

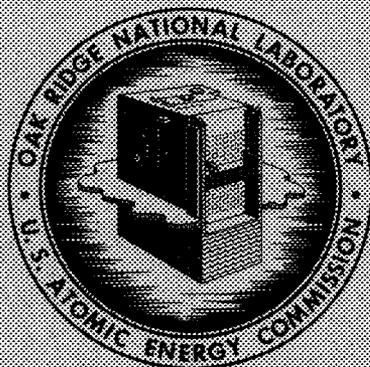
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RECOVERY OF  $^{137}\text{Cs}$  FROM FISSION-PRODUCT  
WASTES AND TRANSPORT BY AN  
ALUMINOSILICATE ION EXCHANGER

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T. A. Butler  
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Isotopes Division

MAY 1965

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ABSTRACT

A method for recovering fission-product cesium from aged basic fission-product waste with an aluminosilicate ion exchanger (Decalso) was developed and demonstrated. Cesium is selectively adsorbed on Decalso from Hanford Purex Supernatant 103A, a basic 9 M  $\text{NaNO}_3$  solution, and concentrated by a factor of about 8.5. The Decalso column is transported from HAPO to ORNL in shielded containers formerly used for shipping solutions, and the cesium is eluted with ammonium salts for purification and source fabrication. In the period April 1961 to August 1964, 2 Mcuries of  $^{137}\text{Cs}$  was recovered from Hanford wastes and transported to ORNL by this procedure.

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INTRODUCTION

This report describes the development and demonstration of an ion exchange procedure for recovering fission-product cesium from basic fission-product wastes and a means for transporting large quantities of  $^{137}\text{Cs}$  from Richland, Washington, to Oak Ridge, Tennessee.

Fission-product cesium has been recovered and purified in multikilocurie quantities at Oak Ridge National Laboratory<sup>1</sup> since 1954. Prior to 1960 aged waste solutions containing fission-product mixtures were transported to ORNL and processed for the individual fission products. When the demand for cesium for use as radiation and heat sources exceeded the demand for associated fission products, wastes that contained mainly fission-product cesium were investigated. Hanford Purex Supernatant 103A, a basic high-molarity- $\text{NaNO}_3$  solution, is low in associated fission products yet contains appreciable quantities of fission-product cesium. Since cesium contains 37-42%  $^{137}\text{Cs}$  and is low in  $^{134}\text{Cs}$ , it is useful for heat and

radiation sources.

A suitable ion exchanger for cesium recovery must be moderately selective for cesium over sodium, stable in basic and neutral solutions, and reusable for many cycles. Cesium sorption and elution rates must be fast enough that solution flow rates of  $\geq 1$  column volume per hour can be maintained, and the cesium must be recoverable by elution with a small volume of eluant. As a medium for transportation, the ion exchanger must be stable to high radiation fields for extended times. The cesium should not be leached from it by tap water or volatilized at high temperatures such as might occur if the cask should be ruptured or exposed to fire during transit.

Among the inorganic ion exchangers showing high selectivity for cesium are heteropoly acids<sup>2-5</sup> and their salts,<sup>6-8</sup> but these are not stable in basic solution. Salts of hydrous oxides and polybasic acids, such as zirconium phosphate,<sup>9-13</sup> have been used on a limited scale. Recovery processes using synthetic aluminosilicates (Linde molecular sieves) and zeolites have been developed at Hanford for recovery and permanent storage of cesium from both acidic wastes<sup>14-17</sup> and basic wastes<sup>16</sup>.

As a result of preliminary studies with 30 inorganic ion exchangers, Decalso, a synthetic aluminosilicate ion exchanger, produced by Ionac Chemical Company, was chosen. The amorphous material is a permutit<sup>18</sup> with the empirical formula  $\text{Na}_2\text{O} \cdot \text{Al}(\text{OH})_3 \cdot 6 \text{Si}(\text{OH})_4 \cdot x \text{H}_2\text{O}$ . It is insoluble in neutral and mildly basic salt solutions, but decomposes in solutions of  $\text{pH} < 2.7$ . Its ion-exchange capacity for cesium is 2.0 meq/g, its specific gravity is 1.66, and 20-30 mesh material has a bulk density of 0.534 kg/liter. The exchangeable ion of Decalso is the sodium ion, which is attached through oxygen to the aluminum. The order of selectivity of Decalso for monovalent ions is  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ . Although Decalso has lower selectivity than several other ion exchangers studied, the rate of sorption and elution of cesium from the amorphous ion exchanger was such that there was little leakage of  $^{137}\text{Cs}$  during the sorption cycle, and  $>97\%$  of the cesium was recovered during elution, even at flow rates of 1 column vol/hr.

## SORPTION STUDIES

The selectivity of Decalso in removing cesium from sodium solutions was determined from static distribution coefficients and in column experiments. The distribution coefficients were useful for determining the effect of variables on the sorption of cesium and in studying the sorption rate; but column studies more closely approximate actual operating conditions. Cesium was concentrated on Decalso from basic 9 M  $\text{NaNO}_3$  by a factor of 8.5.

### Static Distribution Coefficients

Distribution coefficients were measured by contacting a weighed portion of air-dried Decalso with a known volume of solution containing 10 mg/liter of cesium traced with  $^{137}\text{Cs}$ , and varying amounts of  $\text{NaNO}_3$ . The pH was adjusted to 12.6 with NaOH and the solution was left in contact with the ion exchanger for a known length of time before assay. Distribution coefficients were calculated from the relation

$$K_d = \frac{x_1 - x_2}{x_2} \frac{\text{ml of solution}}{\text{g of solid}}$$

where  $x_1$  is the original counting rate (counts/min·ml) and  $x_2$  the rate after the contact.

Effect of sodium concentration. The distribution coefficient of cesium on Decalso decreased with increasing sodium concentration (Table 1).

Table 1. Distribution coefficient of cesium on Decalso as a function of sodium concentration

0.2 g of Decalso per 10 ml of solution,  
pH 12.7, Cs conc. 10 mg/liter, 16 hr  
contact at 25°C, sodium as  $\text{NaNO}_3$

Na Conc, <u>M</u>	Distribution coefficient
0.2	430
1.0	170
2.0	85
2.8	49
4.0	22
6.0	13
8.0	8
9.0	6.7

Effect of radiation damage on selectivity. There was no decrease in selectivity of Decalso for cesium over sodium after exposure to 150 Mrads of gamma radiation, as shown by the distribution coefficients of cesium on Decalso from solutions of various sodium concentrations and by ion-exchange-capacity measurements. The Decalso changed color from white to light tan, and the material was more friable after radiation than before.

Effect of cesium concentration. Cesium concentrations, up to 50 mg/liter, had little effect on the fraction of cesium sorbed (Table 2). The fraction depends, instead, on the selectivity of the ion exchanger and the

sodium concentration. Thus the sodium concentration, which determines  $K_d$ , is the factor limiting the amount of cesium that can be adsorbed rather than the ion exchange capacity of the ion exchanger. Only a few percent of the exchange capacity is represented by cesium because of the presence of the large amount of sodium.

Table 2. Distribution coefficient of cesium on Decalso at various cesium concentrations

0.2 g Decalso per 10 ml of solution,  
pH 12.7, 16 hr contact, 3.7 M  $\text{NaNO}_3$

Cesium conc, mg/liter	$K_d$
Trace	29.8
2	30.1
5	29.0
8	27.0
20	27.2
50	27.0
200	24.0
500	22.2

Effect of anions. There was no significant change in the distribution coefficient of cesium on Decalso from 4.0 M  $\text{NaNO}_3$  containing hydroxide from pH 9.0 to 0.4 M  $\text{NaOH}$ . Also, there was no change after addition of 0.1 M solutions of  $\text{Na}_2\text{SO}_4$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{NaAlO}_2$ , or  $\text{NaNO}_2$ .

Sorption rate. Cesium was rapidly sorbed on 20-30 mesh Decalso from solutions of high sodium concentration. Equilibrium was reached in 1 hr in solutions containing 2-9 M  $\text{NaNO}_3$  and 10 mg of cesium per liter and 90% equilibrium occurred in 15 min.

#### Column Sorption

When cesium is sorbed on a Decalso column, breakthrough depends on the selectivity of the ion exchanger and the sorption rate. If selectivity is high but the rate of approaching equilibrium is slow, cesium will break through immediately. Therefore column experiments give data more applicable to the problem than do distribution coefficients alone. The number of column volumes that could be passed through a Decalso bed was determined by passing a solution containing sodium and cesium tagged with  $^{137}\text{Cs}$  tracer through a 25-ml bed of 20-30 mesh Decalso at a flow rate of 1.0 column vol/hr. Cesium did not break through until the column was

nearly loaded, but then the breakthrough was rapid--usually within 1 column volume, and results were reproducible  $\pm 10\%$ . The number of column volumes having passed through the columns at 50% breakthrough of the  $^{137}\text{Cs}$  was determined at various sodium concentrations.

Effect of sodium concentration. Increasing the sodium concentration decreased the number of column volumes of solution passing through the column before 50% breakthrough (Table 3), as would be expected from distribution coefficient studies.

Effect of temperature. When the sodium concentration was  $>2 \text{ M}$ , more column volumes of solution were passed before breakthrough of cesium at  $25^\circ\text{C}$  than at  $50^\circ\text{C}$ . However, at sodium concentrations below  $2 \text{ M}$ , an increase in temperature increased the number of column volumes before cesium breakthrough (Table 3).

Table 3. Effect of temperature on column sorption of cesium from  $\text{NaNO}_3$  solutions

20-30 mesh Decalso, 1 column vol/hr  
flow rate, 10 mg Cs/liter, pH 12.7

NaNO <sub>3</sub> conc, M	No. of column volumes before 50% breakthrough	
	At 25°C	At 50°C
0.5	142	170
1.0	80	100
2.0	45	50
4.0	20	20
6.0	11	9
9.0	8.5	6.7

The increased number of column volumes of dilute solution passing before breakthrough at  $50^\circ\text{C}$  than at  $25^\circ\text{C}$  is probably due to the increased rate of adsorption. The reverse condition for solutions containing  $>4 \text{ M}$  sodium may be due to a shift in the equilibrium constant resulting from a change in the degree of hydration of the two ions with increasing temperature. Since Hanford Purex Supernatant 103A is very concentrated, ( $9 \text{ M}$  sodium salts), more column volumes of waste can be passed before breakthrough at  $25^\circ\text{C}$  than at  $50^\circ\text{C}$ .

## ELUTION EXPERIMENTS

Elution experiments were run by sorbing cesium on a Decalso column from a solution containing 9 M  $\text{NaNO}_3$  at pH 12.7 and 10 mg of cesium per liter tagged with  $^{137}\text{Cs}$ . After breakthrough, the cesium was eluted. The percentage cesium coming off the column was determined by material balance. When >97% of the cesium had been eluted, the counting rate of  $^{137}\text{Cs}$  on the resin was used to determine the fraction remaining on the Decalso.

### Selection of Eluants

Ammonium nitrate and ammonium sulfate were most effective as eluants. More than 98% of the cesium was eluted with 4 column volumes of 4 M  $\text{NH}_4\text{NO}_3$  or 2 M  $(\text{NH}_4)_2\text{SO}_4$  at flow rates of 2 column volumes per hr at 85°C. Eight column volumes of 4 M  $(\text{NH}_4)_2\text{CO}_3$  was required for the same results. Less than 0.1% of the cesium was removed with 10 column volumes of 4 M  $\text{NH}_4\text{OH}$ .

Dilute nitric acid could not be used because acids attacked the aluminosilicate. A solution containing 0.1 M  $\text{HNO}_3$  dissolved Decalso, forming  $\text{Al}^{+3}$  and silicic acid, which plugged the column. Further tests showed that Decalso dissolves in acid solutions up to pH 2.7.

### Elution of Cesium From Heated and Irradiated Decalso

In the transfer of multikilocuries of  $^{137}\text{Cs}$  on beds of Decalso, the ion exchange material will be subjected to high radiation fields and gamma heating. Studies were made to see if long periods of storage at temperatures greater than ambient would cause partial fixation of the cesium into the structure of the ion exchanger.

Effect of irradiation and heating ion exchanger. Cesium elution was not affected by 150 Mrad gamma irradiation of the cesium form of Decalso. From similarly irradiated samples heated to temperatures below 100°C at atmospheric pressure, >95% of the cesium was released by 4 column volumes of 4 M  $\text{NH}_4\text{NO}_3$  at 25°C. Samples heated to temperatures greater than 100°C at atmospheric pressure were incompletely eluted. This indicates that dehydration of the ion exchanger fixes a fraction of the cesium in the structure (Table 4).

Table 4. Cesium elution from heated and irradiated Decalso

Gamma irradiation	150 Mrad		
Decalso cesium content	0.16 mg/g		
Eluant	4 column vol of 4 M $\text{NH}_4\text{NO}_3$		
Flow rate	2 column vol/hr		
Heat Treatment		Amount Eluted, %	
Temp, °C	Time, hr	25 °C Eluant	85 °C Eluant
62	200	99.7	99.9
100	200	96.0	99.5
125	60	85.0	98.0
400	16	15.0	20.0
1000	16	<<0.1	<<0.1

As shown in Table 4, cesium elution was more efficient at 85°C than at 25°C. Apparently cesium fixed by the heating is more readily released at the higher eluant temperature.

#### APPLICATION OF PROCESS TO RECOVERY AND TRANSPORTATION OF FISSION-PRODUCT CESIUM

Fission-product cesium recovered on Decalso from aged Hanford Purex Supernatant 103A wastes and shipped on the Decalso from HAPO to ORNL has been routinely used for cesium source fabrication at ORNL since April 1961.

The process for recovering this fission-product cesium from Hanford is outlined in Fig. 1. Aged Purex waste, with a sodium concentration of 9 M, is centrifuged and passed through a shielded tank containing 400 gal of Decalso at 25°C until the cesium begins to break through, i.e. when approximately 50,000 curies of  $^{137}\text{Cs}$  has been adsorbed. The beds are then washed with water, and the casks (Fig. 2) are sealed. The casks are loaded, two to a modified gondola car (Fig. 3), and shipped from Hanford to ORNL. At ORNL, more than 97% of the  $^{137}\text{Cs}$  is eluted from the Decalso beds at the Fission Products Development Laboratory with 1000-1200 gal of 5 M  $\text{NH}_4\text{NO}_3$  at 80°C at a flow rate of 4 gal/min. The eluant is stored in underground tanks, which have storage capacity for as much as 0.5 Mcurie of  $^{137}\text{Cs}$ . The ion exchange beds are rinsed and returned to Hanford, in the ammonium form, to be reloaded with cesium. The subsequent purification of the cesium and source compound preparation at ORNL have been described elsewhere.<sup>19</sup>

In the period from April 1961 to August 1964 a total of 1.93 Mcuries of

$^{137}\text{Cs}$  was recovered from Hanford Purex Supernatant 103A wastes and transported to ORNL in 13 shipments of three casks per shipment.<sup>20</sup> After 12 cycles the Decalso in the cask had 90% of its original capacity and showed the same selectivity for cesium over sodium as in the first runs.

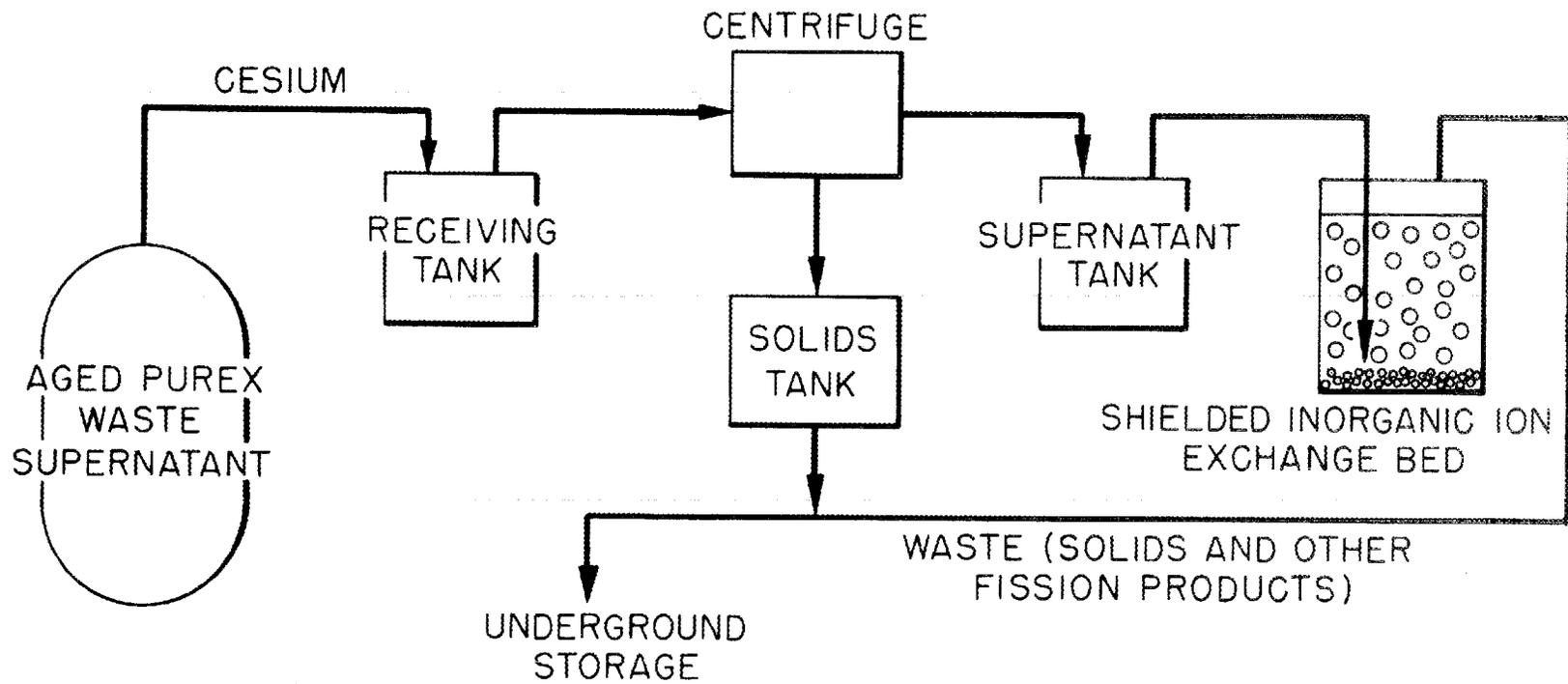


Fig. 1. Cesium-137 Recovery.

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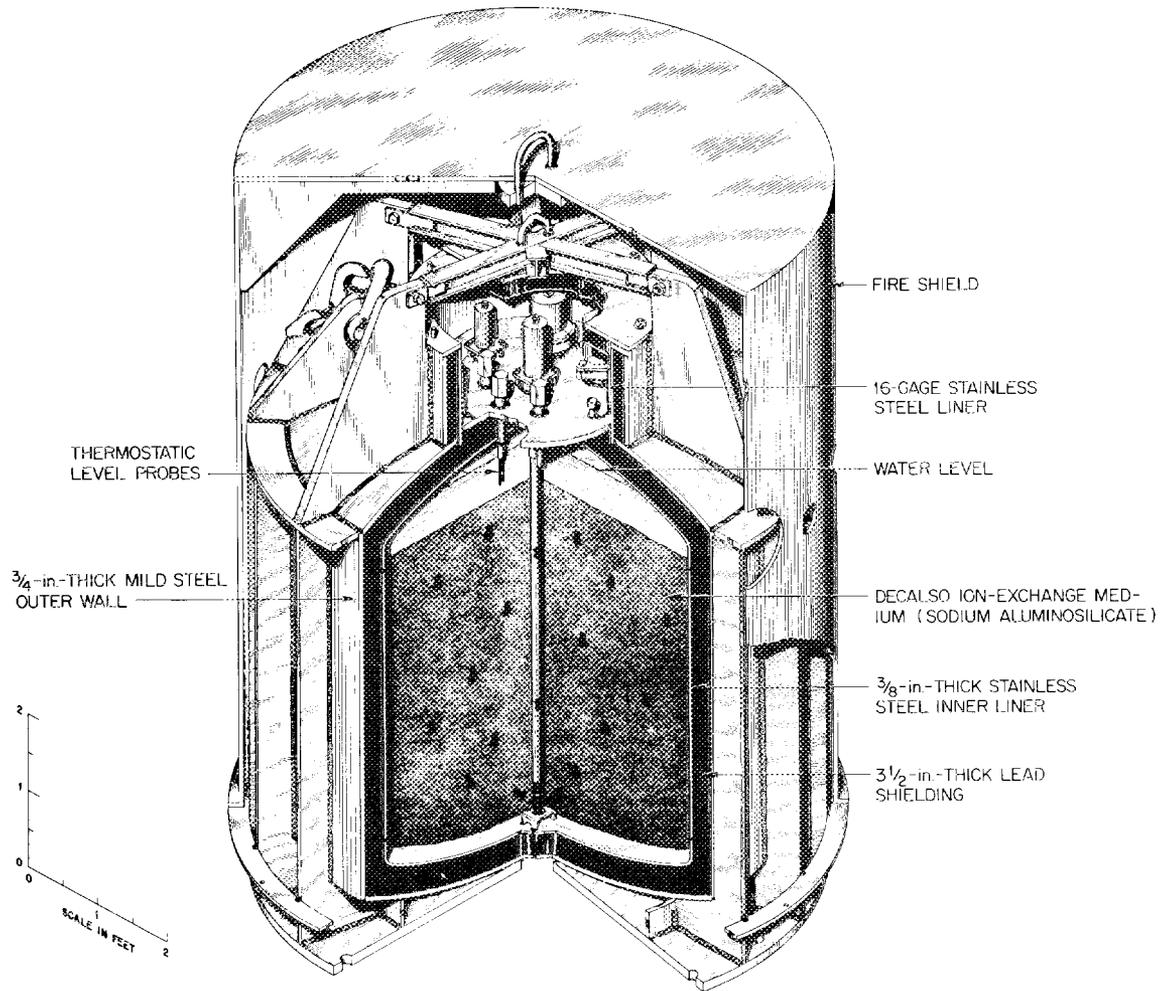


Fig. 2. Cutaway Drawing of Shielded Transfer Tank, Model II (loaded weight 38,800 lb).



Fig. 3. Modified Gondola Car and Transfer Casks  
for Transporting  $^{137}\text{Cs}$ .

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