - A Series of Advances, Vol. 6, Marcel Dekker, New York, 1974.
24. R. Quang and J. O. Cowles, Recovery of the Actinide-Rare Earth Fraction from HUTCH Samples, UCRL-50847 (April 7, 1970).
25. D. E. Ferguson et al., Chem. Technol. Div. Ann. Progr. Rept. May 31, 1966, ORNL-3945, pp. 170-75.
26. D. E. Ferguson et al., Chem. Technol. Div. Ann. Progr. Rept. May 31, 1968, ORNL-4272, pp. 103-8.

27. W. E. Unger et al., Aqueous Fuel Reprocessing Quarterly Report for Period Ending September 30, 1973, ORNL-TM-4394 (February 1974), pp. 13-20. (Available from the U. S. Atomic Energy Commission, Technical Information Center, P. O. Box 62, Oak Ridge, TN 37830).
28. W. E. Unger et al., Aqueous Fuel Reprocessing Quarterly Report for Period Ending December 31, 1973, ORNL-TM-4488 (June 1974), pp. 9-18. (Available from the U. S. Atomic Energy Commission, Technical Information Center, P. O. Box 62, Oak Ridge, TN 37830).
29. W. Ochsenfeld, H. Schmieder, and S. Theiss, Aqueous Reprocessing of Fast Breeder Fuel Elements: Common Extraction and Separation of Macroquantities of Plutonium and Uranium in the Purex Process, EURFNR-888 (October 1970).
30. Liquid Metal Fast Breeder Reactor Program Plan, Element 8-Fuel Recycle, WASH-1108, U. S. Atomic Energy Commission (December 1972).
31. R. I. Newman, "The Barnwell Nuclear Fuel Plant," Nucl. Eng. Intern. 17, 938-41 (1972).
32. D. S. Webster et al., Chemical Engineering Division Fuel Cycle Technology Quarterly Report, January-March 1971, ANL-7799, Argonne National Laboratory (July 1971).
33. G. Koch, W. Ochsenfeld, and E. Schwind, Flowsheet Studies on the Processing of Plutonium Fuels by Solvent Extraction, KFK-990 (May 1969).
34. J. M. McKibben and J. E. Bercaw, Hydroxylamine Nitrate as a Plutonium Reductant in the Purex Solvent Extraction Process, DP-1248, E. I. du Pont de Nemours and Co. (January 1971).
35. R. L. Walser, The Hanford Purex Plant Experience with Reductants, ARH-SA-69 (July 1970).
36. D. A. Orth, J. M. McKibben, and W. C. Schotten, "Progress in Tributyl Phosphate Technology in the Savannah River Plant," pp. 514-33 in Proceedings of the International Solvent Extraction Conference, The Hague, Soc. of Chem. Ind. (1971).
37. H. A. C. McKay et al., Solvent Extraction Chemistry of Metals (Proceedings of the International Conference on the Solvent Extraction Chemistry of Metals, Harwell), Macmillan, New York, 1965.
38. G. F. Best, E. Hasford, and H. A. C. McKay, "Tri-n-Butyl Phosphate as an Extracting Solvent for Inorganic Nitrates - VII. Trivalent Actinide Nitrates," J. Inorg. Nucl. Chem. 12, 136-40 (1959).

39. T. V. Healy, "The Reaction of Nitric Acid with Formaldehyde and with Formic Acid and Its Application to the Removal of Nitric Acid from Mixtures," J. Appl. Chem. 8, 553-561 (1958).
40. W. Bahr, The Extraction Behavior of Neptunium in the Reprocessing of Irradiated Fuels by the Purex Process, KFK-797 (November 1968).