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A STUDY OF METHODS FOR REMOVING STRONTIUM, PLUTONIUM, AND RUTHENIUM FROM SAVANNAH RIVER PLANT WASTE SUPERNATE

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A STUDY OF METHODS FOR REMOVING STRONTIUM, PLUTONIUM, AND RUTHENIUM FROM SAVANNAH RIVER PLANT WASTE SUPERNATE

by

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ABSTRACT

As a part of long-term waste management studies at the Savannah River Laboratory, tests were made to study removal of strontium, plutonium, and ruthenium from simulated and actual waste supernates. Plutonium was sorbed by *Duolite ARC-359* ion exchange resin, the same resin that is used to remove cesium from waste supernate. Strontium was removed from supernate by sorption on a chelating resin *Chelex 100*, or by precipitation as $Sr_3(PO_4)_2$. Activities of ^{137}Cs, ^{90}Sr, and $^{238-241}$Pu remaining in processed waste supernate should be 1-10 nanocuries of each element per gram of salt. Of the methods that were tested, none was adequate for plant-scale removal of ruthenium.

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A STUDY OF METHODS FOR REMOVING STRONTIUM, PLUTONIUM, AND RUTHENIUM FROM SAVANNAH RIVER PLANT WASTE SUPERNATE

INTRODUCTION

Studies are in progress at the Savannah River Laboratory (SRL) to determine methods for possible solidification and storage of Savannah River Plant (SRP) high-level liquid radioactive waste. In one of several options under consideration, solidified waste would be stored in an on-site, retrievable surface storage facility until the waste could be shipped to a federal repository.

An earlier report[1] described in detail the origins and characteristics of SRP waste, the criteria for acceptable solid forms, and potential solid forms for SRP waste. That study was used to formulate the conceptual process outlined in Figure 1.

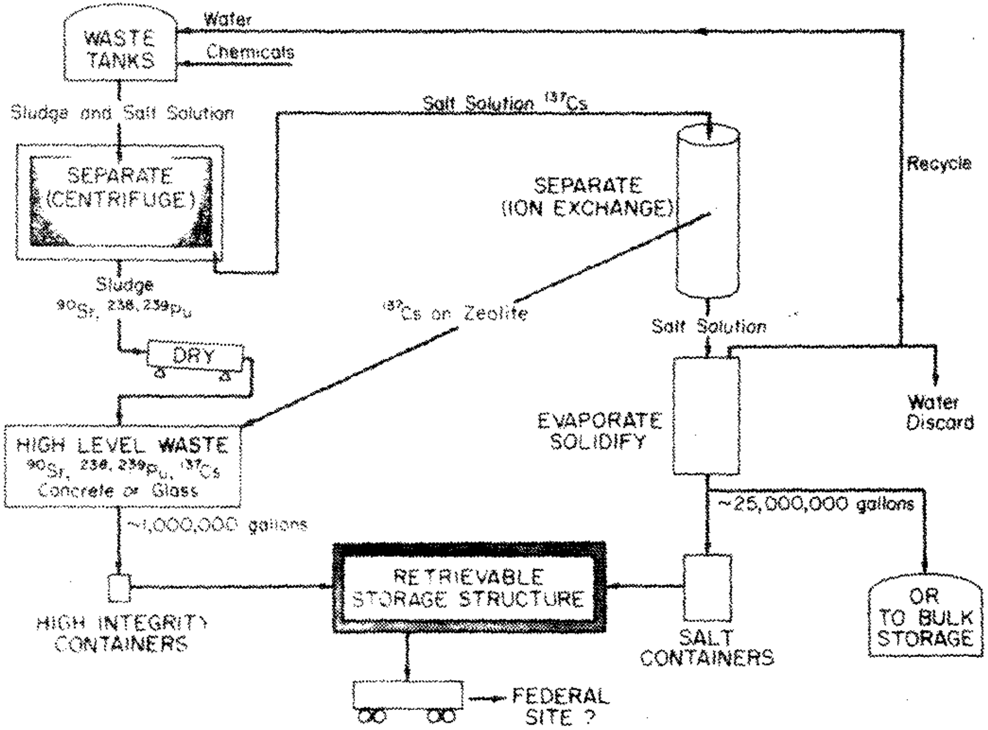

FIGURE 1. Conceptual Waste Solidification Process

SRP waste, stored in underground tanks, consists of an alkaline salt solution, solid salt cake, and an insoluble sludge layer containing large amounts of iron, aluminum, manganese, uranium, and many other elements. In the conceptual process, waste would be removed from a tank by dissolving the salt cake with water and sluicing the slurry of sludge and solution from the tank. Sludge and solution would be separated by centrifugation and filtration. Cesium-137, the principal biological hazard in solution, would be removed by an ion exchange process and sorption on zeolite. Sludge would be washed to remove salts, then dried and blended with the cesium-zeolite for solidification into either concrete or glass. The residual solution from ion exchange would contain ruthenium and small amounts of plutonium and strontium.

This report describes methods that were studied for removing strontium, plutonium, and ruthenium from the alkaline waste supernate solution. Demonstration of cesium removal and of sludge solidification in concrete and glass have been described previously.[2,3,4] Future reports will describe tests of other steps in the conceptual process.

RADIOACTIVITY IN SRP WASTE SALT AFTER CESIUM REMOVAL

The cesium removal process previously demonstrated[2] reduced ^{137}Cs activity in actual waste supernates by a factor (DF*) of 10^5. Analyses of these processed supernates showed that the only significant radioactivities remaining were those of ^{106}Ru, Pu (238, 239, 240), and ^{90}Sr.

In alkaline SRP waste, much of the ruthenium exists as soluble nitrosylruthenium complexes. Plutonium exists primarily as solid $Pu(OH)_4$; strontium exists as $SrCO_3$ and $SrSO_4$ solids, and as Sr^{2+} ions chemisorbed on sludge. However, measurable amounts of plutonium and strontium remain in solution.

In a plant waste treatment process, it may be desirable to reduce radioactivity in the salt to the lowest practicable level. To provide a starting point for further studies, analyses of the Cs-decontaminated supernates, as well as other supernate analyses,[5] were used to estimate the residual activity expected in decontaminated salt (the dry product from evaporation of decontaminated supernate). Residual activity of less than 10 nanocuries/g of salt, the currently accepted limit for low-level transuranic waste, is desirable.

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* Decontamination Factor, DF = $\frac{\text{Nuclide Activity in Feed}}{\text{Nuclide Activity in Product}}$

Estimates of residual activity were based on the assumption that 80 million gallons[1] of salt solution from 10 year old waste would be processed and yield 24 million gallons of salt having a density of 1.8 g/cm^3. Because it is difficult to measure the low levels of Pu and ^{90}Sr in waste supernates and because their concentrations vary widely among the waste tanks, there are large uncertainties in the estimates. They do, however, indicate the degree of further supernate decontamination required to reach the 10 nCi/g level.

Figure 2 shows the estimated residual activities as a function of time after cesium has been removed (DF = 10^5). Initially, ^{106}Ru is the most hazardous of the remaining nuclides; however, ^{106}Ru decays rapidly ($t_{1/2}$ = 369 days). ^{90}Sr and Pu are the dominant activities after about 10 years. The studies discussed in this report were therefore aimed at reducing activities of ^{90}Sr, Pu, and ^{106}Ru to lowest practicable levels.

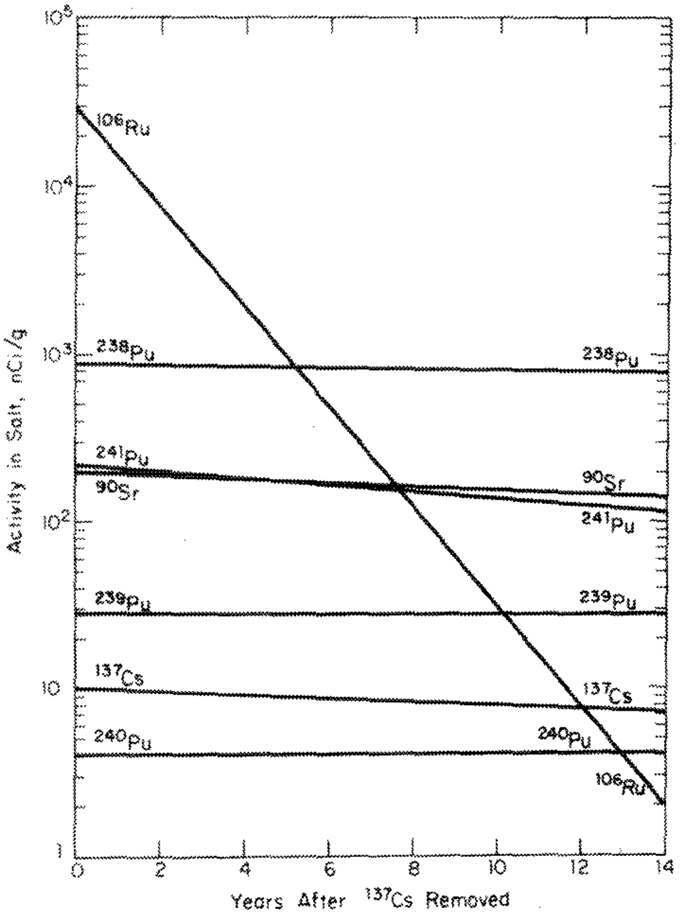

FIGURE 2. Residual Activity in Salt Cake After Cesium Removal

ION EXCHANGE RESINS FOR SUPERNATE DECONTAMINATION

Because an ion exchange separation of cesium from SRP waste supernate has been proposed and demonstrated, addition of columns to remove other nuclides would be straightforward. Equilibrium tests were made to measure the ability of several resins to sorb plutonium, strontium, and ruthenium from supernate. Resins showing promise in these tests were subsequently used in column tests.

The distribution of an ion between ion exchange resin and solution is conveniently measured by equilibrium tests. The distribution coefficient, K_d, is defined as:

$$K_d = \frac{\bar{M}}{M_{eq}} = \frac{M_o - M_{eq}}{M_{eq}} \times \frac{\text{Solution vol (ml)}}{\text{Resin wt (g)}}$$

where $\bar{M}$, M_o, and M_{eq} are the molar concentrations of the sorbed ion (M) in the resin phase, initial solution, and equilibrated solution, respectively. In a solution containing several ions competing for resin sites, K_d is a measure of specificity of the resin for a given ion. K_d is useful for predicting ion exchange column performance because it is proportional to the number of column volumes of feed which will load the column to 50% breakthrough [(M) in instantaneous column effluent = 50% of (M) in feed].[6] All equilibrium tests were conducted by shaking 10 ml of synthetic waste supernate (Table 1) spiked with radioactive tracers and 1 g of resin together overnight. Afterward, resin and supernate were separated by centrifugation. K_d was calculated by determining radioactivity in the supernate before and after equilibration.

TABLE 1

Composition of Simulated Waste Supernate

Constituent	*Concentration, M*
$NaAlO_2$	0.50
$NaOH$	0.75
$NaNO_3$	2.2
$NaNO_2$	1.1
Na_2SO_4	0.3
Na_2CO_3	0.3
$CsNO_3$	0.0002
$Sr(NO_3)_2$	10^{-6}

Results of the equilibrium tests are shown in Table 2. *Duolite ARC-359*[*] resin sorbed plutonium and cesium from simulated supernate. Although zeolite sorbed all three nuclides, its use as a primary sorbent is not recommended because of large volume requirements.[2] Previous column tests with hydrated zirconium oxide gels, such as *HZO-1*,[**] were unsatisfactory because of pluggage from fines. *Chelex-100*,[**] an iminodiacetate chelating resin, sorbed strontium and was chosen for column tests.

TABLE 2

Sorption of Cesium, Strontium, Plutonium, and Ruthenium by Ion Exchange Resins

	K_d			
Resin	*Cesium*	*Strontium*	*Plutonium*	*Ruthenium*
Duolite ARC-359	85	0	240	0
Linde AW-500[a] (Zeolite)	66	122	24	0
Dowex 50W-X8[b]	0	5	0	0
Chelex-100	0	215	7	0
HZO-1	0	>4000	>100	0

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[a] Trademark of Union Carbide.

[b] Trademark of Dow Chemical Company.

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[*] Trademark of Diamond Shamrock Chemical Company.

[**] Trademark of Bio-Rad Laboratories.

REMOVAL OF STRONTIUM FROM SIMULATED WASTE SUPERNATE

Tests were made using simulated supernate (10^{-6}M Sr^{2+}) containing ^{85}Sr tracer to determine strontium removal with a column of *Chelex-100* resin. Removal of strontium by carrier precipitations was also tested.

Chelex-100 Column Tests

Column tests were made to verify that *Chelex-100* would satisfactorily remove strontium from waste supernate, and that the resin could withstand repeated load-elute-regenerate cycles. For these tests, 12.5 ml of Na^+-form, 50-100 mesh *Chelex-100* resin was placed in a 1.3-cm-ID column. Simulated supernate was pumped downflow through the column at 1 column volume (CV) per hour. Strontium DF's, determined by gamma counting, were $>10^4$ after 40 CV and $>10^2$ after 70 CV. Loading was stopped after a throughput of 70 CV, and the resin was washed with 4 CV of water.

Strontium was eluted from the resin at ambient temperature with 1M HNO_3 pumped upflow at 1 CV/hr. All detectable strontium was removed from the column with 10 CV of acid. The 2M $(NH_4)_2CO_3$ - 2M NH_4OH used to elute cesium from *Duolite ARC-359* resin did not efficiently elute strontium from *Chelex-100* resin. A mixed bed of *Duolite ARC-359* and *Chelex-100* cannot be used because *Duolite* slowly dissolves in 1M HNO_3. After strontium was eluted, the *Chelex* resin was washed with 4 CV of water and regenerated with 6 CV of 2M NaOH. Five load-elute-regenerate cycles were completed without change in column performance.

Strontium Precipitation Tests

Precipitation is a promising method for removing strontium from waste supernate. Strontium could be precipitated during or immediately after separation of sludge from supernate. No major equipment would be added to the conceptual solidification process. However, strontium DF's are not as high as can be achieved by ion exchange with *Chelex-100* resin.

Strontium Phosphate Carrier Precipitation

Waste treatment studies at Hanford showed a strontium DF of >100 by carrier precipitation of $Sr_3(PO_4)_2$ from alkaline waste supernates.[7] This method of precipitation provided a strontium DF of about 300 with simulated SRP waste. In the precipitation tests, 10-ml samples of simulated waste supernate were adjusted to 0.025M in PO_4^{3-} by addition of 5M H_3PO_4. Sr^{2+} concentration [originally 10^{-6}M + 10^5 dis/(min)(ml) ^{85}Sr] was adjusted to 0.005M by addition of nonradioactive 1M $Sr(NO_3)_2$. The solutions were mixed and allowed to settle overnight. The mixtures were then centrifuged, and the gamma activities of the supernates were measured. Strontium DF's in these tests ranged from 100 to 500 and averaged 300.

A flocculating agent may be used to facilitate sludge-supernate separation. In a second series of $Sr_3(PO_4)_2$ precipitations, 20 ppm Betz 1120* flocculating polymer was added to the simulated supernate. The average strontium DF (∿300) was not improved, although there was less variation in DF among samples. Additional tests also indicated that 50% changes in PO_4^{3-}, Sr^{2+}, and OH^- concentrations had little effect on the strontium DF.

Calcium Carbonate Carrier Precipitation

$CaCO_3$ (aragonite) is isomorphous with $SrCO_3$. Addition of Ca^{2+} to waste supernate (0.3M CO_3^{2-}) should co-precipitate $SrCO_3$. Removal of carbonate from the waste would also convert soluble plutonium carbonate complexes, presumed to account for plutonium solubility in SRP waste, to insoluble plutonium hydroxides.

Table 3 shows results of tests in which 1M $Ca(NO_3)_2$ was added to 5-ml supernate samples. Strontium DF's are twenty times lower than those obtained by $Sr_3(PO_4)_2$ carrier precipitation, and the plutonium DF's are too low to be useful. The volume of $CaCO_3$ produced is several times larger than that of $Sr_2(PO_4)_3$. Strontium removal by $CaCO_3$ carrier precipitation is therefore not recommended.

TABLE 3

Calcium Carbonate Carrier Precipitation of Strontium and Plutonium from Waste Supernate

$[Ca^{2+}]/[CO_3^{2-}]$	*Strontium DF*	*Plutonium DF*
0.5	4	3
1.0	14	4
1.5	18	4

---

* Product of Betz Laboratory Co.

REMOVAL OF PLUTONIUM FROM SIMULATED WASTE SUPERNATE

Plutonium, like strontium, is found almost entirely in the insoluble phase (sludge) of SRP waste. The formation of complexes probably accounts for the small amount of soluble plutonium found in waste supernates. Carrier precipitation of about 75% of the plutonium with calcium carbonate (Table 3) indicates that carbonato complexes probably constitute a large fraction of the soluble plutonium in SRP waste supernate. On the basis of the equilibrium results in Table 2, column tests were made to determine the plutonium DF with *Duolite ARC-359* resin.

Simulated waste supernate, containing 10^{-6}M ^{238}Pu, was aged for two weeks to ensure that equilibrium was attained. This solution was then pumped at 1 CV/hr through a 25-ml bed (1.3 cm diameter) of *Duolite ARC-359* resin in the Na^+ form, 20-50 mesh. The plutonium DF was 180 after 20 CV; thus, plutonium as well as cesium is sorbed by *Duolite* resin.

A test was then conducted to determine the elution profile of plutonium by 2M NH_4OH - 2M$(NH_4)_2CO_3$, the elutriant used for cesium elution. The resin was washed with 5 CV of water and was eluted upflow at 1 CV/hr and ambient temperature. Plutonium began eluting almost immediately, peaked after 4 CV, and declined. Approximately 95% of the sorbed plutonium was eluted in 10 CV of elutriant. This result agrees closely with elution of cesium from *Duolite* resin.[2]

The column test described above showed that *Duolite ARC-359* sorbs plutonium from simulated waste supernate at the concentration expected in plant processing (5.75M Na^+). In earlier column tests with actual concentrated supernates (9-13M Na^+), significant plutonium DF's were not obtained.[2] Equilibrium tests were therefore made to determine the effects of feed concentration on plutonium sorption. Solid NaOH and $NaNO_3$ were added to samples of simulated supernate (10^{-6}M in ^{238}Pu); distribution coefficients measured in these more-concentrated solutions are shown in Table 4.

The shape of plutonium breakthrough curves in column tests indicates that sorption kinetics of plutonium by *Duolite* resin are slow. Because the plutonium band on a column of this resin is quite diffuse, high distribution coefficients are necessary to produce high DF's. Results in Table 4 show that K_d decreased rapidly for solutions more concentrated than that defined for the conceptual process. *Duolite ARC-359* resin will give good plutonium DF's in waste solutions containing up to 7M Na^+, and poor DF's in more concentrated solutions.

TABLE 4

Effect of Salt Concentration on Plutonium Sorption by *Duolite ARC-359* Resin

Ion Concentration, M			
Na^+	OH^-	NO_3^-	K_d
5.75	0.75	2.2	240
6.75	1.75	2.2	136
7.75	2.75	2.2	76
8.25	3.25	2.2	65
6.75	0.75	3.2	242
7.75	0.75	4.2	49
8.75	0.75	5.2	46

TESTS FOR REMOVAL OF RUTHENIUM FROM SIMULATED WASTE SUPERNATE

Ruthenium in SRP waste tanks is divided almost equally between sludge and supernate. Although the soluble ruthenium species have not been identified, most are probably divalent anions such as $[RuNO(NO_2)_4OH]^{2-}$. ^{106}Ru, with a half-life of 369 days, will not be a significant hazard 12 years after solidification (Figure 2). Tests were made to determine whether ruthenium could be removed by simple modifications of the conceptual process and thus reduce short-term storage hazards from ^{106}Ru. Since none of the materials in the equilibrium tests sorbed ruthenium (Table 2), other methods of removal were tested.

Removal by "Dowex" Resin

Table 5 shows that ruthenium complexes can be sorbed by *Dowex 2-X8* anion exchange resin if the supernate is diluted 8-fold. Such a dilution would place a high load on the evaporators used to convert decontaminated supernate to salt cake and is not recommended.

TABLE 5

Sorption of Ruthenium from Simulated Supernate by *Dowex 2-X8* Resin

Simulated Supernate Diluted by Factor of:	K_d
1	$\sim$0
2	$\sim$1
4	4
8	15

Removal by Activated Charcoal

Activated charcoal was reported to remove nitrosylruthenium complexes from salted solutions over a wide pH range.[8] No significant ruthenium DF was obtained when simulated SRP supernate was pumped at 1 CV/hr through a 25-ml bed of activated charcoal (Barnebey-Cheney, SC L-9281).

Removal by Hydrosulfide Precipitation

Conversion of complexed ruthenium to an insoluble hydrosulfide was attempted by passing H_2S through simulated supernate until $Al(OH)_3$ began to precipitate (pH $\sim$ 11). Approximately half of the ^{106}Ru activity remained in solution after centrifugation.

REMOVAL OF CESIUM, STRONTIUM, AND PLUTONIUM FROM ACTUAL WASTE SUPERNATE BY ION EXCHANGE

Removal of cesium, strontium, and plutonium by ion exchange was demonstrated in a shielded facility, using actual plant waste supernate. No attempt was made to remove ruthenium from the supernate. Supernate from Tank 1-F was chosen for the demonstration because this tank contains a large amount of ^{137}Cs and substantial amounts of ^{90}Sr and ^{239}Pu. Additional ^{90}Sr and ^{238}Pu were added to the supernate to ensure that measurable quantities of these constituents remained after the tests. A solution of nonradioactive salts was also added to adjust the supernate concentrations to those of the conceptual process (Table 1).

The ion exchange apparatus used in these tests consisted of two columns filled with *Duolite ARC-359* resin (20-50 mesh) and one column filled with *Chelex-100* resin (50-100 mesh). Each 1.3-cm-diameter column contained 25 ml of Na^+-form resin. Two separate tests were conducted. In each of these, 20 CV (500 ml) of supernate was pumped downflow through the columns at 1 CV/hr. The *Chelex-100* column was bypassed in the second test, and strontium was removed by $Sr_3(PO_4)_2$ carrier precipitation and by addition of 2 wt % *HZO-1*.

After each test the columns were washed with 5 CV of water and then eluted upflow at 1 CV/hr. Elutriant for the *Chelex-100* column was 10 CV of 1M HNO_3. A second water wash removed acid from the *Chelex-100* resin before all columns were regenerated with 10 CV of 2M NaOH.

Results of these tests are summarized in Figure 3. The cesium DF of 5 × 10^5 confirmed earlier results.[2] This degree of decontamination would give a salt cake containing ~10 nCi ^{137}Cs/g of salt (Figure 2). The plutonium DF of 500 across the *Duolite* columns would reduce the residual Pu activity to ~2 nCi/g of salt. A ^{90}Sr activity of 1-2 nCi/g should be attainable with any of the methods shown in Figure 3.

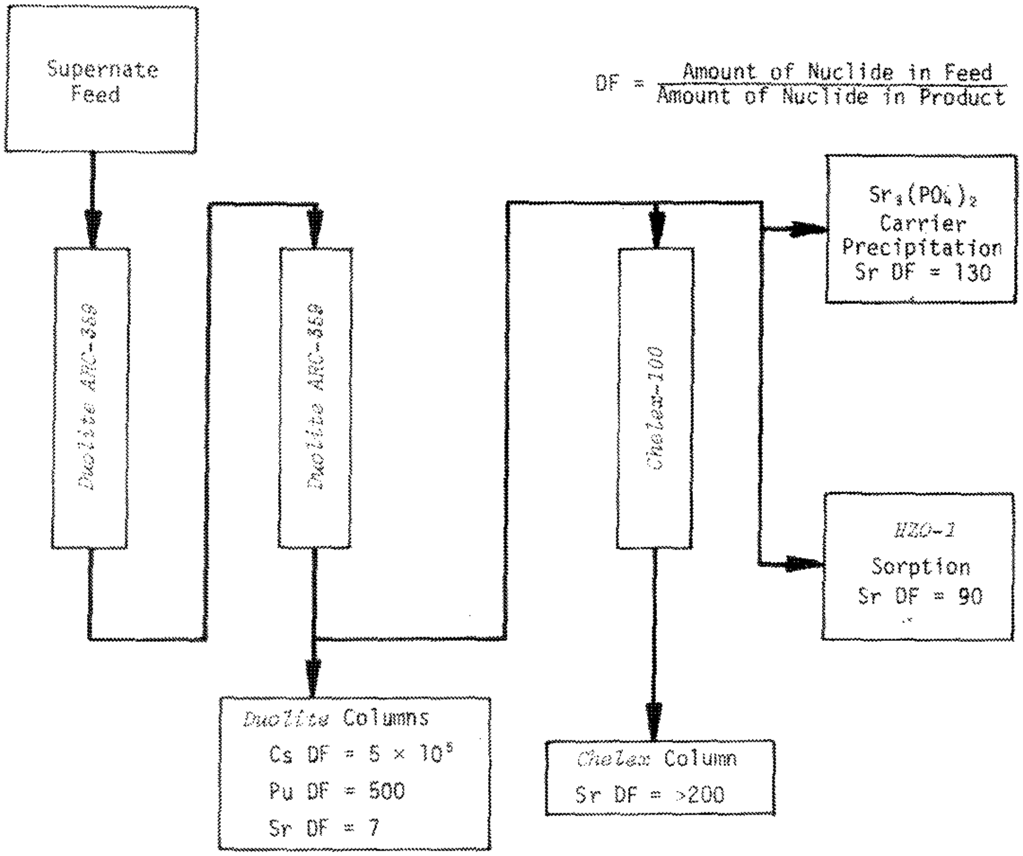

FIGURE 3. Test Results: Removal of Radioactivity from SRP Waste Supernate

SORPTION OF CESIUM, STRONTIUM, AND PLUTONIUM ON ZEOLITE

To demonstrate the final step in the supernate decontamination process, eluates from both tests were combined and evaporated to half the initial volume to expel NH_3 and CO_2. The resulting $NaNO_3$-Na_2CO_3 solution (~375 ml) containing cesium, strontium, and plutonium separated from supernate was pumped at 1 CV/hr through a 25-ml column of *Linde AW-500* zeolite. Analysis of the final five ml of zeolite column effluent gave the results shown in Table 6. All radionuclides were efficiently sorbed by the zeolite.

If concrete is chosen as a matrix for waste solidification, the zeolite will be mixed with sludge and solidified. Effluent from the zeolite column will be recycled to the waste tanks to produce more sludge-supernate slurry. Table 6 therefore indicates the fraction of radionuclides which will recycle through the process. If glass is chosen for waste solidification, evaporated eluate from the *Duolite* and *Chelex* columns will go directly to the glass process and zeolite will not be used. No portion of the evaporated eluate would return to the waste tanks and Table 6 would not apply.

TABLE 6

Fraction of Separated Radionuclides
Remaining in Zeolite Column Effluent

Nuclide	*Fraction Remaining*[a]
^{137}Cs	3×10^{-6}
^{90}Sr	5×10^{-4}
Pu	6×10^{-3}

---

[a] $\frac{\text{Total activity in zeolite effluent}}{\text{Total activity removed from SRP waste}}$

CONCLUSIONS AND FUTURE WORK

Strontium and plutonium were removed from both simulated and actual SRP waste supernate of composition expected for a plant-scale waste solidification process. Removal methods are compatible with other parts of the present conceptual waste solidification process. No method for removal of ruthenium was found. Estimates of radioactivity remaining in decontaminated salt cake were made.

Future tests of supernate decontamination will be part of a demonstration of the entire conceptual process. Supernate separated from actual waste sludge by centrifugation and filtration will be processed by ion exchange. Radionuclides separated from the supernate will be mixed with sludge and solidified in concrete and glass.

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