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DEVELOPMENT AND USE OF A PROCESS FOR CRYSTALLIZATION OF CESIUM TETRAOXALATE: AN INTERMEDIATE FOR PREPARING ^{137}Cs SOURCE COMPOUNDS

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Isotopes Division

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ABSTRACT

A process was developed for crystallization of cesium tetraoxalate, $CsH_3(C_2O_4)_2 \cdot 2H_2O$. Addition of oxalic acid to cesium-rich solutions precipitates more than 90% of the cesium as the tetraoxalate under optimum conditions. Cesium alum is converted to cesium tetraoxalate in 70% yield with cocrystallization of <1% aluminum. Cesium remaining in solution is recycled, giving low process losses. The oxalate was demonstrated to be sufficiently stable to radiation to be useful as an intermediate in processing fission-product ^{137}Cs.

Cesium tetraoxalate is calcined at 450°C to cesium carbonate, which is readily converted to cesium salts or glasses. The process has been used since Jan. 1, 1963, at the Fission Products Development Laboratory, ORNL, for preparing thousand-curie batches of ^{137}Cs chloride and glasses.

INTRODUCTION

This report describes the laboratory development of a process[1] for preparing a useful intermediate compound of cesium -- the tetraoxalate, $CsH_3(C_2O_4)_2 \cdot 2H_2O$ -- which can be crystallized from various cesium recovery process liquors. The starting materials used in this experimental work were cesium chloride, representing the simple salts occurring in solvent extraction raffinates, and cesium alum, the chemical form of fission-product cesium in the purification and recovery steps used at the ORNL Fission Products Development Laboratory.[2]

The behavior of cesium in oxalic acid solutions over a wide range of cesium and oxalic acid concentrations has been described by Foote and Andrews.[3] Processes based on the limited solubility of cesium and rubidium tetraoxalate in oxalic acid solutions have been used to recover these materials from relatively pure solutions.[4] Various processes have been used to convert cesium alum to other cesium compounds. In one of the early ORNL procedures ammonium hydroxide was added to the alum to form aluminum hydroxide and cesium sulfate. After filtering off the insoluble aluminum hydroxide, the cesium sulfate solution was passed through a hydroxide-form anion exchange column to remove the sulfate. In a later process, 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 hydrochloric acid. The platinum metal was removed by filtration, nitric acid was added, and the solution was heated to oxidize the ammonium ion (from hydrazine) and then evaporated to near dryness to allow the CsCl to crystallize.

Since 1954, the fission-product cesium has been recovered from various salt solutions by cocrystallization with ammonium alum[2] at the Fission Products Development Laboratory, ORNL. The process is based on concentration of cesium from solutions by isomorphous crystallization of the cesium with ammonium alum. The more soluble ammonium and rubidium alums are separated from the cesium alum by fractional crystallization.

In the current investigation, the variables in crystallizing cesium tetraoxalate from cesium chloride and cesium alum solutions, calcining the tetraoxalate to cesium carbonate, and preparing cesium salts and glasses from the carbonate were studied, and a process was developed for processing thousand-curie batches of ^{137}Cs.

The advantages of the new process are easy separation of the cesium from aluminum, simple calcination of the tetraoxalate, and ready conversion of the carbonate to usable end-products.

PREPARATION OF CESIUM TETRAOXALATE

Crystallization of Cesium Tetraoxalate from Cesium Chloride Systems

Cesium oxalates crystallized from solutions containing oxalic acid and cesium chloride are not definite compounds, but rather are mixtures of cesium tetraoxalate and oxalic acid. For example, the compound crystallized at 14°C from a 1.0 M oxalic acid solution containing 20 g of cesium per liter contained 33.6% Cs, 9.6 meq of H^+ per gram, 53% oxalate, and 12.6% water. This corresponds to a mixture of 0.4 mole of oxalic acid and 1 mole of cesium tetraoxalate. Recrystallization of this compound from water at 14°C gave a compound containing 38.3% Cs, 8.6 meq of H^+ per gram, 50.6% oxalate, and 10.4% water, corresponding to pure $CsH_3(C_2O_4)_2 \cdot 2H_2O$. These results agree with those found by Foote and Andrews.[3] The cesium was determined gravimetrically as cesium chloroplatinate. The hydrogen ion content was found by titration of a weighed amount of salt with standard sodium hydroxide to a phenolphthalein end-point. The oxalate content was determined by titration with a standard potassium permanganate solution.

<u>Effect of Temperature</u>. The solubility of cesium tetraoxalate in water and in 1.0 M oxalic acid solution increases with increasing temperature from 10 to 60°C (Table 1), with the solubility lower in 1.0 M oxalic acid than in water at any given temperature.

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

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

Effect of Oxalic Acid Concentration. At 14°C, as the oxalic acid concentration increased from 0.6 to 1.25 M, the solubility of cesium tetraoxalate decreased (Table 2). Solutions of oxalic acid and cesium chloride were cooled to 14°C and the resulting crystals were assayed. The cesium/oxalate ratio of the salts that crystallized out was 1:2.0 up to 1.0 M oxalic acid concentration. With oxalic acid concentrations higher than 1.0 M, however, a larger proportion of oxalic acid was cocrystallized.

Table 2. Effect of Oxalic Acid Concentration on Solubility of Cesium Tetraoxalate

Temperature 14°C; 1 hr stirring

Oxalic Acid Conc., M	Solubility of $CsH_3(C_2O_4)_2 \cdot 2H_2O$, g/liter	Cs/C_2O_4 Mole Ratio
0	13.0	1/2.0
0.6	8.7	1/2.0
0.8	5.7	1/2.0
0.9	4.8	1/2.0
1.0	4.8	1/2.4
1.1	4.5	1/2.7
1.2	3.9	1/3.5

Effect of Cesium Concentration. Increasing the cesium concentration of the solution from 10 to 40 g/liters increased the cesium tetraoxalate yield from 84 to 94% (Table 3).

Table 3. Effect of Cesium and Oxalic Acid Concentration on Percentage of Cesium Crystallized

Temperature 14°C; 1 hr stirring

Cs Conc., g/liter	Cs Crystallized, %	Initial Oxalic Acid[a] Conc., M
10	84	1.0
20	88	1.1
40	94	1.4

[a] As the cesium oxalate crystallizes, part of the oxalic acid is removed from the solution. Hence excess oxalic acid equal to the amount removed by the cesium must be added to maintain a free oxalic acid concentration of 0.8-0.9 M.

Effect of Hydrogen Ion Concentration. The percentage of cesium crystallizing out as tetraoxalate was highest in the hydrogen ion concentration range of 0.05-0.10 M H^+ (Table 4) which includes the range of concentrated oxalic acid solutions where no hydrogen ion adjustments are necessary. The effect of hydrogen ion concentration on cesium crystallization was determined at constant oxalate and cesium concentrations by varying it from 6 M to 0.004 M. Adjustments were made with hydrochloric acid or ammonium hydroxide.

Table 4. Effect of Hydrogen Concentration on Percentage of Cesium Crystallized

Temperature 14°C; 30 min stirring; 10 g of Cs per liter as CsCl; 1.0 M oxalic acid

Hydrogen Conc. M[a]	Cs Crystallized, %	Ammonium Conc., M
6.0[b]	0.8	None
1.0[b]	2.0	None
0.70[b]	22.0	None
0.316	57.0	None
0.158	71.0	None
0.100	84.0	None
0.089	88.0	0.08
0.081	88.0	0.15
0.056	89.0	0.2
0.028	55.0	0.33
0.010	20.0	0.5
0.004	4.0	0.8

[a] Adjustments were made with hydrochloric acid or ammonium hydroxide.

[b] These acid concentrations were calculated from acid additions. The remainder were determined from pH measurements.

Cocrystallization of Cesium with Ammonium Tetraoxalate. Since ammonium tetraoxalate also crystallizes from oxalic acid solutions,[5] cocrystallization of cesium with ammonium tetraoxalate was investigated as a method of precipitating cesium at concentrations below the solubility of cesium tetraoxalate. Table 5 shows that as little as 1 μc of ^{137}Cs will cocrystallize to the extent of 89.7% with ammonium tetraoxalate from 1 M oxalic acid solution containing only 0.075 M ammonium.

Table 5. Cocrystallization of Cesium on Ammonium Tetraoxalate

Temperature 14°C; 1 hr stirring; 1 M oxalic acid

Initial NH_4^+ Conc., M	Initial Cs Conc., g/liter	Cs Crystallized, %
0.0	Trace[a]	None
0.075	10	87.7
	2	88.0
	Trace[a]	89.7
0.15	10	87.6
	2	88.0
	Trace[a]	88.3
0.3	10	90.0
	Trace	90.1

[a] Approximately 1 μc of ^{137}Cs per milliliter.

Effect of Ethyl Alcohol. Oxalic acid is soluble in ethyl alcohol but cesium tetraoxalate is not. Thus with optimum concentrations for >90% cesium tetraoxalate recovery from cesium chloride solutions (40 g of cesium per liter and 1.4 M oxalic acid),the addition of sufficient alcohol to make a 50% solution increased the yield of cesium to >95% (Table 6). Above 1.0 M oxalic acid the acid did not cocrystallize with the cesium tetraoxalate from alcoholic solutions as it did from aqueous solutions. The cesium salt contained 39% Cs, 50.6% oxalate, 10.4% water, and 8.6 meq of titratable hydrogen per gram.

Table 6. Effect of Ethyl Alcohol on Crystallization of Cesium Tetraoxalate

Temperature 14°C; 1 hr stirring

Cs Conc., g/liter	Ethyl Alcohol in Aqueous, %	Oxalic Acid Conc., M	Cs Crystallized, %	Cs/C_2O_4 Mole Ratio
10	None	1.0	84	1/2.4
40	None	1.4	94	1/2.6
10	50	1.0	95	1/2.0
40	50	1.4	97.2	1/2.0
40	75	1.4	98.7	1/2.0

Crystallization of Cesium Tetraoxalate from Cesium Alum Solutions

The aluminum content of cesium tetraoxalate recovered from cesium alum solution must be sufficiently low that cesium glasses and other salts can be prepared from it. Cesium tetraoxalate containing less than 1% of the initial aluminum in solution was recovered from cesium alum solutions in 65-70% yield under optimum conditions, i.e., 20-25 g of cesium per liter, 1.25 M oxalic acid, and 0.05 M NH_4^+. The solution was heated to 70°C to effect solution of the alum and then cooled at a rate of 1°C/min to a temperature of 25°C and held there for 15 min while seed crystals formed. The temperature was then lowered 0.5°C/min to a final temperature of 14-15°C. The cesium tetraoxalate was filtered off and air dried. It had a bulk density of 1.1 kg/liter and contained 33 wt % cesium.

Effect of Cesium Alum Concentration. Crystallization of cesium tetraoxalate from concentrated solutions of cesium alum and oxalic acid is hindered by the tendency of the solution to become supersaturated. Under these conditions cesium tetraoxalate crystals form slowly and, once crystallization starts, the tetraoxalate has a tendency to cocrystallize with aluminum oxalate. With cesium concentrations below 25 g/liter, less than 2% of the aluminum cocrystallized; however, at higher cesium concentrations the percentage of aluminum cocrystallizing increased rapidly to >80% (Table 7).

Table 7. Effect of Cesium Alum Concentration on Cocrystallization of Aluminum Oxalate with Cesium Tetraoxalate

Temperature 14°C; 1 hr stirring

Initial Cs Conc., g/liter	Cesium Crystallized, %	Al Carried, % of Initial Al in Solution	Initial Oxalic Acid Conc., M[a]
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

[a] See footnote, Table 3.

Effect of Hydrogen Ion Concentration. Since the hydrogen ion concentration of solutions of cesium alum and oxalic acid is higher than that of solutions of cesium chloride and oxalic acid, the cesium tetraoxalate yield in the alum system is lower than that in the corresponding cesium chloride system (see Table 4). From solutions of 1.0-1.2 M oxalic acid containing 10-25 g of cesium per liter as cesium alum, and at a hydrogen ion concentration of 0.3 to 0.5 M, only 60-65% of the cesium crystallized as cesium tetraoxalate.

Effect of Ammonium Ion. The presence of as little as 0.05 M ammonium ion increased the cesium precipitation from a 20 g/liter solution from 65 to 75% and decreased the aluminum carried from 2.5 to only 0.5% of the aluminum in the solution (Table 8). Apparently, ammonium tetraoxalate crystals form and act as seed crystals which prevent supersaturation. On the other hand, larger amounts of ammonium ion increase the volume of crystals, which is not desirable.

Table 8. 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°/min

Cs Conc., g/liter	NH_4^+ Conc., M	Hydrogen Ion Conc., M	Cs Crystallized, %	Al Carried, % of Al Initially in Solution
2.5	0.075	0.16	77.2	0.1
10	0.035	0.25	75.0	0.1
20	0.0	0.32	65	2.5
20	0.05	0.32	75	0.1
20	0.3	0.32	77	0.5

Effect of Ethyl Alcohol. Ethyl alcohol increased the cocrystallization of aluminum oxalate with cesium tetraoxalate. When a 1.2 M oxalic acid solution containing 20 g of cesium per liter, as alum, and 50% ethyl alcohol was cooled to 14°C, 94% of the cesium crystallized, but 95% of the aluminum also cocrystallized as aluminum oxalate.

RADIATION STABILITY OF CESIUM TETRAOXALATE

Beta and gamma irradiation for a time equal to that in which an intermediate precipitate would be needed did not cause significant weight loss due to radiolysis of cesium tetraoxalate. About 4.5 grams of cesium containing 150 curies of ^{137}Cs was precipitated as the tetraoxalate, filtered off, and air dried for 24 hr. Since there was no detectable weight loss (limit of detection 0.01 g) during the 24-hr period, there apparently was little or no radiolysis of the compound. Hence cesium tetraoxalate seems to be sufficiently stable to permit crystallization of thousand-curie batches of ^{137}Cs without appreciable weight loss.

CESIUM RECOVERY FROM OXALIC ACID SOLUTIONS

Since crystallization of cesium tetraoxalate is only 80-90% complete from simple salt solutions and 65-75% from cesium alum solutions, the cesium remaining in the solution must be recovered and recycled. The method used depends on whether the cesium was crystallized from a simple salt solution or from an alum solution.

Solutions Containing Simple Salts

The 10-20% cesium remaining in the mother liquor was recovered in laboratory experiments by cocrystallization with ammonium tetraoxalate. After the cesium tetraoxalate had been filtered, the supernatant liquid was heated to approximately 70°C and sufficient NH_4OH added to give a final NH_4^+ concentration of 0.1 $\underline{M}$. When this solution was cooled to 14-16°C, 90% of the remaining cesium was cocrystallized with the ammonium tetraoxalate. This scavenging step can be repeated as many times as necessary.

Solutions Containing Alum

Cesium in the supernatant alum solution was also recovered by cocrystallizing cesium with ammonium tetraoxalate. After heating to 70°C, 0.1 mole per liter of NH_4^+ as NH_4OH was added and the solution cooled to 14-16°C; of the remaining cesium, 90% cocrystallized with the ammonium tetraoxalate.

Cesium losses can be prevented by recycle of the supernatant containing 25-35% of the cesium to the cesium — ammonium alum crystallization step. In laboratory studies, more than 97% of the cesium present was recovered by one such crystallization. In the cesium — ammonium alum process, the cesium is recovered by three crystallizations, each time from the mother liquor of the preceding crystallization. The ammonium alum concentration (saturated) is sufficiently high and the volume is so much larger than that of the oxalic acid solution that the oxalic acid does not hinder the cesium — ammonium alum crystallization. Repeated recrystallization of the alum then gives cesium alum, which is the feed material for the tetraoxalate process.

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.

Cesium tetraoxalate was heated for various times at various 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, oxalate, and carbonate. From these studies, the reactions at different temperatures were determined to be

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

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

$$2CsHC_2O_4 \xrightarrow{200\text{-}400^\circ C} Cs_2C_2O_4 + H_2C_2O_4$$

$$Cs_2C_2O_4 \xrightarrow{400\text{-}450^\circ C} \text{Mixture of } Cs_2CO_3,\ Cs_2O,\ CO, \text{ and } CO_2$$

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

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, $CsHC_2O_4$. This compound is not deliquescent and is useful as an intermediate for preparing cesium glasses. At temperatures above 400°C cesium oxalates are converted to mixtures of cesium carbonate and cesium oxide. The conversion is complete after 2 hr at 450°C. In the laboratory, cesium tetraoxalate was converted to cesium carbonate by heating in a shallow nickel tray at 125°C in an air stream for 2 hr and then at 450°C for 2 hr. The cesium compounds prepared from cesium tetraoxalate are free of Al_2O_3 and Fe_2O_3, two of the major contaminants of cesium prepared by methods discussed earlier, since oxalic acid complexes both aluminum and ferric iron and keeps the ions in solution. Aluminum (~0.1 mg/g cesium tetraoxalate) that cocrystallizes with the cesium tetraoxalate is converted to the insoluble oxide at 450°C and is removed by filtration of the cesium carbonate solution prior to making the source compounds. Carbon, which also forms from the calcination of ammonium tetraoxalate, is removed by filtration. The resulting cesium carbonate solution contains no detectable alkaline earth, trivalent metal ions, or ammonium ions. The alkaline metal content is dependent on the separation obtained by the cesium alum purification.

PREPARATION OF CESIUM SALTS AND GLASSES FROM CESIUM CARBONATE

Cesium chloride[2b] and cesium sulfate[6] are used as source forms for ^{137}Cs radiation sources. For some uses, the more inert cesium glass may be preferred for radiation sources. Recent work at ORNL on glasses containing 40-50% fission-product cesium for use as heat sources has been reviewed.[7]

These source materials and other cesium salts are easily prepared from cesium carbonate (last part of process shown in Fig. 1). The carbonate prepared from cesium tetraoxalate is first dissolved in water and

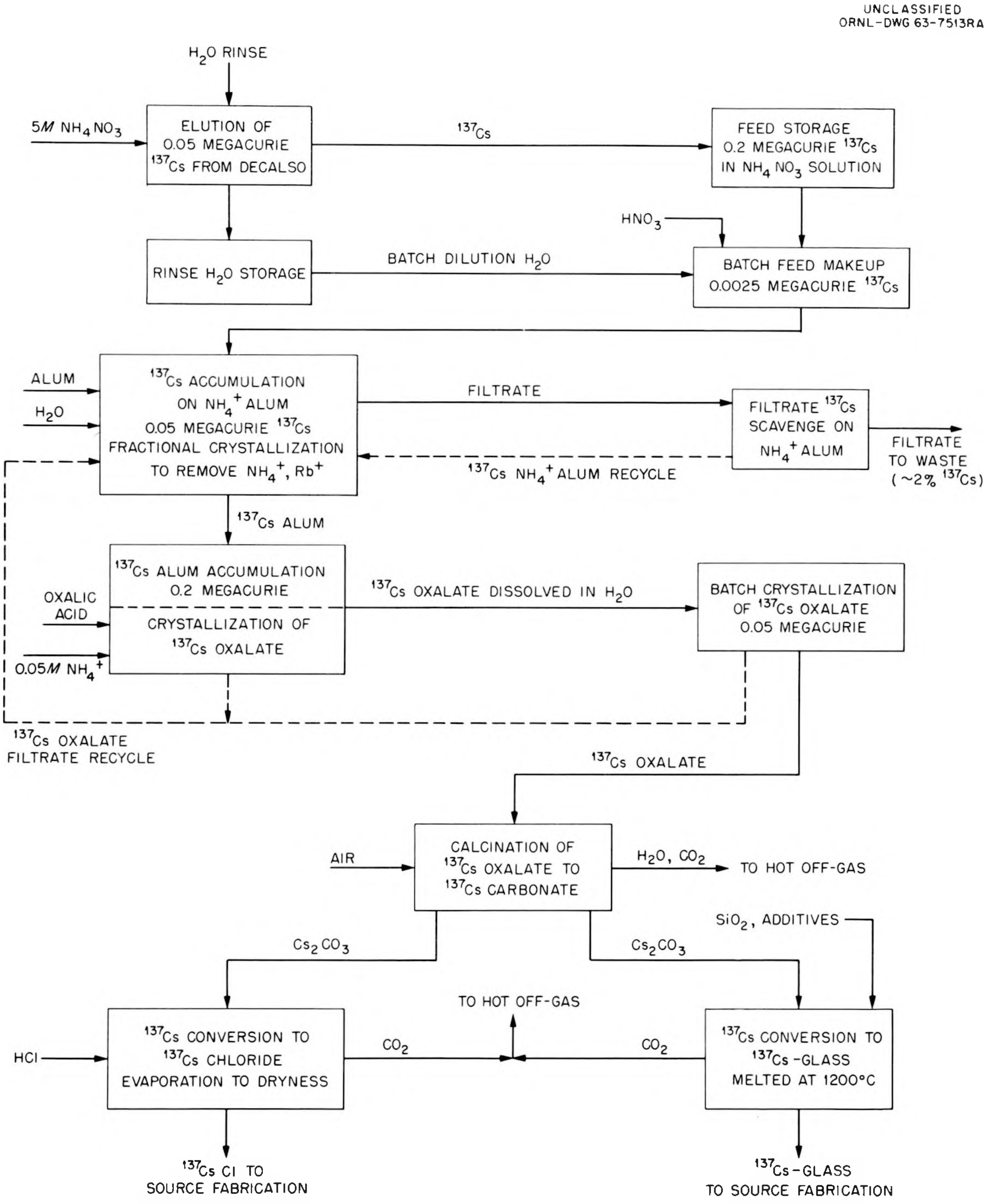

Fig. 1. FPDL ^{137}Cs Processing.

filtered to remove trace amounts of aluminum oxide and carbon. In preparing cesium chloride the carbonate is decomposed by adding a stoichiometric amount of HCl. The solution is warmed to expel CO_2 and finally evaporated to dryness. Cesium chloride prepared by this procedure contained <0.1% Al and <0.1% Fe, and did not contain any other detectable impurities.

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. Cesium phosphate is prepared similarly.

Cesium carbonate is also useful in preparing ^{137}Cs sources as glasses. To prepare a 100-g batch of glass with the empirical formula,

$$0.8\ Cs_2O \cdot 0.2\ BaO \cdot 3.5\ SiO_2,$$

56.0 g of Cs_2CO_3, 8.5 g of $BaCO_3$, and 45.0 g of SiO_2 were blended and the mixture was heated at 1200°C for 3 hr and annealed at 500°C for 2 hr. Cesium oxide volatilized from the melt at a rate of approximately 0.5 $mg/cm^2 \cdot hr$ at 1200°C. The glass contained approximately 43% cesium and had a density of 3.2 g/cm^3. The ^{137}Cs content of the glass was approximately 45 curies per cc. Cesium was leached from the surface of the glass at a rate of 1.3 $mg/cm^2 \cdot day$ by a moving film of distilled water at 25°C during the first day, and at a rate of 0.2 $mg/cm^2 \cdot day$ for a one-week period.

APPLICATION OF CESIUM TETRAOXALATE PROCESS TO FISSION-PRODUCT CESIUM PROCESSING

The process for converting cesium alum to cesium tetraoxalate and subsequently to other cesium compounds[1] is used routinely in the Fission

Products Development Laboratory at ORNL. Fission-product cesium is purified by the alum process in 0.05-megacurie batches until 0.2 megacuries of pure cesium alum was accumulated. The cesium alum was then converted to cesium tetraoxalate, dissolved, and recrystallized in smaller batches. The first crystallization was not necessary for purification but was very useful in the transfer of cesium from the cesium alum crystallizers and aided in getting representative samples of the solution for radiochemical analysis.

The first crystallization was made in a 400-liter volume in 0.2-megacurie batches with 1.2 to 1.25 $\underline{M}$ oxalic acid and 15 to 25 g of cesium per liter. The cesium tetraoxalate was dissolved in water and transferred in smaller batches to a 100-liter vessel.

The second crystallization was made in the 100-liter vessel in 0.05-megacurie batches, with 1.1 to 1.2 $\underline{M}$ oxalic acid and 15 to 25 g of cesium per liter. The solution was cooled to 25°C at a rate of 1°C/min. The cooling rate was halted at 25°C for 15 min and then cooled to 16°C at a rate of 0.5°C/min. Yields of cesium tetraoxalate in both crystallizations were 65-70%. In later runs, the addition of sufficient ammonium ion to make the solution 0.05 $\underline{M}$ NH_4^+ increased the yields of cesium to 70% on the first crystallization and to 92% on the second crystallization. Cesium not crystallized was recycled to the alum system for recovery as cesium alum. Twenty runs were made with an average yield of 0.03 megacuries of ^{137}Cs as cesium tetraoxalate per run. The integrated cesium process used at the Fission Products Development Laboratory, ORNL, is shown in Fig. 1. The cesium tetraoxalate is calcined at 350°C in a shallow nickel tray in a muffle furnace having an air sweep. Volatility of cesium is no problem during calcination. The fission-product cesium tetraoxalate forms Cs_2CO_3 by calcination at a lower temperature than stable cesium. Also, during storage of large quantities of cesium tetraoxalate, the compound decomposes to Cs_2CO_3 in a two-week period. The cesium carbonate is assayed by calorimetric methods[8] and made into cesium chloride, cesium glass, or cesium sulfate.

In the period from Jan. 1, 1963, to Jan. 1, 1964, 0.6 megacurie of ^{137}Cs as alum was converted to cesium tetraoxalate and subsequently made into various source compounds.[9] Three thousand curies as Cs_2SO_4, 0.114 megacuries as cesium glass, and the remainder as cesium chloride were prepared during this period. During continuous operation, cesium alum has been converted to cesium chloride at a rate greater than 0.05 megacuries/week.

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