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A COMBINED CESIUM-STRONTIUM EXTRACTION / RECOVERY PROCESS

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ABSTRACT

A new solvent extraction process for the simultaneous extraction of cesium and strontium from acidic nitrate media is described. This process uses a solvent formulation comprised of 0.05 M di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6), 0.1 M Crown 100' (a proprietary, cesium-selective derivative of dibenzo-18-crown-6), 1.2 M tributyl phosphate (TBP), and 5% (v/v) lauryl nitrile in an isoparaffinic hydrocarbon diluent. Distribution ratios for cesium and strontium from 4 M nitric acid are 4.13 and 3.46, respectively. A benchtop batch countercurrent extraction experiment indicates that >98% of the cesium and strontium initially present in the feed solution can be removed in only four extraction stages. Through proper choice of extraction and strip conditions, extracted cesium and strontium can be recovered either together or individually.

INTRODUCTION

Recently, there has been considerable interest in the development of improved processes for the chemical pretreatment of nuclear wastes generated by the American defense establishment (Bell and Bell, 1994). Chemical pretreatment, by segregating most or all of the radioactive components from the inactive, bulk constituents of the waste, can reduce the quantity of waste requiring vitrification and subsequent burial in a deep geologic repository. Because of the diversity and complexity of nuclear wastes, however, the demands on any separation process employed in its treatment are great.

Previous work in this laboratory has led to the development of solvent extraction (SX) processes for the removal and recovery of transuranic elements (Horwitz et al., 1985), strontium (Horwitz et al., 1991; Dietz et al., 1995a), and cesium (Dietz et al., 1995b) from acidic nitrate media. In an effort to minimize the number of treatment steps and the size of the waste processing facility required, we have recently focused on combining these individual acid-side solvent extraction processes into a single process. In a previous report, a means of combining the transuranic extraction process (TRUEX) and the strontium extraction process (SREX) into a single TRU-Sr extraction/recovery process (Horwitz et al., 1993; Horwitz et al., 1994) was described. In this report, an acid-side SX process for the simultaneous extraction of Cs and Sr from acidic nitrate

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media is described. This combined CSEX-SREX process, which relies on a mixture of a strontium-selective macrocyclic polyether and a novel cesium-selective extractant based on dibenzo-18-crown-6, offers two potential advantages over possible alternatives in a chemical processing scheme for high-level waste treatment. First, if the process is applied as a first step in chemical pretreatment (Figure 1), the radiation level for all subsequent processing steps (e.g., TRUEX) will be significantly reduced. In addition, because the recovered Cs-Sr fraction is non-TRU, it will decay to low-level waste after only a few hundred years. As a result, it may not be necessary to bury it in a deep repository.

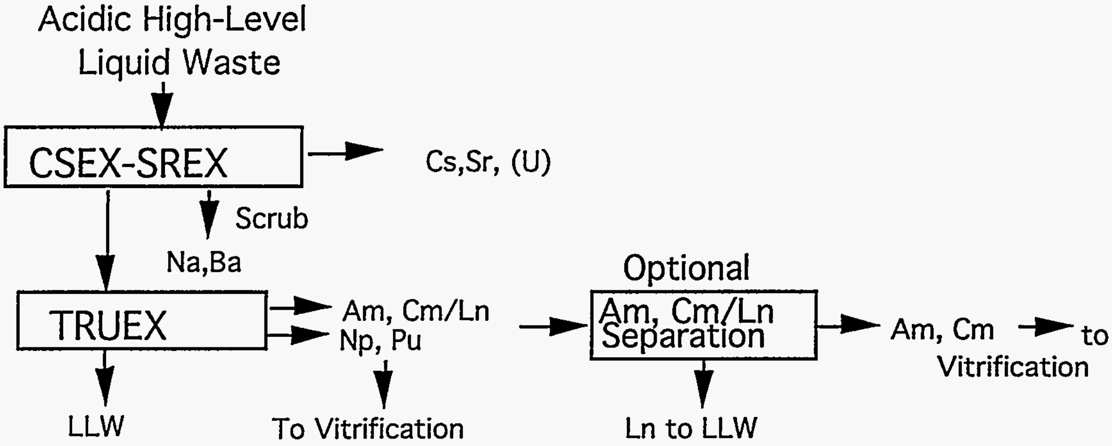


Figure 1. Treatment of acidic high-level liquid wastes using a front-end Cs-Sr solvent extraction process.

EXPERIMENTAL

Materials. Calcine Waste simulant (Hogg et al., 1993) was kindly supplied by Dr. R. Scott Herbst of Lockheed Idaho Technology Company (Idaho Falls, ID, USA). The approximate composition of this waste simulant is shown in Table 1.

TABLE 1

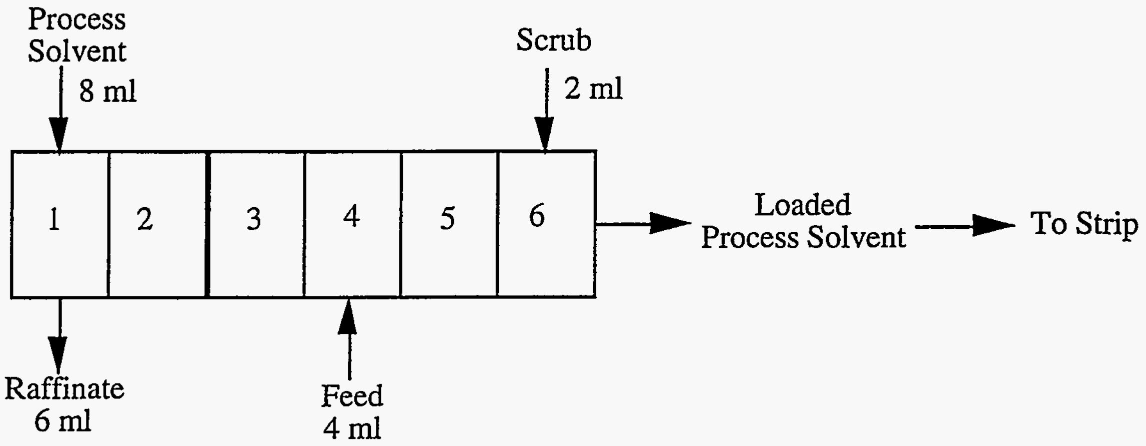
Composition of Dissolved Calcine Waste from LITCO

Simulated Zirc Calcine	
Component	Moles/L
Acid	3.781
Al	0.486
B	0.086
Ca	0.778
Cs	0.005
F	1.24
Fe	0.0149
Nitrate	6.39
Na	0.015
Sr	0.0039
Zr	0.225

The strontium extractant, di-t-butylcyclohexano-18-crown-6 (DtBuCH18C6), was obtained from Eichrom Industries (Darien, IL, USA) and used without purification. The cesium extractant precursor, of proprietary composition, was synthesized by Dr. Richard A. Bartsch of Texas Tech University, (Lubbock, TX, USA) and appropriately modified at ANL to yield a compound designated hereafter as Crown 100'. Details of the modification procedure will be presented in a forthcoming publication (Dietz et al., 1995b).

Procedures. Distribution ratios were measured either radiometrically or by ICP-AES, as described previously (Huff and Horwitz, 1985).

The combined CSEX-SREX process was tested in a batch countercurrent mode using 25 ml graduated separatory tubes fitted with teflon stopcocks and stoppers. The flow diagram is shown in Fig. 2.



Process Solvent: 0.1 M Crown 100' - 0.05 M DtBuCH18C6 - 1.2 M TBP - 5% (v/v) lauryl nitrile in Isopar™-L.
Feed: Calcine waste from LITCO
Scrub : 4 M HNO_3

Figure 2. Flow diagram for batch countercurrent test of the combined CSEX-SREX process.

RESULTS AND DISCUSSION

Previous work in this laboratory has established that strontium may be efficiently and selectively extracted from acidic nitrate media by solutions of DtBuCH18C6 dissolved in either a combination of a paraffinic hydrocarbon and an appropriate phase modifier (e.g., tributyl phosphate) (Dietz et al., 1995a) or any one of a number of oxygenated aliphatic diluents (e.g., alcohols, ketones) (Horwitz et al., 1991). Because preliminary studies indicated that several crown ethers of possible utility in cesium extraction lack sufficient solubility in certain oxygenated aliphatic solvents, however, and because a paraffinic hydrocarbon-based solvent is preferrable in any large-scale solvent extraction process, our efforts to combine cesium and strontium extraction into a single operation have focused on the use of process solvents comprised of a mixture of DtBuCH18C6 and Crown 100' in an isoparaffinic hydrocarbon modified by addition of TBP. (The use of isoparaffinic hydrocarbons (IPHs) rather than normal paraffinic hydrocarbons (NPHs), it should be noted, was prompted by results obtained in the development of the combined TRUEX-SREX process which indicated superior solvent loading for extractant formulations based on IPHs (Horwitz et al., 1993).) The concentrations of Crown 100'(0.1 M), DtBuCH18C6 (0.05 M), and

TBP (1.2 M) utilized in the process solvent represent a compromise between the need to maximize cesium and strontium extraction, to minimize third-phase formation, and to achieve rapid phase disengagement.

Figure 3 shows the influence of aqueous nitric acid concentration on the extraction of cesium and strontium, as measured by their distribution ratios, using the combined CSEX-SREX process solvent. As can be seen, strontium extraction rises steadily with nitric acid concentration, as expected from previous results for DtBuCH18C6 alone in 1-octanol or TBP-paraffinic hydrocarbon mixtures (Horwitz et al., 1991; Dietz et al., 1995a). D_{Sr} reaches a value of 3.46 at 4 M nitric acid, the acidity of the synthetic feed solution. Cs extraction, as indicated by D_{Cs}, exhibits a similar increase with rising acidity up to ca. 4 M acid. The efficiency of cesium and strontium extraction at high acidity, the low distribution ratios at low acidity, and the reasonably good selectivity over other fission products and trivalent actinides make this process well suited to the treatment of certain acidic high-level waste streams.

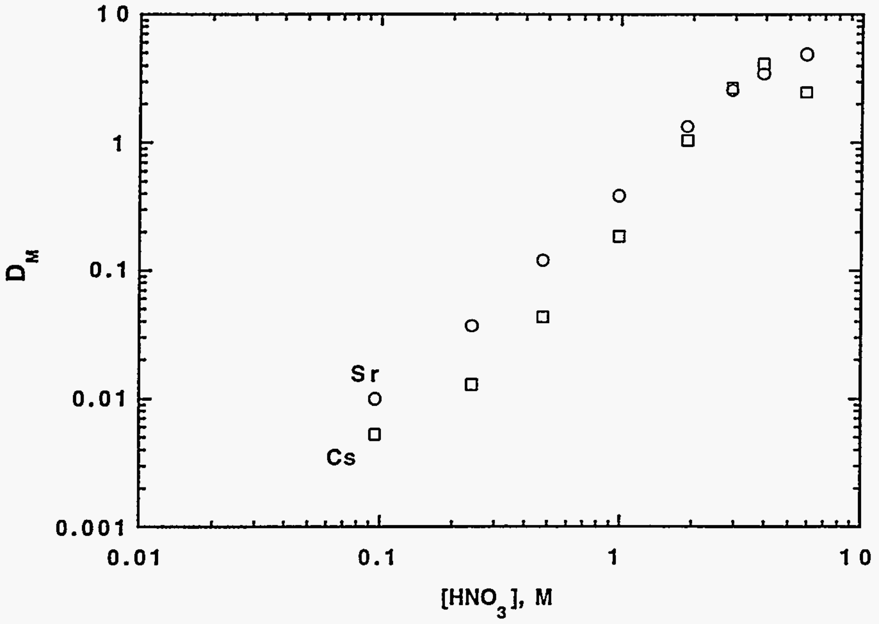


Figure 3. Nitric acid dependencies of Cs and Sr extraction by the CSEX-SREX Combined Process Solvent (0.1 M DtBuCH18C6-0.05 M Crown 100'-1.2 M TBP-5 % (v/v) lauryl nitrile-Isopar™ L) ; T = 22 ± 1 °C

Table 2 summarizes the cesium and strontium distribution ratios and the corresponding extraction factors for each of the four extraction and two scrub stages in the batch countercurrent extraction test, carried out as outlined in Figure 2. The results are, in each case, consistent with the acid dependency data (Figure 3).

The decontamination factors (DFs) achieved in the countercurrent test for the various waste constituents are summarized in Table 3. The values indicate that despite the relatively high concentrations of aluminum, calcium, and zirconium in the feed solution, none of these elements would be expected to constitute a major portion of the final product.

Table 2

Cesium and Strontium Distribution Ratios and Extraction Factors per Stage in Batch Countercurrent Experiment (99.8% Sr and 98.6% Cs Extracted)

Stage Number	Stage Type	D_{Sr}	E_{Sr}	D_{Cs}	E_{Cs}
1	Extraction	3.38	4.5	2.49	3.3
2	Extraction	3.41	4.6	1.77	2.4
3	Extraction	3.48	4.6	1.49	2.0
4	Extraction	3.11	4.2	1.26	1.7
5	Scrub	3.41	4.6	1.53	2.0
6	Scrub	3.41	4.6	1.72	2.3

Table 3

Decontamination Factors for Selected Calcine Waste Constituents in the Cs/Sr Product

Component	Decontamination Factor [1]
Al	6.0×10^3
Ca	5.9×10^3
Cs	--
Fe	4.2×10^3
Na	19
Sr	--
Zr	2.0×10^2

[1] Taken as the ratio of the concentration of the constituent of interest to that of strontium in the feed solution divided by the same ratio for the strip solution.

Table 4

Successive Stripping of Loaded CSEX-SREX Process Solvent [1]

Contact no.	D_{Sr}	Organic Phase Activity (cpm/mL)	D_{Cs}	Organic Phase Activity (cpm/mL)
1	0.72	1.07×10^5	0.39	3.02×10^5
2	0.14	2.21×10^4	0.095	4.66×10^4
3	0.041	1.49×10^3	0.023	1.94×10^3
4	0.019	6.50×10^1	0.021	1.20×10^2
5	not measureable	-- [2]	not measureable	-- [2]

[1] Fully loaded process solvent contains ca. 2.1×10^{-3} M Cs and 3.9×10^{-3} M Sr.

[2] Measured activity is within 2 ó of the background count rate.

Results obtained in the successive stripping of ^{137}Cs and ^{85}Sr-spiked samples of the organic phase from the last scrub stage are shown above in Table 4. These data clearly demonstrate that highly effective stripping of the loaded process solvent can be achieved. The final distribution ratios for cesium and strontium are approaching the values expected for 0.1 M nitric acid, the strip solution employed, indicating that the initial strips serve also to reduce the nitric acid content of the organic phase.

CONCLUSIONS

The results of this study demonstrate that it is possible to combine the extraction of cesium and strontium from acidic nitrate media into a single operation. This combined CSEX-SREX process offers several advantages over the individual processes carried out in tandem. First, the combined process requires less equipment and space. In addition, it requires the handling of only one process stream. Next, extraction and recovery of both cesium and strontium are straightforward. Both are extracted from solutions containing high nitric acid concentrations and stripped using dilute acid. Finally, the separation sequence is flexible. Uranium can be co-extracted with Cs and Sr or rejected to the raffinate, for example, and if desired, any barium present can be scrubbed from the loaded Cs-Sr process solvent, thereby reducing the weight of the Cs-Sr fraction.

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