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THE RECOVERY OF Cs^{137} FROM ORNL RADIOCHEMICAL WASTE

A. T. GRESKY

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LABORATORY SECTION

THE RECOVERY OF Cs^{137} FROM ORNL RADIOCHEMICAL WASTE

A. T. Gresky

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1.0 Abstract

This report describes a method for the recovery of 37 year Cesium^{137} from ORNL waste solutions by co-crystallization with potassium aluminum sulfate.

2.0 Introduction

Alkaline radiochemical waste solutions containing the fission products, 37 year Cs^{137} and 1.0 year Ru^{106}, represent the starting solution for the experiments described here.

It is found in the following decay chain:

$$Te^{137} \xrightarrow[\beta]{1\ min} I^{137} \xrightarrow[\beta]{22S} Xe^{137} \xrightarrow[\beta]{3.9m} Cs^{137} \xrightarrow[\beta]{37Y} \underset{stable}{Ba^{137}(i.t.)}$$

Cs^{137} emits a 0.52 Mev beta particle which is essentially in equilibrium with a 0.66 Mev gamma formed by the internal transition of Ba^{137} with a half-life of 158 seconds.(1)

A process was developed for concentrating Cesium^{137} activity by volume reduction and crystallization of the bulk solids from methanol solutions.(2) This procedure was effective in removing solids and yielded a solution containing about 80% of the cesium, but necessitated complicated operational facilities.

The possibility of using a carrying technique based on the low solubility of cesium alum, especially in the presence of high concentrations of the lighter alkali-alums was suggested(3) and this report presents a simple cesium recovery process based on this principle. The process described has not as yet been extended to the production of carrier-free tracer. However, preliminary scouting experiments indicate that cesium can be separated from aluminum and alkali metal contaminants by ion exchange methods.

3.0 Summary

A process has been demonstrated on a one liter scale for the recovery of Cs^{137} from ORNL alkaline radiochemical wastes. The process involves co-crystallization, or carrying, of cesium on potassium alum at a pH of 4.5. Yields of 95-100% have been obtained.

It is recommended that the process be developed further as an initial step in the production of carrier-free tracer or as a method for removing Cs from waste solutions before storage.

4.0 Experimental

4.1 Neutralization of the Alkaline Waste with Sulfuric Acid

Concentrated sulfuric acid was added to the alkaline solution to neutralize the sodium hydroxide and destroy carbonates. An amorphous precipitate formed at about pH 6.0 but redissolved at pH 4.5. This was the optimum pH for the crystallization. Crystallization of the potassium alum at a higher pH resulted in contamination of the crystals by the precipitate. It was found that 50 milliliters of 98% H_2SO_4 per liter of supernatant liquid were necessary to attain this pH.

4.2 Crystallization of Potassium Alum for Cesium Carrying

The neutralized solution was heated to 60°C, 350 grams $KAl(SO_4)_2 \cdot 24H_2O$/liter were added, and the solution was agitated until the salt dissolved. On cooling, crystallization began at about 32°C, and at 25°C about one-half of the salt had recrystallized and was found to carry 95-100% of the cesium present. Only about 5% of the Ru^{106} carried with the crystals.

4.3 Continuous Recrystallization Studies

By replenishing the potassium alum in amounts equal to its solubility in a single batch of the alkaline waste, it was found that salt could be used repeatedly to carry cesium from several batches of supernatant. By this means a very high concentration of cesium was effected and the quantity of reagent required reduced by a factor of two. Losses were not increased significantly.

Using one liter batches of the neutralized waste solutions, ten successive runs were made to determine the feasibility of this continuous concentration method. The first run was made using 350 gm $KAl(SO_4)_2 \cdot 24H_2O$/liter, and the supernatant liquor was decanted and analyzed. Then 200 grams of potassium alum was added to the crystals from the first run and another liter of alkaline waste, at 60°C, was used to dissolve the crystals. After cooling to 25°C, it was again observed that the crystals carried essentially all of the cesium from the two batches. This procedure was followed through eight additional runs employing the same quantity of $KAl(SO_4)_2 \cdot 24H_2O$. Analysis of the decanted supernatant indicated less than 5% cesium loss.

5.0 Recommendations and Procedure

This procedure is recommended for scavenging Cesium^{137} from waste solutions and thereby provides a source of relatively high specific activity for carrier-free tracer production. Ion exchange is recommended for

further purification of the tracer. It has been demonstrated that aluminum and alkali metal contaminants can be separated from cesium using Dowex 50 resin[4][5].

It is proposed that further work be carried out using commercial grade dehydrated potassium alum if large-scale development is desired. Use of an inexpensive reagent is important on a production scale because of the relatively large amounts required. Use of refrigeration to obtain temperatures below 25°C reduces the amount of alum necessary, although this does not seem to be economical (Table I).

The wide variation in composition of different waste solutions may demand small changes in the procedure; but, in general, the process is as follows:

(1) Neutralize the alkaline waste solution with 98% H_2SO_4 to a pH of 4.0-4.5.

(2) To the neutralized supernatant, at 60°C, add an amount of $KAl(SO_4)_2 \cdot 24H_2O$ equivalent to twice its solubility at 25°C.

(3) Cool, with agitation, to 25°C to allow crystallization; discard the supernatant liquor.

(4) Add to the crystals an amount of $KAl(SO_4)_2 \cdot 24H_2O$ equivalent to that soluble in the previous batch; add a fresh volume of supernatant solution, heat to 60°C, and again crystallize.

(5) Repeat this procedure on as many batches as are required for the concentration desired.

Table I

Solubility Data for Alkali Alums[6]

Temp. (deg.C)	Solubility, (% by weight in water)		
	Potassium Alum	Rubidium Alum	Cesium Alum
0	2.87	0.715	0.21
15	4.80	1.25	0.35
30	7.74	2.15	0.60
45	12.48	3.85	1.04
60	19.85	6.89	1.96
80	-	17.77	5.21
100	-	-	18.60
M.P.	54.45	58.5	62.0

Table II

Solubility of Potassium Alum in the Presence of Various Concentrations of Sodium Alum at 25°C (6)

Solubility (% by weight of each component)	
Sodium Alum	Potassium Alum
4.8	7.8
10.0	6.1
12.1	5.7
15.4	5.3
21.1	4.7
33.7	3.8
55.6	2.7
76.7	1.7

6.0 Bibliography

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