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W. R. Wilmarth[a]; J. T. Mills[a]; V. H. Dukes[a]; M. C. Beasley[a]; A. D. Coleman[a]; C. C. Diprete[a]; D. P. Diprete[a]

[a] Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, South Carolina, USA

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Caustic-Side Solvent Extraction Batch Distribution Coefficient Measurements for Savannah River Site High-Level Wastes[#]

W. R. Wilmarth,[*] J. T. Mills, V. H. Dukes, M. C. Beasley, A. D. Coleman, C. C. Diprete, and D. P. Diprete

Savannah River Technology Center, Westinghouse Savannah River
Company, Aiken, South Carolina, USA

ABSTRACT

The cesium distribution coefficients for extraction, scrubbing, and stripping of the caustic-side solvent extraction flowsheet were measured for a number of tank waste supernates from both the F- and H-Area Tank Farms. The measured distribution coefficients, D_{Cs}s, indicate that the caustic-side

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[*] Correspondence: W. R. Wilmarth, Savannah River Technology Center, Westinghouse Savannah River Company, Aiken, SC 29808, USA; E-mail: bill.wilmarth@srs.gov.

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solvent extraction flowsheet will successfully decontaminate the supernate and produce a concentrated, dilute nitric acid product. Because of the difficulty in performing the experiments on a 40-mL scale in the shielded cells, some caustic carryover into the scrub acid occurred and contributed to the higher-than-expected scrub distribution coefficients.

Comparing the measured extraction distribution coefficients to recently published data by Oak Ridge National Laboratory (ORNL) personnel showed agreement between the model and experiments with two actual tank wastes. However, tests with three other tank wastes gave extraction D_{Cs}s that deviated from the model predictions. Additional refinements of the model are planned in FY 2002. Two of these measurements were below the flowsheet requirement for extraction. Several aspects of the waste chemistry (e.g., anion concentrations) were examined; however, no distinct correlation was found for extraction distribution coefficient behavior.

Testing also examined the affinity of the calixarene-solvent system for actinide removal. Plutonium and uranium extraction distribution coefficients measured around 2. However, additional analytical work is needed to measure the mass of the actinides in the organic phase (Wilmarth, W.R., Hobbs, D.T. *Task Technical and Quality Assurance Plan Supporting CSSX Pilot Plant Critically Issues*; WSRC-RP-2001-0076; Westinghouse Savannah River: Aiken, SC, 2001).

INTRODUCTION

Since the cessation of the in-tank precipitation process, various researchers across the Department of Energy (DOE) complex evaluated three options for removing radiocesium from Savannah River Site (SRS) high-level waste. One of these options uses caustic-side solvent extraction (CSSX) with a solvent system developed at Oak Ridge National Laboratory (ORNL).[2] This solvent consists of a calix[4]arene-crown-6 extractant dissolved in an inert hydrocarbon matrix. A modifier, an alkylphenoxy alcohol added to the solvent, enhances the extraction power of the calixarene, increases solubility, and minimizes formation of a third phase. Addition of trioctylamine improves stripping performance and mitigates the effects of any surfactants present in the feed stream.[3] The solvent system proved successful for removing and concentrating cesium in batch tests using a simulant of the SRS waste.[4]

Only a single data set exists from measurements of the solvent system's performance with actual tank waste. The first measurements completed on SRS tank waste supported the real waste demonstration with a composite of Tank 44F and 37H wastes.[5] Therefore, samples were collected from several high-level waste storage tanks at SRS and processed to measure the cesium distribution coefficients for sequential extraction, scrubbing, and stripping steps in the CSSX flowsheet.

EXPERIMENTAL METHODOLOGY

Experiments used samples obtained from several high-level waste Tanks 13H, 26F, 35H, 33F, and 46F. These tanks represent Waste Removal, Concentrate Receipt, and Canyon Receipt Tank, respectively. The samples were placed into the shielded cells, diluted with the intention of reaching approximately 5.6-M sodium-ion concentration, and filtered through 0.45-μm filters prior to testing. The 5.6-M sodium-ion concentration is the reference concentration for the proposed facility.[6]

The solvent was supplied by the ORNL (lot number PVB B000894-31W). The solvent consisted of the cesium extractant, calix[4]arene-bis(*tert*-octylbenzo-crown-6) (0.01 M), a modifier, 1-(2,2,3,3-tetrapfluoropropoxy)-3-(4-*sec*-butylphenoxy)-2-propanol (0.5 M), and trioctylamine (0.001 M) dissolved in Isopar L. Scrubbing and stripping acid solutions came from 2 × and 100 × gravimetric dilution of certified 0.1-M nitric acid (Fisher Scientific, lot number 003535-2Y, expiration 7/02), respectively.

Sequential extraction, scrubbing, and stripping operations were performed on each of the diluted tank wastes; and cesium distribution coefficients were measured. Testing occurred in duplicate with targeted organic-to-aqueous (O/A) volume ratios of 0.33 for the extraction step and 5 for the scrub and strip steps. Polypropylene tubes (40 mL or 15 mL) were used during the batch contacts. The additions of aqueous and organic phases were performed gravimetrically. Samples were analyzed by gamma-spectroscopy analysis using ORTEC high-purity germanium detectors (30 to 40% efficient). Most of the electronics are Canberra. Resultant spectra are analyzed using Canberra Genie 2K software. The aqueous phase was diluted into 0.2-M nitric acid, and the organic phase into either the complete solvent system or octanol. All dilutions were determined gravimetrically.

Organic samples that were too radioactive to analyze directly were further diluted. The only exception was as they were organic, dilutions used organic solvents, not dilute nitric acid as is customary. The initial organic solvent chosen was octanol. However, as the results proved inconsistent, octanol was compared to Isopar L containing the ORNL modifier and to paraffin as solvents for the gamma-counting vials. The gamma-counting vials contained 0.1 mL of the ^{137}Cs loaded calixarene extractant diluted in Isopar L with the modifier, and 2.9 mL of the solvent of choice.

Elemental metals measurements were performed based on atomic emission from excited atoms and ions using Applied Research Laboratories, Model Number 3580 inductively coupled plasma atomic emission spectrometer (ICP-ES). Free hydroxide analysis was determined via an inflection point titration using a contained Radiometer "TIM 900" automated titration system.

RESULTS AND DISCUSSION

Dip and variable depth samples from Tanks 13H, 26F, 33F, 35H, and 46F were placed into the shielded cells and composited, diluted, and filtered, as previously described. Table 1 contains the measured densities of the diluted composites and the measured sodium-ion concentration, along with the measured anion concentrations for each of the tank samples. The measured sodium-ion concentrations show that three tanks (13H, 46F, and 35H) were close to the 5.6-M target. The sodium-ion concentration of Tank 26F proved significantly higher than the target and measured 8.2 M. In general, anion balances were good; however, the anion balance for Tank 26F indicates the measured sodium concentration is slightly high.

The flowsheet calculations[7] use values of 8, 0.6, and 0.16 for the cesium-distribution coefficient (D_{Cs}) for the extraction, scrubbing, and stripping steps at 25°C, respectively. Table 2 contains the cesium-distribution coefficients determined in this study for Tanks 13H, 26F, 33F, 35H, and 46F. These coefficients represent the average of replicate tests. The measured distribution coefficients were temperature corrected from the ambient shielded cell temperature of 20 ± 2°C using Eq. (1). The equation and the values of

Table 1. Densities (g/mL) of tank sample composites.

Tank	Density	Estimated Na^+ concentration (M)
13H	1.2439	5.6
26F	1.3336	7.7
35H	1.2653	6.3
33F	1.1995	4.5
46F	1.2458	5.6

Table 2. Waste tank sample results.

Nitrate	M	0.60	1.04	0.59	0.03	0.72
Nitrate	M	0.81	1.10	0.42	1.50	1.60
Sulfate	M	<0.013	0.008	<0.013	0.040	0.020
OH	M	3.05	5.16	3.99	2.05	2.80
Anion sum	M	4.46	7.31	5.00	3.62	5.14
Measured Na	M	5.1	8.2	5.2	3.6	5.5
Measured Cs-137	dpm/mL	2.37E + 0.9	2.58E + 0.9	2.05E + 0.9	5.92 + 0.7	1.65E + 0.9

enthalpy (H) are taken from a research by Bonnesen et al.[8]

$$D_1 = D_0 \exp[(H/R)\{(1/T_1) - (1/T_0)\}] \qquad (1)$$

where T_i is absolute temperature in K, D_I is the distribution coefficient at T_I, and R is 0.0083144 kJ/mol-K.

The distribution coefficients for extraction ranged from 7.7 to 13.8, compared to the baseline value of 8. The lowest values of D_{Cs} measured 7.7 for Tank 26F and 7.9 for Tank 35H. Tank 13H and Tank 46F had D_{Cs}s for extraction above 10, with the D_{Cs} for Tank 33F measuring 8.8. Examination of the data does not reveal a correlation between cesium recovery and the extraction distribution coefficients for Tanks 26F and 35H.

Researchers[9] at ORNL developed a multivariant mathematical model of the cesium extraction from SRS waste simulants. Table 3 shows a comparison of the ORNL model prediction and the temperature-corrected batch extraction coefficients for each of the five tank wastes. The model prediction for cesium extraction and experiment agree for the tank wastes from Tank 13H and Tank 46F. However, for the other three tank wastes (26F, 33F, and 35H), there was significant disagreement. There are several possible reasons for this discrepancy. For two of these wastes (Tanks 26F and 33F), the sodium-ion concentration fell outside the data used in the development of the model, potentially leading to the high model prediction (Table 4). Examining the tank chemistry data supplied in Table 1, no correlation is observed to hydroxide, nitrate, or nitrite concentration. The only correlation observed related to the sulfate concentration. For Tanks 13H and 46F, no measurable sulfate concentration was detected. For the three remaining tanks, each had a measurable sulfate concentration that ranged from 0.01 M to 0.04 M. Although these concentrations are low, sulfate is not in the ORNL model. The amount of deviation from the model does increase with increasing sulfate concentration. Additional testing to improve the predictive model is underway and may provide a higher correlation between tank chemistry and extraction.

Table 3. ^{137}Cs distribution coefficients for tank waste samples at 25°C.

D_{Cs}	Tank 13H	Tank 26F	Tank 46F	Tank 35H	Tank 33F
Extraction	10.1 ± 2.4	7.7 ± 1.9	13.8 ± 2.8	7.9 ± 0.9	8.8 ± 0.5
Scrub	4.4 ± 0.9	1.1 ± 0.5	1.6 ± 1.3	0.7 ± 0.6	1.1 ± 0.05
Strip 1	1.1 ± 0.1	0.10 ± 0.10	0.27 ± 0.19	0.14 ± 0.001	0.07 ± 0.01
Strip 2	0.25 ± 0.01	0.23 ± 0.09	0.10 ± 0.02	0.17 ± 0.13	0.04 ± 0.005
Strip 3	0.12 ± 0.02	0.04 ± 0.02	0.04 ± 0.05	0.16	0.06 ± 0.005

Table 4. Comparisons of extraction data for actual[a] and predicted tank wastes.

Tank	ORNL predicted D_{Cs}	Actual D_{Cs}	Na^+ concentration (M)
13H	8.8	10.1	5.1
26F	14.95	7.7	8.2
33F	23.71	8.8	3.6
35H	22.02	7.9	5.5
46F	16.55	13.8	5.2

[a] Measured D_{Cs} corrected to 25°C.

The temperature-corrected distribution coefficients for the scrub step of each of the samples appeared higher than anticipated and range from 4.4 for Tank 13H to 0.7 for Tank 35H. The values for D_{Cs} for the scrub step exceeded the flowsheet value of 0.6. The scrub D_{Cs}s, with the exception of Tank 13H, proved lower than those measured for the real-waste demonstration, where Walker et al.[5] measured 8.8 and 3.67. After discussions with various personnel, we measured the pH of selected scrub aqueous phases, and the pH measured between 4 and 10. This finding indicates some aqueous phase carryover from the extraction step. This phase carryover may cause the high distribution coefficients.

With the exception of the distribution coefficients for the stripping step in Tank 13H, the first strip of the cesium from the organic phase resulted in fairly low D_{Cs} and ranged from 0.07 to 0.27. The first strip D_{Cs} for Tank 13H produced a value of 1.1. The strip D_{Cs} value for this tank decreased for the second (0.25) and third contact (0.12) with the acid. This was the general trend for the strip measurements. In all cases, the batch distribution coefficient for the third strip fell below the flowsheet requirement of 0.16. All of the measured D_{Cs}s for stripping agreed well with the real-waste demonstration,[5] indicating that the process can successfully decontaminate these wastes and concentrate the cesium as desired.

The solvent-extraction flowsheet currently designed utilizes monosodium titanate to remove the strontium and actinide components of the tank waste. Decontamination factors for the actinides are not large, generally less than 10. If the calixarene-solvent system would remove the actinides, the flowsheet could be simplified. Therefore, the aqueous and organic phases were analyzed for plutonium-238 by alpha spectroscopy. Table 5 shows the extraction distribution coefficients measured for the various SRS tank wastes at ambient cell temperature (20 ± 2°C). In general, the extraction D_{Pu}s measured around 2, with the exception of Tank 13H. The D_{Pu} for Tank 13H was 0.045 ± 0.049. The low

Table 5. Pu extraction distribution coefficient measurements.

Tank	D_{Pu}	Standard deviation
13H	0.045	0.049
26F	2.87	—
33F	2.905	2.74
35H	1.68	0.45
46F	2.55	0.21

concentration of ^{238}Pu in the wastes resulted in large uncertainties in the alpha measurements. For Tank 26F, only one measurement is reported due to the inability to close the material balance. If indeed, the actinides are extracted into the organic phase, the behavior of these actinides is the scrub and strip contacts needs to be understood to prevent build-up in the recycled organic phase.

Additionally, the aqueous sample from the tank with the highest ^{238}U concentration (Tank 35H) was submitted for inductively couple plasma-mass spectroscopy. There is no method for analyzing the organic phase for uranium mass. A distribution coefficient for the extraction of uranium by the calixarene-solvent system was calculated from the starting and final aqueous phase concentrations. The extraction D_U measured 2.6 ± 0.2 at ambient cell temperature.

CONCLUSION

Caustic-side solvent extraction[5] (CSSX) was shown to successfully decontaminate SRS wastes and concentrate the cesium in a dilute nitric-acid stream to be fed to the Defense Waste Processing Facility. However, only a limited data set exists for actual tank wastes. Therefore, the cesium-distribution coefficients for extraction, scrubbing, and stripping were measured for a number of tank-waste supernates from both the F- and H-Area Tank Farms. The measured D_{Cs}s indicate the caustic-side solvent extraction flowsheet will successfully decontaminate the supernate and produce a concentrated, dilute nitric-acid product. Because of the difficulty in performing the experiments on a 40-mL scale in the shielded cells, some caustic carryover into the scrub acid occurred and contributed to the higher-than-expected scrub distribution coefficients.

Comparing the measured extraction distribution coefficients to recently published data by ORNL personnel, showed agreement between the model and experiment for two actual tank wastes. Experiments on three wastes did not show agreement with the model. Additional work is planned to measure batch-distribution coefficients in several wastes, including dissolved saltcake.

The affinity of the calixarene-solvent system for actinide removal was also tested. Plutonium extraction distribution coefficients measured around 2. A single measurement of the extraction of uranium showed a D_U of 2.6. The uranium analysis had to rely only on aqueous phase measurements because no method existed for the organic phase.

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