Selection and Evaluation of Processes for Recovery of Beneficial Isotopes from Commercial Reactor Wastes

by
D. K. Davis
J. A. Partridge
O. H. Koski

December 1977

Prepared for the
U.S. Department of Energy
under Contract EY-76-C-06-1830

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, 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.

The views, opinions and conclusions contained in this report are those of the contractor and do not necessarily represent those of the United States Government or the United States Department of Energy.

PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.50
026-050	\$5.00
051-075	\$5.50
076-100	\$6.00
101-125	\$6.50
126-150	\$7.00
151-175	\$7.75
176-200	\$8.50
201-225	\$8.75
226-250	\$9.00
251-275	\$10.00
276-300	\$10.25

3 3679 00062 4827

SELECTION AND EVALUATION OF
PROCESSES FOR RECOVERY OF
BENEFICIAL ISOTOPES FROM
COMMERCIAL REACTOR WASTES

by
D. K. Davis
J. A. Partridge
O. H. Koski

December 1977

PACIFIC NORTHWEST LABORATORY
OPERATED BY BATTELLE MEMORIAL INSTITUTE
RICHLAND, WASHINGTON 99352

SUMMARY

Conceptual processes were prepared for recovering isotopes from stored high-level liquid wastes to define equipment and facility requirements. Capital costs were estimated for each process. Four different facilities were studied for potential isotope recovery. The processes were for the recovery of:

- 1) cesium only
- 2) strontium only
- 3) cesium and strontium, and
- 4) cesium, strontium, promethium, americum, curium, neptunium, and the platinum metals.

The selection of these recovery processes was determined by their possible effect on the waste management system. The isotope recovery processes selected tended to have a minimal effect on this system.

Preliminary capital investment costs for the four types of facilities processing HLLW from a 5 MT/day reprocessing plant were estimated to be:

- \$37 million for a cesium or a strontium recovery facility
- \$51 million for a facility recovering cesium and strontium, and
- \$143 million for a multi-product facility.

In all cases the recovery facility was assumed to be closely integrated with a fuel reprocessing plant and designed along with the reprocessing plant.

Recovery costs were estimated for the various products, assuming 50% recovery from the HLLW for all of the products, except the platinum metals; 25% recovery was assumed for these metals. In general, product price estimates (in 1977 dollars) assumed a market for all of the recovered materials. Estimates for cesium ranged from 45¢/Ci of ¹³⁷Cs (at 69 MCi/yr) in a cesium-only recovery facility to 31¢/Ci in a plant recovering both cesium and strontium. Strontium estimates ranged from 60¢/Ci of ⁹⁰Sr (at 51 MCi/yr) in a strontium-only recovery facility to 42¢/Ci in a cesium and strontium recovery facility.

CONTENTS

SUMMARY	iii
INTRODUCTION	1
RECOVERY PROCESS	3
CESIUM.	3
STRONTIUM.	6
CESIUM AND STRONTIUM	8
INTEGRATED FLOWSHEET	9
Neptunium	9
Platinum Metals	11
Cesium and Strontium	12
Promethium, Americium, and Curium	12
IMPACT ON WASTE MANAGEMENT	13
PRODUCTION COST ESTIMATE	15
CONCLUSIONS.	23
REFERENCES	24

FIGURES

1	Concept for Cesium Recovery	4
2	Concept for Strontium Recovery	8
3	Concept for Recovery of Both Cesium and Strontium at a Single Facility	9
4	Concept for Multi-Isotope Recovery Plant	10

TABLES

1	Cesium Recovery by Ion Exchange	5
2	Strontium Recovery by Ion Exchange	8
3	Capital Costs for a Cesium or a Strontium Recovery Plant	17
4	Cost Estimate for Cesium Recovery	18
5	Cost Estimate for Strontium	18
6	Capital Costs for a Recovery Plant for Cesium and Strontium	19
7	Cost Estimates for Cesium and Strontium Produced in a Single Recovery Plant	20
8	Capital Costs for a Multi-Product Plant	20
9	Cost and Production Estimates for a Multi-Product Isotopes Recovery Plant	21
10	Cost Estimates for Products from a Multi-Product Recovery Plant - 25% Market	22
11	Cost Estimates for Products from a Multi-Product Recovery Plant - 100% Market	22

SELECTION AND EVALUATION OF PROCESSES FOR RECOVERY OF BENEFICIAL ISOTOPES FROM COMMERCIAL REACTOR WASTES

INTRODUCTION

High-level liquid waste (HLLW) from nuclear fuel reprocessing contains several isotopes which have potential value. Two isotopes that have received considerable attention for potential beneficial applications are cesium-137 (as a gamma irradiation source) and strontium-90 (as a heat source). Other elements having isotopes with potential value include neptunium (Np), promethium (Pm), americium (Am), curium (Cm), technetium (Tc), and the platinum metals, rhodium (Rh), palladium (Pd), and ruthenium (Ru).

Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute for the Department of Energy (DOE), developed preliminary conceptual flowsheets to define equipment and facilities required to recover these isotopes from stored HLLW. Approximate nuclide costs were also estimated. This report summarizes the results of that study.

Although the fission products krypton (Kr) and xenon (Xe) have potential value and evolve from spent reactor fuel early during fuel reprocessing, they were not considered in this study. The economic feasibility of their recovery appears to depend on regulatory decisions (whether or not to require recovery of ^{85}Kr) that have not yet been finalized.

Processing concepts were prepared for the recovery of:

- 1) cesium only,
- 2) strontium only,
- 3) cesium and strontium in a single plant, and
- 4) Cs, Sr, Np, Pm, Am, Cm and the fission product precious metals in one multi-product plant.

Isotope production costs were estimated for the facilities utilizing these recovery concepts based on extrapolations of the basic cost figures

reported for a curium and a curium-neptunium recovery facility at the Barnwell Nuclear Fuel Plant.⁽¹⁾ In this estimate, as in Reference 1, it was assumed that the facilities would process all of the HLLW from a 5-tonne/day fuel reprocessing plant for by-product recovery. It was also assumed that the waste would be stored for three years prior to processing.

These recovery concepts were not limited to proven technology; some are based on processes demonstrated in some cases only in the laboratory. Further R&D will be required to fully define the processes. In choosing the processes, prime emphasis was given to minimizing the impact of the isotope recovery on management of the HLLW (i.e., on waste solidification). The considerations were to allow a minimum of nonvolatile chemicals, a minimum of chemicals which hamper glass formation, and a minimum of chemicals which act to increase the volume of waste produced. Time constraints were not considered in evaluating these processes. The study's objective was not to recommend specific operational flowsheets, but to identify potential isotope recovery processes. The use of alternative concepts would not greatly affect most of the cost estimates.

RECOVERY PROCESSES

Four process concepts were prepared for the recovery of various isotopes from stored HLLW resulting from nuclear fuel reprocessing. Using these concepts, preliminary cost estimates were made for the recovery of the various products. All four concepts use inorganic cation exchangers for cesium and strontium recovery and solvent extraction processes for recovery of the other products, except the platinum metals; the platinum metals are recovered from the solids separated from the HLLW. These concepts all require additional research and development work to be suitable for plant application.

CESIUM

Possible techniques for recovering cesium from HLLW fall into three categories: precipitation, solvent extraction, and ion exchange. In this study, all three of these types of processes were considered. However, the precipitation and solvent extraction processes in general were rejected because of their adverse effect on waste management, due to the added chemicals and/or because they are not effective in the acid range easily obtainable in HLLW. The acidity of denitrated HLLW can be reduced by caustic addition with complexants added to minimize solids formation. This, however, has an adverse effect on the waste management process. Therefore, ion exchange was selected as the process of choice for cesium recovery (Figure 1).

The first of three operations in this cesium recovery process is to reduce the nitric acid concentration in the HLLW to approximately 1M to permit efficient sorption of cesium by the ion exchanger. Direct neutralization with caustic cannot be considered because the enormous quantity of sodium required would adversely affect final waste solidification (fluidized bed calcination and glass making) and also interfere with cesium sorption by the exchanger. Denitration of a solution such as the HLLW with 1M sucrose at 100°C has been demonstrated to be a safe, reliable process and is recommended for this application.⁽²⁾ The denitration is terminated at 1M HNO_3 to avoid the formation of excessive solids.

FIGURE 1. Concept for Cesium Recovery

The second phase of cesium recovery is feed clarification. Stored HLLW will contain suspended solids, principally compounds of zirconium, molybdenum, the platinum metals and insoluble phosphates.⁽¹⁾ As the acid concentration is reduced by denitration, additional solids (mostly platinum metals) will be formed.⁽¹⁾ Because solids cause plugging in ion-exchange beds, a feed clarification step is required, which could be performed by centrifugation.

The third phase of this process is to remove cesium from the aqueous stream with an ion exchanger. Inorganic exchangers have at least two advantages over organic ion exchange resins. First, they are more resistant to radiation damage, and second, several have greater selectivity for cesium than do the organic resins. Kourism and Vijtech⁽³⁾ have reviewed the selectivity for cesium of some phosphate exchangers and salts of heteropoly acids, such as the phosphotungstates.

Factors influencing the choice of an exchanger include availability, the exchanger's selectivity for cesium, its mechanical stability in the acid environment, and the eluant required. An eluant should be selected that would have a minimum impact on the waste management process. In a preliminary study of cesium sorption from acid HLLW solutions,⁽⁴⁾ encouraging results were obtained with a titanium phosphate exchanger, ABEDEM TiA.^(a) Additional R&D will be required to determine the optimum inorganic exchanger for cesium removal.

In our study of cesium recovery, ABEDEM TiA was selected as the ion exchanger. This process is conservatively assumed to recover 50% of the available cesium or 69 MCi/year (0.787 MT/yr).⁽⁵⁾ The resin has a capacity of 29.8 gCs/ ℓ resin.⁽⁴⁾ Allowing a safety factor of 33%, to ensure proper recovery, the required volume of resin is 304 ℓ . The HLLW flows through the column at the rate of 5 column volumes/hr. The loaded column is then washed, using 4 column volumes of 0.5M nitric acid. The cesium is eluted from the column, using 6 column volumes of a 5M NH_4NO_3 - 0.1M HNO_3 solution. The eluate is treated further to convert cesium to the final form. The column is regenerated using 5 column volumes of 1M HNO_3 .

The actual operating conditions for the cesium recovery process will be obtained during an in-depth study to determine if ABEDEM TiA is the exchanger to be actually used. Table 1 gives some of the estimated process information.

TABLE 1. Cesium Recovery by Ion Exchange

Column Size	50.78 Cm ID.x 150 Cm
Exchanger Volume	304 ℓ
% Cesium Loaded	53
% Cesium Eluted	95
Cesium Loading	29.8 g/ ℓ Exchanger ⁽⁴⁾
Recovery	50%
Cycle Time	8 hr

^(a) $\text{\textcircled{R}}$ SERAI group, Brussels⁽⁶⁾

STRONTIUM

Strontium could potentially be recovered by precipitation, solvent extraction, or ion exchange processes.

Co-precipitation of strontium and rare earth sulfates, with lead sulfate as a carrier, was developed and implemented on a large scale at Hanford for removing strontium from acidic Purex process waste. The process involved adjusting the acidity to pH 1 and adding a complexing agent to prevent co-precipitation of iron. The precipitated product was metathesized by NaOH or Na_2CO_3 and further processed by ion exchange or solvent extraction to produce a purified strontium product. From an operational standpoint, the complexity of this approach makes precipitation the least desirable of the processes considered.

Solvent extraction has also been used to remove strontium from Purex waste. The most frequently used solvent has been di-(2 ethylhexyl) phosphoric acid (HDEHP). However, use of HDEHP requires that complexants be added and the aqueous stream be buffered in the pH range of 4 to 6. These added chemicals would have an adverse impact on waste management. Similarly, other solvent extractants require aqueous phase complexants and a buffered solution. Thus, solvent extraction does not appear attractive for this application, although it is more desirable than precipitation.

The ion exchange process proved to be the most desirable of the three processes for strontium recovery. Both organic resins and inorganic ion exchangers were reviewed for the extraction of strontium.⁽⁷⁻¹¹⁾ Inorganic exchangers were shown to be preferable.

The disadvantages of organic ion exchangers for this application are that they are damaged by radiation and are not selective for strontium, nor are they effective for strontium sorption from an acid medium. A strontium recovery process using organic resins generates a significant amount of contaminated chemical waste. At Hanford, for example, Dowex 50W, X-12 has been used for purifying a crude strontium fraction.⁽¹¹⁾ To prevent the uptake of cerium, iron, lead, zirconium and niobium by the resin during the adsorption cycle, a complexant was added. The acidity was adjusted to pH 4

by the addition of caustic. Elution took place through a series of columns in the Ca^{2+} or Y^{3+} form (Ca^{2+} or Y^{3+} serving as "barrier ions") with EDTA and HEDTA eluant solutions. These added complexants and sodium ions affected the waste management system by adding chemicals to the waste stream.

Recovery of strontium from HLLW by means of an inorganic cation exchanger appears to be the most desirable method, and polyantimonic acid is a promising exchanger. It shows selectivity for the strontium ions present in HLLW and is effective in an acid medium. Because it is inorganic, polyantimonic acid is also resistant to radiation damage. Its disadvantage is that elution of strontium from polyantimonic acid is relatively difficult. Solutions of silver or lead nitrates have proved effective as strontium eluants from this exchanger. It is then possible to separate the strontium values from the eluate and recycle the eluant ion. Further R&D is required to develop the technology necessary for in-plant use of this exchanger for strontium recovery.

The concept for strontium recovery from HLLW is shown in Figure 2. It is similar to that for cesium recovery: a denitration step to lower the acid concentration, a feed clarification step, and a selective removal of strontium by an inorganic cation exchanger. The denitration and feed clarification steps are required in this process for the same reasons that they are needed in cesium recovery (discussed in the preceding section).

The process conservatively assumes 50% recovery of the available strontium, 51 MCi or 0.37 MT/yr.⁽⁵⁾ The polyantimonic acid exchanger has a strontium capacity of 17 g/l exchanger.⁽¹²⁾ The required volume of exchanger is 234 l. Due to the slow strontium adsorption-desorption kinetics of the exchangers, there is a need for two columns operating on cycles independently of each other; each processes 1 day's feed. The feed solution flows through the column at the rate of 210 l/hr. The loaded column is washed using 5 column volumes of 2M HNO_3 acid. Strontium is eluted from the column using 17.5 column volumes of a 2M $\text{Pb}(\text{NO}_3)_2$ - 1M HNO_3 solution. Using 20 column volumes of 6M HNO_3 , the exchanger is regenerated to 80% capacity. Estimated system information is given in Table 2, based on the very limited amount of process R&D reported in the literature for this exchanger.

FIGURE 2. Concept for Strontium Recovery

TABLE 2. Strontium Recovery by Ion Exchange

Column Size	44.5 Cm ID x 150 Cm (2 sets)
Exchanger Volume	234 ℓ
% Sr Loaded	59
% Sr Eluted	84.5
Sr Loading	17 g/ℓ Exchanger ⁽¹²⁾
Recovery	50%
Cycle Time	45 hr

This adsorbent has not been well studied. Additional work in the area of strontium recovery from acid solution is needed to find an adsorbent with better kinetics. The slow kinetics of the polyantimonic acid severely hampers its use.

CESIUM AND STRONTIUM

For recovery of both cesium and strontium at a single facility, the two concepts previously discussed could be combined into one facility, as

shown in Figure 3. The raffinate from cesium recovery would serve as feed to the strontium recovery process.

FIGURE 3. Concept for Recovery of Both Cesium and Strontium at a Single Facility

INTEGRATED FLOWSHEET

A concept for recovery of selected isotopes in addition to cesium and strontium is shown in Figure 4. Recovery processes are included in this flowsheet for neptunium, the platinum metals, promethium, americium, and curium.

Neptunium

Neptunium is removed from the HLLW by a solvent extraction system using 30% tri-n-butylphosphate (TBP) in a normal paraffin hydrocarbon (NPH) diluent. This is the process proposed by Wheelwright et al. for plutonium, neptunium and uranium removal from HLLW, in conjunction with a curium recovery process.⁽⁵⁾ To obtain sufficiently pure neptunium, an ion exchange cycle will likely be required, in addition to two 30% TBP-NPH solvent

FIGURE 4. Concept for Multi-Isotope Recovery Plant

extraction cycles. Because solids cause operational difficulties in solvent extraction processing, the initial step involves removal of solids from HLLW by centrifugation.

The individual processing steps are based on the Hanford Purex Plant solvent extraction flowsheet for neptunium concentration, decontamination and purification. A detailed description of this process is given by Wheelwright et al.⁽⁵⁾ An anion exchange process for removal of neptunium and plutonium from HLLW is also discussed by Wheelwright et al., but it seemingly has no advantage over the solvent extraction process.

Platinum Metals

The proposed method for recovery of the platinum metals from HLLW, as shown in Figure 4, is by processing the collected solids. These solids include those which were initially present in the HLLW and those produced during the denitration step. Both types of solids contain some of the fission product platinum metals. However, data is lacking which would define the percentage of the total platinum metals expected in the solids. Thus, further measurement of the platinum metal content is needed. In the absence of such data, it is estimated that 25 to 75% of the fission product platinum metals will be in these solids. Additional R&D will be required to develop processes for recovery and isolation of the platinum metals.

Recovery of the soluble fraction of the platinum metals from HLLW is not believed to be practical. With the current market, extensive processing is not economically viable. It is possible that most of the platinum metals could be removed from the HLLW with the solids, so that the soluble platinum species might represent only a small fraction of the total platinum metals. However, even if most of these metals are soluble, there is no economically attractive method for their recovery from an acidic nitrate solution. There is the possibility of adding an oxidizing agent and distilling volatile RuO_4 ⁽¹³⁾ and Tc_2O_7 ,⁽³⁾ but successful removal of these metals, as well as rhodium and palladium, has not been demonstrated. Methods have been

demonstrated for removing precious metals from alkaline waste solutions,⁽¹⁴⁻¹⁷⁾ but neutralization of the HLLW for recovery of these products does not appear warranted.

The denitration operation should be carried out in a manner which will maximize recovery of the platinum metals on the solids formed. Additional R&D will be required to define the optimum operating conditions. R&D may also demonstrate that small chemical additions during this operation will increase the yield of platinum metals.

Cesium and Strontium

The cesium and strontium recovery processes in this integrated flow-sheet would be the same as those previously discussed.

Promethium, Americium, and Curium

The concept chosen for recovery of Pm, Am, and Cm involves the use of solvent extraction for removal from HLLW and for the partial separation of many of the lanthanides from these three products. These solvent extraction processes are envisaged as operating with nitric acid solutions (containing no added complexants) so that no nonvolatile materials will be added to the HLLW during the operations. Solvents considered for such operations include 100% TBP and diluted extractants, such as phosphonates (e.g., dibutylbutyl phosphonate, DBBP), phosphinates (e.g., butyldibutyl phosphinate, BDBP), and bidentate organophosphorus compounds (e.g., dihexyl-N, N-dimethylcabamylmethylene phosphonate, DHDECMP).^(5,22) While the concept shown in Figure 4 involves solvent extraction of the Am, Cm and lanthanides from the HLLW after Cs and Sr have been removed, the optimum integrated process could well involve a reverse order; that is, the Am, Cm, and lanthanides could be extracted from the HLLW prior to denitration and Cs and Sr removal operations.

Final purification of the Am, Cm, and Pm is achieved by cation exchange chromatography employing complexants and a solution buffered at a pH of about 8.6.^(18, 19, 20) Because of the partial separation of many of the lanthanides achieved in the solvent extraction processes, the amount of complexant required is markedly reduced and the quantity of sodium ion required for

pH adjustment could fall below the amount required for conversion of the HLLW into a desired glass composition. While it may be possible to obtain complete separation of Am, Cm, and Pm without using complexants, it would be highly speculative to propose such separations at this time.

IMPACT ON WASTE MANAGEMENT

The conceptual flowsheets discussed in the previous sections require additional R&D to adequately assess their impact on waste solidification processes. For example, further work is necessary to determine which eluants and other process chemicals can be recycled. In general, these isotope recovery processes were selected with the main objective being to minimize the amount of chemicals added to the HLLW during the recovery processes. Thus, any adverse effect on calcination and glass-making would be minimized.

PRODUCTION COST ESTIMATES

Estimates of production costs for the various isotopes were made based on extrapolations from the basic cost figures presented by Carney⁽¹⁾ for curium and for curium-neptunium recovery plants. The flowsheet of Wheelwright et al,⁽⁵⁾ discussed earlier in this report was developed for these plants. Carney's costs were based on flowsheet and process descriptions, and on plant designs provided by an architectural engineering firm (AE). A detailed cost analysis by an AE is beyond the scope of this study, therefore the Carney report was used as a reference point.

While there are certain risks in estimating plant costs based on cost figures of another plant using different flowsheets, we felt that this was a reasonable approach for making very preliminary estimates of the production costs for the four facilities considered here. The feed solution to each plant is the same (HLLW), and many of the chemical processing unit operations are the same or are very similar (i.e., ion exchange, solvent extraction, denitration, etc.). Thus, the shielding and types of process cells and equipment for the plants based on our concepts would be similar to those used in the curium and curium-neptunium plants.

The capital cost estimates for the plants in this study were based on the assumption that our isotope recovery plants would be processing HLLW from a 5-MT/day reprocessing plant. It was also assumed that the waste would be aged 3 years before being processed for isotope recovery. Thus, our recovery plants would have the same operating capacity as the reference (curium and curium-neptunium) plants. The following factors were then used to estimate costs, based on analysis of the reference plants and their costs (including contingencies):

- 1) volumes of process space were computed for each identified chemical unit operation or process in the reference plants.
- 2) volumes were computed for auxiliary space, such as operating galleries, control rooms, offices, etc., in the reference plants.
- 3) an estimate was made of the cost of process volume with contained equipment (~\$40/ft)(1974 dollars).

- 4) an estimate was made of the cost of auxiliary and support space ($\sim \$20/\text{ft}^3$)(1974 dollars).
- 5) estimates were made of the volume of process space required by the various segments (unit operations) and expressed as a factor of that used in with the reference plants.
- 6) the following formula, which involves the basic costs of $\$40/\text{ft}^3$ for process space including equipment and $\$20/\text{ft}^3$ for auxiliary and support space, was developed:

For each chemical unit operation:

$$\text{Unit Operation Cost} = \$40(\text{Process Vol in ft}^3) + \$20(\text{Aux. Vol})$$

For the total plant:

$$\text{Total Plant Cost} = \sum (\text{Unit Operation Cost})$$

where:

$$\text{Auxiliary volume} = 4 \times \text{Process volume}$$

- 7) for the encapsulation facilities, a flat addition of \$8.4 million per product was made, based on the cost of the neptunium encapsulation facility in the reference plant.

The total estimated cost using the above relationship was $\$24/\text{ft}^3$ of plant volume. The average cost per ft^3 for the reference curium plant was $\$22.8/\text{ft}^3$ and for the reference curium-neptunium plant was $\$22.7/\text{ft}^3$; each one being slightly less than the estimated cost based on our formula. Although estimating total plant costs on the basis of process volume may appear to be a hazardous method, the ratio of equipment costs to total building costs is roughly one-third or less. Therefore, the cost for a given size unit operation is surprisingly stable with respect to variations in process equipment.

Using the method outlined above for estimating capital costs, the values shown in Table 3 were obtained for a cesium or a strontium recovery plant (see Figures 1 and 2 for flowsheets). A plant cost of \$36.7 million was obtained after applying an escalator factor of 36% to convert April 1974

dollars (reference plant cost basis) to December 1977 dollars. The escalation factor was obtained by using Engineering News Report index values.

TABLE 3. Capital Costs for a Cesium or a Strontium Recovery Plant

<u>Unit Operation</u>	<u>Reference Plant Cost (millions, 1974\$)</u>	<u>Factor</u>	<u>Strontium or Cesium Plant Cost (millions, 1974\$)</u>
HLLW Pumps and Exchangers	9.6	1	9.6
HLLW Concentrators	1.1	0.5	0.6
HLLW Treatment	2.9	0.5	1.5
HLLW Denitration	5.2	1.0	5.2
Ion Exchange	3.4	0.5	1.7
Encapsulation	8.4	1	<u>8.4</u>
	Sub-Total		27.0
Escalator, 1974 dollars to 1977 dollars (+36%)			+ <u>9.7</u>
	Total Cost		36.7

In comparison, McKee⁽²¹⁾ made a detailed analysis of the economics of ^{137}Cs and ^{90}Sr recovery by private industry. In that analysis the cesium recovery plant (29 MCi/yr ^{137}Cs) was smaller than the one considered here. Updating the capital investment from 1970 dollars and using the capacity cost scaling technique supplied by McKee, a capital investment of \$37.2 million was estimated for a 69 MCi/yr ^{137}Cs plant.

For the reference plant, the ratio of annual sales to initial capital costs required to yield 10-year profitability was 0.84. Applying this ratio to a cesium or strontium recovery plant costing \$36.7 million, required annual sales were estimated at \$30.8 million (1977\$).

Table 4 shows the price per curie of ^{137}Cs required to yield annual sales of \$30.8 million, depending on the size of the market. A conservative estimate of 50% cesium recovery^(a) was used [137 MCi of ^{137}Cs /year in the

(a) While a 50% recovery rate is considered conservative for this type of process, a process developed to give high recovery (90-100%) would probably be uneconomical.

HLLW, which was cooled for 3 years].⁽⁵⁾ Assuming a market for 100% of production results in a cost of \$0.45/Ci of ^{137}Cs . As the market decreases the cost per curie of cesium increases.

TABLE 4. Cost Estimate for Cesium Recovery

Cesium Plant Costs	\$36.7 million
Required Annual Sales to Give 10-yr Profitability	\$30.8 million
Annual Production (Assuming 50% Recovery)	69 MCi

<u>Market as a Percent of Production</u>	<u>MCi</u>	<u>\$/Ci ^{137}Cs</u>
100%	69	0.45
75%	52	0.59
50%	34.5	0.89
25%	17	1.81

Table 5 shows a similar analysis for ^{90}Sr . In this case, a price of \$0.60/Ci of ^{90}Sr is estimated, assuming: 1) a market for 100% of production, and 2) 50% strontium recovery from the HLLW.

TABLE 5. Cost Estimate for Strontium

Strontium Plant Costs	\$36.7 million
Required Annual Sales to Give 10-yr Profitability	\$30.8 million
Annual Production (Assuming 50% Recovery)	51 MCi

<u>Market as a Percent of Production</u>	<u>MCi</u>	<u>\$/Ci of ^{90}Sr</u>
100%	51	0.60
75%	38	0.81
50%	25	1.23
25%	13	2.37

Table 6 shows the estimated costs for a plant recovering both cesium and strontium (see Figure 3 for flowsheet). The main difference between this plant and a plant for either cesium or strontium recovery is an additional ion exchange facility and an additional encapsulation facility. The total estimated capital cost for this plant is \$50.6 million, as shown in Table 6. Updating McKee's⁽²¹⁾ cesium and strontium plant (29 MCi/year of ¹³⁷Cs and 28 MCi/year of ⁹⁰Sr) results in a capital cost of \$50.2 million for a plant producing 69 MCi/year of ¹³⁷Cs and 51 MCi/year of ⁹⁰Sr. Our estimate corresponds well to the estimate made by McKee.⁽²¹⁾

TABLE 6. Capital Costs for a Recovery Plant
for Cesium and Strontium

<u>Unit Operation</u>	<u>Reference Plant Cost (millions, 1974\$)</u>	<u>Factor</u>	<u>Cs/Sr Plant Cost (millions, 1974\$)</u>
HLLW Pumps and Exchangers	9.6	1	9.6
HLLW Concentrators	1.1	0.5	0.6
HLLW Treatment	2.9	0.5	1.5
HLLW Denitration	5.2	1	5.2
Ion Exchange	3.5	1	3.5
Encapsulation	8.4	2	<u>16.8</u>
	Sub-Total		37.2
	Escalator, 1974 dollars to 1977 dollars (+36%)		<u>+ 13.4</u>
	Total Cost		50.6

The estimated costs for cesium and strontium are somewhat reduced if they are both produced at the same recovery plant, (Table 7 compared to Tables 4 and 5). The cesium price would range from \$0.31 to \$1.25/Ci of ¹³⁷Cs as the market varied from 100% to 25% of production. This is approximately 30% lower than the estimated costs of cesium from a cesium-only recovery plant. Strontium-90 prices are estimated to range from \$0.42 to \$1.63 as the market decreases from 100% to 25% of production. McKee⁽²¹⁾ included a detailed market/product price analysis which, when updated, resulted in similar price ranges.

TABLE 7. Cost Estimates for Cesium and Strontium
Produced in a Single Recovery Plant(a,b)

Market as a Percent of Production	MCi ¹³⁷ Cs	MCi ⁹⁰ Sr	1977\$/Ci ¹³⁷ Cs	1977\$/Ci ⁹⁰ Sr
100%	69	51	0.31	0.42
75%	52	38	0.41	0.56
50%	34.5	25	0.62	0.85
25%	17	13	1.25	1.63

(a) Bases:	Plant Costs	\$50.6 million
	Required Sales to Give 10-yr Profitability	\$42.5 million
	Annual Production (Assuming 50% Recovery)	69 MCi ¹³⁷ Cs 51 MCi ⁹⁰ Sr

(b) Assumptions: 1/2 of Sales for each isotope

Table 8 shows the estimated capital costs for an integrated plant recovering multiple products (flowsheet on Figure 4). The total capital costs for such a plant are estimated to be \$143.3 million.

TABLE 8. Capital Costs for Multi-Product Plant^(a)

Unit Operation	Reference Plant Cost (millions, 1974\$)	Factor	Multi-Product Plant Cost (millions, 1974\$)
HLLW Pumps and Exchangers	9.6	1	9.6
HLLW Concentrators	1.1	1	1.1
HLLW Treatment	2.9	1	2.9
HLLW Denitration	5.2	1	5.2
Solvent Extraction	3.8	3	11.4
(Auxiliary)	3.2	2	6.4
Platinum Metals Recovery Process	--	--	3
Ion Exchange	3.5	2	7.0
Encapsulation	8.4	7 ^(a)	58.8
		Sub-Total	105.4
		Escalator, 1974 dollars to 1977 dollars (+36%)	+ 37.9
		Total Cost	143.3

(a) Cesium, strontium, platinum metals, curium, promethium, neptunium, and americium.

Table 9 shows the cost and isotope production estimate for a multi-product facility using the conceptual flowsheet. For the purpose of making some cost estimates, we have assumed two scenarios. In the first, shown in Table 10, we have assumed that there will be a market for four of the products and no market for the other three products, and that each of the four must bring in 1/4 of the required annual sales. The cost of each of the products shown in Table 10 is based on each product being one of the four for which there is a market.

TABLE 9. Cost and Production Estimates for a Multi-Product Isotopes Recovery Plant

Plant Costs	\$143.3 million
Required Annual Sales to Give 10-yr Profitability	\$120.4 million
Annual Production (Assuming 50% Recovery)	69 MCi ¹³⁷ Cs 51 MCi ⁹⁰ Sr 1.41 MCi ²⁴⁴ Cm 0.89 MCi ²⁴¹ Am .360 kg ²³⁷ Np 25 MCi ¹⁴⁷ Pm
(Assuming 25% Recovery)	1940 kg Ru, Rh, Pd, Tc

TABLE 10. Cost Estimates for Products from
a Multi-Product Recovery Plant -
25% Market(a)

<u>Product</u>	<u>Cost (\$)</u>
¹³⁷ Cs	0.44/Ci
⁹⁰ Sr	0.59/Ci
²⁴⁴ Cm	21.3/Ci
²⁴¹ Am	33.8/Ci
²³⁷ Np	83.6/g
¹⁴⁷ Pm	1.20/Ci
Ru, Rh, Pd, Tc	15.5/g

- (a) Assumptions:
- Four products will pay off and three will not.
 - Each of the four must bring in sales of \$120.37/4 million or \$30.1 million.
 - A market exists for 100% of the production of each of the four.

In the second scenario, we assume that there is a market for 100% of the production of each of the seven products and that each product produces one-seventh of the required annual sales. The cost estimates based on this scenario are shown in Table 11.

TABLE 11. Cost Estimates for Products from a Multi-Product
Recovery Plant - 100% Market(a)

<u>Product</u>	<u>Cost (\$)</u>
¹³⁷ Cs	0.25/Ci
⁹⁰ Sr	0.34/Ci
²⁴⁴ Cm	12.2/Ci
²⁴¹ Am	19.3/Ci
¹³⁷ Np	47.7/g
¹⁴⁷ Pm	0.69/Ci
Ru, Rh, Pd, Tc	8.8/g

- (a) Assumptions:
- A market exists for 100% of production of each of the seven products.
 - One-seventh of total sales come from each product -- \$120.37 million = \$17.2 million

CONCLUSIONS AND RECOMMENDATIONS

The results of this study show that beneficial isotopes could be recovered from HLLW with minimal impact on waste calcination and vitrification. For the four facility types studied, three techniques were considered for recovering the isotopes: precipitation, solvent extraction and ion exchange.

For ^{137}Cs recovery, ion exchange with ABEDEM TiA exchanger seemed to be the best method. In recovering ^{90}Sr , the inorganic cation exchanger polyan-timonic acid appeared to be the most promising. These two methods could be combined to recover both cesium and strontium in series with the raffinate from the ^{137}Cs recovery serving as the feed to the ^{90}Sr recovery process.

This study indicates that a multi-isotope recovery facility is also possible. To recover Np, a solvent extraction system based on the Purex process seems the most practical. For Pm, Cm, and Am, solvent extraction with nitric acid solutions for crude cuts combined with cation exchange using complexants for the fine cuts appears to be the best recovery technique. Recovering the platinum metals could be possible by processing the collected solids from HLLW processing.

Estimates of process costs are only preliminary. They indicate the probable magnitude of selling price required for recovery of beneficial isotopes from HLLW.

Although the recovery processes are promising, further research and development is needed to precisely define these processes and to develop accurate cost estimates to determine if the recovery of the isotopes is economically worthwhile. Included in such research should be an analysis of the potential market for these isotopes.

REFERENCES

1. H. C. Carney, Editor, Curium-244/Neptunium-237 Recovery from the Barnwell Nuclear Fuel Plant. GA-A13348, General Atomic Company, San Diego, CA 92138, February 1975.
2. E. A. Coppinger, Pilot Plant Denitration of Purex Waste with Sugar. HW-77080, General Electric Company, Richland, WA 99352, March 1973.
3. V. Kourim and O. Vojtech, "Methods of Fission Product Separation from Liquid Radioactive Wastes." Atomic Energy Review. 12(2):215, 1974.
4. Yvonne M. Jones, A Preliminary Study of Cesium Sorption from Acid Waste Solutions Utilizing Phosphate Exchangers. BNWL-270, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, November 1966.
5. E. J. Wheelwright, L. A. Bray, H. H. Van Tuyl and H. T. Fullam, Flow-sheet for Recovery of Curium from Power Reactor Fuel Reprocessing Plant Waste. BNWL-1831, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, May 1974.
6. G. Balon, G. A. Beaudet and J. Piret, "A New Inorganic Ion Exchanger for the Separation of Cesium from High-Level Radioactive Wastes." Euronuclear. pp. 85-88, 1966.
7. L. H. Baetsle and D. Huys, Ind. Chim. Belge. 32(2):3, 1967.
8. Charles Aubertin et al., "Process for Separating Strontium from Fission Product Solution by Fixing an Antimonic Acid." U.S. Patent 3,399,030, August 27, 1968.
9. L. H. Baetsle and D. Huys, "Structure and Ion-Exchange Characteristics of Polyantimonic Acid." J. Inorg. Nucl. Chem. 30:639, 1968.
10. C. Knoecny and V. Kourim, Radiochem, Radioanal. Letters. 2(2):47, 1969.
11. E. J. Wheelwright, "A Generic Ion Exchange Process for the Recovery and Purification of Valuable Elements from the Nuclear Industry." Proc. Conf. Ion Exchange in the Process Industries, Society of Chemical Industry, London, 1970.
12. V. Kourim, J. Stejakal, M. Santanora, "Improved Inorganic Ion Exchanges," J. of Radioanalytical Chem., 30:187, 1976.
13. A. Fontaine and D. Berger, Application of the Chemical Properties of Ruthenium to Decontamination Processes. Commissariat a l'Energie Atomique, Chusclan, France, CEA-R-2842, December 1965.

REFERENCES (cont'd)

14. J. V. Panesko, Process for Recovery of Rhodium, Palladium and Technetium from Aged Reprocessing Wastes at Hanford. ARH-733, Atlantic Richfield Hanford Company, Richland, WA 99352, August 1968.
15. J. V. Panesko, Recovery of Rhodium, Palladium and Technetium on Strongly Basic Anion Exchange Resin. ARH-1279, Atlantic Richfield Hanford Company, Richland, WA 99352, July 1969.
16. C. A. Colvin, Recovery of Palladium from Nuclear Waste Solutions Using a Packed Column of Tricapryl Monomethyl Ammonium Chloride on an Inert Support. ARH-1346, Atlantic Richfield Hanford Company, Richland, WA 99352, September 1969.
17. J. V. Panesko, Anion Exchange Recovery of Rhodium from Palladium-Free Alkaline Solutions. ARH-1982, Atlantic Richfield Hanford Company, Richland, WA 99352, March 1972.
18. E. J. Wheelwright and F. P. Roberts, The Use of Alternating DTPA and NTA Cation-Exchange Flowsheets for the Simultaneous Recovery and Purification of Pm, Am, and Cm, USAEC Report No. BNWL-1072, July 1969.
19. R. M. Harbour, W. H. Hale, G. A. Burney, and J. T. Lower, "Large-Scale Separation of Transplutonium Actinides by Pressurized Cation Exchange," At. Energy Rev., No. 10, pp. 379-399, 1972.
20. J. A. Kelley, Ion Exchange Process for Separating Americium and Curium from Irradiated Plutonium, USAEC Report No. DP-1308, November 1972.
21. R. W. McKee, Technical, Economic and Policy Considerations Affecting Future Production Marketing and Use of Cesium-137 and Strontium-90. BNWL-1686, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, December 1972.
22. E. J. Wheelwright et al., Partitioning of Long Lived Nuclide from Radioactive Waste - FY 1975 Annual Report, BNWL-1926, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, April 1976.

DISTRIBUTIONNo. of
CopiesNo. of
Copies

A. A. Churm
DOE Chicago Patent Attorney
9800 S. Cass Avenue
Argonne, IL 60439

W. C. Remini
DOE Division of Advanced Systems
and Materials Production
Washington, DC 20545

D. C. Bauer
DOE Division of Advanced Systems
and Materials Production
Washington, DC 20545

B. J. Rock
DOE Division of Advanced Systems
and Materials Production
Washington, DC 20545

C. A. Cooley
DOE Waste Management Division
Washington, DC 20545

E. J. Wahlquist
DOE Division of Advanced
Systems and Materials
Production
Washington, DC 20545

G. W. Cunningham
DOE Waste Management Division
Washington, DC 20545

D. C. Davis, Jr.
DOE Oak Ridge Operation
Office
P. O. Box E
Oak Ridge, TN 37830

T. J. Dobry, Jr.
DOE Division of Advanced Systems
and Materials Production
Washington, DC 20545

T. W. Goldsten
DOE Savannah River Operations
Office
P. O. Box A
Aiken, SC 29801

T. J. Holleman
DOE Division of Advanced Systems
and Materials Production
Washington, DC 20545

27 DOE Technical Information
Center

R. N. Kostoff
DOE Division of Advanced Systems
and Materials Production
Washington, DC 20545

W. M. Pardue
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201

A. P. Litman
DOE Division of Advanced Systems
and Materials Production
Washington, DC 20545

W. J. Zielenback
Battelle Columbus Laboratories
505 King Avenue
Columbus, OH 43201

J. N. Maddox
DOE Division of Biomedical
and Environmental Research
Washington, DC 20545

C. J. Francis
EXXON Nuclear Co., Inc.
Research and Technology Center
2955 George Washington Way
Richland, WA 99352

G. A. Newby
DOE Division of Advanced Systems
and Materials Production
Washington, DC 20545

No. of
Copies

No. of
Copies

M. E. Spaeth
EXXON Nuclear Co., Inc.
Research and Technology Center
2955 George Washington Way
Richland, WA 99352

H. C. Carney
General Atomic Company
P. O. Box 81601
San Diego, CA 92138

P. E. Brown
General Electric Company MSVD
P. O. Box 8555
Philadelphia, PA 18101

G. E. Robinson
General Electric Company,
Vallecitos Laboratory
P. O. Box 846
Pleasanton, CA 94566

J. W. Anstee
Industrial Products Group
Atomic Energy of Canada, Ltd.
Ottawa, Canada

3 Los Alamos Scientific Laboratory
P. O. Box 1663
Los Alamos, NM 87544

S. E. Bronisz
R. A. Kent
R. N. Mulford

2 Monsanto Research Corporation
Mound Laboratory (DOE)
Nuclear Operations
P. O. Box 32
Miamisburg, OH 45342

W. T. Cave
R. Dewitt

2 Oak Ridge National Laboratory
Oak Ridge, TN 37830

E. Lamb
A. C. Schaffauser

ONSITE

DOE Richland Operations

W. A. Burns
W. C. Johnson
H. E. Ransom

Rockwell Hanford Operations

L. I. Brecke
H. H. Hopkins
L. M. Knights
E. J. Kosiancie
C. W. Malody
J. D. Moore
H. P. Shaw
R. W. Spencer

Battelle-Northwest

J. W. Bartlett
W. F. Bonner
D. K. Davis
H. T. Fullam
E. R. Irish
J. H. Jarrett
D. E. Knowlton
O. H. Koski
R. C. Liikala
J. L. McElroy
R. W. McKee
J. E. Minor
R. E. Nightingale
D. E. Oleson
A. M. Platt
W. E. Sande
J. L. Swanson
H. H. Van Tuyl
L. D. Williams
Technical Information Files (5)
Technical Publications

HEDL

5 J. A. Partridge