UNCLASSIFIED

DPST-66-433

IRC INDEX NO.: TB255

E. I. DU PONT DE NEMOURS & COMPANY
INCORPORATED

AIKEN, SOUTH CAROLINA

(TEL. & TEL. ADDRESS, AUGUSTA, GA.)

EXPLOSIVES DEPARTMENT

SAVANNAH RIVER LABORATORY

Distribution

1. V. R. Thayer, Wilm.
2. L. Squires-M. H. Wahl
3. C. W. J. Wende-J. W. Croach
4. M. H. Smith-W. H. Holstein
5. J. B. Tinker-R. J. Christl
6. W. P. Bebbington-E. B. Sheldon, SRP
7. J. K. Lower
8. W. P. Overbeck-A. A. Johnson, SRL
9. C. H. Ice-D. S. Webster
10. L. H. Meyer
11. C. S. Schlea
12. E. R. Russell
13. H. J. Groh
14. J. F. Proctor
15. TIS File Copy
16. Vital Records Copy

~~This document consists of~~
~~8 Pages, Copy No. 16 of~~
~~16 Copies, Series A~~

CLASSIFICATION REVIEW FOR
DECLASSIFICATION BUT LEFT
UNCHANGED

June 22, 1966

V. R. THAYER, DIRECTOR
CHEMICAL PROCESS SECTION
TECHNICAL DIVISION
AED-EXPLOSIVES DEPARTMENT
WILMINGTON

By: *B. F. O. Mealy*
Date: *12/13/73*
U.S. REC Division of Classification
CG 752

DPST--66-433

DE86 015854

**THE RECOVERY OF CESIUM, TECHNETIUM, RHODIUM, AND PALLADIUM
FROM STORED WASTE SUPERNATES**

This letter presents the results of our assessment of the processing methods and costs for the recovery of cesium, technetium, rhodium, and palladium from aged waste supernates. The original request for this information from R. C. Blair⁽¹⁾ gave the following guidelines for the assessment of costs:

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

1. R. C. Blair to L. Squires, November 24, 1965.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Received by OSTI

SEP 22 1986

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

UNCLASSIFIED

DPST-66-433

V. R. THAYER

- 2 -

June 22, 1966

1. Assume that "in-line" recovery facilities would be installed to recover the desired products from the supernates as they are transferred from the storage tanks to other locations. No costs associated with the movement of the supernates are to be charged against recovery of the fission products.
2. Facilities and costs should not extend beyond those operations necessary to the production of a crude recovered concentrate.
3. Costs for vessels capable of storing up to 2 years production of the recovered concentrates should be included.
4. In considering fission product quantities, include current inventories plus the estimated output from four reactors operating at power through 1972.
5. The capacity of the installed equipment should be sufficient to process the total supernate inventory within a four to six-year period.

Cesium can be readily absorbed from alkaline waste supernates without prior treatment using Linde AW-500, a synthetic zeolite. Technetium, present in the supernate as the pertechnetate anion, together with rhodium and palladium, probably present as anionic nitrite complexes, can be absorbed from untreated waste supernates using Dowex 1-X4 or similar anion resins. Although the behavior of cesium and technetium is reasonably well understood, the behavior of the anionic complex that accounts for the presence of rhodium and palladium in this strongly alkaline solution is not well understood. Further work is required before a process can be outlined for the clean separation of rhodium and palladium from the technetium-rhodium-palladium crude fraction sorbed on the anion resin.

An assessment of capital and operating costs for the recovery of cesium only, technetium only, or both cesium and technetium are presented in Table 1 below. No costs are shown for rhodium and palladium, since the technology for their separation is not sufficiently advanced. However, the incremental cost for their separation from technetium is expected to be small. Process flow diagrams for the recovery of cesium and technetium by ion exchange are shown in Figure 1.

UNCLASSIFIED

V. R. THAYER

- 3 -

June 22, 1966

TABLE IExpected Capital and Annual Operating Costs

	<u>Capital Cost*</u>	<u>Incremental Annual Operating Cost</u>
Recovery of ^{137}Cs Only	\$ 1,400,000	\$ 150,000
Recovery of ^{99}Tc Only	1,800,000	100,000
Recovery of both ^{137}Cs and ^{99}Tc	2,700,000	210,000

*Costs include installation of duplicate facilities in both F and H Areas.

Inventories

In F Area about 4×10^7 curies of ^{137}Cs (400 kg) are contained in about 5×10^6 gallons of supernate (8 curies/gallon). Technetium is present in amounts equivalent to that of the cesium (0.02 g/liter). Based on a single analysis of Tank 10 in H Area (0.2 ppm Rh, $\sim 2 \text{ c } ^{137}\text{Cs}/\text{gal}$), the average concentration of rhodium expected in F Area is between 0.6 and 1.0 ppm, corresponding to a total of 15 to 25 kilograms of rhodium. The amount of palladium present is expected to be about one-half that of the rhodium. Both ^{103}Rh and the several palladium isotopes in the waste are stable. Trace quantities of radioactive ^{103}Rh and ^{103m}Rh resulting from (n,2n) reactions on rhodium will cause the bulk rhodium to be slightly radioactive, but the level has not yet been established. Since most of the future reactor charges through 1972 are expected to be fueled with enriched uranium, the inventory of waste in F Area is assumed to remain essentially constant during the next five years.

In H Area about 2×10^7 curies of cesium (200 kg) are contained in some 5×10^6 gallons of supernate (about 4 curies/gallon) and an additional 1×10^7 curies are contained in salt cake. If converted to the same salt concentration as in supernate, the total volume of waste will be about 7×10^6 gallons and will contain 300 kg of cesium. If all future production involves burning enriched uranium, an additional $4\text{--}5 \times 10^7$ curies of ^{137}Cs (400-500 kg) will be produced and stored in H Area by 1972; this newer waste will probably be stored at an average cesium concentration of about 8 curies/gallon as liquid or 25 curies/gallon as salt. The amounts of technetium, rhodium, and palladium will be in proportions similar to those given above for F Area. Table II below summarizes the total amounts of each isotope in each area as of 1972, under the assumption that all future processing is enriched uranium in H Area.

TABLE II

Inventory of Cs, Tc, Rh*, and Pd* as of 1972

	<u>Kilograms</u>	
	<u>F Area</u>	<u>H Area</u>
Cesium-137	400	~ 800
Technetium-99	400	~ 800
Rhodium-103	(20)	(40)
Palladium-106/108	(10)	(20)

*These results for Rh and Pd are based on one sample from a single waste tank and, although they correspond roughly to the expected amounts based on exposure, they should be considered tentative.

Cesium Recovery

A crude, partially decontaminated cesium concentrate can be recovered directly from the waste supernate without any pretreatment of the feed by passing the supernate through an ion exchange column loaded with Linde AW-500, a synthetic zeolite. The equivalent of about 50 column volumes of supernates can be passed through the column before significant breakthrough of cesium occurs (a residence time of 7 to 10 minutes in the column is required). The loaded column is then washed with 2 to 3 column volumes of 0.2M $(\text{NH}_4)_2\text{CO}_3$ and the cesium eluted with 3-4 column volumes of 1.5M $(\text{NH}_4)_2\text{CO}_3$ to yield a crude solution containing greater than 98% of the cesium in the feed at a concentration between 50 and 100 curies/gallon (0.2 to 0.3 g/liter). This crude will be stored for eventual loading into transportable ion exchange shipping casks similar to those now used for transporting cesium between Isochem and ORNL.

The capacity of a column containing about 100 gallons of zeolite will be adequate to process the inventory contained in either area within a 3 to 4-year period. Separate installations of ion exchange columns and associated tankage would be needed in each area. Since recovery is assumed to be performed during the movement of wastes from their present location, and since large volumes of water will have to be added to redissolve existing salt cake, there seems to be little incentive for minimizing waste volumes; no attempt will therefore be made to reduce the volume of wash solution. Instead, the 300,000-600,000 gallons of dilute ammonium carbonate wash will be added to the waste being moved in each area. Over the full campaign some 600,000 to 800,000 gallons of 1.5M $(\text{NH}_4)_2\text{CO}_3$ eluate containing cesium will be produced. This material can either be stored in existing waste tanks that have been cleaned and reserved for this purpose, or be evaporated and stored in each area as about 5,000 gallons of concentrate in cooled tanks constructed for this purpose. The latter method has been assumed in arriving at capital costs for the recovery operation. The heat load from the total cesium inventory in both areas will be about 300 kw.

The ion exchange zeolite is expected to require replacement after about 10 cycles (a total of 500 bed volumes or 50,000 gallons of supernate). For the full campaign the two areas will accumulate a total of 30,000 gallons of spent zeolite that will have to be disposed of in a manner similar to that for sludge now present in the tanks.

Technetium Recovery

Technetium is present in the waste as the pertechnetate anion and can be absorbed directly from the alkaline waste on Dowex 1-X4 anion resin. Rhodium and palladium are both expected to sorb on the resin at the same time, although the fraction recovered is not currently known. The loaded column is then washed with 3 to 5 bed volumes of water followed by 3 to 5 bed volumes of 0.25 molar nitric acid, and eluted in 3 to 5 bed volumes of 8 molar nitric acid. Some of the rhodium and palladium is expected to follow this same route. The acidic eluate will be evaporated and steam stripped to produce a concentrate containing 10 to 30 grams of technetium per liter. Provisions must be made for neutralizing the column wash and the evaporator overheads before combining them with the remainder of the wastes. The reduction of waste volumes in the operation of this column is, again, of only marginal economic significance. Acid will be recovered and reused only if economically justified at the time these operations are undertaken. The cesium DF of the crude technetium concentrate is expected to be about 10^4 if cesium recovery precedes technetium recovery (5 millicuries of Cs per liter).

The technetium recovery column will contain about 40 gallons of resin in which the supernate will have a residence time of about 4 minutes. The capacity of the column will be about 150 column volumes; this batch size is compatible with the operation of the cesium column described above, in that both columns will accept a 5,000 to 6,000-gallon batch that can be fed first to the cesium and then to the technetium column.

Provisions must also be made for nitric acid and caustic storage, solution make-up, neutralization of washes, evaporation of eluate, storage of concentrate, and neutralization of evaporator condensate. Storage of several years accumulation of concentrate will require a 5,000-gallon tank, as will the storage of a batch of column feed; the neutralization tank, the evaporator, and the condensate tank should each be about 500 gallons. The heat load from the total technetium inventory in both areas is negligible because of the 2×10^5 year half-life of ^{99}Tc . The ion exchange resin is expected to have a life of some 20 batches. A total of 6,000 gallons of spent resin that must be treated as a sludge will be generated in processing the waste for technetium recovery.

Costs

Expected capital costs for cesium and technetium recovery are summarized in Table III below. The cost for recovery of both isotopes is expected to be less than the sum of the cost shown for each isotope because of certain shared costs and common overhead charges.

UNCLASSIFIED

DPST-66-433

V. R. THAYER

- 6 -

June 22, 1966

TABLE III

Capital Costs for Cesium and Technetium Recovery

<u>Equipment</u>	<u>Installed Cost</u>	
	<u>Cesium</u>	<u>Technetium</u>
Ion Exchange Column	\$ 25,000	\$ 25,000
Cold Feed Tankage	15,000	20,000
Crude Storage Tanks	30,000	25,000
Concentrate Storage Tanks	30,000	20,000
Waste Hold Tank	20,000	-
Evaporator and Condenser	-	80,000
Neutralizer	-	20,000
Piping	100,000	150,000
Instrumentation	75,000	100,000
Shielding	200,000	200,000
Subtotal Installed	\$ 495,000	\$ 640,000
Distributives (@ 40% installed)	205,000	260,000
Area Total	\$ 700,000	\$ 900,000
Grand Total F and H Areas	\$1,400,000	\$1,800,000
Combined Cesium and Technetium (@ 0.85 times sum of individual)	<u>\$2,700,000</u>	

Operating costs for the recovery of fission products depends in large measure upon the date that recovery is initiated. If operations at the plant site have been discontinued and the waste is being transferred to its final storage location, the rate of transfer will probably be governed by the ion exchange operations unless much larger facilities than those currently envisioned are installed. Under these conditions the added operating cost incurred because of the extended transfer time would be charged against the recovered isotopes. If, however, normal plant operations are in progress during the recovery period, then incremental costs for the recovery operation will be relatively low and will consist principally of a materials cost for zeolite and anion resin together with a small labor charge. It is this latter case that is itemized in Table IV below and summarized in Table I. As in the case of capital costs, operating costs for the combined recovery of Cs and Tc are less than the sum for the individual isotope recovery because of shared labor costs.

UNCLASSIFIED

V. R. THAYER

- 7 -

June 22, 1966

TABLE IVAnnual Incremental Operating Costs for Cesium and Technetium Recovery

<u>Item</u>	<u>Incremental Cost (Annual)</u>		
	<u>Cesium</u>	<u>Technetium</u>	<u>Cesium & Technetium</u>
Essential Materials			
Chemicals	\$ 10,000	\$ 10,000	\$ 20,000
Resin*	80,000	30,000	110,000
Operating Labor	30,000	30,000	40,000
Maintenance Labor & Materials	<u>30,000</u>	<u>30,000</u>	<u>50,000</u>
Annual Incremental Cost	\$ 150,000	\$ 100,000	\$ 220,000

*Costs based on current prices for 100-lb batches of commercial grade resin. In the quantities required for this purpose, lower bulk prices may be obtainable.

J. F. Proctor
Separations Engineering Division

H. G. Groh
Separations Chemistry Division

JFP/HJG:mc

110-100-113

FIGURE 1 - CESIUM AND TECHNETIUM RECOVERY