

RECOVERY OF CESIUM AND STRONTIUM FROM ACIDIC HLW FROM POWER REACTORS WITH INORGANIC ION EXCHANGERS

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ABSTRACT

Recovery of Cs-137 and Sr-90 from 1AW acidity waste solution have been studied by using Titanium Phosphate-Ammonium Molybdophosphate (TiP-AMP) and Polyantimonic acid (PAA). These inorganic ion exchangers show favorable performance for the adsorption and elution of Cs-137 and Sr-90. The product, Cs-137 has more than 99% radioactive purity and there is a high decontamination factor for Ru-103, Zr-95, Sr-90, Na-22, Am-241, but less so for Rb-86 and Ce-144. The product, Sr-90 has more than 98% radioactive purity and there is a high decontamination for Ru-103, Zr-95, Cs-137, Na-22 and Am-241, but less so for Ce-144.

A design of the recovery process of Cs-137 and Sr-90 is suggested from the individual experimental results with TiP-AMP and PAA.

INTRODUCTION

The utilization of high-level radioactive liquid waste from spent fuel reprocessing containing useful isotopes is a matter of great importance for their potential nuclear application and radioactive waste disposal. (1-4)

Two nuclides that have received considerable attention are Cesium-137 and Strontium-90. Possible techniques for separation of Cs-137 and Sr-90 from radioactive waste solution (1AW) fall under three categories; precipitation, solvent extraction and ion exchange. In general, the precipitation and solvent extraction processes are rejected because of their adverse effect on waste management due to chemical reagents added or they are not effective collectors of Cs and Sr in the acid range compared to the easily attainable in 1AW with extraction. Furthermore, radiation decomposition also easily occurs in extractant.

Since inorganic ion exchangers and adsorbents usually have high ion selectivities and high radiation resistances, several inorganic ion exchangers have been developed for removing Cs-137 and Sr-90 from the 1AW waste solution. Also Ammonium molybdophosphate (AMP), titanium phosphate (TiP), and Ferro-Cyanide Zinc are used for Cs-137 and polyantimonic acid (PAA) for Sr-90.

As is well known, these inorganic ion exchangers have some shortcomings. Ammonium molybdophosphate is powdered material and cannot be loaded in column. Zirconium phosphate and Titanium phosphate are amorphous or semi crystalline ion exchangers with mono functional phosphate groups. They easily block up the exchange column due to released micro amounts of phosphate groups combined with trivalent action in the feed solution.

Ferro-Cyanide Zinc is more of a crystalline material, but the ion exchange irreversibility can not elute Cs-137 from the column; possibly, these facts are favorable to disposal.

Separation of Sr-90 from 1AW waste solution is a more difficult parting process. None of the inorganic ion exchangers permit adsorption of Sr-90 with the high acidity, except for polyantimonic acid. Due to the polyantimonic acid there's a high selectivity for Sr-90. Eluting of Sr-90 from the column is more difficult. There are no alternatives for the elution of Sr-90: 8.0 mol/L HNO₃ + 0.5 mol/L AgNO₃ elutriant was

employed with about 98% of the Sr-90 extracted from the column.

This paper describes our preliminary laboratory tests with the new inorganic ion exchangers TiP-AMP and PAA for recovery of Cs-137 and the Sr-90 unique Sr-90 procedure. Based on individual tests, there is a possible design of a combination of these techniques for recovery of Cs-137 and Sr-90.

Experimental Procedures

• Preparation of Inorganic Ion Exchangers:

Titanium phosphate (TiP) was prepared in the laboratory according to the literature methods with good size granules (50-100 mesh). Then the TiP was loaded in a column or beaker and combined with AMP using ammonium molybdate via a dynamic or static method resulting in a yellow complex ion exchanger TiP-AMP. The exchanger was washed with distillation water to remove the free acid until the effluent Ph was neutral and then dried in air for several days (9). Polyantimonic acid (PAA) was prepared by hydrolyzing antimony pentochloride in excess water with various ratios. The precipitate was allowed to age several days, product washed by 1.0 mol/L HCl and dried 3 days at various temperature (10).

• Determination of Breakthrough Curves of Cesium and Strontium:

A 1 gm exchanger (50-100 mesh) was loaded in a glass column. The bed volume being 1.0 ml/g for TiP-AMP and 1.1 ml/g for PAA. The column was washed by 10 BV of 1.0 mol/L HNO₃.

The simulated solution containing tracer Cs-137 and Sr-85 + 89 was pressed through the individual column at a fixed rate 2.0-3.0 ml/hr at 13°C. Each part of the effluent (1 ml) from the column was collected with an automatic collector until the C/C₀ reached approximately 1. The breakthrough capacity were calculated from the curves. The results show 0.47 m mol/g (C/C₀ = 0.01 BV = 85) for Cs and 0.22 m mol/g (C/C₀ = 0.01 BV = 40) for Sr at 64°C. The results are shown in Figs. 1 and 2 and Table I.

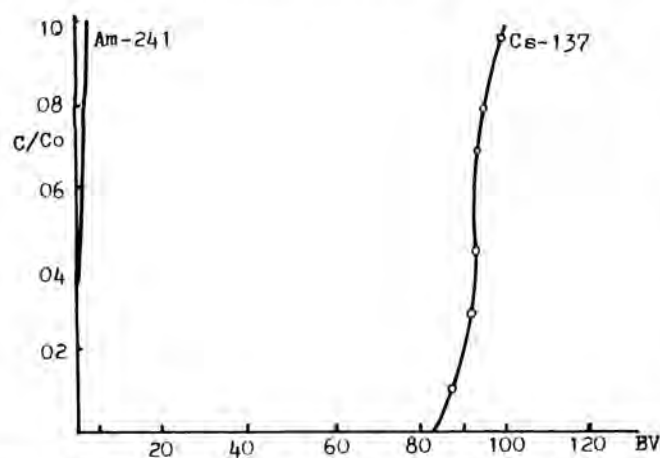


Fig. 1. Breakthrough curves of Am-241 and Cs-137 from the TiP-AMP column.

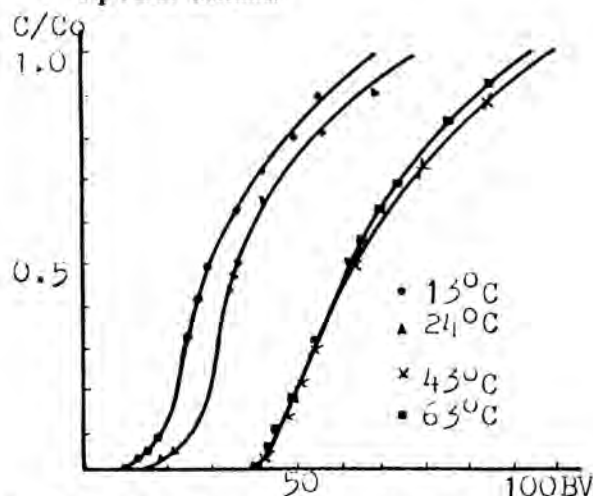


Fig. 2. Breakthrough curves of Sr-89 in different temperatures from the PAA column.

- Effect of Acidity on the Cesium and Strontium Capacity of the TiP-AMP and PAA:

The effect of the feed acidity on the Cs and Sr capacity was investigated via the above static method. The results are shown in Table II.

- Effect of Temperature and Flow Rate on the Strontium Capacity of the PAA:

The exchange capacity of the PAA depends on the temperature and flow rate. This was studied with the above static column exchange method. The results are shown in Tables III & IV.

- Effect of Sodium Ion Concentration on the Capacity of TiP-AMP:

Both sodium and Cesium belong to the alkali metals. It is very meaningful to observe the ion exchange competition between Na^+ and Cs^+ ; hence, the exchange capacity was evaluated with the dynamic method at different Na^+ concentrations. It was found that the sodium ion concentration of feed solution greatly influenced the cesium capacity of the TiP-AMP. Results are shown in Fig. 3.

- Effect of Cycle Use on the Cesium Capacity of the TiP-AMP and Strontium Capacity of the PAA:

TABLE I

Composition of Simulated Feed Solution

Ion	Concentration (g/L)	Ion	Concentration (g/L)
Na^+	2.5	Ce^{3+}	3.75
Cs^+	0.75	Fe^{3+}	2.0
Rb^+	0.075	Zr^{4+}	2.0
Sr^{2+}	0.5	UO_2^+	0.25
Ba^{2+}	0.25	HNO_3	1 mol/L

TABLE II

The Exchange Capacity of Various Acidities (in m mol/g)

Exchanger	Acidity mol/L				Breakthrough %
	0.5	1.0	2.0	4.0	
TiP-AMP (for Cs)	0.5	0.47	0.46	0.45	1
PAA (for Sr)	0.22	0.22	0.20	0.17	1
	0.35	0.37	0.36	0.38	50

TABLE III

Effect of Temperature on the Sr^{2+} Capacity of PAA

Temperature $^{\circ}\text{C}$	Breakthrough 1% m mol/g	Breakthrough 50% m mol/g
13	0.05	0.17
24	0.10	0.20
43	0.22	0.35
63	0.22	0.35

TABLE IV

Effect of Flow Rate on the Sr Capacity of PAA

Flow Rate BV/hr	Breakthrough 1% m mol/g	Breakthrough 50% m mol/g
0.5	0.220	0.35
1.0	0.220	0.37
2.0	0.200	0.35
3.0	0.170	0.39
4.0	0.150	0.38

After the ion exchange column eluted Cs and Sr individually, it was regenerated with 10 BV of 1.0 mol/L HNO_3 for TiP-AMP and concentrated HNO_3 10 BV for the PAA at 60°C . These exchanger cycles were investigated. The results are shown in Table V.

Recovery of Cesium-137 and the Decontamination Factor of Ce-141, Ce-144, Ru-106, Ru-103, Zr-95 and Nb-95:

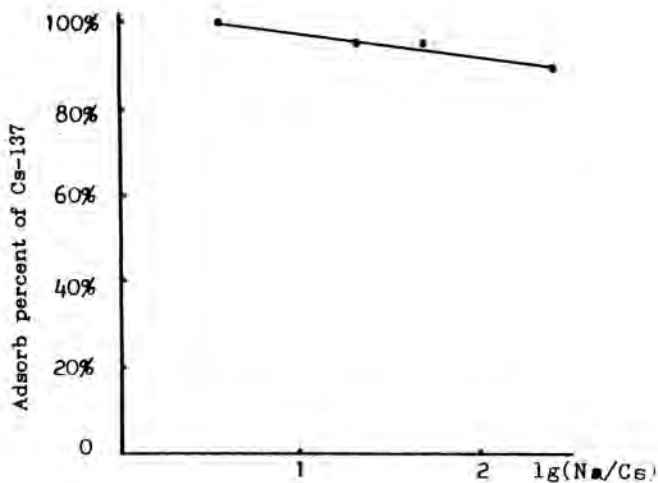


Fig. 3. Effect of Na/Cs on the adsorb percent of Cs-137.

TABLE V

Regeneration Studies on TiP-AMP and PAA Columns

Cycle	Capacity of Cs C/C0 = 0.01 m mol/g	Capacity of Sr C/C0 = 0.01	C/C0 = 0.5 m mol/g
1	0.47	0.22	0.35
2	0.49	0.17	0.24
3	0.50	0.15	0.24
4	0.49	0.10	0.25
5	0.47		
6	0.48		

To simulated feed solution a fresh fission product was added as an indicator. The feed solution passed through with a flow rate 2.0-3.0 ml/hr at room temperature until 70 BV. The loaded column was washed with 5 BV of 0.5 mol/L HNO₃ and 15 BV 0.5 mol/L (H₂C₂O₄ + HNO₃) for removing Ce-144, Ca-141, Ru-106, Ru-103, Zr-95 and Nb-95 and the purpose of the decontamination was achieved.

Then Cesium was eluted by passing 10 BV 5.5 mol/L NH₄NO₃ + 0.5 mol/L HNO₃ at 60°C. The total Cesium elutriant was examined on its activity with a 4096 channel analyzer with the results shown in Table VI and Fig. 4.

- Recovery of Strontium-90 and the Decontamination Factor of Ce-141, Ce-144, Ru-103, Ru-106, Zr-95 and Nb-95:

Feed solution (containing a fresh fission product) was passed through the column was at a flow rate of 3.0-4.0 ml/hr at 60°C, the loaded column was washed by 5 BV of 2.0 mol/L HNO₃ and 15 BV of 1.0 mol/L H₂C₂O₄ for removing Ru-103, Ru-106, Ce-144, Ce-141, Zr-95 and Nb-95. Strontium was eluted by passing 20 BV of 8.0 mol/L HNO₃ + 0.5 mol/L AgNO₃ at 60°C. The total strontium was examined with a

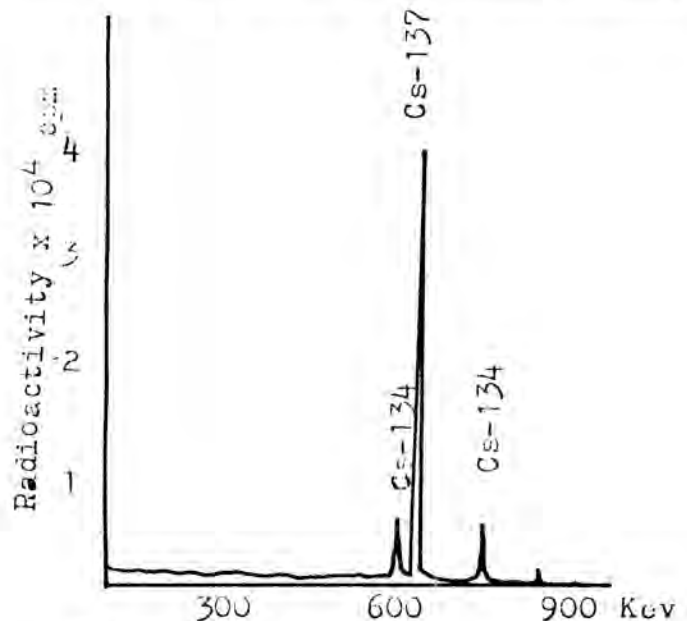


Fig. 4. Gamma spectrometry of recovered Cs-137.

TABLE VI

Decontamination Factor of Nuclides in the Cs and Sr Process

Nuclides	D.F for Cs	D.F for Sr
Ce-141	undetected	-
Ce-144	undetected	72
Ru-103	106	undetected
Zr-95	2300	undetected
Nb-95	-	undetected
Na-22	1164	11
Sr-85 + 89	850	
Am-241	758	61
Rb-86	1.5	undetected
Cs-137 *	undetected	

4096 channel analyzer. The results are given in the Table and Fig. 5.

RESULTS AND DISCUSSIONS

The results reveal that the combined TiP-AMP is much better than titanium phosphate (TiP) or ammonium molybdophosphate (AMP) alone. The advantage are:

- solved the TiP exchange column block-u problem
- AMP combined with TiP, solved an outstanding issue of granulation of the AMP
- behavior of the exchange was much better than an individual TiP and AMP

Polyantimonic acid is a better ion exchanger for the recovery of Strontium than other inorganic ion exchangers with acid radioactive waste; but, some shortcomings need to be studied in the future.

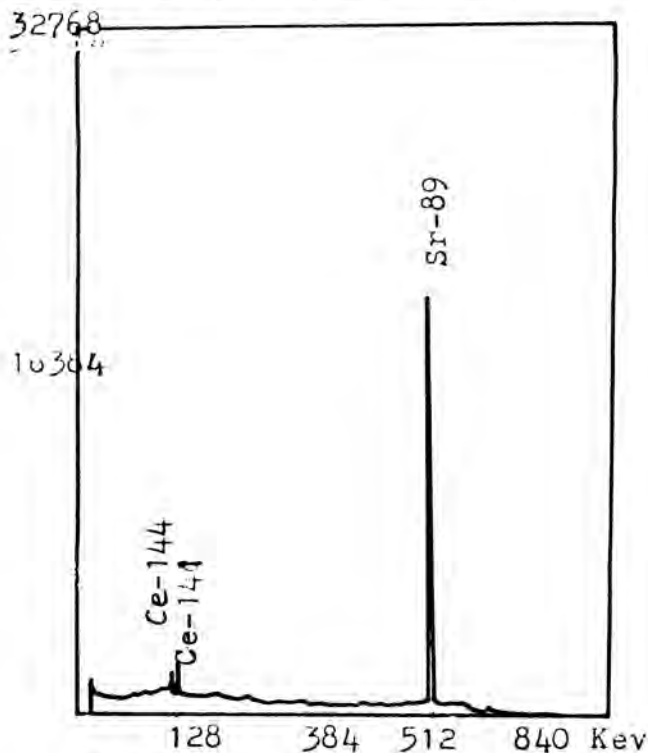


Fig. 5. Gamma spectrometry of recovered Sr-89.

From the above results, we can make a design of a processing system for the recovery of Cesium and Strontium from 1AW waste in a hotcell test for verification as shown in Fig. 6.

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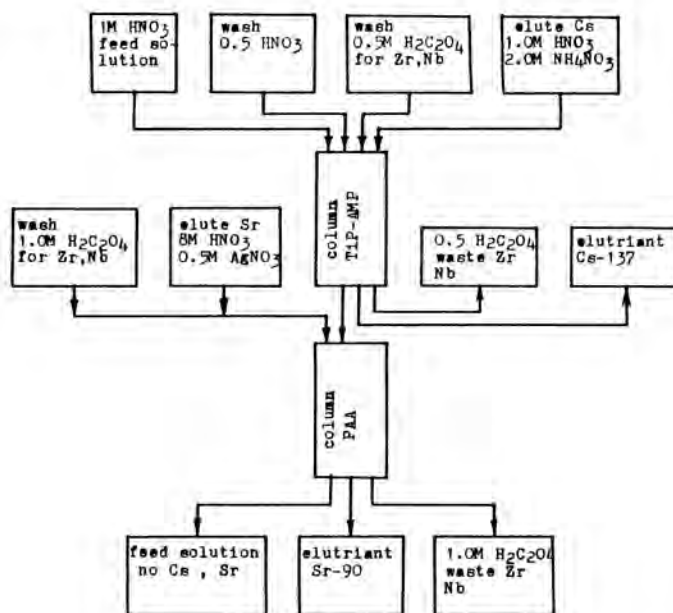


Fig. 6. Recovery process of Cs-137 and Sr-89 from 1AW.