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FISSION PRODUCT ACTIVITIES IN AGED SAVANNAH RIVER PLANT WASTE SOLUTIONS

by

J. R. Wiley

Savannah River Laboratory
E. I. du Pont de Nemours & Co.
Aiken, S. C. 29801

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SUMMARY

Since the early 1950's, the Savannah River Plant (SRP) has produced nuclear materials for national defense programs, and stored radioactive waste from plant operations in large, underground tanks. Scientists at Savannah River Laboratory are developing a process for removing waste from the tanks and solidifying the hazardous radioactive isotopes in a highly stable form. An important part of this process is to remove radioisotopes from the water-soluble portions of the waste to minimize the volume of material that must be solidified.

Most waste isotopes are contained in an insoluble sludge in the waste tanks. The bulk of the waste, however, is a water-soluble salt (mainly $NaNO_3$) that is contaminated with cesium-137 and several other radioisotopes. Present plans are to decontaminate this large volume of salt (about 25 million gallons) rather than to solidify it. That way only the insoluble sludge and the radioisotopes removed from the salt will be solidified. Decontaminating the salt would greatly reduce the cost of waste treatment because fabricating, transporting, and storing the solid waste forms is very expensive.

To ensure that SRP waste salt can be satisfactorily decontaminated, 800 liters of actual waste solution was removed from the waste tanks and used to demonstrate the decontamination process. This ion exchange process reduced the combined radio activity of cesium-137, strontium-90, and plutonium to below 6 nanocuries/gram in the salt product. By comparison the potassium-40 activity, in sylvite, a naturally-occurring salt, is about 0.45 nanocuries/gram. Further tests using this treated waste are being made to determine what traces of radioisotopes remain and how they can be removed.

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Aiken, South Carolina

ABSTRACT

Fission products with activities ≥10 nCi/mL were identified in 10-year-old defense waste solutions stored at the Savannah River Plant. Measured activities of ^{137}Cs, ^{106}Ru, ^{90}Sr, ^{99}Tc, and lanthanide isotopes provided information about fission product distribution between alkaline supernatant solution and insoluble sludge, mainly $Fe(OH)_3$. ^{137}Cs, the principal source of radioactivity (∿1 mCi/mL) in solution, was removed by cation exchange resin so that other isotopes could be measured without its interference. ^{106}Ru was divided almost evenly between sludge and solution (∿10^{-2} mCi/mL). Ion exchange behavior of the soluble nitrosylruthenium complexes showed that 60% are divalent anions and the rest are probably uncharged. Conversion to anionic sulfide complexes by refluxing the diluted supernate with 0.01 M Na_2S allowed anion exchange resin to remove >99% of the Ru complexes from solution. ^{90}Sr activity in supernate (∿500 nCi/mL)

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was 100 times lower that predicted from the solubility of $SrCO_3$, the least soluble Sr salt in the waste. Adsorption of ^{90}Sr onto sludge accounts for this difference. Ion exchange resins containing chelating groups remove ^{90}Sr from the supernatant solution. Activity of ^{99}Tc (∿50 nCi/mL) from soluble TcO_4^- was about half of that expected from fission yields. The remaining Tc is probably insoluble; residues from HNO_3 dissolution of irradiated UO_2 fuels contain appreciable amounts of Tc. The combined activity of trivalent lanthanide isotopes, ^{144}Ce-^{144}Pr, ^{147}Pm, and ^{151}Sm, (∿40 nCi/mL) was many orders of magnitude greater than expected from the solubility of their hydroxides. This enhanced solubility may be caused by the high salt concentration in the waste.

INTRODUCTION

Two nuclear fuel reprocessing facilities have operated at Savannah River Plant (SRP) since the early 1950's to produce nuclear materials for national defense programs. Acidic wastes that contain fission products, traces of actinides, and larger quantities of nonradioactive chemicals, are produced by fuel dissolution and subsequent separation processes. The waste is made alkaline with NaOH so it can be stored in carbon steel tanks. Addition of NaOH causes oxides and hydroxides of fission products, waste actinides, and metals (principally iron, aluminum, and managanese) to precipitate and form a sludge on the bottom of the waste tank.

The insoluble sludge confines most of the hazardous radionuclides and comprises about 10% of the waste volume. The supernatant solution of soluble salts, however, retains almost all of the ^{137}Cs, about half of the ^{106}Ru, and traces of other isotopes that are in chemical equilibrium with the sludge.

Current plans for long-term waste management at SRP are to remove waste from the storage tanks and use ion exchange to separate radionuclides from the salt solution. The separated nuclides would be mixed with the highly radioactive sludge and then solidified in a borosilicate glass. The decontaminated solution would be evaporated, and the salt could be stored relatively inexpensively in bulk form if its residual radioactivity were sufficiently low.

An ion exchange method that reduced ^{137}Cs and ^{90}Sr activity to <6 nCi/mL in samples of actual SRP waste solution was described previously.[1] In this method ^{137}Cs and trace amounts of soluble plutonium (probably carbonate complexes) are removed by a phenol-sulfonic acid cation exchange resin and ^{90}Sr is removed by a chelating resin.

Further tests to define the chemistry of fission products in SRP waste were developed in this study. Factors affecting the distribution of ^{90}Sr between sludge and supernate were determined so that the ion exchange column for ^{90}Sr removal could be properly sized relative to the ^{137}Cs-removal columns. A laboratory method for removing nitrosyl-^{106}Ru from alkaline solutions was developed to facilitate handling and further analysis of actual waste solutions processed in ion exchange tests. Activities of ^{99}Tc and lanthanide isotopes were measured in initial tests to determine the residual activity that would remain in salt cake after ion exchange treatment.

STRONTIUM-90

^{90}Sr is the principal biological hazard in SRP waste sludge, but only a small amount of ^{90}Sr is found in solution (500 nCi/mL). The maximum strontium concentration in actual SRP waste solutions sampled from different waste tanks ranged from 10^{-7} to 10^{-9}M as calculated from ^{90}Sr activity in these solutions and fission yields of ^{90}Sr, ^{89}Sr, and ^{88}Sr. In simulated waste solutions (Table 1), however, strontium solubility is 10^{-6}M. This solubility limit, determined primarily by the carbonate concentration, is 10 to 1000 times greater than that observed in actual waste.

Actual waste solutions are in chemical equilibrium with the insoluble sludge. Hydrous oxides of metals that comprise the bulk of SRP sludge (Table 2) can act as ion exchangers. To test the adsorption properties of SRP sludge, a solution of simulated acid waste was prepared (Table 3). This solution was neutralized and increased to a 2M excess of NaOH. When the simulated waste sludge that precipitated from this solution was equilibrated with simulated waste solution, the apparent solubility of strontium in solution was reduced as low as 6×10^{-10}M, depending on the sludge to solution ratio. The presence of sludge in SRP waste tanks therefore reduces the amount of ^{90}Sr in the supernate to a level well below the limit determined by the solubility of strontium in alkaline-carbonate solutions.

RUTHENIUM-106

^{106}Ru is divided almost evenly between sludge and supernatant solution. In 10-year-old waste solution, ^{106}Ru is a biological hazard second only to ^{137}Cs. Because of its one-year half-life this ^{106}Ru will decay during an additional 10 to 12 years of storage to a level comparable to that of residual ^{137}Cs after decontamination by ion exchange.[1] Control of the waste for this short time is quite certain, so there is no incentive for plant-scale ^{106}Ru removal. ^{106}Ru, however, interferes with analyses of low-level activities in 10-year-old waste and complicates handling this material. Therefore, a laboratory method to remove ^{106}Ru was developed.

During Purex processing, fission-product ruthenium is converted to a variety of nitrosylruthenium complexes. A series of monomeric complexes with the general formula

$$[RuNO(NO_3)_x(OH)_y(H_2O)_z]^q$$

where $x + y + z = 5$ and $q = 3 - x - y$ have been identified.[2] When SRP waste is made alkaline these complexes probably convert to divalent anions, e.g.

$$[RuNO(NO_3)_4OH]^{2-}$$

and to uncharged polymers, e.g.

$$RuNO(NO_3)(OH)(H_2O) \begin{smallmatrix} \diagup OH \diagdown \\ \diagdown OH \diagup \end{smallmatrix} RuNO(NO_3)(OH)(H_2O) .$$

Indirect evidence for these species is provided by the ion exchange behavior of the ruthenium. When SRP waste is equilibrated with anion exchange resin, the distribution between ruthenium on the resin and in ambient solution is given by the distribution coefficient, k_d.

$$k_d = \frac{\overline{Ru}}{Ru} .$$

The bar indicates that the ion is adsorbed on the resin. For a simple exchange of ruthenium with some monovalent anion, A,

$$Ru^{-n} + \overline{A} \rightarrow \overline{Ru} + nA .$$

If small amounts of ruthenium are loaded onto the resin, k_d is related to the equilibrium constant for adsorption onto the resin and the concentration of A in solution by

$$k_d \; \alpha \; \frac{Keq}{[A]^n} .$$

This model shows that if waste solution is diluted k_d will increase faster than [A] decreases if n is >1. The increase of k_d from near zero in undiluted waste to 15 in waste diluted 8-fold suggests that a large fraction of the nitrosylruthenium complexes in SRP waste are anions with n>1 (Table 4).

An anion exchange column* removed ∿60% of the ruthenium from diluted SRP waste solution (Table 4). Futher treatment with cation resin** did not remove additional ruthenium; therefore, remaining complexes were probably uncharged.

Nitrosylruthenium forms stable sulfide complexes,[3] and although the concentration of ruthenium in SRP waste is too low for these complexes to precipitate, converting the uncharged complexes to sulfides would make them likely to adsorb onto anion exchange resin.

To test this method, actual waste solutions were diluted 10-fold, made 0.01M in Na_2S, and refluxed 2 hours. The k_d for the treated solutions increased markedly to between 200 and 300 (Table 4). Refluxing the solutions was necessary because k_d did not increase for a solution stored two days at room temperature. An anion exchange column removed >99.3% of the ruthenium from treated, refluxed solutions.

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* Column contained Dowex 1 x 2 resin, Dow Chemical Co., Midland, Mich.

** Dowex 50W-X8 resin, Dow Chemical Co., Midland, Mich.

TECHNETIUM-99

Comparing the fission yield of ^{99}Tc with yields of ^{137}Cs and ^{90}Sr shows that similar molar quantities of all three nuclides should be present in SRP waste. Although ^{137}Cs and ^{90}Sr are well known biological hazards, ^{99}Tc is only slightly hazardous because its specific activity is very low.

Because the soluble pertechnetate ion, TcO_4^-, is stable in alkaline solutions, a significant fraction of the ^{99}Tc is expected to be in the waste solution. Based on the assumption that all technetium is soluble, a maximum of 93 nCi/mL of solution can be expected, as calculated from the fission yields of ^{137}Cs and ^{99}Tc, their half-lives, and the measured activity of ^{137}Cs in SRP waste.

^{99}Tc in waste solutions from each reprocessing facility (after ion exchange removal of ^{137}Cs and ^{90}Sr, but not ^{106}Ru) was measured by extracting TcO_4^- into tetrapropylammonium hydroxide and counting the extractant by liquid scintillation.[4] Measured ^{99}Tc activities were 39 nCi/mL and 58 nCi/mL in the two samples. Comparing these results with the calculated 93 nCi/mL indicates that about half of the ^{99}Tc is in an insoluble form. Insoluble residues from laboratory dissolution tests of irradiated UO_2 fuels are rich in ^{99}Tc. Failure of all ^{99}Tc to go into solution during fuel dissolution probably accounts for the reduced ^{99}Tc activity in SRP waste solutions.

LANTHANIDE ISOTOPES

The total activity of the lanthanide isotopes was measured by acidifying samples of waste solutions that had been treated by ion exchange, adjusting the nitrate ion concentration to 6M, and extracting the lanthanides into 50% TBP (tri-n-butylphosphate) in n-paraffin.[5] The mixed isotopes were then back-extracted into 0.1M HNO_3 and counted by liquid scintillation. The total activity of lanthanide isotopes was 40 nCi/mL.

Fission yield calculations, corrected for 10-year decay, show that ^{147}Pm activity should be at least 10 times that of other lanthanide activities, such as ^{144}Ce-^{144}Pr and ^{151}Pm. This was confirmed by comparing the beta-particle spectrum of the extractant with that of a ^{147}Pm tracer. The spectra appeared to be identical; there were no significant counts corresponding to beta-decay energies greater than that of ^{147}Pm (0.225 MeV), and the shape of the spectrum at lower energies indicated that significant amounts of ^{151}Sm were not present.

An activity of 40 nCi/mL corresponds to about 2×10^{-5}M of ^{147}Pm. This concentration is many orders of magnitude greater than that expected from solubility products of lanthanide hydroxides ($K_{so} \times 10^{-20}$).[6] This enhanced solubility may be caused by the high salt concentration in SRP waste.

CONCLUSION

Activities of the major fission products in 10-year-old SRP waste were measured. These tests helped to determine fission product behavior in alkaline solutions and to predict residual radioactivity that would remain if ^{137}Cs and ^{90}Sr were removed from the waste by ion exchange.

ACKNOWLEDGMENTS

^{90}Sr solubility in simulated SRP waste was measured by N. E. Bibler. The method for removing nitrosyl-^{106}Ru was suggested by R. M. Wallace.

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TABLE 1

Composition of Simulated Supernate

Component	*Concentration, M*
$NaNO_3$	2.2
$NaNO_2$	1.1
NaOH	0.75
$NaAlO_2$	0.5
Na_2SO_4	0.3
Na_2CO_3	0.3
$CsNO_3$	0.0002

TABLE 2

Composition of SRP Sludges Sampled from SRP Waste Tanks

Component	*Unit*	*Average*	*Range*
Fe	Wt %	22.0	3.1 - 32.8
Al	Wt %	9.9	1.5 - 33.5
U	Wt %	6.7	0 - 15.4
Mn	Wt %	5.4	1.7 - 10.8
Ni	Wt %	2.8	0.3 - 6.3
Hg	Wt %	1.2	0.1 - 2.8
^{90}Sr	mCi/g	-	30.0 - 180
^{144}Ce	mCi/g	-	0.5 - 30
^{106}Ru	mCi/g	-	0.1 - 10
Alpha Act.	mCi/g	-	0.1 - 0.7

TABLE 3

Composition of Simulated Acid Waste

Component	*Concentration (M)*
$Fe(NO_3)_3$	0.68
$Al(NO_3)_3$	0.52
$Ca(NO_3)_2$	0.32
$Ni(NO_3)_2$	0.18
$Sr(NO_3)_2$	10^{-3}
HNO_3	4.0

TABLE 4

Results of ^{106}Ru Removal Tests

Waste Treatment	*Distribution Coefficient, k_d*	*Ru Removed in Column Test, %*
None	~ 0	-
Diluted 8-fold	15	58
Diluted 10-fold and refluxed	12	-
Diluted 10-fold; excess (0.01M) Na_2S; room temperature; two days standing	13	-
Diluted 10-fold; excess (0.01M) Na_2S; refluxed 2 hr	200 to 300	99.3