PREPARATION OF MEGACURIE QUANTITIES OF CESIUM-137 SALTS AND SOURCE COMPOUNDS AT OAK RIDGE NATIONAL LABORATORY*

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ABSTRACT

Processes used at the Fission Products Development Laboratory, Oak Ridge National Laboratory, for recovery, purification, and conversion of megacurie quantities of ^{137}Cs to salts and source compounds are reviewed with special emphasis on the conversion of cesium alum to cesium carbonate by the cesium tetraoxalate process. Subsequent conversion of cesium carbonate to source compounds is discussed.

INTRODUCTION

Fission-product ^{137}Cs has been recovered and purified at Oak Ridge National Laboratory since 1948 to provide gamma-ray sources for teletherapy, radiography, and irradiation units. The first large source was a teletherapy unit fabricated in 1954 which contained 1540 curies of ^{137}Cs in the form of compacted CsCl encapsulated in stainless steel. Within a few years, ^{137}Cs teletherapy sources were widely accepted by medical facilities and there was a demand for sources containing 1000 to 3000 curies. The number of teletherapy sources prepared annually at ORNL has increased to about 25; in addition ORNL also sells considerable quantities of ^{137}Cs to private firms who fabricate teletherapy and radiography sources.

In the past three years, the increased supply of purified ^{137}Cs and reduction in price (presently \$0.125/curie in quantities >200,000 curies) has made ^{137}Cs more attractive for industrial-scale irradiators.[1,2] Two large sources recently prepared that are of special significance are a 200,000-curie $^{137}CsCl$ source, in the form of rectangular wafers (Fig. 1), for the Radiation Laboratory, Brookhaven National Laboratory, and a 176,000-curie source for Saint-Gobain Techniques Nouvelles, Seine, France. Inquiries from a number of irradiation facilities have indicated current interest in sources of 100,000 to 300,000 curies of ^{137}Cs and long-range plans for even larger quantities in the range of 0.4 to 1.0 megacurie of ^{137}Cs. Cesium-137 and its daughter, ^{137}Ba, decay by beta and gamma emission to yield ~4.8 watts thermal power per 1000 curies, which makes it potentially useful as a heat source.

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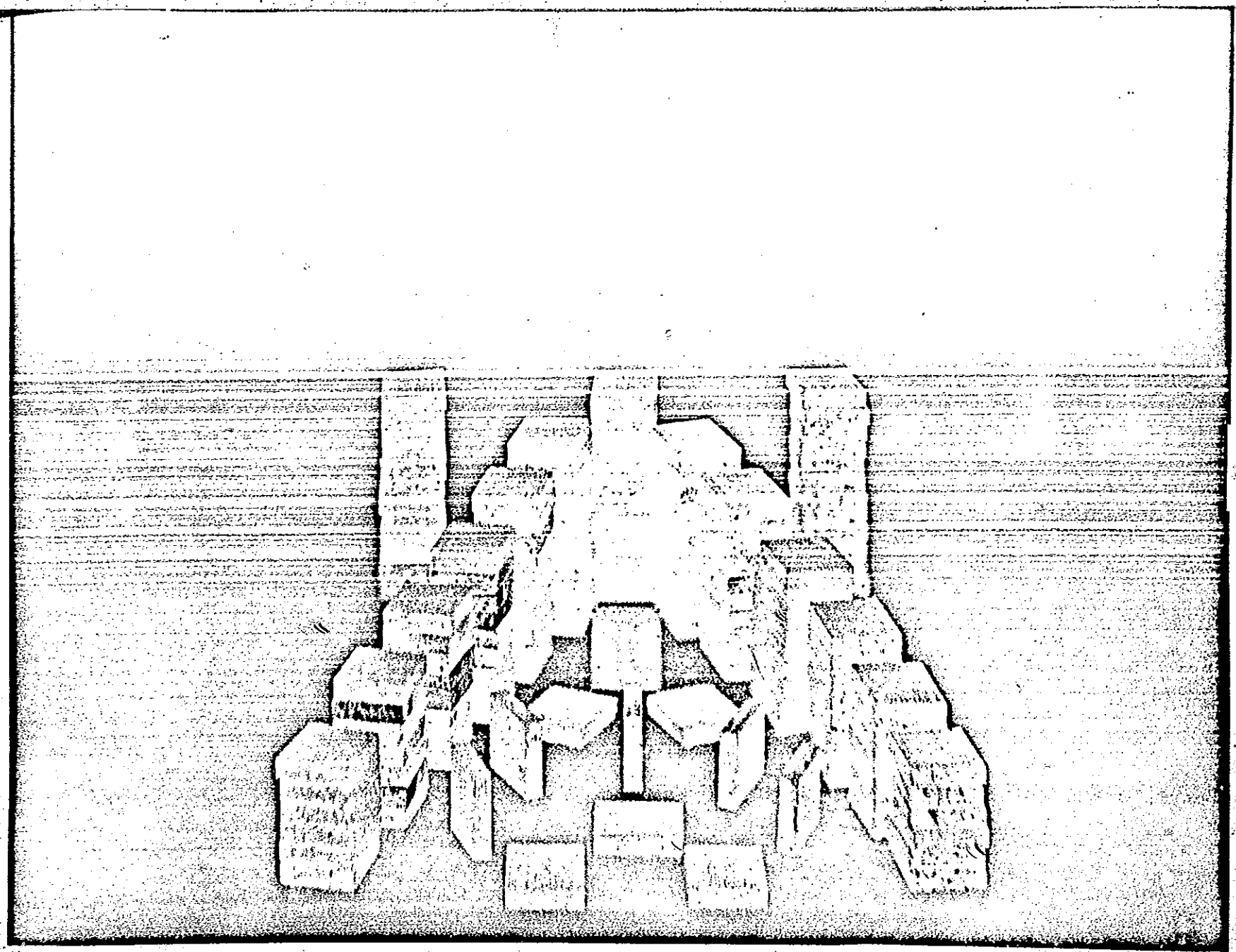

Fig. 1. 70,000 Curies of ^{137}Cs as Square Wafers (Radiation Source).

Prior to 1961, fission products were first recovered from waste solutions generated by pilot plant processing of irradiated uranium at ORNL and from liquid waste shipped to ORNL.[7] In order to meet the growing demand for ^{137}Cs, a technique was developed for selective sorption of ^{137}Cs on an inorganic ion exchanger (Decalso) from the supernatant of neutralized fission-product wastes. Shipment of crude ^{137}Cs concentrated from waste tanks located at Hanford was begun in 1961. Purification of the crude ^{137}Cs and conversion to compounds useful as radiation or heat sources are accomplished at ORNL in the Fission Products Development Laboratory (FPDL) at a rate of 1.0 megacurie/year.

DISCUSSION

Recovery of Cesium-137 From Fission-Product Wastes by Decalso Process

In recovery of ^{137}Cs by the Decalso process,[3,4] neutralized Hanford Purex Supernatant 103A, with a sodium ion concentration of 5 to 7 M, is passed through a radiation-shielded tank containing 400 gal of 20-30 mesh Decalso at 25°C until the cesium begins to break through or when ~50,000 curies of ^{137}Cs has been sorbed. The beds are then covered 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}Cs is eluted from the Decalso beds at FPDL with 1000-1200 gal of 5 M NH_4NO_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 megacurie of ^{137}Cs. The ion-exchange beds are rinsed and returned to Hanford, in the ammonium form, to be reloaded with cesium. The original Decalso beds placed in the shipping casks in 1961 are still being used after twelve loading and elution cycles and have shown no loss of selectivity for sorbing cesium.

The ^{137}Cs processing rate in the FPDL is dependent primarily on the shipping schedule for the feed. Four shipping casks are presently in use. Each 400-gal Decalso bed will transport 50,000 curies; and with a shipping cycle of eight weeks per four STT's, the ^{137}Cs processing rate is about one megacurie of ^{137}Cs per year. In the period from April 1961 to January 1965, over 2.5 megacuries of ^{137}Cs has been processed at ORNL.

Purification of Cesium-137 by Alum Process

The alum process[5-12] is based on the isomorphous cocrystallization of small amounts of cesium with large amounts of ammonium alum. The concentration of ammonium alum in solution also decreases the cesium alum solubility, resulting in high ^{137}Cs recovery. After collecting the cesium in the ammonium alum beds, the more soluble alums are removed by a heating and cooling cycle to effect fractional crystallization of the alums. After three to five such cycles, and removal of the aqueous phase each time, the more insoluble cesium alum is obtained in a relatively pure form, free of other alums and other fission products. Cesium losses recycled from subsequent processing steps are also collected by the alum process for reprocessing. This multiple use of the alum process makes it the key process in the FPDL ^{137}Cs integrated process (Fig. 4).

The 5 M NH_4NO_3 eluant resulting from the elution of the ^{137}Cs from the Decalso beds is diluted to 2.5 M NH_4NO_3 and the 2,500-curie batch of ^{137}Cs is then transferred to a vessel containing an ammonium alum bed. Cesium-137 is then collected

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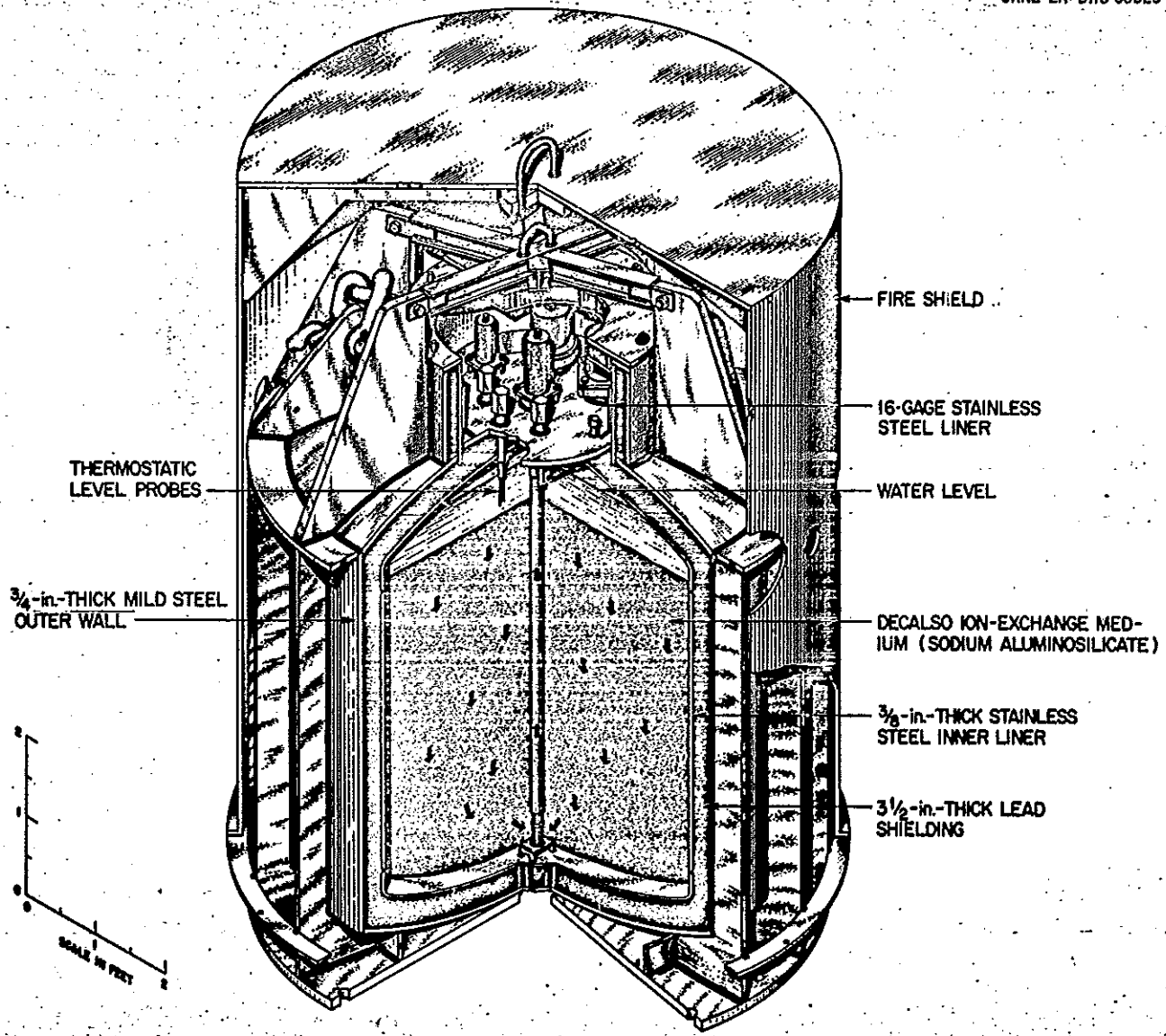

Fig. 2. STT Model II (Loaded Weight – 38,800 lbs)

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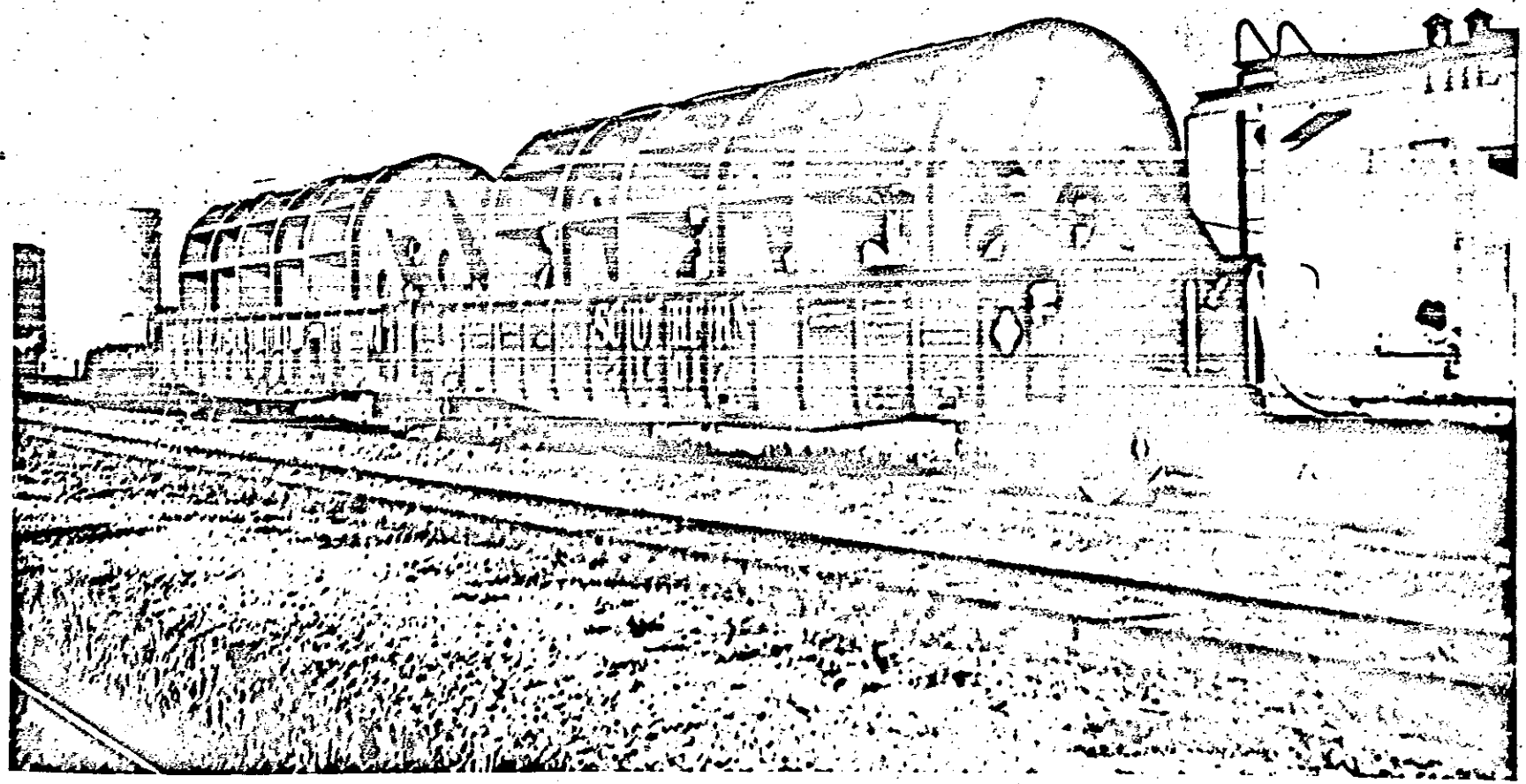

Fig. 3. Gondola Cars for Transporting Shipping Casks (STT) from Hanford, Washington to Oak Ridge, Tennessee.

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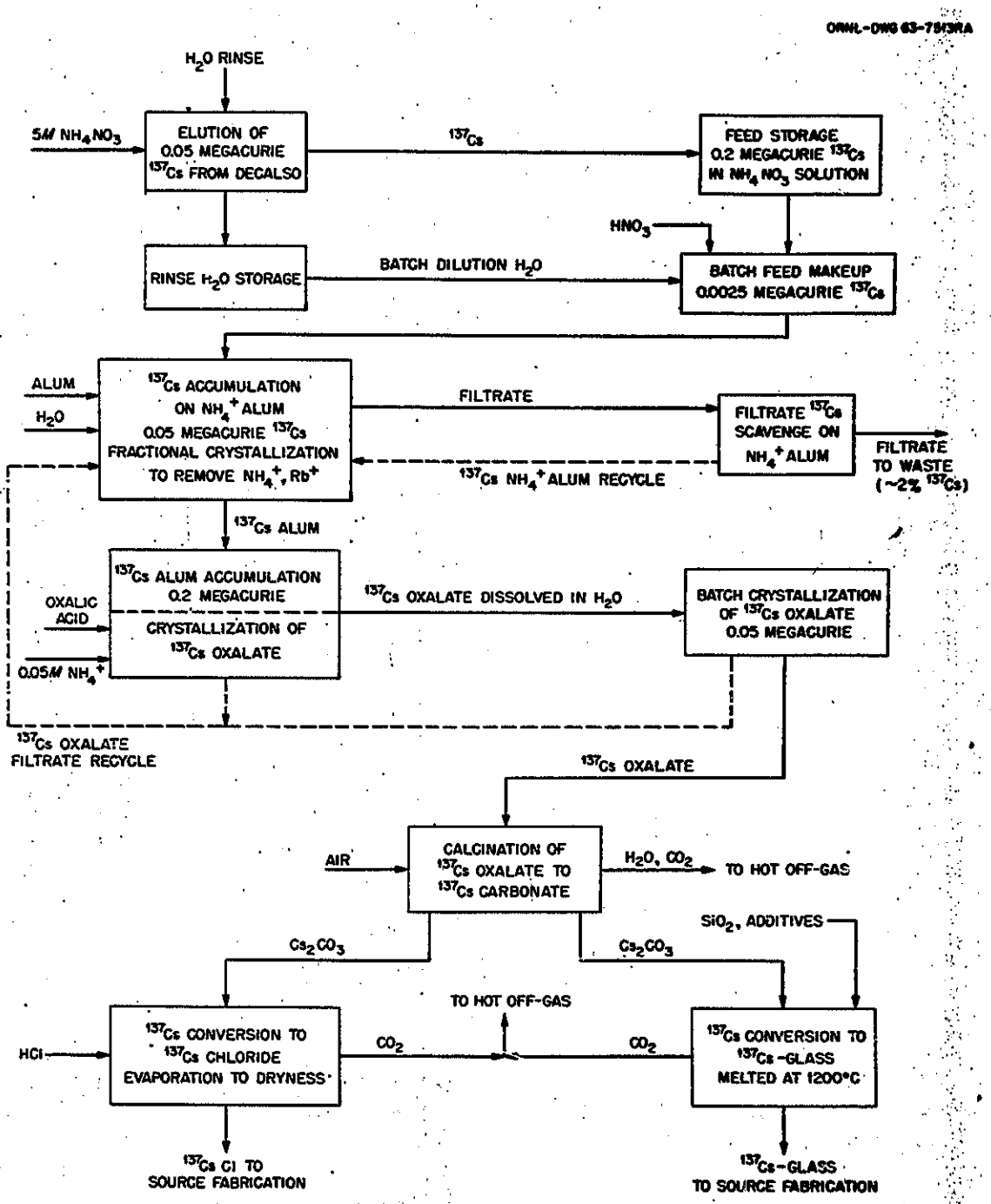

Fig. 4. FPDL ^{137}Cs Processing Flow Diagram.

on the ammonium alum beds by a heating and cooling procedure. The solution remaining from this crystallization is transferred to a second vessel also containing ammonium alum, and the same process repeated two times to effect recovery of >98% of the ^{137}Cs. Subsequent batches of 2,500 curies of ^{137}Cs are transferred to the alum crystallizers and the process is repeated.

When ~50,000 curies of ^{137}Cs has been collected on the alum beds (about one week's operation at FPDL), water is added to the mixed alums and the more soluble ammonium and fission-product rubidium alums, as well as traces of fission products, are removed by several fractional crystallizations. The more insoluble cesium alum is then transferred to an accumulation vessel. The alum cocrystallization and fractional crystallization process is repeated until ~200,000 curies of ^{137}Cs has been accumulated. It is then converted to cesium tetraoxalate by a subsequent process (Fig. 4).

Conversion of Cesium-137 Alum to Source Compounds by Cesium Tetraoxalate Process

Various processes have been used at FPDL to convert cesium alum to other cesium compounds. In one of the early ORNL procedures,[7] ammonium hydroxide was added to the alum to form aluminum hydroxide, ammonium sulfate, and cesium sulfate. After the insoluble aluminum hydroxide had been filtered off, the cesium sulfate solution was heated with HNO_3 to oxidize the residual NH_4^+. Hydrochloric acid was added to remove the HNO_3 and the Cs_2SO_4 solution was passed through a hydroxide-form anion-exchange column to remove the sulfate ion. The resulting cesium hydroxide was neutralized with HCl and evaporated to prepare CsCl crystals.

In a later process,[8] cesium alum was converted to cesium chloroplatinate which was recovered and then converted by an aqueous solution of hydrazine hydrate to platinum metal, cesium chloride, and ammonium chloride. The platinum metal was removed by filtration, nitric acid was added, and the solution was heated to oxidize the ammonium ion. Hydrochloric acid was then added and the solution heated to remove the excess HNO_3; the cesium chloride was evaporated to recover the CsCl. Because of the necessity of handling relatively large quantities of HCl and HNO_3 and the time required for evaporating the acids and recovering the platinum, this method has been replaced by the cesium tetraoxalate process.[13-15]

The advantages of the tetraoxalate process are the easy separation of the cesium from aluminum, simple calcination of the tetraoxalate to cesium carbonate, and the ready conversion of the carbonate to usable end-products. The process is amenable to large-scale processing of fission cesium and the soluble fraction of cesium is recycled to the preceding alum process to effect high recoveries of product.

Cesium tetraoxalate, $CsH_3(C_2O_4)_2 \cdot 2H_2O$, can be crystallized from simple salt solutions such as those occurring in solvent extraction raffinates or from the cesium alum process. The solubility of cesium tetraoxalate in water and 1.0 M oxalic acid solution at various temperatures is shown in Table 1. Laboratory studies show that cesium is crystallized as cesium tetraoxalate from cesium alum–oxalic acid solution, with little coprecipitation of Al(III) at cesium concentrations of <20 g cesium per liter (Table 2). It was found that the addition of small amounts of NH_4^+ ion increased the yield of cesium tetraoxalate and decreased the percentage of the aluminum that coprecipitated (Table 3).

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Table 1. Effect of Temperature on Solubility of Cesium Tetraoxalate in Water and in 1.0 M Oxalic Acid Solution

Temperature, °C	$CsH_3(C_2O_4)_2 \cdot 2H_2O$ solubility, g/liter	
	1.0 M Oxalic acid	Water
10	2.65	8.8
14	4.60	13.0
20	5.00	22.6
30	11.7	40.0
40	30.8	67.5
50	61.6	117.0
60	83.2	--

Table 2. Effect of Cesium Alum Concentration on Cocrystallization of Aluminum Oxalate with Cesium Tetraoxalate

(Temperature 14°C; 1 hr stirring)

Initial cesium concentration, g/liter	Cesium crystallized, %	Al carried, % of initial Al in solution	Initial oxalic acid concentration, M
10	60	<1.0	1.0
15	64	1.0	1.1
20	65	2.1	1.1
25	67	5.2	1.2
30	69	22.0	1.25
40	70	35.0	1.5
50	73	72.0	1.8
100	89	83.0	2.9

Table 3. Effect of Ammonium Ion on Crystallization of Cesium Tetraoxalate from Cesium Alum and Oxalic Acid Solution

(Temperature 14°C; 1 hr stirring; 1.25 M oxalic acid; cooling rate 1°C/min)

Cesium concentration, g/liter	NH_4^+ concentration, M	Cesium crystallized, %	Al carried, % of initial Al in solution
20	0.0	65	2.5
20	0.05	75	0.1
25	0.0	67	5.2
25	0.05	77	0.2

In the ^{137}Cs processing at FPDL, the cesium alum is converted to cesium tetraoxalate after 200,000 curies of pure cesium alum has been accumulated by crystallization in a 400-liter volume of 1.2 to 1.25 M oxalic acid, 0.05 M NH_4^+, and 15 to 25 g of cesium per liter. The first crystallization is not necessary for purification but is very useful in the transfer of ^{137}Cs from the cesium alum crystallizers and aids in getting representative samples of the solution for radiochemical analysis. The cesium tetraoxalate is dissolved in water and transferred in 50,000-curie batches to a 100-liter vessel.

The second crystallization is made in the 100-liter vessel from 1.1 to 1.2 M oxalic acid. The solution is cooled to 25°C at a rate of 1°C/min. The cooling rate is halted at 25°C for 15 min and then cooled to 14-16°C at a rate of 0.5°C/min. Yields of cesium tetraoxalate are 70% on the first crystallization and 92% on the second crystallization. The increased yield on the second crystallization is due primarily to the lower concentration of aluminum ions.

The soluble cesium in the supernatant fraction is recycled to the alum system for recovery as cesium alum. The integrated cesium process used at FPDL is shown in Fig. 4.

Preparation of Cesium Carbonate from Cesium Tetraoxalate

Cesium carbonate is easily prepared by heating cesium tetraoxalate to a sufficiently high temperature to volatilize excess oxalic acid and water and decompose the oxalate to carbonate and carbon monoxide. The calcination is endothermic and there is no danger of uncontrolled burning.

In laboratory studies of the calcination, cesium tetraoxalate was heated for different times and temperatures in a shallow nickel tray in a muffle furnace with an air stream passing through. The resulting compounds were assayed for cesium, titratable hydrogen ion, oxalate, and carbonate. From these studies, the reactions in different temperature ranges were determined to be:

$$CsH_3(C_2O_4)_2 \cdot 2H_2O \xrightarrow{105\text{-}120^\circ C} CsH_3(C_2O_4)_2 + 2H_2O$$

$$CsH_3(C_2O_4)_2 \xrightarrow{120\text{-}200^\circ C} CsHC_2O_4 + H_2C_2O_4$$

$$2CsHC_2O_4 \xrightarrow{200\text{-}300^\circ C} Cs_2C_2O_4 + H_2C_2O_4$$

$$Cs_2C_2O_4 \xrightarrow{300\text{-}450^\circ C} \text{Mixture of } Cs_2CO_3, Cs_2O, CO, \text{ and } CO_2$$

$$Cs_2CO_3 \xrightarrow{>450^\circ C} Cs_2O + CO_2$$

When cesium tetraoxalate is heated to 100°C, the crystals melt. Continued heating at 120°C sublimes the excess oxalic acid, leaving cesium acid oxalate, $CsHC_2O_4$. The conversion of $CsHC_2O_4$ to Cs_2CO_3 is complete after 2 hr at 300°C. This procedure is used to convert fission-product cesium tetraoxalate to cesium carbonate.

The cesium compounds prepared from cesium tetraoxalate are low in Al_2O_3 and Fe_2O_3 since oxalic acid complexes both aluminum and ferric iron and keeps these ions in solution. Trace amounts of iron and aluminum (~0.1 mg/g cesium tetraoxalate) that do cocrystallize with the cesium tetraoxalate are converted to the insoluble oxides at 300°C and are removed by filtration of the dissolved cesium carbonate

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solution prior to making other cesium compounds. Carbon, which also forms from the calcination of ammonium tetraoxalate, is also removed by the filtration. The resulting cesium carbonate solution contains no detectable alkaline earth, trivalent metal ions, or ammonium ions.

Preparation of Cesium Source Compounds from Cesium Carbonate

Cesium carbonate is used to prepare a variety of source compounds. Cesium chloride is the primary form for radiation sources, but other salts or compounds can be prepared for heat sources or special application.

Dry powdered $^{137}CsCl$ is prepared in 50,000-curie batches by reacting the filtered Cs_2CO_3 solution with a slight excess of hydrochloric acid.[12-14] The $^{137}CsCl$ solution is again filtered, and the filtrate is evaporated in tantalum equipment to yield the dry salt. The powder is baked with constant stirring at 300°C for 4 hr to remove the last traces of HCl; it is then stored in lots of 10,000 curies in stainless steel cans in water-cooled storage wells. The cesium chloride has an activity concentration of ~25 curies ^{137}Cs per gram CsCl, as measured by calorimetric methods;[16,17] this varies slightly due to differences in the ^{137}Cs isotopic concentration.

The cesium chloride is pressed[18] into a variety of sizes and shapes such as right cylinders, square wafers (Fig. 1), or segments of a ring, and then hermetically sealed in Type 316 LC stainless steel capsules by fusion welding techniques.[19,20] Long-term compatibility studies[21] have shown fission-product cesium chloride is compatible with Type 316 stainless steel capsules.

Cesium sulfate is prepared by adding a stoichiometric amount of dilute sulfuric acid to the cesium carbonate solution and evaporating to near dryness. An equal volume of ethyl alcohol is added to the concentrate to decrease the solubility of the cesium sulfate, and the crystals are filtered from the solution and dried. This procedure is better than the procedure[22] of evaporating acid cesium sulfate solutions to dryness because the cesium sulfate prepared from cesium carbonate does not contain $CsHSO_4$, which is highly corrosive.

Several types of cesium glasses[23,24] containing 40-45% cesium have been prepared from cesium carbonate. About 100,000 curies of ^{137}Cs glass has been prepared, but experience has shown that fabrication of cesium glass as small rods or special shapes is very difficult. Cesium glass in the form of right cylinders for use as a heat source[25] was prepared (Fig. 5).

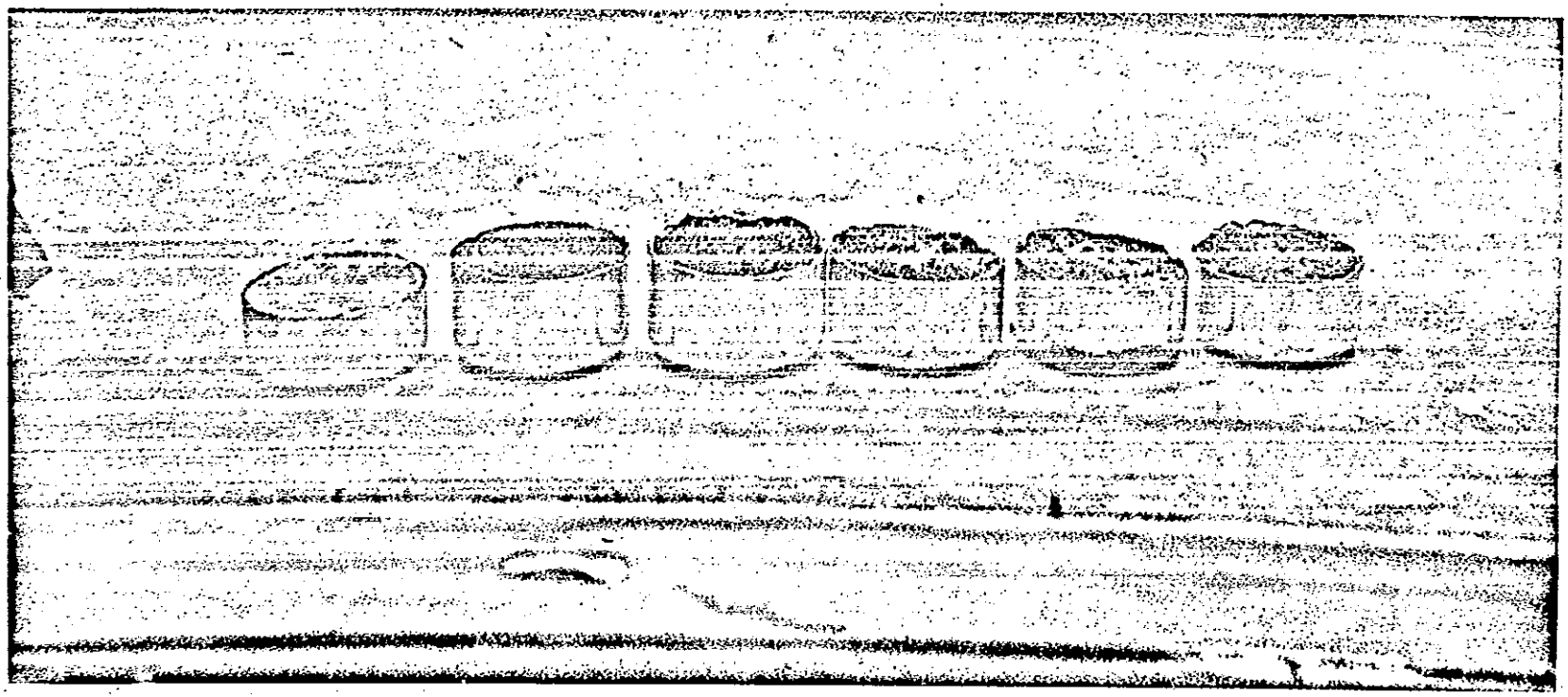

Fig. 5. 28,000 Curies of ^{137}Cs Borosilicate Glass for Use as Heat Source.

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