

INEL 100N-97-10785

CONF-971004--

ACTINIDE PARTITIONING FROM ACTUAL IDAHO CHEMICAL PROCESSING PLANT ACIDIC TANK WASTE USING CENTRIFUGAL CONTACTORS

Jack D. Law, Ken N. Brewer, Terry A. Todd
Lockheed Martin Idaho Technologies Company
P. O. Box 1625
Idaho Falls, ID 83415-5218
Tel: 208-526-3130 Fax: 208-526-5937 E-mail: jdlaw@ineel.gov

RECEIVED

NOV 21 1997

OSTI

waste streams. A recent peer review identified the most promising radionuclide separation technologies for evaluation.¹ The Transuranic Extraction (TRUEX) process, developed by Horwitz and Schulz², was identified as a primary candidate for separation of the actinides from ICPP SBW.

A major emphasis at the ICPP has been directed toward evaluating actinide separation from SBW using the TRUEX process. The active extractant used in the TRUEX process solvent is octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO). Tributylphosphate (TBP) is added to the solvent as a phase modifier to prevent third phase formation and a paraffinic hydrocarbon is used as a diluent. The process has been effectively demonstrated to remove actinides from acidic SBW simulants and actual SBW solution to well below the 10 nCi/g U. S. Nuclear Regulatory Commission (NRC) Class A low-level transuranic waste requirements. Previously, all testing at the INEEL has been performed using batch contacts with actual and simulated SBW³, and using small-scale centrifugal contactors (2-cm and 5.5-cm rotor diameter) with SBW simulant.⁴ This report summarizes the results of TRUEX flowsheet testing for the separation of actinides from actual SBW solution (tank WM-183) using 2-cm diameter centrifugal contactors in a shielded cell facility.

II. PURPOSE AND SCOPE

MASTER

The purpose of this study was to demonstrate the applicability of the TRUEX process for the treatment of ICPP SBW under continuous, countercurrent conditions using actual ICPP tank waste. Once the applicability of this process to SBW has been established, a comparison of the flowsheet to other technologies currently under development will be possible.

Installation of the 2-cm centrifugal contactors in the ICPP Remote Analytical Laboratory (RAL) hot cell allowed the use of actual SBW in testing of the TRUEX process. Consequently, the scope of this study was to evaluate the TRUEX technology using actual ICPP tank waste. This allowed the removal efficiencies of the actinides to be determined and the effectiveness of the process in reducing the actinide activity to below U. S. NRC Class A LLW requirements to be evaluated. In addition, the behavior of H⁺, Fe, Hg, and ⁹⁹Tc in the process was evaluated.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ph

ABSTRACT

The TRUEX process is being evaluated at the Idaho Chemical Processing Plant (ICPP) for the separation of the actinides from acidic radioactive wastes stored at the ICPP. These efforts have culminated in a recent demonstration of the TRUEX process with actual tank waste. This demonstration was performed using 24 stages of 2-cm diameter centrifugal contactors installed in a shielded hot cell at the ICPP Remote Analytical Laboratory. An overall removal efficiency of 99.97% was obtained for the actinides. As a result, the activity of the actinides was reduced from 457 nCi/g in the feed to 0.12 nCi/g in the aqueous raffinate, which is well below the U. S. NRC Class A LLW requirement of 10 nCi/g for non-TRU waste. Iron was partially extracted by the TRUEX solvent, resulting in 23% of the Fe exiting in the strip product. Mercury was also extracted by the TRUEX solvent (76%) and stripped from the solvent in the 0.25 M Na₂CO₃ wash section.

I. INTRODUCTION

The Idaho Chemical Processing Plant (ICPP), located at the Idaho National Engineering and Environmental Laboratory (INEEL), formerly reprocessed spent nuclear fuel to recover fissionable uranium. The radioactive raffinates from the solvent extraction uranium recovery processes were converted to granular solids (calcine) in a high temperature fluidized bed. During the course of reprocessing, a secondary waste stream, acidic liquid sodium-bearing waste (SBW), was also generated primarily from equipment decontamination between campaigns and solvent wash activities. This SBW cannot be directly calcined due to the high sodium content and has historically been blended with reprocessing raffinates or non-radioactive aluminum nitrate prior to calcination. Fuel reprocessing activities are no longer being performed at the ICPP, thereby eliminating the option of waste blending to deplete the SBW inventory. Currently, approximately 5.7 million liters of liquid SBW are temporarily stored at the ICPP in large underground stainless-steel tanks. As part of a 1995 agreement between the State of Idaho, the U. S. Department of Energy, and the U. S. Department of Navy, the SBW must be removed from the tanks by 2012.

Several technologies are currently being evaluated for the treatment and final disposition of SBW inventories. These technologies include radionuclide partitioning followed by immobilization of the resulting high-activity and low-activity

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

III. EXPERIMENTAL PROCEDURE

A. WM-183 waste.

Sodium-bearing waste, obtained from tank WM-183, was used as feed solution for this testing. Currently, approximately 5.7 million liters of SBW are stored in six tanks. The composition in each tank varies; however, the composition of the solution in tank WM-183 is representative of the solution in all the tanks. The chemical composition of the WM-183 waste is shown in Table I.

Table I. WM-183 waste composition.

Component	Conc.	Component	Conc.
Acid (M)	1.72	SO ₄ (M)	0.066
Al (M)	0.62	Zr (M)	<6.6E-03
B (M)	0.013	Alpha (nCi/g)	456.8
Ca (M)	0.042	²⁴¹ Am (nCi/g)	33.86
Cl (M)	0.011	²³⁸ Pu (nCi/g)	327.3
Cr (M)	0.016	²³⁹ Pu (nCi/g)	125.9
Fe (M)	0.051	U (mg/L)	114
Hg (M)	0.0023	²³⁷ Np (nCi/g)	<6.5
K (M)	0.096	⁹⁹ Tc (Ci/m ³)	0.036
Na (M)	0.77	¹³⁷ Cs (Ci/m ³)	218
NO ₃ (M)	5.24	⁹⁰ Sr (Ci/m ³)	240
Pb (M)	0.0015		

B. TRUEX solvent.

The composition of the TRUEX solvent used in these tests was 0.2 M CMPO and 1.4 M TBP in Isopar L[®]. Isopar L[®] is an isoparaffinic hydrocarbon diluent manufactured by Exxon, Inc. The purity and composition of the TRUEX solvent were established prior to use in the centrifugal contactors. Impurities in the CMPO, resulting from acid hydrolysis, radiolytic degradation, or residual manufacturing impurities, may hinder the ability to strip the actinides from the TRUEX solvent.⁵ The distribution coefficient for ²⁴¹Am is particularly sensitive to CMPO impurities. Therefore, the distribution coefficient for ²⁴¹Am was evaluated as a function of nitric acid concentration from HNO₃ solutions to evaluate CMPO purity and solvent composition. This method of determining ²⁴¹Am distributions as a function of nitric acid concentration was established as a quality control procedure and was used to test the initial TRUEX solvent and the TRUEX solvent from each flowsheet test.⁶ If the results were comparable to literature values, the solvent was suitable for extraction studies.

C. TRUEX Flowsheet Demonstration

Based on the results of TRUEX flowsheet development studies performed at the ICPP using a non-radioactive SBW simulant in 2-cm and 5.5-cm diameter centrifugal contactors, a TRUEX flowsheet was recommended for testing in the 2-cm centrifugal contactors using actual ICPP SBW.⁴ This flowsheet consists of eight stages of extraction at an O/A of 0.33, five stages of 0.1 M HNO₃ scrub at an O/A of 1.5, six stages of 0.04 M 1-hydroxyethane 1,1-diphosphonic acid (HEDPA) in 0.04 M HNO₃ strip at an O/A of 1.0, three stages of 0.25 M Na₂CO₃ wash at an O/A of 0.67, and two stages of 0.1 M HNO₃ rinse at an O/A of 3.0. There is no benefit for the fractionation of individual actinides (i.e., Am from Pu) since all the actinides will be disposed of in the high-activity waste glass. Therefore, a gross actinide stripping agent (HEDPA) was used. The resulting flowsheet used for the TRUEX flowsheet testing is shown in Figure 1. It should be noted that this flowsheet was developed for testing with 24 stages of centrifugal contactors, which is expected to be more stages than is required for processing SBW.

The goals of the TRUEX flowsheet testing were to:

- (1) Demonstrate the overall operability of the 2-cm centrifugal contactors in a remote environment with the TRUEX flowsheet.
- (2) Determine the removal efficiencies and distribution coefficients of ²⁴¹Am, Pu, U, ⁹⁹Tc, H⁺, Fe, and Hg at steady-state conditions.
- (3) Evaluate the effectiveness of the TRUEX flowsheet in separating the actinides from actual SBW.
- (4) Determine if any precipitate or third phase formation problems exist with this flowsheet.

TRUEX flowsheet testing was performed as follows. The centrifugal contactor motors were started at 3,600 rpm. All aqueous solution flows, except for the actual SBW, were established. Simulant flow, consisting of 1.9 M HNO₃, 0.6 M Al₂NO₃, and 0.6 M NaNO₃ was established for the SBW feed. Thirty minutes after the start of the aqueous feeds, solvent feed flow was established. Once solvent flow was seen exiting stage 24, actual SBW feed (WM-183) was started. Level readings on each of the feed tanks were noted in order to determine actual solution flowrates based on tank depletion rates. Approximately 100 minutes after the start of WM-183 feed, samples were taken of the aqueous raffinate, strip product, Na₂CO₃ wash, HNO₃ rinse, and solvent effluent streams. The centrifugal contactors were then shutdown by simultaneously stopping the feed pumps and contactor motors. Each stage remains approximately at steady-state operating conditions with this type of shutdown. This allowed aqueous and organic samples to be taken from each stage and distribution coefficients to be determined for each of the 24 stages.

After shutdown, individual stage samples were taken as follows. The solution from each stage was drained into individual 60 mL sample bottles. The phases were re-

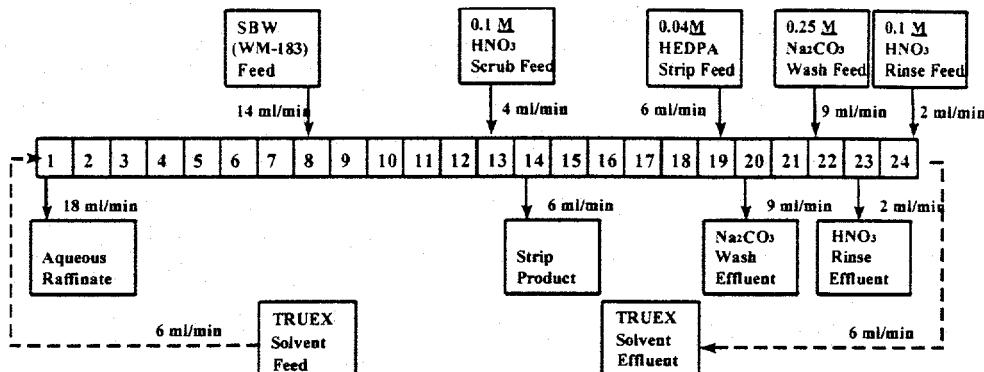


Figure 1. TRUEX flowsheet

equilibrated by shaking the bottles with a manipulator for several minutes each. Re-equilibration of the phases serves to evaluate distribution coefficients of the individual species under hypothetical conditions of 100% stage efficiency. The re-equilibrated solution from each stage was then poured into a clean separatory funnel, allowed to stand for five to ten minutes, and the aqueous and organic phases were separated.

IV. RESULTS AND DISCUSSION

A. Contactor Operation

Precipitate or third phase formation was not observed during testing or after shutdown. Flooding was not observed during testing. Material balance calculations indicated that the actual strip product flowrate was 4 mL/min higher than the strip feed flowrate and that the aqueous raffinate flowrate was equal to the feed flowrate (indicating no scrub flow). This indicates that one of the scrub section contactor motors was not operating during the test. While preparing the centrifugal contactors for unrelated flowsheet tests after the completion of this testing it was discovered that the stage 13 rotor was not spinning. It is suspected that this was also the case during the TRUEX testing. With an inoperable contactor motor, the aqueous and organic solutions entering the stage are not mixed and the solution level increases until the two phases exit out the light phase (organic) weir. Very little solution overflows out of the heavy phase (aqueous) weir. With stage 13 (scrub feed inlet stage) not operating, the scrub feed would have overflowed with the solvent into the strip section where it would have separated from the solvent and exited with the strip product solution. As a result, the flowsheet test was essentially performed without a scrub section.

B. Concentrations at Shutdown

The removal efficiencies obtained for gross alpha, ^{241}Am , ^{238}Pu , ^{239}Pu , ^{235}U , ^{99}Tc , Fe, and Hg are given in Table II. Distribution coefficients were calculated for gross alpha, ^{241}Am , ^{238}Pu , ^{239}Pu , ^{235}U , ^{238}U , H^+ , Fe, and Hg for each of

the 24 stages. The resulting distribution coefficients are given in Table III. Data for Zr are not presented since all samples were below the Zr detection limit. ^{237}Np analyses were not performed due to analytical difficulties associated with the low Np activity. A discussion of the behavior of each component follows.

Table II. Removal efficiencies.

Component	Removal Efficiency
Alpha	99.97%
^{241}Am	>99.9%
^{238}Pu	99.96%
^{239}Pu	99.98%
^{235}U	>98.9%
^{99}Tc	89%
Fe	23.1%
Hg	76%

1) Nitric Acid. Distribution coefficients of H^+ in the extraction section ranged from 0.66 to 0.88, resulting in an H^+ concentration of 1.2 M in the TRUEX solvent exiting the extraction section. The 0.1 M HNO_3 scrub typically will back-extract the HNO_3 from the TRUEX solvent prior to the solvent entering the strip section. H^+ was not scrubbed from the TRUEX solvent as a result of the inoperable stage in the scrub section, and the H^+ concentration remained at 1.2 M.

2) Gross Alpha. The gross alpha activity was reduced from 2.01E+04 dps/mL in the feed to 5.1 dps/mL in the aqueous raffinate immediately prior to shutdown. This corresponds to a removal efficiency of 99.97%. A gross alpha activity of 5.1 dps/mL corresponds to 0.12 nCi/g which is well below the NRC Class A LLW requirement of 10 nCi/g for non-TRU waste. The strip section was very effective in back-extracting the actinides from the TRUEX solvent, removing 99.9998% of the gross alpha activity from the solvent with six strip stages.

Table III. Gross alpha, ^{241}Am , ^{238}Pu , ^{239}Pu , ^{235}U , ^{238}U , H^+ , Fe , and Hg distribution coefficients.

Stage	D _{alpha}	D _{Am-241}	D _{Pu-238}	D _{Pu-239}	D _{U-235}	D _{U-238}	D _{H+}	D _{Fe}	D _{Hg}
Extraction	1	nd ^a	nd	3.6	41	nd	0.88	0.30	3.4
	2	nd	nd	2.0	<2.1	nd	0.70	0.63	1.7
	3	nd	nd	>32	nd	nd	0.72	0.60	1.0
	4	nd	<12	>18	>51	nd	0.69	0.71	0.45
	5	102	<59	<10	<21	nd	0.66	0.67	1.0
	6	24	13	10	34	nd	0.70	0.72	0.44
	7	16	59	1.1	1.3	nd	0.75	0.75	0.38
Scrub	8	671	38	305	299	790	280	0.69	nd
	9	nd	13	716	660	nd	nd	nd	0.58
	10	180	11	5340	7060	nd	0.26	nd	0.45
	11	179	12	7300	6910	nd	0.85	nd	0.39
	12	49700	857	16500	12100	nd	0.48	nd	>54
Strip	13	1930	48	17800	15300	nd	0.79	nd	1.6
	14	1.5	6.8	0.091	0.093	23	19	0.76	nd
	15	0.34	1.4	0.012	0.014	1.2	1.2	0.51	nd
	16	0.040	nd	0.0014	0.0017	0.02	0.02	nd	nd
	17	0.0044	nd	0.0018	0.010	0.004	0.004	nd	nd
Wash	18	0.012	<0.20	nd	0.13	0.08	0.06	nd	nd
	19	0.022	nd	nd	0.52	0.2	0.8	nd	nd
	20	0.10	nd	0.17	0.87	3.4	35	nd	nd
	21	0.049	nd	0.044	0.91	11	64	nd	nd
Rinse	22	0.056	nd	0.0070	0.015	25	414	nd	nd
	23	13	0.37	9.2	8.5	233	65	nd	nd
	24	87	<0.05	60	71	320	124	nd	0.96

^anot determined

3) Americium. The activity of ^{241}Am was reduced from $1.49\text{E}+03$ dps/mL in the feed to <16 dps/mL in the aqueous raffinate immediately prior to shutdown. A lower detection limit was achieved for the stage 1 aqueous sample (drained from stage 1 after shutdown), yielding an activity of <1.54 dps/mL. This corresponds to a removal efficiency of $>99.90\%$.

Extraction distribution coefficients for ^{241}Am ranged from <12 to 59. The strip section was very effective in back-extracting the ^{241}Am from the TRUEX solvent, removing $>99.99\%$. As a result of the inoperable contactor stage in the scrub section, acid was not scrubbed from the solvent and the distribution coefficients on the first two strip stages were greater than one (6.8 and 1.4).

4) Plutonium. The activity of ^{238}Pu was reduced from $1.44\text{E}+04$ dps/mL in the feed to <50 dps/mL in the aqueous raffinate immediately prior to shutdown. An improved detection limit was achieved for the stage 1 aqueous sample (drained from stage 1 after shutdown), yielding an activity of 5.1 dps/mL. This corresponds to a removal efficiency of 99.96%.

The activity of ^{239}Pu was reduced from $5.54\text{E}+03$ dps/mL in the feed to <44 dps/mL in the aqueous raffinate immediately prior to shutdown. An improved detection limit was achieved for the stage 1 aqueous sample (drained from stage 1 after shutdown), yielding an activity of 1.1 dps/mL. This corresponds to a removal efficiency of 99.98%.

Distribution coefficients for Pu in the extraction section varied considerably. However, most of the Pu was extracted in the first extraction contact, resulting in Pu activities near the detection limit. Also, residual Pu activity from previous testing is expected to be present in the contactors, resulting in contamination of the stage samples. As a result, distribution coefficients for stages 1 through 7 are expected to have a large uncertainty associated with them. The distribution coefficients for ^{238}Pu and ^{239}Pu on the first extraction stage (stage 8) were approximately 300. Strip distribution coefficients were <0.1 . As a result, $>99.99\%$ of the Pu extracted by the TRUEX solvent was back-extracted with the 6 strip stages.

5) Uranium. The activity of ^{235}U was reduced from 12 ppm in the feed to <0.13 ppm in the aqueous raffinate

immediately prior to shutdown. This corresponds to a removal efficiency of >98.89%. A much higher removal efficiency was expected for U. However, residual U activity from previous testing in the centrifugal contactors is expected to be present in the contactors, resulting in contamination of the raffinate sample.

The distribution coefficients for ^{235}U and ^{238}U on the first extraction stage (stage 8) were 790 and 280, respectively. As a result of the inoperable contactor stage in the scrub section, acid was not scrubbed from the solvent and the distribution coefficients on the first two strip stages were greater than 1.0. The distribution coefficients dropped to less than 0.1 on the remaining strip stages since the acid was stripped from the solvent on the first two strip stages. As a result, >99.9% of the U extracted by the TRUEX solvent was back-extracted with the 6 strip stages.

6) Technetium. The activity of ^{99}Tc was reduced from 1,310 dps/mL in the feed to 147 dps/mL in the aqueous raffinate immediately prior to shutdown. This corresponds to a removal efficiency of 89%. Distribution coefficients were not determined for ^{99}Tc on each of the stages. However, an average ^{99}Tc extraction distribution coefficient of 2.3 on each of the eight extraction stages results in a removal efficiency of 89%. The strip section was moderately effective in back-extracting the ^{99}Tc from the TRUEX solvent, with 26% of the extracted ^{99}Tc exiting in the strip product stream. The remainder of the ^{99}Tc (74%) was stripped from the solvent in the Na_2CO_3 wash section, preventing any buildup of ^{99}Tc in the TRUEX solvent.

It is important to note that the ^{99}Tc activities in ICPP tank wastes are anticipated to be below NRC Class A LLW requirements (0.3 Ci/m³). Technetium removal is of concern due to its mobility, as TcO_4^- , in the environment. It is therefore advantageous to be able to fractionate ^{99}Tc from the wastes.

7) Iron. Twenty four percent of the Fe was extracted by the TRUEX solvent and exited with the strip product. The HEDPA strip was effective in back-extracting the Fe from the solvent, resulting in < 1.9% of the Fe remaining in the solvent effluent. Solvent sample analyses were below the Fe detection limit so distribution coefficients could not be calculated directly. Using solvent concentrations obtained from material balances, extraction distributions ranging from 0.3 to 0.75 were obtained.

Results from previous flowsheet testing with simulated SBW indicated that < 1% of the Fe exits with the strip product. Fe is typically back-extracted from the TRUEX solvent in the scrub section. However, no Fe was scrubbed from the solvent due to the inoperable contactor stage in the scrub section.

8) Mercury. The TRUEX solvent extracted 76% of the Hg from the WM-183 waste. Extraction distribution coefficients ranged from 0.4 to 3.4. The HEDPA strip was ineffective in back-extracting Hg from the solvent, resulting in only 1.2% of the Hg exiting with the strip product (high-

activity waste fraction). However, the three stages of 0.25 M Na_2CO_3 wash removed 99.9% of the Hg from the TRUEX solvent. As a result, 98.8% of the Hg in the WM-183 feed was partitioned between the low-activity waste Na_2CO_3 wash effluent and raffinate streams.

V. CONCLUSIONS

An overall removal efficiency of 99.97% was obtained for the actinides. As a result, the activity of the actinides was reduced from 457 nCi/g in the feed to 0.12 nCi/g in the aqueous raffinate, which is well below the NRC Class A LLW requirement of 10 nCi/g for non-TRU waste. Removal efficiencies of >99.9%, 99.96%, 99.98%, >98.89%, and 89% were obtained for ^{241}Am , ^{238}Pu , ^{239}Pu , ^{235}U , and ^{99}Tc , respectively.

The 0.04 M HEDPA strip section was very effective in back-extracting the actinides from the TRUEX solvent. Six strip stages removed 99.9998% of the actinide activity from the solvent.

Nitric acid was not scrubbed from the TRUEX solvent with the six scrub stages due to the scrub feed stage not operating. As a result, all of the scrub feed overflowed with the solvent into the strip section, effectively eliminating the scrub section.

Iron was partially extracted by the TRUEX solvent, resulting in 23% of the Fe exiting in the strip product. The inoperable contactor stage in the scrub section prevented the Fe from being scrubbed from the solvent.

Mercury was also extracted by the TRUEX solvent (76%) and stripped from the solvent in the 0.25 M Na_2CO_3 wash section. Only 1.2% of the Hg exited with the high-activity waste strip product.

Flooding, precipitate formation, or third phase formation were not observed during the flowsheet testing.

VI. ACKNOWLEDGMENT

This work was performed with support from the U. S. Department of Energy under contract DE-AC07-94ID13223.

VII. REFERENCES

1. A. L Olson, W. W. Schulz, L. A. Burchfield, C. D. Carlson, J. L. Swanson, and M. C. Thompson, "Evaluation and Selection of Aqueous Based Technology for Partitioning Radionuclides from ICPP Calcine," WINCO-1071, February 1993.
2. E. P. Horwitz, et. al., *Solvent Extr. & Ion Exch.*, 3(1&2), 75, 1985.
3. R. S. Herbst, K. N. Brewer, T. J. Tranter, and T. A. Todd, "TRUEX Partitioning from Radioactive ICPP Sodium Bearing Waste," INEL-95/0224, March 1995.

4. J. D. Law and R. S. Herbst, "TRUEX Flowsheet Development as Applied to ICPP Sodium-Bearing Waste Using Centrifugal Contactors," INEL-95/0130, February 1995.
5. R. Chiarzia and E. P. Horwitz, *Solvent Extr. & Ion Exch.*, 8(6), 907, 1990.
6. K. N. Brewer, R. S. Herbst, T. J. Tranter, and T. A. Todd, "CMPO Purity Tests in the TRUEX Solvent Using Americium-241," WINCO-1177, December 1993.