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Fission Product Solvent Extraction*

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Bruce A. Moyer,[1] Peter V. Bonnesen,[1]
Richard A. Sachleben,[1] Tamara J. Haverlock,[1] and Derek J. Presley[1]
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
P. O. Box 2008, Bldg. 4500S, MS-6119
Oak Ridge, Tennessee 37831-6119

Ralph A. Leonard[2] and Cliff Conner[2]
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 205
Argonne, IL 60439-4837

Gregg J. Lumetta[3]
Pacific Northwest National Laboratory
P.O. Box 999
Richland, WA 99352

Terry A. Todd[4] and Donald J. Wood[4]
Idaho National Engineering and Environmental Laboratory
P.O. Box 1625
Idaho Falls, Idaho 83415

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DISCLAIMER

Fission Product Solvent Extraction

Presenter: *Bruce A. Moyer, Oak Ridge National Laboratory*
Co-investigators: *P. V. Bonnesen and, R. A. Sachleben, Oak Ridge National Laboratory (ORNL); R. A. Leonard and C. Conner, Argonne National Laboratory (ANL); G. J. Lumetta, Pacific Northwest National Laboratory (PNNL); T. A. Todd and D. J. Wood, Idaho National Engineering and Environmental Laboratory (INEEL).*

Description

Overview. Two main objectives concerning removal of fission products from high-level tank wastes will be accomplished in this project. The first objective entails the development of an acid-side Cs solvent-extraction (SX) process applicable to remediation of the sodium-bearing waste (SBW) and dissolved calcine waste (DCW) at INEEL. The second objective is to develop alkaline-side SX processes for the combined removal of Tc, Cs, and possibly Sr and for individual separation of Tc (alone or together with Sr) and Cs. These alkaline-side processes apply to tank wastes stored at Hanford, Savannah River, and Oak Ridge.

This work exploits the useful properties of crown ethers and calixarenes and has shown that such compounds may be economically adapted to practical processing conditions. Potential benefits for both acid- and alkaline-side processing include order-of-magnitude concentration factors, high rejection of bulk sodium and potassium salts, and stripping with dilute (typically 10 mM) nitric acid. These benefits minimize the subsequent burden on the very expensive vitrification and storage of the high-activity waste. In the case of the SRTALK process for Tc extraction as pertechnetate anion from alkaline waste, such benefits have now been proven at the scale of a 12-stage flowsheet tested in 2-cm centrifugal contactors with a Hanford supernatant waste simulant. SRTALK employs a crown ether in a TBP-modified aliphatic kerosene diluent, is economically competitive with other applicable separation processes being considered, and has been successfully tested in batch extraction of actual Hanford double-shell slurry feed (DSSF).

Efforts to extend the success with SRTALK to the development of processes for a) the separation of Cs alone from acid or alkaline wastes and b) the combined separation of Cs and Tc (and optionally Sr) from alkaline waste have so far yielded promising results and potentially offer benefits equivalent to those already shown for the SRTALK process. Our alkaline-side Cs extractant is a hybrid calixarene-crown ether (Fig. 1), which is a close relative of compounds developed by French and Italian investigators but which has been derivatized to be soluble in practical alkane diluents. The family of calix[4]arene-crown-6 compounds has been known to be extraordinarily selective for Cs^+ vs. Na^+ ions[1] but until now has not been adapted to practical SX applications. With use of certain alcohol modifiers in the aliphatic kerosene Isopar® L, our extractant calix[4]arene-bis(*t*-octylbenzo-crown-6) attains useful cesium distribution ratios (i.e., D_{Cs} in the range of 1-10) at extractant concentrations of above 20 mM, even for the extremely severe conditions extant in Hanford DSSF waste. Such solvents may be stripped with 10 mM nitric acid, are stable for at least 1 month in continuous contact with non-radioactive DSSF simulant, and give good phase disengagement. Extraction and stripping tests of a candidate solvent for Cs extraction alone and for combined Cs, Tc, and Sr have so far been successfully conducted on a batch scale on actual Hanford DSSF waste. On the acid-side, tests on simulants of INEEL SBW and DCW have so far shown that good extraction and stripping performance is indeed achievable with the calix[4]arene-crown-6 class of

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[1] Ungaro, R.; Casnati, A.; Ugozzoli, F.; Pochini, A.; Dozol, J.-F.; Hill, C.; Rouquette, H. *Angew. Chem. Int. Ed. Engl.*, 33, 1506-1509 (1994).

compounds. However, increased resistance to nitration of the extractant is needed, resulting in renewed synthesis efforts targeted at proposed nitration-resistant analogs. Specific results from the past year under this TTP are given in the Accomplishments section below.

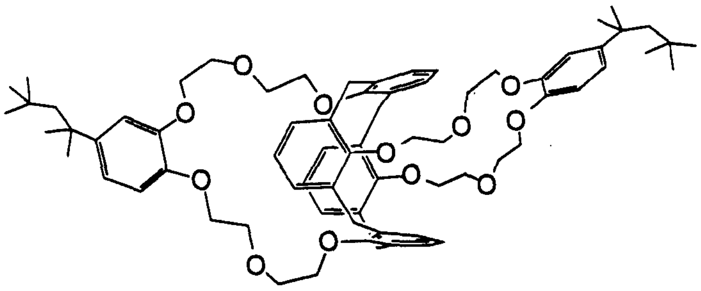

Fig. 1. Alkane-soluble Cs extractant calix[4]arene-bis(*t*-octylbenzo-crown-6) synthesized at ORNL. IBC Advanced Technologies is currently producing a commercial batch of this extractant.

Technology Needs

EM Focus Area: High Level Waste Tank Remediation

Acid-Side Cs Process. Acidic SBW and DCW stored at INEEL contain high levels of both ^{137}Cs and ^{90}Sr, with required DFs of 1240 and 27500, respectively. The waste also contains dissolved lead and mercury, and as such is classified as mixed waste under the Resource Conservation and Recovery Act (RCRA). The RCRA classification of this waste is a driver for its timely treatment, and technologies for removing the cesium and strontium are urgently needed. The removal of strontium using the SREX process has already been successfully demonstrated,[2] but there are no satisfactory methods for removing the cesium.

Alkaline-Side Processes. The need for separating the fission products ^{99}Tc, ^{90}Sr, and ^{137}Cs from the Hanford tank wastes has arisen in connection with plans to concentrate these radionuclides together with transuranic elements in the high-activity fraction of the waste to be vitrified and stored in a geologic repository.[3] In the absence of fission-product separations, vitrification and storage of the full 55 million gallons of waste has been estimated to cost in the range $100-200B, presenting a prohibitive burden on the U.S. taxpayer. A more rational approach recognizes that only ca. 0.01% of the mass of the waste is radioactive and that separation of this small mass fraction into a manageable volume of high-activity waste (HAW) can greatly reduce the overall cost of disposal. The value of applicable technologies will obviously be dominated by their impact on the number of HAW glass canisters, whose cost to produce will probably be on the order of $1.0M per 1650-kg canister. Although other fission-product separation methods have been proposed for alkaline tank-waste treatment, this work seeks higher economic performance through a) reducing the inventory of sodium and potassium salts reporting to the high-activity glass, potentially reducing vitrification and storage costs, b) combining Cs, Tc, and Sr removal into a single unit process, reducing space requirements, chemical consumption, and secondary waste production, and c) reducing risk of system failure by offering viable alternative technologies.

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[2] Wood, D.J.; Tranter, T.J.; Todd, T.A. *Solvent Extr. Ion Exch.*, 13, 829-844 (1995).

[3] Bunker, B.; Virden, J.; Kuhn, B.; Quinn, R. in *Encylcopedia of Energy Technology and the Environment*, Wiley, 1995; pp. 2023-2032.

Accomplishments

Selected results from the past year are reported in this section. Because of limited space, experimental details are omitted and will be published in the near future in the open literature.

Tc SX by the SRTALK Process. A 12-stage SRTALK flowsheet has been developed and tested on a simplified Hanford DSSF simulant at ANL using 2-cm centrifugal contactors (Fig. 2). The flowsheet utilized a solvent consisting of 0.04 M DtBuCH18C6 in 1:1 v:v TBP:Isopar® L. A 2-stage scrub section employed 0.5 M NaOH to reduce the sodium and potassium nitrate loading of the solvent and to improve the performance of the stripping with 0.01 M HNO_3. The SRTALK centrifugal-contactor test performed as designed, demonstrating the clean separation of Tc from the bulk waste constituents, especially sodium. While Tc was concentrated by a factor of 9.9 with a DF of 10.7, the sodium concentration was reduced by a factor of 5850 to 0.0010 M in the strip solution. Potassium

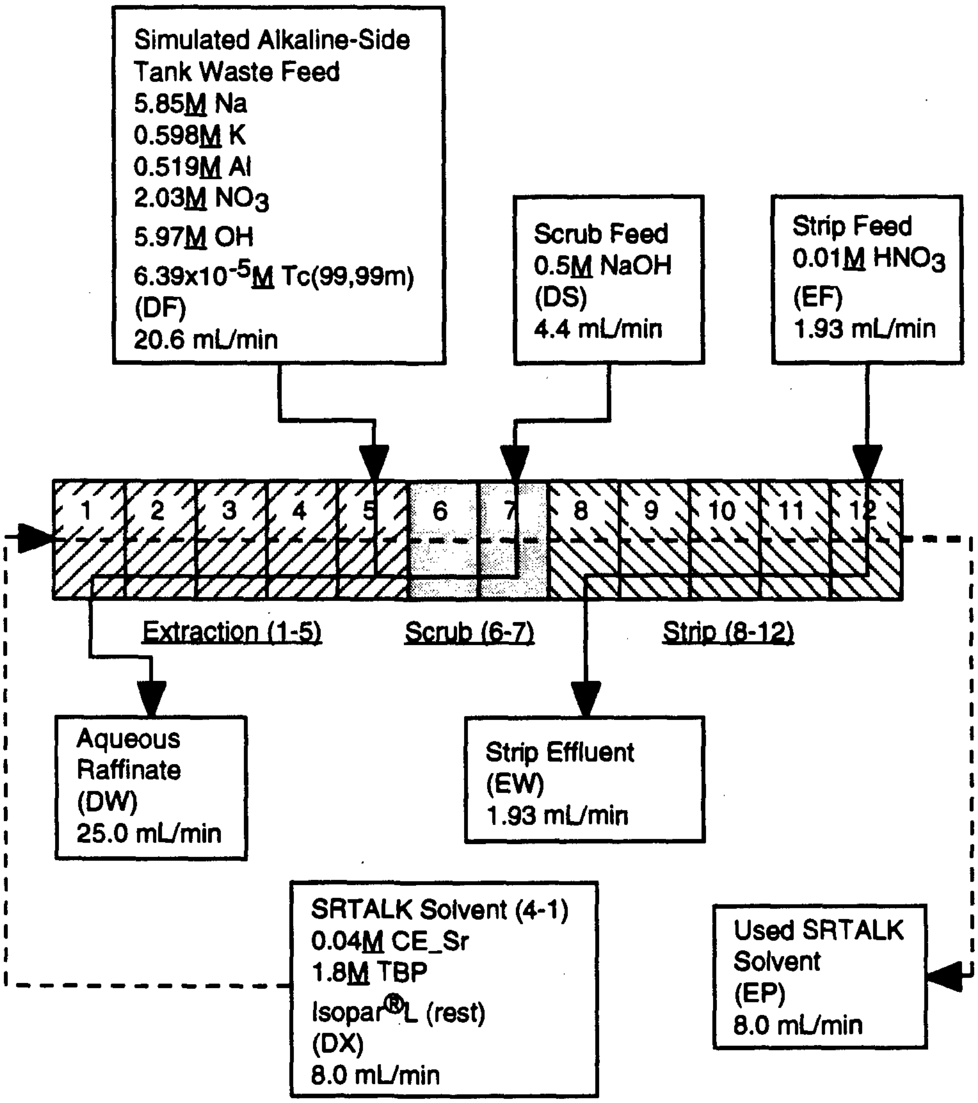

Fig. 2. Twelve-Stage SRTALK flowsheet for 2-cm centrifugal contactor test at ANL.

and aluminum were rejected to an even greater degree. Assuming that the alkaline supernatant solutions, dissolved salt solutions, and sludge-washing solutions from the entire Hanford tank inventory could be treated with comparable performance by the SRTALK process, the total amount of sodium that would be carried along with technetium would be only 1400 kg, reducing the sodium burden on vitrification. Batch test results performed at PNNL on actual Hanford DSSF waste showed that pertechnetate extraction and stripping occur much as expected based on tests with waste simulants. Using a solvent consisting of 0.04 M DtBuCH18C6 in 1:1 v:v TBP:Isopar® M, the technetium distribution ratio was 9.3 on extraction and 0.3 on stripping with distilled water.

Alkaline-Side Cs Extraction. As shown in Table 1, the extraction of Cs from two Hanford supernatant tank wastes by a candidate solvent developed at ORNL and stripping with 10 mM nitric acid have been proven experimentally at PNNL. A number of solvents containing alcohol modifiers of varying structure in Isopar® L have been subjected to tests on DSSF waste simulant. Two candidate solvents currently show good extraction and stripping behavior, good phase disengagement, and stability to at least one month on continuous contact with the simulant.

Table 1. Cesium extraction and stripping from Hanford tank waste by ORNL extractant.[a]

Tank	D_{Cs} Extract #1	D_{Cs} Extract #2	Total % Extracted	D_{Cs} Strip #1	D_{Cs} Strip #2	Total % Stripped
AW-101[b]	1.8	2.0	89%	0.7	0.3	90%
SY-101[c]	18	20	99.7%	0.8	0.6	85%

[a] Two extractions each with fresh solvent, coded OR-Cs-3, followed by two strips each with fresh 10 mM HNO_3; 5-minute contacts at 1:1 phase ratio by vortexing. [b] Blend of supernatant liquids: 70% AW-101, 20% AP-106, and 10% AP-102. [c] Undiluted complexant concentrate supernatant.

Alkaline-Side Combined Cs, Tc, and Sr Extraction.

Combined extraction of Cs, Tc, and Sr has been demonstrated in simulant tests, proving that solvents capable of removing the three fission products in a single step may indeed be formulated based on our extraction methodology. Results of PNNL tests of the same solvent on Hanford DSSF show in Table

Table 2. First example of combined extraction and stripping from alkaline supernatant tank waste[a]

Metal	D_M Extract #1	D_M Extract #2	Total % Extracted	D_M Strip #1	D_M Strip #2	D_M Strip #3	Total % Stripped
Tc	2.2	0.4	77.7%	0.8	0.046		98.0%
Cs	7.5	7.0	98.2%	1.6	1.2	1.0	85%

[a] Two extractions of DSSF from Hanford tank AW-101 (diluted to 5 M Na) were performed by 5 minutes of vortexing at a 1:1 phase ratio with fresh solvent coded OR-CsSrTc-3/3 followed by two strips with fresh 0.05 M HNO_3.

2 that Cs and Tc may be extracted and stripped successfully from actual waste; Sr was present at insignificant levels and was not reliably measured in the test. The Tc results indicate that 15-20% of the Tc is not extractable as pertechnetate.

Acid-Side Cs Extraction. Efforts since Oct., 1997, have successfully shown that our Cs extractant (Fig. 1) dissolved in Isopar® L modified with selected alcohols indeed has the capability to effect the reversible Cs extraction from simulants of both INEEL acidic tank wastes, SBW and DCW. As an example of numerous tests performed, a solvent consisting of 0.01 M extractant together with 0.25 M modifier Cs-4 gave the respective D_{Cs} values 2.64 and 0.19 on extraction and stripping. However, tests of stability showed that the extractant undergoes nitration and forms a third phase on approximately 100 hours of continuous exposure to SBW simulant. Since the nitration reaction takes place at the benzo substituent on the polyoxyethylene chain of the extractant, straightforward nitration-resistant analogs have been proposed and are currently being synthesized for testing.

Benefits

The beneficiary of our acid-side Cs extraction process is EM-30 at INEEL, charged with removing Cs and Sr from SBW and DCW. Advantages of our Cs technology include high selectivity over Na and stripping with 10 mM nitric acid. Beneficiaries of the development of our alkaline-side SX processes include the Tanks Focus Area, TWRS, the Hanford privatization vendors, and the Savannah River site. At Hanford, improved technologies will be needed for Phase II of privatization. At Savannah River, the failure of the in-tank precipitation process has necessitated the consideration of alternative Cs removal technologies. Specific benefits and cost savings have been described in previous sections.

Proposed Future Activities

Acid-Side Cs Process. Work initiated at ORNL in FY 1998 is focusing on solvent development, aimed at obtaining optimal Cs distribution behavior, rapid phase disengagement, and chemical stability in batch tests with simulants. Under separate funding, collaborators at INEEL (T. A. Todd and D. J. Wood) will conduct batch tests on actual SBW and DCW. Flowsheet development will be performed under INEEL's funding in FY 1999, with ORNL providing distribution measurements in support of the flowsheet. It is proposed for FY 1999 to begin development of a solvent suitable for the combined extraction of Cs and Sr from SBW and DCW.

Alkaline-Side Combined Process. Major emphasis in FY 1998 is being devoted to combined Cs and Tc extraction, whereas Sr may be added as an option. Work to be accomplished in collaboration with ANL (R. A. Leonard and C. Conner) includes developing an economical SX flowsheet for the combined process and conducting engineering tests of the performance of the combined process on suitable alkaline Hanford waste simulants in centrifugal contactors. PNNL (G. J. Lumetta) is conducting supporting batch tests of Tc, Cs, and Sr extraction from samples of actual Hanford tank supernatant waste. ORNL tests are focusing on optimizing the solvent composition and on obtaining distribution measurements to support the flowsheet development. For FY 1999, we propose to optimize and test a flowsheet applicable to the removal of Cs from Savannah River alkaline waste as an alternative to the in-tank precipitation process.

Contact for Further Information

Bruce A. Moyer, Principal Investigator, TTP 3TEE OR16C341
Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6119; 423-574-6718 (ph.), 423-574-4939 (fax); moyerba@ornl.gov (email)

Patent and Technology Transfer Status

Moyer, B. A.; Sachleben, R. A.; Bonnesen, P. V. "Process for Extracting Technetium from Alkaline Solutions," U. S. Patent 5,443,731, August 22, 1995.

Kilambi, S.; Robinson, R. B.; Moyer, B. A.; Bonnesen, P. V. "Supported Liquid Membrane Separation," application to U.S. Patent Office, Sept. 15, 1997. Technology licensed by Commodore Technologies, Mar., 1997. U.S. Provisional Application Serial No. 60/026,196, submitted by Commodore Technologies, Sept. 16, 1996. ORNL disclosure ERID No. 0241, Sept. 10, 1996.

Moyer, B. A.; Bonnesen, P. V.; Sachleben, R. A.; Presley, D. J. "Solvent and Process for Extracting Cesium from Alkaline Waste Solutions," provisional application to U.S. Patent Office, Sept. 5, 1997. ORNL disclosure ERID No. 0325, Jan. 23, 1997. IBC Advanced Technologies, Inc. has signed a non-disclosure agreement and has expressed an interest in licensing the technology (see Fig. 1).

Selected Publications (11 total since 1994)

Leonard, R. A.; Conner, C.; Liberatore, M. W.; Bonnesen, P. V.; Presley, D. J.; Moyer, B. A.; Lumetta, G. J. "Developing and Testing an Alkaline-Side Solvent Extraction Process for Technetium Separation from Tank Waste," *Sep. Sci. Technol.* (Submitted).

Haverlock, T. J.; Bonnesen, P. V.; Sachleben, R. A.; Moyer, B. A. "Applicability of a Calixarene-Crown Compound for the Removal of Cesium from Alkaline Tank Waste," *Radiochim. Acta.* 76, 103-108 (1997).

Bonnesen, P. V.; Moyer, B. A.; Haverlock, T. J.; Armstrong, V. S.; Sachleben, R. A. "Removal of Technetium from Alkaline Waste Media by a New Solvent Extraction Process," in *Emerging Technologies in Hazardous Waste Management VI*, D. William Tedder and Frederick G Pohland, Eds., American Academy of Environmental Engineers, Annapolis, MD, 1996; pp. 245-262.

Bonnesen, P. V.; Moyer, B. A.; Presley, D. J.; Armstrong, V. S.; Haverlock, T. J.; Counce, R. M.; Sachleben, R. A. "Alkaline-Side Extraction of Technetium from Tank Waste Using Crown Ethers and Other Extractants," Report ORNL/TM-13241, Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A., June, 1996.

Selected Presentations (38 total since 1994)

Leonard, R. A.; Conner, C.; Vandegrift, G. F.; Bonnesen, P. V.; Moyer, B. A.; Presley, D. J. "Development and Testing of the SRTALK Process," Tenth Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, Oct. 20-24, 1997.

Bonnesen, P. V.; Presley, D. J.; Haverlock, T. J.; Sachleben, R. A.; Das, G.; Moyer, B. A. "Development of an Alkaline-Side Solvent Extraction Process for the Removal of Cesium from Tank Waste," Tenth Symposium on Separation Science and Technology for Energy Applications, Gatlinburg, TN, Oct. 20-24, 1997.

Moyer, B. A.; Bonnesen, P. V.; Sachleben, R. A.; Presley, D. J.; Leonard, R. A.; Conner, C.; Vandegrift, G. F.; Lumetta, G. J. "Alkaline-Side Solvent Extraction of Cs, Sr, and Tc," The Symposium on Science and Technology for Disposal of Radioactive Tank Wastes, 214th American Chemical Society National Meeting, Las Vegas, NV, Sept. 7-11, 1997.

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