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SEPARATION OF STRONTIUM-90 FROM HANFORD HIGH-LEVEL RADIOACTIVE WASTE

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ABSTRACT

Current guidelines for disposing of high-level radioactive wastes stored in underground tanks at the U.S. Department of Energy's Hanford Site call for vitrifying high-level waste (HLW) in borosilicate glass and burying the glass canisters in a deep geologic repository. Disposition of the low-level waste (LLW) is yet to be determined, but it will likely be immobilized in a glass matrix and disposed of on site. To lower the radiological risk associated with the LLW form, methods are being developed to separate ^{90}Sr from the bulk waste material so this isotope can be routed to the HLW stream. A solvent extraction method is being investigated to separate ^{90}Sr from acid-dissolved Hanford tank wastes. Results of experiments with actual tank waste indicate that this method can be used to achieve separation of ^{90}Sr from the bulk waste components. Greater than 99% of the ^{90}Sr was removed from an acidic dissolved sludge solution by extraction with di-t-butylcyclohexano-18-crown-6 in 1-octanol (the SREX process). The major sludge components were not extracted.

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INTRODUCTION

Methods are being developed to treat and dispose of large volumes of radioactive wastes stored in underground tanks at the U.S. Department of Energy's (DOE) Hanford Site. The treatment methods used must be effective for a wide variety of waste compositions because the compositions of the wastes generally vary from tank to tank. The current baseline scenario for treating and disposing of these wastes would partition the wastes into high-level waste (HLW) and low-level waste (LLW) streams. The HLW will be vitrified into borosilicate glass and disposed of in a geologic repository while the LLW will be immobilized in a glass matrix and will likely be disposed of by shallow burial at the Hanford Site.

Separating various radionuclides from the bulk waste components is desirable for both economic and environmental reasons. Because vitrifying and disposing of HLW is expected to be considerably more costly than disposing of LLW, it would be beneficial to minimize the volume of HLW by segregating the radionuclides into a concentrated waste stream. Furthermore, maximum removal of radionuclides from the LLW stream would lower the risk of radioactive material leaching from the LLW matrix into the surrounding environment.

The Hanford tank wastes are highly alkaline (typically with pH >13), and consist of three general physical forms: 1) supernatant liquid, 2) salt cake,(c) and 3) sludge. Except for ^{137}Cs and ^{99}Tc, the majority of the radionuclides are in the tank sludges. Thus, separation techniques for radioisotopes other than ^{137}Cs and ^{99}Tc are generally directed at treating the tank sludge materials.

The transuranic extraction (TRUEX) process for separating the transuranic elements (primarily Am and Pu) from acid-dissolved

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(c) The salt cake, consisting primarily of sodium salts (nitrate, nitrite, aluminate, and hydroxide), was formed by evaporation of tank supernatant liquids.

Hanford tank sludges has been investigated for a number of years (1-9). More recently, di-t-butyl-cyclohexano-18-crown-6 (DtBC18C6) has been investigated for extracting ^{90}Sr from acid-dissolved Hanford tank sludges. The process in which Sr is extracted with DtBC18C6 was developed by workers at Argonne National Laboratory; this has been termed the SREX process (10).

This paper describes the results of experiments conducted to test the SREX process for separating ^{90}Sr from the bulk constituents of Hanford tank sludge. Portions of an actual Hanford tank sludge were used in these experiments. The sludge used was taken from tank number B-110; this sludge contained ~220 μCi (8.1 x 10^6 Bq) ^{90}Sr per gram of sludge. The primary waste type stored in Tank B-110 was from the bismuth phosphate process, which was performed at Hanford in the 1940s and 1950s to recover and purify plutonium from irradiated fuel. The sludge formed when this waste was adjusted to high pH and contains Na, Bi, Cr, Fe, Si, phosphates, sulfates, and other constituents.

EXPERIMENTAL

The SREX process was examined in two different tests. The batch solvent extraction contacts performed in these tests are summarized in Figures 1 and 2 and in Tables 1 and 2. Composite core samples from two different locations within the tank were used for these tests. The DtBC18C6 was purchased from Parish Chemical Company (Vineyard, Utah) and the 1-octanol (99+%) was obtained from Aldrich Chemical Company (Milwaukee, Wisconsin). The SREX process solvent was prepared by dissolving the DtBC18C6 in 1-octanol to a concentration of 0.2 M; the resulting solvent mixture was used without any pretreatment. The TRUEX process solvent[d] was provided by Westinghouse Hanford Company (Richland,

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[d] The TRUEX process solvent consisted of 0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide plus 1.4 M tributyl phosphate in a normal paraffin hydrocarbon.

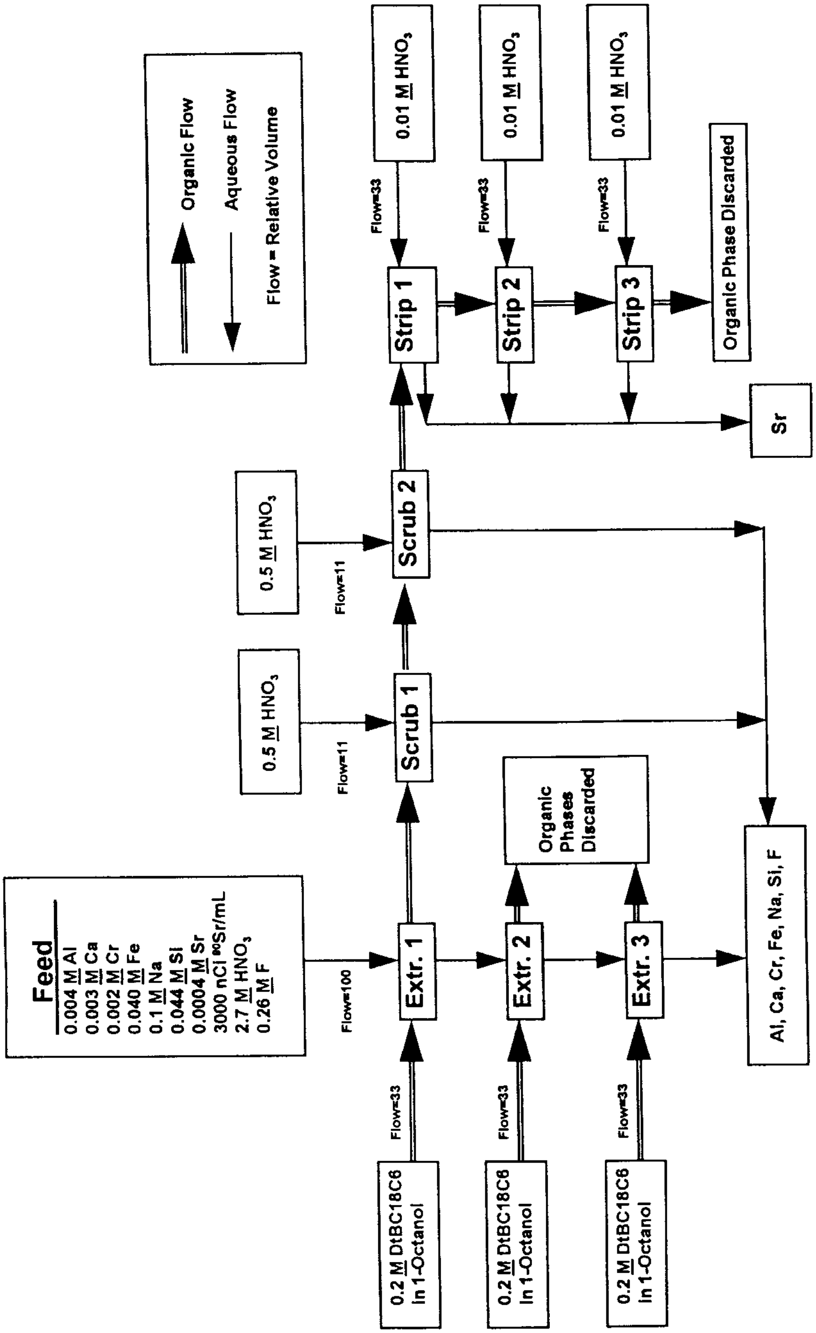

FIGURE 1. Schematic of the First SREX Test with Tank B-110 Sludge

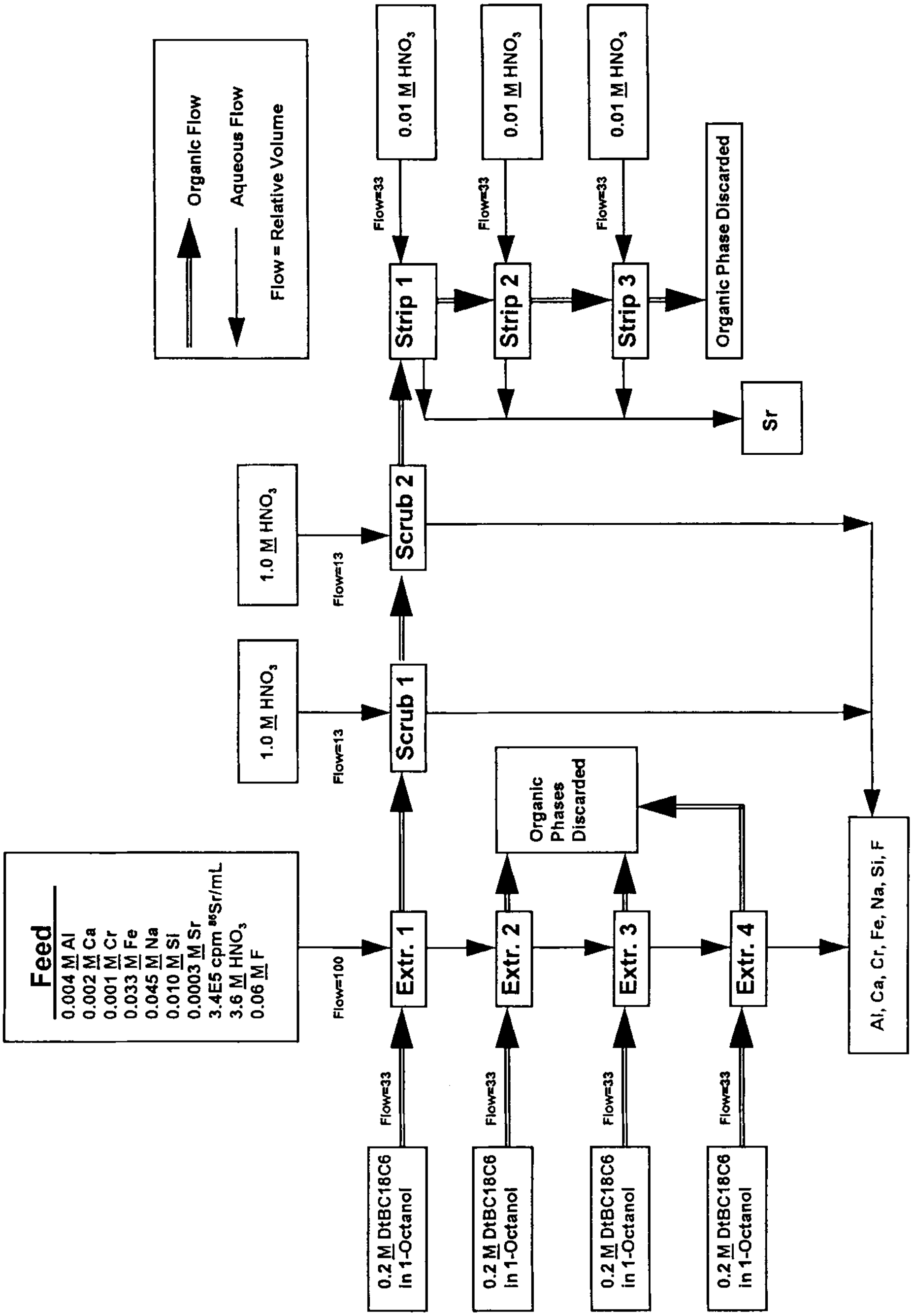

FIGURE 2. Schematic of the Second SREX Test with Tank B-110 Sludge

TABLE 1. SOLVENT EXTRACTION CONTACTS PERFORMED IN THE FIRST SREX TEST (REFER TO FIGURE 1)

Step	Aqueous Phase	Aq. Vol., mL	Organic Phase	Org. Vol., mL
EXTR-1	Solution 3	9.00	0.2 M DtBC18C6	3.00
SCRUB-1	0.5 M HNO_3	0.83	From EXTR-1	2.50
SCRUB-2	0.5 M HNO_3	0.67	From SCRUB-1	2.00
STRIP-1	0.01 M HNO_3	1.50	From SCRUB-2	1.50
STRIP-2	0.01 M HNO_3	1.00	From STRIP-1	1.00
STRIP-3	0.01 M HNO_3	0.50	From STRIP-2	0.50
EXTR-2	From EXTR-1	3.00	0.2 M DtBC18C6	1.00
EXTR-3	From EXTR-2	1.50	0.2 M DtBC18C6	0.50

TABLE 2. SOLVENT EXTRACTION CONTACTS PERFORMED IN THE SECOND SREX TEST (REFER TO FIGURE 2)

Step	Aqueous Phase	Aq. Vol., mL	Organic Phase	Org. Vol., mL
EXTR-1	Solution 8	19.80	0.2 M DtBC18C6	6.53
SCRUB-1	1.0 M HNO_3	2.17	From EXTR-1	5.50
SCRUB-2	1.0 M HNO_3	1.77	From SCRUB-1	4.50
STRIP-1	0.01 M HNO_3	3.50	From SCRUB-2	3.50
STRIP-2	0.01 M HNO_3	2.50	From STRIP-1	2.50
STRIP-3	0.01 M HNO_3	1.50	From STRIP-2	1.50
EXTR-2	From EXTR-1	5.00	0.2 M DtBC18C6	1.65
EXTR-3	From EXTR-2	3.00	0.2 M DtBC18C6	1.00
EXTR-4	From EXTR-3	1.50	0.2 M DtBC18C6	0.50

Washington). Before use, the TRUEX process solvent was washed with three successive 0.5 volumes of 0.25 M Na_2CO_3, then twice with 0.5 volumes of deionized water.

Procedure for the First SREX Test

For the first test, a 5.24-g portion of sludge from Tank B-110 was washed twice with 10-mL portions of 0.1 M NaOH at room temperature. These washes were performed by mixing the sludge with the 0.1 M NaOH for 1 to 2 h, centrifuging, and then decanting the wash liquor from the sludge.

To dissolve the washed sludge, water was added to give a total volume of 10 mL; then HNO_3 (2.9 mL of 15.7 $\underline{M}$) and HF (0.15 mL of 10 $\underline{M}$) were added along with enough water to give a total volume of 15 mL. After stirring at 100°C for 1 h, another 0.15 mL of 10 $\underline{M}$ HF was added to increase dissolution of the sludge. The dissolver mixture was heated for another 2 h, then was allowed to cool. After centrifuging, the solution (Solution 1) was decanted. Water (5 mL) and 10 $\underline{M}$ HF (1 mL) were added to the undissolved solid. The mixture was stirred at room temperature overnight, which resulted in most of the solid being dissolved. More was dissolved by heating the mixture for 1 h at 100°C. The solution (Solution 2) was cooled and centrifuged, then was decanted from the small amount of residual solid. Solutions 1 and 2 were filtered through 0.2-μm filters. The amount of residual solid was too small to allow for its characterization, so it was discarded.

The feed solution (Solution 3) was prepared by mixing 2.5 mL of Solution 1, 2.5 mL of Solution 2, 1 mL of 15.7 $\underline{M}$ HNO_3, and 4 mL of water. The composition of Solution 3 is given in Figure 1. The feed solution was contacted with 3 mL of 0.2 $\underline{M}$ DtBC18C6 in 1-octanol (the SREX process solvent); then portions of each phase were taken for subsequent contacts, as outlined in Table 1. In general, the contacts were performed by mixing the two phases for 30 to 60 sec. The mixtures were centrifuged before sampling to ensure complete phase separation.

The aqueous phases from each contact were sampled. The concentration of the bulk sludge components was determined by inductively coupled plasma/atomic emission spectroscopy (ICP). Acid concentrations were determined by potentiometric titration with standard NaOH. Fluoride concentrations were determined potentio-metrically using a fluoride-selective electrode. Strontium-90 concentrations for Solution 3 and each aqueous phase were determined by radiochemical analyses.

Procedure for the Second SREX Test

For the second test, a 3.43-g portion of Tank B-110 sludge was used. The sludge was slurried in ~15 mL of 0.1 M NaOH and heated at 100°C for 1 h. After cooling to room temperature, the mixture was centrifuged, and the clear supernatant solution was decanted. The sludge was washed in a similar manner with another 10-mL portion of 0.1 M NaOH, then was dissolved in acid as follows.

The washed sludge was mixed with 10 mL of water, giving a slurry with pH = 11.9. Nitric acid (0.27 mL of 15.7 M) was added to lower the pH to 1.0. An additional 1.8 mL of 15.7 M HNO_3 was added to yield an effective HNO_3 concentration of approximately 2 M. The dissolution mixture was heated at 100°C for 1 h, then was allowed to cool to ambient temperature. Nearly all of the solids dissolved.

The dissolution mixture was centrifuged, and the dissolved sludge solution (Solution 4) was decanted from the small amount of residual solids. The residual solids were treated with 5.3 mL of 1.9 M HNO_3/0.6 M HF at 100°C for 1 h, resulting in complete dissolution of the remaining solids (Solution 5). The two dissolved sludge solutions (Solutions 4 and 5) were combined for use in the solvent extraction test (Solution 6).

Before conducting the second SREX test, Solution 6 was used in a test of the TRUEX process (1,2) for separating the transuranic elements from the dissolved sludge solution. Solution 6 (13.8 mL) was mixed with 2.2 mL of 2.0 M HNO_3 and 4.4 mL of a solution that was 0.01 M HNO_3 and 0.01 M ascorbic acid to give Solution 7. The latter two solutions were added to represent the blending of the TRUEX scrub solutions with the feed solution that would occur in the TRUEX extraction stages. Solution 7 was contacted two successive times with the TRUEX process solvent at an organic-to-aqueous phase ratio equal to 0.5.(e)

(e) Because the focus of this paper is on Sr separation, detailed results of the TRUEX test are not reported here. The results TRUEX test can be found in reference 11.

Fourteen milliliters of the aqueous phase from the second TRUEX extraction were mixed with 1) 3.3 mL of 15.7 M HNO_3 (to increase the HNO_3 concentration, and thus, increase the Sr distribution coefficient), 2) 2.6 mL of 1.0 M HNO_3 (to represent blending with the scrub stream), and 3) ^{85}Sr tracer solution (so that the behavior of Sr could be followed by gamma counting techniques). The resulting solution (Solution 8) was subjected to a series of extraction, scrub, and strip steps as outlined in Figure 2 and Table 2.

RESULTS AND DISCUSSION

First SREX Test

In the first SREX test, a dissolved B-110 sludge solution (Solution 3, above) was contacted three successive times with the SREX process solvent at an organic-to-aqueous phase ratio equal to 0.33. The results are shown in Figure 3. Greater than 99% of the Sr was extracted from the aqueous feed solution; the decontamination factor(f) for ^{90}Sr was 250. Of the major sludge components present, only Na extracted to any extent, and this did not occur until the third extraction contact. Because the scrub steps were only tested on the organic phase from the first extraction contact, the behavior of Na in the scrubbing stages was not determined. But based on published distribution coefficients (10), Na should have been readily scrubbed from the extract. The amount of H^+ extracted was consistent with published data on the SREX process (10). Barium and Pb, which are minor constituents of the waste, were extracted along with the Sr.

The organic phase from the first extraction was subjected to a series of scrub and strip contacts as outlined in Table 1. The concentration profile for ^{90}Sr for all the contacts is given in

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(f) The decontamination factor (DF) is defined as the quantity of a certain component initially present in the waste divided by the quanitity of that component present after treatment.

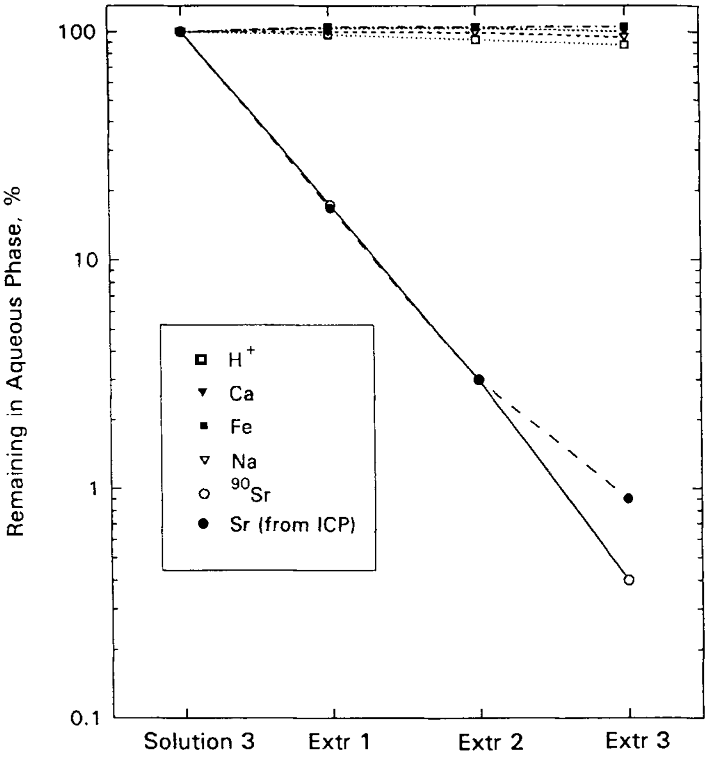

FIGURE 3. Extraction Results from the First SREX Test with Tank B-110 Sludge

Figure 4. The behavior of ^{90}Sr can be summarized as follows:

- Greater than 99% of the ^{90}Sr was extracted from the acid-dissolved sludge solution.
- Eighty-eight percent of the extracted ^{90}Sr remained in the organic phase after the second scrub contact.
- Strontium-90 was stripped easily with 0.01 M HNO_3.

This initial SREX test served as a proof-of-principle that the SREX process can be used to separate ^{90}Sr from dissolved

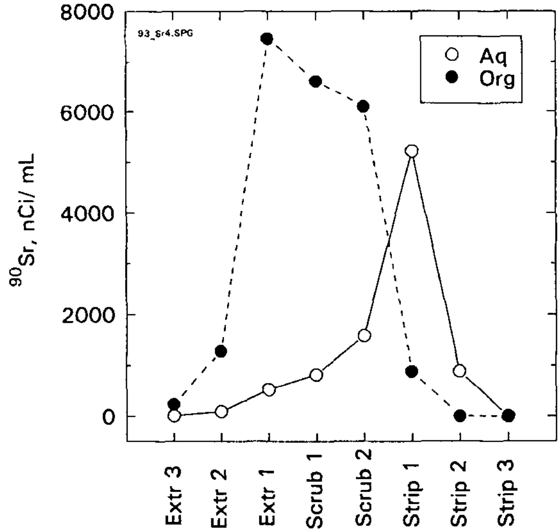

FIGURE 4. Strontium Concentration Profile from the First SREX Test with Tank B-110 Sludge

Hanford tank sludges. Significant loss of ^{90}Sr from the extract during the scrub steps indicated that a different scrub solution might be needed to improve the process performance. Another test was conducted (Figure 2, Table 2) using 1.0 M HNO_3 as the scrub solution.

Second SREX Test

In the second SREX test, a dissolved B-110 sludge solution was contacted four successive times with the SREX process solvent at an organic-to-aqueous phase ratio equal to 0.33. The organic phase from the first extraction was subjected to a series of scrub and strip steps. The Sr concentration profile is given in Figure 5. The process performed as expected. Strontium was extracted efficiently (DF ~9,000), retained in the extract during the scrubbing contacts, and stripped with 0.01 M HNO_3. The distribution coefficient for Sr in the first strip contact was

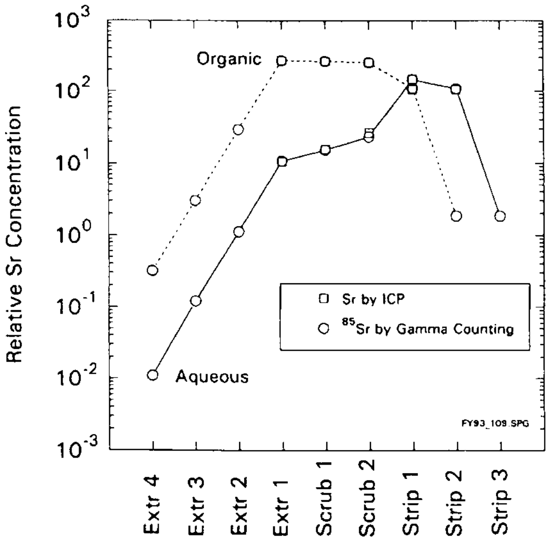

FIGURE 5. Strontium Concentration Profile from the Second SREX Test with Tank B-110 Sludge

0.8, which is somewhat high for efficient stripping, especially at the organic-to-aqueous phase ratio of 1 use here. Under continuous counter-current conditions, a flowsheet employing a 0.5 $\underline{M}$ HNO_3 scrub solution may be more desirable. As was indicated in the first test (Figure 4), the Sr distribution coefficients remained well above 1 during scrubbing when 0.5 $\underline{M}$ HNO_3 was used as the scrub solution, and stripping was much more efficient (the Sr distribution coefficient was 0.2 in the first strip contact of the first SREX test).

The Sr distribution coefficients measured during this experiment are compared to those reported in the literature (12) in Figure 6. The results obtained here agree very well with the literature values.

Lead was extracted along with Sr; however, the extracted Pb was not stripped from the solvent. The Pb distribution coefficient in the first strip contact was >11. This implies that

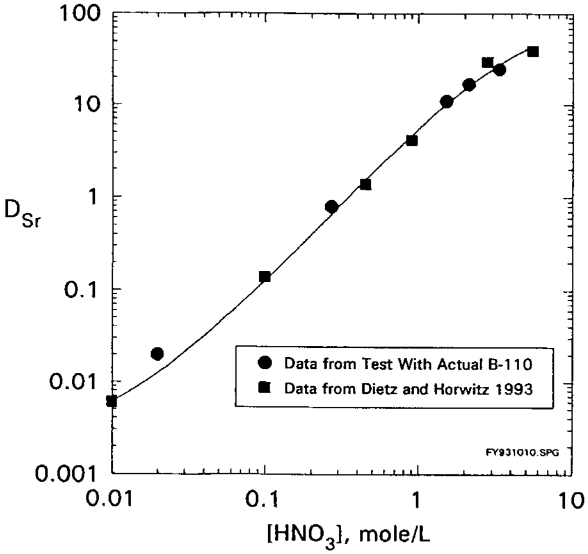

FIGURE 6. Comparison of Sr Distribution Coefficients Determined in SREX Tests with Actual Tank B-110 Sludge to Those Reported in the Literature

Pb can be separated from the Sr, but a second strip section must be added to the process flowsheet to strip Pb from the solvent.

Conclusion

The results of SREX tests with actual B-110 sludge indicate that, in principle, this process can be used to separate ^{90}Sr from the bulk non-radioactive components of Hanford tank sludges. Using the SREX process, in combination with the TRUEX process, could greatly reduce the volume of HLW glass produced in disposing of Hanford tank wastes. Additional flowsheet optimization and continuous counter-current tests with a variety of Hanford tank wastes will be required to fully demonstrate the process.

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