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CESIUM ABSORPTION FROM ACIDIC SOLUTIONS USING AMMONIUM MOLYBDOPHOSPHATE ON A POLYACRYLONITRILE SUPPORT (AMP-PAN)

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ABSTRACT

Recent efforts at the Idaho Chemical Processing Plant (ICPP) have included evaluation of cesium removal technologies as applied to ICPP acidic radioactive waste streams. Ammonium molybdophosphate (AMP) immobilized on a polyacrylonitrile support (AMP-PAN) has been studied as an ion exchange agent for cesium removal from acidic waste solutions. Capacities, distribution coefficients, elutability, and kinetics of cesium extraction have been evaluated. Exchange breakthrough curves using small columns have been determined from 1M HNO_3 and simulated waste solutions. The theoretical capacity of AMP is 213 g Cs/kg AMP. The average experimental capacity in batch contacts with various acidic solutions was 150 g Cs/kg AMP. The measured cesium distribution coefficients from actual waste solutions were 3287 mL/g for dissolved zirconia calcines, and 2679 mL/g for sodium-bearing waste. The cesium in the dissolved alumina calcines was analyzed for; however, the concentration was below analytical detectable limits resulting in inconclusive results. The reaction kinetics are very rapid (2-10 minutes). Cesium absorption appears to be independent of acid concentration over the range tested (0.1M to 5M HNO_3).

INTRODUCTION

The Idaho Chemical Processing Plant (ICPP), located at the Idaho National Engineering Laboratory, reprocessed spent nuclear fuels to recover fissionable uranium, until a mission change in 1992. The radioactive liquid wastes were solidified in a fluidized bed calciner at 500°C. The resulting granular solid (calcine) is composed of mainly of metal, actinide, lanthanide, and fission product oxides and fluorite. The radioactive components comprise <1 wt.% of the total calcine volume [1]. Approximately 3800 m^3 of calcined waste is presently stored in stainless steel bins placed within concrete vaults [2]. An additional 1.5 million gallons of acidic liquid waste that has a high concentration of sodium are being stored in tanks prior to final disposal. This liquid sodium-bearing waste was primarily generated from decontamination and solvent wash activities. Direct calcination is difficult to perform because of the high sodium content. The waste was previously blended with aluminum nitrate or raffinates from aluminum or zirconium fuel dissolution before calcination. Cesium and strontium are the major heat producers and contributors of the radiation field for both calcine and sodium-bearing waste. Radioactive and nonradioactive cesium are formed in the fission and decay processes and are present in ICPP waste.

ICPP calcines and sodium-bearing waste may undergo pretreatment by separating the radioactive constituents from the matrix prior to immobilization and final disposition. The inert matrix materials could then be disposed of as low level waste and the radioactive components (contained within a ceramic or glass form) would be disposed of as high- level waste in a geological repository. Removal of the cesium and strontium would significantly decrease the radioactivity level of the waste; however, removal of transuranic elements is required to decrease the alpha radioactivity level to meet Nuclear Regulatory Commission Class A requirements for the final waste form.

EXPERIMENTAL PROCEDURES

Reagent Preparation. The dissolution of pilot plant calcines was performed as outlined by the parameters of Herbst, et al. [3]. The dissolution of actual zirconia and alumina calcine was performed as outlined by the parameters of Brewer, et al. [4]. The actual sodium-bearing waste was taken from tank WM-185. This tank is representative of the various tanks containing sodium-bearing waste. Solutions of 2 g Cs/L in 3M HNO_3 and 20 g Cs/L in 3M HNO_3 were used for capacity tests. Other solutions of various cesium concentrations in 1M HNO_3 were also used and are listed with the respective experiments.

Sample Preparation for Analytical Analysis. The resin was used wet, as shipped, in all of the experiments performed. All batch test samples were mixed on a vortex mixer or a rotary wheel for the desired contact time (generally 30 minutes). The post-contact solution was filtered through a 0.45μm acrodisk filter attached to a 10 milliliter syringe. Nonradioactive cesium, sodium, and potassium analyses were performed by atomic emission. Radioactive cesium was determined by gamma spectroscopy. All other metals were analyzed by ICP techniques. The cesium concentration in each feed solution was measured as well as the cesium concentration in each post-contact solution. The amount of cesium on the resin was determined by subtracting the cesium concentration in the post-contact solution from the cesium concentration in the feed [5]. These tests were all performed at room temperature, 27^0 C ± 3^0 C.

AMP-PAN. Ammonium molybdophosphate, $(NH_4)_3PO_4 \bullet 12MoO_3 \bullet 3H_2O$, was obtained on a polyacrylonitrile support (0.4-0.8mm, bulk density≈1.4 g/mL). Polyacrylonitrile aids in shape modification and improves the granulometric properties and therefore hydraulic properties of powders. Binding polymers such as polyacrylonitrile have several advantages such as low price of the polymer, easy preparation of the composite exchanger, and the possibility of shaping it into grains, fibers, or membranes. The hydrophilicity, porosity, and cross-linking can typically be changed to meet most requirements [7]. AMP-PAN is 85% ammonium molybdophosphate loaded on a polyacrylonitrile support. The AMP-PAN is shipped and stored in water. The AMP-PAN used in this study was obtained from the Department of Nuclear Sciences and Physical Engineering, Czech Technical University, Brehova 7, CS-115 19 Prague 1, Czech Republic. It is not currently being produced commercially.

Batch Tests

Kinetic tests. Ten milliliters of a feed solution containing ^{137}Cs (3210 dps/mL or 9.97E-10 g/mL) in 1M HNO_3 was added to each of eight tubes containing nominally 0.75 g of AMP-PAN. The contact time for each sample varied from 1 to 60 minutes to determine the effect of time on cesium absorption. The cesium retention on the resin was calculated from post-contact solution analyses.

Absorption of metals from simulated and actual waste solutions. Six batch contacts were performed. Each batch contact had ten milliliters of a different feed, simulated and actual wastes, combined with nominally 0.75 g of resin. The distribution coefficients (K_ds) were measured for eight major elements and cesium and strontium. The waste compositions for the feed solutions can be found in Table 1. The resin was contacted by mixing with the feed for 60 minutes on a mechanical shaker for the simulated waste tests. The resin and feed were mixed on a rotary wheel for 60 minutes for the actual waste tests.

AMP-PAN stability tests. One-half gram of AMP-PAN was weighed into each of sixteen test tubes. Five milliliters of water were added to four tubes, five milliliters of 1M HNO_3 were added to four tubes, five milliliters of 3M HNO_3 were added to four tubes, and five milliliters of 5M HNO_3 were added to the remaining four tubes. The samples were placed on a mechanical shaker for dynamic contact times of 96 hours, 264 hours, 432 hours, and 600 hours at $28^0 \pm 3^0$ C. The post-contact solution was analyzed for molybdenum.

Equilibrium tests. In these tests, the resin weight was varied for a constant 10 mL feed solution. The resin and feed solutions were combined in test tubes and

TABLE 1: Waste compositions for test feed solutions

Species	Sodium Bearing Waste Tank (SBW) WM-185	Sodium Bearing Waste Simulant	Dissolved Zirconia Calcine	Simulated Zirconia Calcine	Dissolved Alumina Calcine	Simulated Alumina Calcine
Units in Molar						
Acid	1.63	1.31	2.58	3.78	1.75	2.41
Al	0.374	0.556	0.716	0.486	1.23	0.767
B	0.019	0.013	0.983	0.086	0.035	0.096
Cd	<0.002	2.05E-6	--	--	0.009	--
Ca	0.065	0.0327	0.568	0.57	0.371	0.439
Cs	3.4E-5	9.78E-5	3.31E-5	0.005	3.4E-5	6.32E-6
Cr	0.005	0.006	0.002	5.75E-3	--	--
F	0.035	0.097	0.64	1.24	0.174	0.621
Fe	0.021	0.023	0.01	0.015	0.011	0.01
Nitrate	5.17	4.22	4.33	6.39	4.438	5.45
K	0.19	0.148	0.012	5.88E-4	0.005	0.021
Na	1.41	1.13	0.196	0.012	0.043	0.161
Total Sr	5.9E-4	6.3E-4	1.66E-3	0.004	1.69E-3	3.5E-4
Zr	0.01	5.12E-4	0.066	0.225	0.009	0.066

placed on a rotary wheel to continuously mix the contents for a contact time of 30 minutes. Four feed solutions containing nitric acid and cesium were used. Two different cesium feed concentrations were used; 2 g Cs/L labeled with 4.41E6 dps/mL ^{137}Cs and 20 g Cs/L labeled with 3.28E6 dps/mL of ^{137}Cs. The test was repeated using 0.5$\underline{M}$ HNO_3 and 3.0$\underline{M}$ HNO_3 as feed solutions. Additionally, actual sodium-bearing waste (SBW) (1.63$\underline{M}$ HNO_3) was spiked with 100 g Cs/L in 3$\underline{M}$ HNO_3 to bring the final cesium concentration to 2 g Cs/L in and 20 g Cs/L in to provide two additional feeds. These feeds provided data for three isotherms at

TABLE 2: Tests conditions for capacity tests

Grams AMP-PAN	Feed Solutions		
	Test 1	Test 2	Test 3
0.5	2 g Cs/L in 3$\underline{M}$ HNO_3	2 g Cs/L in 0.5$\underline{M}$ HNO_3	2 g Cs/L SBW
1	2 g Cs/L in 3$\underline{M}$ HNO_3	2 g Cs/L in 0.5$\underline{M}$ HNO_3	2 g Cs/L SBW
1	20 g Cs/L in 3$\underline{M}$ HNO_3	20 g Cs/L in 0.5$\underline{M}$ HNO_3	20 g Cs/L SBW
1.25	20 g Cs/L in 3$\underline{M}$ HNO_3	20 g Cs/L in 0.5$\underline{M}$ HNO_3	20 g Cs/L SBW
1.65	2 g Cs/L in 3$\underline{M}$ HNO_3	2 g Cs/L in 0.5$\underline{M}$ HNO_3	2 g Cs/L SBW
1.65	20 g Cs/L in 3$\underline{M}$ HNO_3	20 g Cs/L in 0.5$\underline{M}$ HNO_3	20 g Cs/L SBW
2.5	20 g Cs/L in 3$\underline{M}$ HNO_3	20 g Cs/L in 0.5$\underline{M}$ HNO_3	20 g Cs/L SBW
3.3	20 g Cs/L in 3$\underline{M}$ HNO_3	20 g Cs/L in 0.5$\underline{M}$ HNO_3	20 g Cs/L SBW
5	2 g Cs/L in 3$\underline{M}$ HNO_3	2 g Cs/L in 0.5$\underline{M}$ HNO_3	2 g Cs/L SBW

different nitric acid concentrations. Table 2 lists the feed solutions and test conditions used for these tests.

Column Tests

Breakthrough capacity. Pyrex 1 x 30 cm columns (Corning No. 38452-10) with a fitted glass frit and stopcock to adjust flow were used to determine the breakthrough capacity at various flow rates. Table 3 lists the conditions used to determine breakthrough capacity.

Reduced AMP Studies (Molybdenum Blue): It has been noted during these studies that at times a blue color instead of the characteristic yellow is present. The blue color is a result of the reduction of the ammonium molybdophosphate [6]. Therefore, tests were performed to see if AMP performed differently in the reduced state. Six milliliters of 0.1$\underline{M}$ ascorbic acid in 0.1$\underline{M}$ HNO_3 was added to ~26 g of AMP-PAN in a batch contact. The reduced AMP-PAN was packed into two pyrex 1 x 30 cm columns, each having a bed volume of 5.8 cm^3. Each of the columns were then washed with 30 mLs of 0.1$\underline{M}$ HNO_3 to remove any residual ascorbic acid. One column was then loaded with 1.8 g Cs/L in 1$\underline{M}$ HNO_3 (Feed E) and the other column

TABLE 3: Test Conditions for Determining Cesium Breakthrough Capacity of AMP-PAN

Column Size/Bed Volume	Average Flow Rate (mL/min•cm^2)	Feed Solution	Feed Solution
1 x 30 cm/14.1 cm^3	7.6	C	0.96 g Cs/L
1 x 30 cm/14.2 cm^3	1.3	A	0.72 g Cs/L
1 x 30 cm/14 cm^3	4.5	B	0.68 g Cs/L
1 x 30 cm/12.5 cm^3	5.95	E	1.8 g Cs/L
1 x 30 cm/12.5 cm^3	13.1	D	0.64 g Cs/L

was loaded with 0.64 g Cs/L in 1M HNO_3 (Feed D). All color changes in the columns throughout the experiment were noted.

Elution Tests: Nine 1.5cm x 7.5cm Varian polyethylene columns (part no. 1213-1010) were each loaded with 4 g AMP-PAN (6.6 cm^3 bed volume). Forty-five milliliters of 1.0 g Cs/L in 1M HNO_3 were added to each column. Each column was eluted with a different ammonium compound at a flow rate of 1.5 mL/min•cm^2. The following ammonium compounds were used: 7M NH_4NO_3, 10M NH_4NO_3, 3M NH_4Cl, 5M NH_4Cl, 3M NH_4F, and 5M NH_4F. Elution tests were also performed in a pyrex 1 x 30 cm column (bed volume=14cm^3) using 1.5M $(NH_4)_2CO_3$ at a flowrate of 1.7 mL/min•cm^2. Each ten milliliter aliquot was collected for cesium analysis to determine the extent of elution occurring.

RESULTS AND DISCUSSION

Kinetics: Results of the kinetic tests are shown in Figure 1. It can be seen that the exchange of cesium with ammonium is rapid from these results. Equilibrium

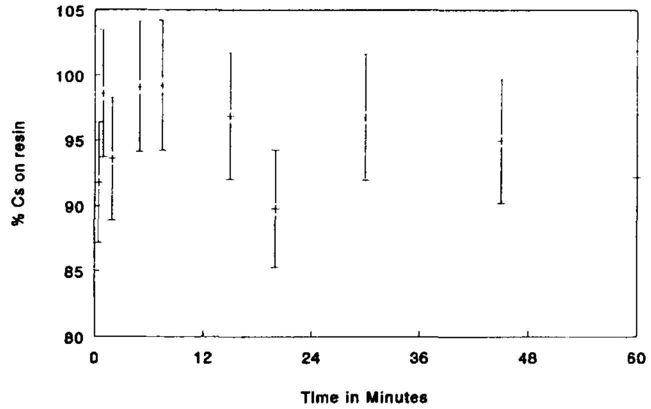

Figure 1: Cesium absorption as a function of time

has been reached within the first two minutes. This agrees favorably with results reported by Sebesta and Stefula [6] of 2 minutes on AMP powder and 10 minutes on AMP-PAN.

Distribution Coefficients: Ion distribution coefficients (K_ds) are a measure of a species partitioning between the aqueous and the solid phases. The ion distribution coefficient represents the affinity for different ions to attach to a resin. As the K_d increases, the greater the partitioning efficiency. Ion distribution coefficients are determined at equilibrium for this study by the equation [5]:

$$K_d = \frac{\text{Amount of solute on resin}}{\text{Amount of solute in solution}} \times \frac{\text{Volume of solution, mL}}{\text{Weight of AMP, g}}$$

Table 4 contains results of the tests to determine ion distribution coefficients for selected constituents in the simulated and actual waste solutions. The distribution coefficients have been corrected for 67% fluid weight of the AMP-PAN, followed by an 85% correction to reflect the loading of the ammonium molybdophosphate on the support. It appears that AMP-PAN is selective for cesium in the solutions tested. The cesium distribution coefficient reported for alumina calcine and alumina calcine simulant was calculated from uncorrected analytical data. The reported analytical

TABLE 4: Distribution Coefficients (mL/g) of the Major Components of Simulated and Actual Wastes

Element	Zirconia Calcine Simulant	Zirconia Calcine	Alumina Calcine Simulant	Alumina Calcine	Sodium Bearing Waste Simulant	Sodium Bearing Waste (Tank WM-185)
Al	6	4	0	0	18	1
B	10	4	1	0	0	1
Ca	6	4	1	1	3	0
F	6	2	0	0	6	15
Fe	2	2	0	0	1	1
K	0	4	4	2	5	2
Na	16	29	0	2	1	2
Zr	2	2	2	0	0	1
Sr	0	0	0	0	2	1
Cs	483	3287	57	57	360	2679

NOTE: The experimental uncertainty for these tests is ±5%.

values were less than detection limits; therefore, this value may be erroneous. Tests have been repeated using all of the waste solutions to verify the discrepancy in the reported cesium distribution coefficients between simulated and actual waste solutions. The results were comparable to the original test results. Due to time constraints, further work has not been performed to determine the cause of this discrepancy.

Stability: The chemical stability of AMP-PAN when exposed to nitric acid was investigated by placing the AMP-PAN into different concentrations of nitric acid for various amounts of time at $28^0 \pm 3^0$ C. The data from this test appears in Figure 2. There is a significant increase in the amount of molybdenum in the post-contact solution as time increases. There is a loss of up to 82.8 % of the molybdenum in a 3M HNO_3 solution over a period of 600 hours (3.6 weeks) It also appears that, in the

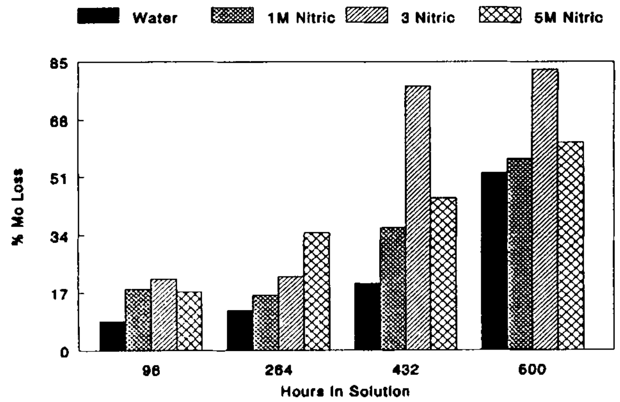

Figure 2: AMP-PAN stability in acidic conditions determined by molybdenum loss

solutions tested, the greatest loss of molybdenum from the AMP-PAN occurs in a 3M HNO_3 solution. A sample of the solution the AMP-PAN was shipped in was analyzed as a reference point. The AMP-PAN had been stored in the solution for eight months with a molybdenum loss of <2%. Therefore, agitation appears to play a major role in the breakdown of the AMP-PAN.

Capacity: The theoretical capacity of ammonium molybdophosphate for cesium is 213 g Cs/kg AMP [8]. The capacity curves are shown in Figure 3. Tests determined the capacity to be 169 g Cs/kg AMP from 0.5M HNO_3 feed solution, 157 g Cs/kg AMP from 3M HNO_3 feed solution, and 151 g Cs/kg AMP from sodium-bearing waste tank WM-185 (1.63M HNO_3) that had been spiked with nonradioactive cesium to increase the total cesium concentration. These results favorably agree with those obtained by Sebesta and Stefula [7] of 120-135 g Cs/kg AMP. All of the test results have been corrected for 67% fluid weight of the AMP-PAN and the 85% loading of the AMP onto the PAN support. Based on the data obtained in these tests, it is apparent that cesium sorption is independent of the nitric acid concentration.

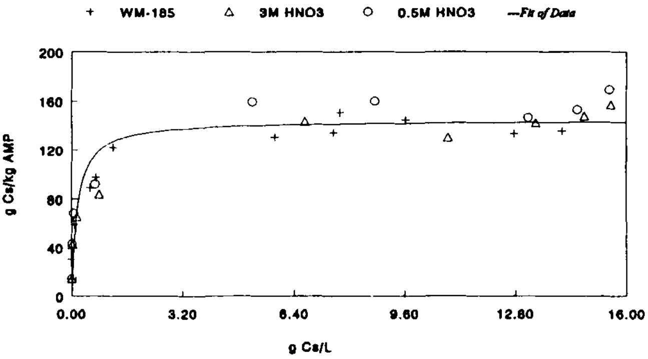

Figure 3: Sorption isotherms for cesium on AMP as a function of acid concentration

Breakthrough Capacity: The breakthrough capacity is the quantity of solute which can be taken up by the column under test or operating conditions. It is always lower than the total capacity. Breakthrough capacities were determined at the point where Cp/Co=0.5; Cp=ion in raffinate and Co= ion in feed solution [9]. Results from column breakthrough tests are seen in Figure 4. The breakthrough capacities at Cp/Co=0.5 were determined to be 39.4 g Cs/kg AMP, 47.0 g Cs/kg AMP and 44.2 g Cs/kg AMP for flow rates of 7.64 mL/min•cm^2, 1.32 mL/min•cm^2 , and 4.53 mL/min•cm^2, respectively. The breakthrough capacities for simulated sodium waste and simulated alumina calcines were never reached due to the low cesium concentration in these feed solutions. Five hundred milliliters of sodium bearing waste was passed over a bed volume of 16 cm^3. Five hundred seventy-five milliliters of alumina calcine simulant was passed over a bed volume of 15 cm^3. However, the breakthrough capacity for simulated zirconia calcine was determined to be 39 g Cs/kg AMP at Cp/Co=0.5. The simulated zirconia feed has a cesium concentration of 14 and 20 times higher than that of sodium-bearing waste simulant and alumina calcine simulant, respectively. These agree favorably with the column breakthrough capacity results obtained by Sebesta and Stefula [7] of 0.23 mmole/g

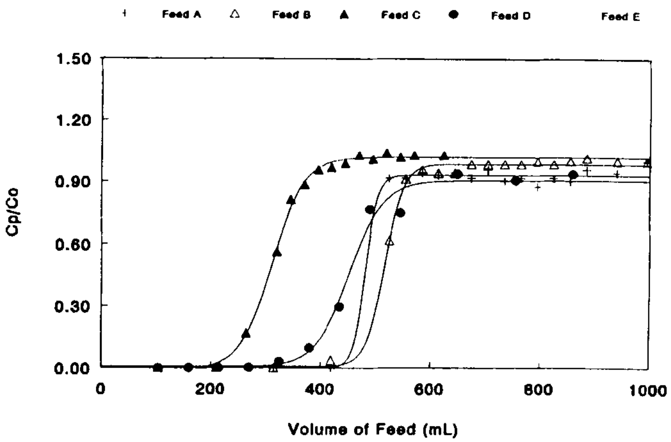

Figure 4: Cesium breakthrough curves for various test conditions

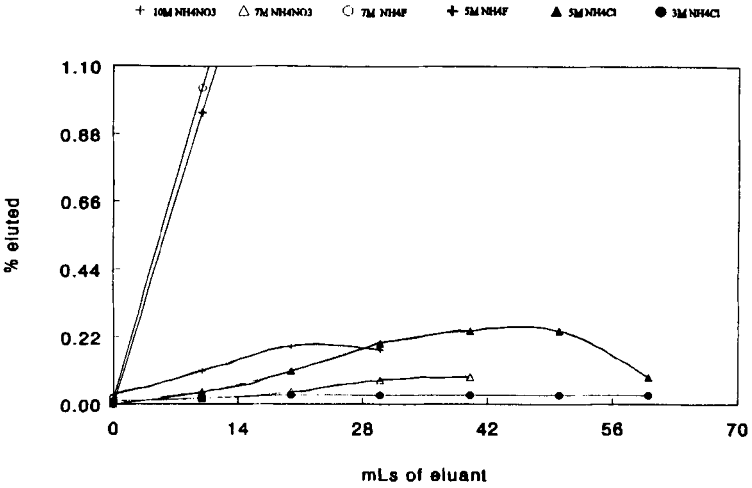

Figure 5: Cesium elution using various eluants

(30.3 g Cs/kg) of swollen AMP-PAN or 0.65 mmole/g AMP (86.5 g Cs/kg AMP) [7].

Reduced AMP studies: The results of the column tests using reduced AMP-PAN are also seen in Figure 4. The reduction of the AMP-PAN does not significantly change the performance. The breakthrough capacities at Cp/Co=0.5 were 36.73 g Cs/kg AMP and 25.68 g Cs/kg AMP for flow rates of 1.3 mL/min•cm^2 and 5.95 mL/min•cm^2, respectively in 1x30 cm columns. These results also favorably compare to the previous reported results of Sebesta and Stefula [7]. The oxidation of the molybdenum began upon contact with the nitric acid solutions, as noted by a color change from blue to yellow. After 20 hours the column with the flow of 1.3 mL/min•cm^2 was 66% oxidized. Complete oxidation had occurred within 48 hours. As expected, the column with the flow of 5.95 mL/min•cm^2 oxidized slower. Within 20 hours 6% had oxidized. Complete oxidation of the column occurred within 60 hours.

Elution tests: The results from the elution tests appear in Figure 5. The ammonium fluoride compounds tended to turn the columns white. It appeared that the AMP was removed from the PAN support. When ammonium carbonate was used to elute cesium, the AMP was removed from the PAN support and carbon dioxide gas formed causing the resin to sputter from the top of the column.

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