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MASTER

METHODS FOR SEPARATING ACTINIDES FROM REPROCESSING AND REFABRICATION  
PLANT WASTES\*

D. W. Tedder, \*\* B. C. Finney, J. O. Blomeke

Oak Ridge National Laboratory  
Oak Ridge, Tennessee 37830

## ABSTRACT

Chemical processing flowsheets have been developed to partition actinides from all actinide-bearing LWR fuel reprocessing and refabrication plant wastes. These wastes include high-activity-level liquids, scrap recovery liquors, HEPA filters and incinerator ashes, and chemical salt wastes such as sodium carbonate scrub solutions, detergent cleanup streams, and alkaline off-gas scrubber liquors. The separations processes that were adopted for this study are based on solvent extraction, cation exchange chromatography, and leaching with  $Ce^{4+}$ - $HNO_3$  solution.

## INTRODUCTION

A research and development program<sup>1,2</sup> coordinated by Oak Ridge National Laboratory has been under way since 1977 to evaluate, for waste management purposes, the feasibility and incentives for partitioning (separating) the actinides from fuel reprocessing and refabrication plant waste streams and recycling them to reactors for transmutation to short-lived and stable fission products. This paper describes the processes that were chosen to establish the technical feasibility of carrying out such separations.<sup>3</sup>

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\*\* Present address: School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Ga. 30332.

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A four-point strategy was adopted in order to develop actinide partitioning flowsheets that are defensible from the standpoint of chemical feasibility:

1. utilize only demonstrated technology that is readily applicable to commercial recycle operations,
2. develop generic capabilities to deal with all types of wastes,
3. choose processing systems that complement each other and provide actinide recovery opportunities in depth, and
4. experimentally evaluate the proposed methods.

Although the experimental work was limited to laboratory and hot-cell investigations of the various treatment subsystems, we believe that the selected processes and flowsheets are sufficiently advanced to permit recoveries of greater than 99% of the actinides.

#### WASTE TREATMENT SUBSYSTEMS

It is envisioned that the separations processes would be incorporated into separate waste treatment facilities (WTFs) that are located adjacent to the fuel reprocessing and refabrication plants.

A schematic diagram depicting fuel reprocessing with actinide partitioning is shown in Fig. 1. The various wastes are transferred to the WTF for actinide partitioning and afterward are returned to the reprocessing plant for immobilization and packaging. The partitioned actinides are returned as a concentrated nitrate solution to the reprocessing plant for conversion to the oxides.

The subsystems incorporated in the WTF are: (1) High-Level Solid Waste Treatment, (2) High-Level Liquid Waste Treatment, (3) Solid Alpha Waste Treatment, (4) Cation Exchange Chromatography, (5) Salt Waste Treatment, (6) Actinide Recovery, (7) Solvent Cleanup and Recycle, (8) Off-Gas Treatment, (9) Actinide Product Concentration, and (10) Acid and Water Recycle. The WTF supporting a fuel refabrication facility, although similar, does not contain subsystems (1) and (2).

#### High-Level Solid Waste Treatment

Cladding hulls and dissolver solids are generated as wastes during the reprocessing of LWR fuels. Although the alpha activity in these wastes is generally low, the WTF has the provisions for giving them an additional leach with  $\text{HNO}_3$ -HF solution.

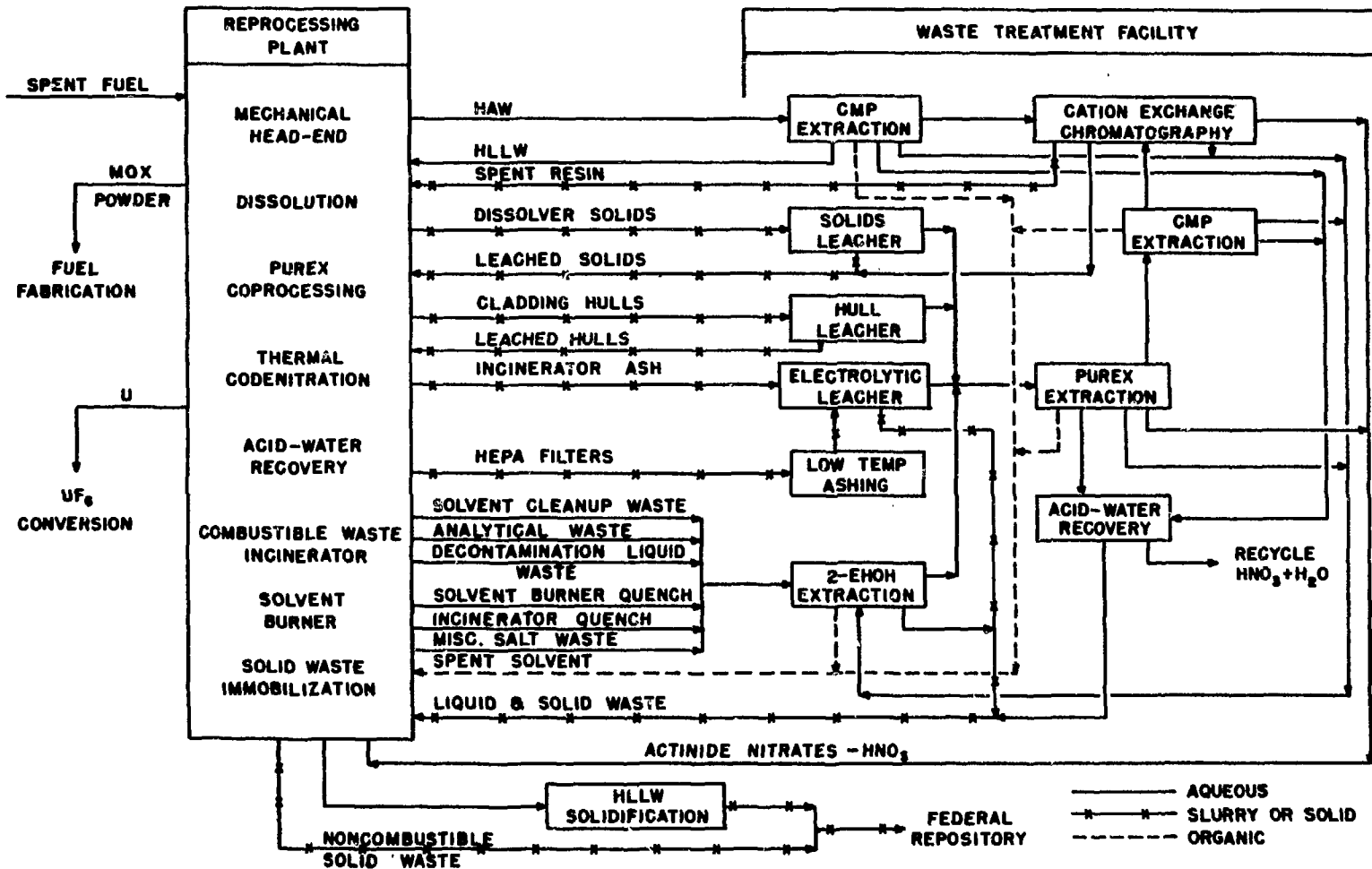


Fig. 1. Schematic diagram of LWR fuel reprocessing with actinide partitioning.

### High-Level Liquid Waste (HLLW) Treatment

The HLLW, after generation, is transferred to the WTF where it is contacted with a bidentate extractant composed of 30% dihexyl-N, N-diethylcarbonylmethylene phosphonate (CMP) in diisopropylbenzene. All the actinides and lanthanides are removed from the HLLW to some degree under high acid conditions,<sup>4</sup> and all other fission products that tend to be extracted can be controlled by scrubbing or by adjusting the extraction conditions to reject those that exist as anions.

The coextracted actinides and lanthanides are stripped from the solvent by sequential treatment in two columns: a dilute nitric acid strip column containing a reductant, followed by a dilute oxalic acid strip column. After the oxalic acid has been destroyed, the two strip solutions are combined with other recycle streams, partially denitrated, concentrated, and finally sent to Cation Exchange Chromatography for lanthanide removal.

Experimental results<sup>4</sup> using actual HLLW suggest that greater than 99.99% of the tetravalent actinides and 99.9% of the trivalent actinides may be removed using CMP extraction.

### Solid Alpha Waste Treatment

Solid Alpha Waste Treatment consists of the processing steps that have been developed to recover actinides from HEPA filters and incinerator ashes. Such wastes are generated primarily in the nitrate-to-oxide conversion step during reprocessing, the oxide powder handling and pellet grinding operations in fuel fabrication, and the incineration of alpha-contaminated combustible wastes in both reprocessing and fabrication.

For the purposes of this study, it is assumed that the HEPA filters are dismantled and the filter media are then shredded and packaged in 55-gal drums at the incinerator area. The incinerator ashes are also packaged in drums and then transferred from the incinerator area to the WTF.

At the WTF, the shredded HEPA media are first metered through a low-temperature ( $\sim 300^{\circ}\text{C}$ ) asher to oxidize any high-molecular-weight glues or binders that may be present. The asher product is collected in a hopper and loaded into the leaching equipment, which consists of a vertical, cylindrical column and a stirred electrolytic oxidizer tank. A leaching cycle consists of successively loading the vertical column with a batch of waste and circulating a mixture of nitric acid, cerous nitrate, and gadolinium nitrate by thermosiphon through the fixed bed and back to the oxidizer tank. As the leachant circulates and approaches reflux temperatures, an electrical potential is applied across the electrodes in the oxidizer tank to convert the cerous nitrate to ceric nitrate.

On completion of the leaching, oxalic acid is added to the leachant to reduce the corrosive ceric ion. The leachant is then transferred to a holding tank for subsequent centrifugation and actinide removal. The leached HEPA material is washed with nitric acid and water, compacted to near its original volume with air pressure, and discharged into drums. The drums are sent to the on-site immobilization and storage area for ultimate disposal.

Incinerator ashes are decontaminated simply by loading them into a separate, stirred electrolytic oxidizer tank and subjecting them to essentially the same leaching operations as those described for the HEPA waste.

The leaching of HEPA filter waste and incinerator ashes with  $Ce^{4+}$ - $HNO_3$  is complex, but results of experimental studies<sup>5,6</sup> suggest that this method is probably technically feasible and, in some respects preferable to leaching with fluoride. The  $Ce^{4+}$ - $HNO_3$  is about as effective as fluoride in accelerating the dissolution of all transuranic actinides but does not dissolve or greatly soften the HEPA filter waste. Fluoride converts the fiberglass into a viscous, sticky mass and totally dissolves the incinerator ashes, whereas the ceric acid does not affect the fiberglass and only partially dissolves the incinerator ashes. In terms of decontamination, the ceric acid has achieved 99.99% dissolution of all actinides in the filter media; however, as much as 5% of the alpha activity initially in the incinerator ashes does not dissolve.

#### Cation Exchange Chromatography

Separation of the actinides and, in particular, the trivalent actinides from the lanthanides is accomplished by cation exchange chromatography (CEC).<sup>7</sup> A number of small batches must be run in parallel in order to deal with the large quantities of curium and associated heat that build up due to the recycle of the transuranics. Conceptually, this problem is dealt with by a modular approach in the design of cation exchange racks. Each rack (or module) consists of a single sorption column and two elution columns mounted on a balanced frame that has overall dimensions about the size of an office file cabinet. In this manner, the number of watts per batch of radioactive material loaded onto the module is kept acceptably small.

The experimental work relating to this processing area has focused on identifying any interactions between the CEC area of the WTF and the HLLW Treatment area that produces the CEC feed, and on determining the elution sequence for the tetravalent actinides.<sup>8</sup> The expected impurities in the feed to the CEC will not significantly affect system performance, and there is no evidence that CEC feed adjustment beyond the control of acidity level is necessary. Also, results of tests have confirmed that the tetravalent actinides will

elute ahead of the barrier ion in CEC; therefore, these elements will report to the Salt Waste Treatment system as desired.

Although CEC is capable of a very high degree of actinide partitioning, its principal disadvantage lies in the high rate of ion exchange resin replacement caused by radiation degradation.

### Salt Waste Treatment

Both alkaline and acidic salt wastes are produced during fuel reprocessing and refabrication. The most important of these, with respect to actinide losses, is the alkaline sodium carbonate scrub solution that is generated during the cleanup of tributyl phosphate (TBP) for recycle. This waste may contain up to 0.5% of the actinides in the feed. Difficulties have also been experienced with the alkaline detergent wastes containing surfactants that extract into TBP and the sodium carbonate scrub wastes resulting from CMP recycle and cleanup.

A process was developed to recover actinides from these wastes that consists of first acidifying them and then contacting them with 2-ethylhexanol.<sup>9</sup> This alcohol extracts the acidic degradation products such as dibutyl and monobutyl phosphoric acids but leaves the actinides in the raffinate. Subsequently, the raffinate may be contacted with TBP and CMP for actinide recovery since it no longer contains those acidic degradation products that would interfere with the separation. The alcohol extractant, containing the degradation products and detergents, is recycled after the acidic species have been removed by washing with sodium carbonate.

### Actinide Recovery

Both WTFs require an Actinide Recovery area where actinides are recovered from the liquors being produced in the above-mentioned separation processes. The WTF supporting the fuel reprocessing plant requires both TBP and CMP extraction cycles, but the WTF supporting the fuel refabrication plant can be operated with a CMP extraction cycle alone by utilizing the existing, on-site TBP scrap recovery system.

In each case, the various actinide-bearing liquors are concentrated, acidified, and clarified by centrifugation as needed. Subsequently, the concentrate is contacted with TBP and then with CMP. The raffinate, now essentially actinide-free, is further concentrated and denitrated with formic acid; the resulting slurry is then converted to a concrete and packaged in drums. The TBP is stripped in the usual manner, and the recovered actinides are sent back to the main processing facility. The CMP is stripped in two columns, similar to the operation of the HLLW treatment strip columns, to recover the stable cerium and gadolinium for recycle to the Solid Alpha Waste Treatment area. Low concentrations of trivalent actinides are maintained in the cerium recycle stream by bleeding a fraction of this stream to the CEC system. Thus, the major differences between the Actinide Recovery area and the HLLW Treatment area are the somewhat higher levels of radioactivity in the latter system.

#### Miscellaneous Support Systems

Both TBP and CMP solvents are cleaned with water and sodium carbonate washes and then equilibrated with acid before they are recycled. This treatment aids in the operation of the extraction columns and also serves to strip the ruthenate and pertechnetate anions from the CMP solvent. Activity levels are controlled in the Actinide Recovery Area by bleeding a fraction of the CMP to the HLLW Treatment Area; a small fraction of the CMP from the HLLW Treatment Area is sent to the on-site solvent burner.

Both WTFs require extensive off-gas treatment. Acid denitration requires the recovery of nitrogen oxides. Ruthenium absorption beds are provided in the event of ruthenium volatilization in the Solid Alpha Waste Treatment areas. The WTF associated with a fuel reprocessing plant will also require iodine retention systems. Both WTFs utilize HEPA filtration and catalytic destruction of  $\text{NO}_x$ .

Extensive acid and water recycle is carried out in both WTFs. The process streams generated internally are voluminous, have low levels of alpha activity, and contain large quantities of dissolved solids. Thus, large quantities of dilute acid and water need to be recycled as evaporator overheads.

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