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Methods for Removal of Actinides from High-Level Wastes*

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Methods for Removal of Actinides from High-Level Wastes

Fractionation of radioactive wastes into a long-lived fraction (or fractions) and a short-lived fraction is a necessary part of some of the potential waste management alternatives presently under study by the USAEC. The removal of actinides from high-level wastes is an important step in waste fractionation. The purpose of the waste fractionation program at ORNL is to investigate the technical feasibility of removing actinides from the high-level, radioactive wastes from the processing of commercial power reactor fuels. The feasibility study provides a part of the technological basis that is necessary for the evaluation of waste management alternatives. Specifically, we are examining the possibility of removing actinides to such a degree that the calculated hazard index of the solidified, high-level fission product wastes after storage periods of about 1000 years would be comparable to that for naturally occurring minerals and ores of uranium. The actinides that are recovered would receive special treatment for storage or may be recycled to reactors where they are burned to less hazardous fission products.

Investigations thus far have consisted of determination of the degree of removal required for the actinides and a partial evaluation of the feasibility of accomplishing these removals. A considerable amount of work is yet to be done before technical feasibility can be established.

On the basis of the duration of the long-term hazard of radioactive wastes from conventional plants that process spent reactor fuels, the long-lived actinides are the much larger contributors. After these actinides are removed, certain long-lived fission products in the high-level fission

product wastes such as ^{129}I , ^{99}Tc , ^{93}Zr , and ^{135}Cs become the dominant contributors. The magnitude of the contribution of the actinides to the long-term hazard of the wastes is quite large. After the actinides have been removed to an extent so that the long-lived fission products are the dominant hazard, the resultant wastes have a calculated hazard index values at times of 500-1000 years and greater that are less than those for uranium ores. The hazard index is defined as the volume of water that could be contaminated to the RCG-allowable value by one volume of waste or other radioactive material.

SLIDE 1 illustrates the possible merits of such removals of actinides from the high-level wastes. The hazard index of high-level waste from conventional processing of spent fuel from a typical LWR are compared with the same wastes after further postulated removal of actinides by secondary treatment. In conventional processing 99.5% of the U and Pu are removed and in the combined conventional and secondary processing 99.9% of the U, 99.99% of the Pu, 95% of the Np, and 99.9% of the Am and Cm are removed. Assumptions made in calculating the hazard index of the wastes are: (1) the total quantity of unrecovered actinides from 1 MT of fuel from conventional and from combined conventional and secondary processing was present in 2 ft^3 of solidified, high-level fission product waste, (2) 100% of the rare gases, 100% of the tritium and 99.9% of iodine was removed in the conventional processing.

For reference, this slide also shows the hazard index associated with the mineral pitchblende and with a uranium ore containing 0.2% U,

typical of the large deposits that occur on the Colorado Plateau. Note that the hazard index of the waste from conventional processing decreases rapidly over the first thousand years (due to the decay of ^{90}Sr and ^{137}Cs) but remains as great or greater than pitchblende for more than a million years. The waste resulting after secondary treatment, however, falls within the range of naturally occurring radioactive materials after only several hundred years, a time span for which the effects of geologic, climatic, and other natural phenomena can be reliably extrapolated. Equivalent reductions are obtained in the calculated hazard index values of wastes from processing liquid metal fast breeder reactor (LMFBR) and high-temperature gas-cooled reactor (HTGR) fuels when actinides are further removed by secondary processing to an extent where the fission products control the hazards. One way of disposing of the separated actinides and iodine would be to recycle them with fresh fuel to power reactors, and our calculations show that even after sustained recycle of these materials, the wastes, while having a slightly higher index would still lie within the range of naturally occurring radioactive species.

SLIDE 2 presents the percentage removal of each actinide element in different reactor fuels that would be required to reduce the hazard index of the wastes to less than 5% of that of pitchblende after storage for about 1000 years. Further reduction of actinides would not be warranted unless one also removed the very long-lived fission products: ^{99}Tc , ^{93}Zr , ^{135}Cs , and additional ^{129}I . Wastes from all of the fuel types require removal

of U, Pu, Np, Am, and Cm and, in addition, HTGR wastes require removal of Th and Pa. It was assumed in all of the calculations (Slides 1 & 2) that all unrecovered actinides from the conventional processing of 1 metric ton of LWR, LMFB, and HTGR fuels were present in 2, 3, and 6 cubic feet, respectively of solidified high-level fission product waste. It was also assumed that 100% of the volatile tritium, krypton, and xenon and 99.9% of the volatile iodine was removed during processing and did not report to the solidified waste. Separating processes currently used to recover actinides normally have given U, Pu, and Th recoveries of 99.5% and neptunium, americium, and curium recoveries in the range of 90 to 99%.

It is, therefore, apparent that a comprehensive development program will be required to reduce this proposed waste management concept to practice. This program must be designed (SLIDE 3) to (1) solve problems that are obvious from previous experience, (2) increase the removal of actinides to the desired levels, (3) determine the most desirable method to integrate the needed process cycles into an overall system, (4) choose chemical processes and reagents that minimize high-level waste treatment problems, and (5) determine the composition of all waste streams that will be generated and ways to recycle these streams.

We have begun our investigations on removal methods by limiting our considerations to wastes from LWR fuels because this is the only type for which experience on large-scale reprocessing exists. In conventional, commercial processing by the Purex process about 99.5% of fissile and fertile values are recovered from solutions of the fuel (SLIDE 4). All

the other actinides are not recovered and are discharged to the high-level fission product waste along with the 0.5% of the unrecovered fissile and fertile values of the fuel. The high-level aqueous fission product waste contains the major fraction of the actinides that are discharged to waste in conventional processing and >99.9% of the non-volatile fission products. The schematic Purex Plant shown typifies the Nuclear Fuel Services Plant which has operated. In the Midwest Fuel Recovery Plant, not yet operating, neptunium will also be recovered by the Purex process. Concentrations of key constituents in the high-level waste stream and the required actinide recovery factors are shown in SLIDE 5. In order to achieve the overall required removal of actinides from spent LWR fuels in which plutonium is recycled, minimum additional recovery factors from the high-level wastes of 5, 20, 50, 1000, and 1000 are needed for uranium, plutonium, neptunium, americium, and curium, respectively.

Although the recoveries of actinides that will be required from the high-level wastes may be feasible by modifications of existing plant processes and by additions of extra recovery processes, some difficult chemical problems will have to be solved (SLIDE 6). In addition to the residues from fuel dissolution, these chemical problems are largely associated with chemical changes that occur in solutions of actinides and fission products during conventional processing and additional processing and the recycle of all waste streams from the processing. In the past, more complete recovery of plutonium has been inhibited by nonextractable forms of plutonium. These nonextractable forms consist of the residues from fuel dissolution and of forms generated during processing, yet unidentified,

which may include colloids, precipitates, sorbed species and complex ions. Certain fission products, such as zirconium, tin, and molybdenum, are easily hydrolyzed and precipitated and present many difficulties in processing with regard to actinide losses and operation. Separations of americium and curium from fission products require process solutions of low acidity, and hydrolysis and precipitation of actinides and fission products must not be allowed to occur during the course of processing. The conceptual processing sequence for removal of actinides from the high-level waste have not been finalized as studies are still in progress. SLIDE 7 illustrates our current concept. Neptunium is removed by recovering it along with the economic values of uranium, using the existing Purex solvent extraction process. If technically feasible, essentially complete removal of the reactor bred plutonium, uranium, and neptunium will be accomplished using extra stages of Purex in which exhaustive extraction is carried out. We expect to recover 95% of the neptunium in the primary extraction but a more complete recovery of neptunium will be obtained in the exhaustive extraction. The actinides removed by exhaustive extraction would probably be recycled to the primary Purex plant after appropriate treatment of the solution of removed actinides. The actinides recovered by exhaustive extraction would probably have a poor decontamination from fission products.

Next the wastes are stored for a period of 3 to 4 years to reduce radiation damage to process reagents, solvents or ion exchange resins to be used in subsequent operations. The problem here is that not only are large inventories of wastes in liquid form accumulated, but also that plutonium grows back into the wastes during storage and will again require removal.

In the following step it is visualized that the daughter plutonium and any plutonium not extracted in the exhaustive extraction would be removed. We are not sure what this step will include. It would probably consist of removing any actinide-bearing solids such as undissolved fuel fines, and treating them for recovery and chemical treatment of any inextractable solubilized forms of plutonium (i.e., colloids or complex ions).

Provided the separated solids can be solubilized in nitric acid, the dissolved solids would be recycled to the primary Purex plant but if the solids cannot be dissolved, they would be processed by special processing from molten salts or nitric-hydrofluoric acid solutions. The solubilized but inextractable plutonium which may exist is also a very difficult problem. This problem can only be solved by laboratory development studies in which the inextractable species are identified and methods for rendering them extractable are developed.

Following final removal of the plutonium, the americium and curium are removed. Again we are not sure what the specific recovery process will be. Existing processes for the removal of americium and curium from fission products are deficient in one or more ways. Although, several of the processes have the potential for the final removal step from the rare earth fission products, methods for preparing a satisfactory feed solution to these processes will have to be developed. Conventional processes for separating americium and curium from fission products utilize high concentrations of metal salts or organic chemicals and methods for eliminating these materials from the final fission product solid waste by

appropriate recycle or combustion processes will have to be developed. The processes that are being evaluated for the removal of americium and curium from the wastes are ion exchange chromatography, tributylphosphate extraction from feed solutions salted with aluminum nitrate, and extraction from carboxylic acid solutions with di(2-ethylhexyl)phosphoric acid (Talspeak process).

Conceptual flowsheet studies for Am and Cm removal have pointed out several specific problems to be solved. SLIDE 8 shows one of the candidate flowsheets for solvent extraction removal of Am and Cm - the Talspeak process. In this process, a group separation of lanthanides and trivalent actinides is made; hence it has the potential for the final removal step for Am and Cm. The group separation is effected by extracting a carboxylic acid solution with HDEHP. The aqueous phase acidity is maintained at a pH value of 2.5 to 3.0. The Am and Cm and rare earths are coextracted by the HDEHP from 1 M lactic acid. The complexing agent diethylenetriamine-pentacetate (DTPA) is used to partition the rare earths and trivalent actinides. The actinides are partitioned to the aqueous phase where they may be further purified and concentrated by another cycle of solvent extraction or by oxalate precipitation. This process utilizes a large quantity of process chemicals which ultimately appear in low level waste streams. These process chemicals will need to be partially recycled or the waste streams treated in a satisfactory manner for ultimate solidification with all of the high-level wastes. Other than sodium, the components of the process chemical are organic materials and have the potential for being converted to non-contaminated gaseous chemical wastes.

The other candidate solvent extraction process TBP extraction from feed solutions salted with $\text{Al}(\text{NO}_3)_3$ has similar problems with recycle of the bulk chemical used -- the $\text{Al}(\text{NO}_3)_3$. It is also a low acidity flowsheet.

The cation exchange chromatography (CEC) process also has the problems associated with low acidity and large quantities of process chemicals (SLIDE 9). In this process the actinides and rare earths are sorbed on a loading column. Chromatographic separation is effected by band displacement through a series of ion exchange columns with an eluant containing a complexing agent, usually DTPA. Zinc is used as a barrier ion so that the developing bands remain "sharp" for the individual elements over many the 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 losses due to end-cutting and hence the quantity of material that must be reworked or recycled.

Because of the large quantity of zinc that is required for providing the barrier ion, this material will need to be recycled when employed for our application. Also, significant amounts of actinide contaminated resin waste will be generated because of mechanical, chemical, and radiation damage to the resin particles. Solutions to these problems will require further study of both a conceptual and an experimental nature.

The CEC process has been developed at SRL to a scale of 20 moles of RE's and actinides. This is about 1/4 the capacity necessary for processing 1 MT of LWR fuel. At 1/4 scale, the columns are 8, 6, 4, and 2-in.-diam and each in column was 5 ft long.

Since the attractive candidate methods of extraction of actinides from lanthanides require acidities considerably lower than 1 N, we are carrying out studies of both a conceptual and experimental nature for achieving low acidity feed. Low acidity cannot be achieved without effecting precipitation of certain fission product elements. For example, we observe that destruction of nitric acid by reduction with formic acid results in the precipitation of the noble metals, zirconium, and molybdenum. Since the zirconium and molybdenum solids are quite voluminous, separation and washing of the solids free of trivalent actinides would be a cumbersome and difficult process even if technically feasible. We are therefore looking for processes which can remove the troublesome fission products. Methods currently under study include (1) HDEHP extraction of Zr and Mo from 6 N HNO_3 solution, (2) TBP extraction of actinide-lanthanide fraction from solutions salted with $\text{Al}(\text{NO}_3)_3$. The HDEHP process has been successively tested for Zr and Mo removal in the laboratory. However, we have not yet developed a method for recovery of the HDEHP solvent. It is known that the TBP process works - the problem here is to adjust the process so that higher recoveries can be achieved and the $\text{Al}(\text{NO}_3)_3$ can be recycled.

So far we have dealt only with the HAW waste stream in the Purex plant (SLIDE 10). We have tacitly assumed that the liquid streams from the partition and purification cycles can be recycled in the processing and we have only one high-level raffinate stream the HAW. This we believe can be done by use of suitable reductants in partitioning and purification. We will eventually have to deal with the wastes from purifying the solvents. The caustic scrubber wastes contain 0.01% of the Pu -- and methods of recovering this Pu will have to be developed or a more satisfactory alternate solvent purification method will have to be used.

In summary we can say that based on our investigations thus far, it appears that it will be feasible to reduce the long-term hazards of waste by more complete removal of actinides. However, many challenging problems must be solved before satisfactory processes can be developed and in turn demonstrated on a "hot-pilot" plant scale. It appears the necessary U and Np removals can probably be accomplished by modification and addition to the current Purex process. A number of specific chemical problems have been identified which must be solved before satisfactory chemical process flowsheets can be developed for the very high degrees of removal required for Pu and Am and Cm.

EFFECT OF AGE AND METHOD OF TREATMENT ON THE HAZARD INDEX OF HIGH-LEVEL WASTES FROM LWR'S

~~SLIDE 6~~

SLIDE 1

PERCENTAGE REMOVALS REQUIRED TO REDUCE HAZARD INDEX
OF AGED WASTES TO <5% OF THAT OF PITCHBLEND^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	99.0	99.9	99.9	95.0

^a MINERAL CONTAINING 60% U.

OBJECTIVES OF ACTINIDE SEPARATIONS PROGRAM

1. SOLVE PROBLEMS OBVIOUS FROM PREVIOUS EXPERIENCE.
 2. INCREASE REMOVAL OF ACTINIDES TO DESIRED LEVELS.
 3. DETERMINE HOW TO INTEGRATE NEEDED PROCESS CYCLES INTO AN OVERALL SYSTEM.
 4. CHOOSE PROCESSES AND REAGENTS THAT MINIMIZE HIGH-LEVEL WASTE TREATMENT PROBLEMS.
 5. DETERMINE HOW TO RECYCLE ALL GENERATED WASTE STREAMS.
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SLIDE 8

OUTLINE OF CONVENTIONAL PROCESSING

Slide 4

**COMPOSITION OF HIGH-LEVEL WASTE FROM REPROCESSING
LWR FUEL AND ACTINIDE RECOVERY FACTORS REQUIRED**

CONSTITUENT	CONCENTRATION (g/LITER)	RECOVERY FACTOR REQUIRED
U	0.93	≥ 5
Np	0.15	≥ 20
Pu	0.009	≥ 50
Am	0.03	≥ 1000
Cm	0.007	≥ 1000
TOTAL F.P.	5.60	
R.E.'s	2.03	

**BASIS: 33,000 MWd EXPOSURE; 5175 LITERS WASTE PER TON OF
FUEL; 0.5% LOSS OF U AND Pu TO WASTE.**

SLIDE 5

MAJOR PROBLEMS TO BE SOLVED

1. UNDISSOLVED RESIDUES OF FUEL.
 2. INEXTRACTABLE FORMS OF PLUTONIUM.
 3. *Development of a ^{low} level waste recovery process*
 - 4 - 3. ACTINIDE LOSSES TO SOLIDS GENERATED IN THE PROCESSING.
 - 5 - 4. CONTROL OF VALENCE OF NEPTUNIUM DURING EXTRACTION.
 - 6 - 5. DEVELOPMENT OF ALTERNATE REDUCTANTS FOR U, Pu, Np PARTITIONING.
 - 7 - 6. RECYCLE OF ALL WASTE STREAMS GENERATED BY THE PROCESSING.
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SLIDE 6

CONCEPTUAL PROCESSING SEQUENCE FOR THE
REMOVAL OF ACTINIDES

Slide 7

Slide 8

FLWSHEET FOR RECOVERY OF AMERICIUM AND CURIUM
BY THE ORIGINAL TAISPEAK PROCESS

SCHEMATIC FLOWSHEET OF CATION EXCHANGE CHROMATOGRAPHIC PROCESS FOR RECOVERY OF AMERICIUM AND CURIUM

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Slide 10

OUTLINE OF CONVENTIONAL PROCESSING

Slide 10