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# DISSOLUTION OF ORNL HLW SLUDGE AND PARTITIONING OF THE ACTINIDES USING THE TRUEX PROCESS

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## ABSTRACT

Experiments were conducted to evaluate acid dissolution of actual high-level radioactive waste sludge and to evaluate the transuranium extraction (TRUEX) process for partitioning actinides from the dissolved sludge solution. All tests were performed at a temperature of 24 °C.

Samples of sludge from Melton Valley Storage Tank W-25 were rinsed with mild caustic (0.2 *M* NaOH) to reduce the concentrations of nitrates and fission products associated with the interstitial liquid. In one campaign, the rinsed sludge was leached in nitric acid and about 50% of the dry mass of the sludge was dissolved. The resulting solution contained total metal concentrations of ~1.8 *M* with a nitric acid concentration of 2.9 *M*. The solution began gelling immediately, and a visible gel layer was observed after 8 days. In the other campaign, the sludge was neutralized with nitric acid to destroy the carbonates and was subsequently leached with 2.6 *M* NaOH for ~6 h before rinsing with the mild caustic. The sludge was then leached in nitric acid, and about 80% of the sludge dissolved. The resulting solution contained a total cation concentration (excluding $H^+$) of ~0.6 *M* and a nitric acid concentration of 1.7 *M*. This solution became hazy in ~8 days, indicating gel formation, but did not display separated gel layers after aging for 20 days.

Batch liquid-liquid equilibrium tests of the extraction and the stripping operations were conducted. Chemical analyses of both phases were used to evaluate the process. Evaluation was based on two metrics: the fraction of TRU elements removed from the dissolved sludge, and comparison of the results with predictions made with the Generic TRUEX Model (GTM). The fractions of Eu, Pu, Cm, Th, and U removed from aqueous solution in only one extraction stage were >95% and were close to the values predicted by the GTM. Mercury was also found to be strongly extracted, with a one-stage removal of >92%. In one test, vanadium appeared to be moderately extracted.

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## INTRODUCTION

Production operations at many Department of Energy (DOE) sites throughout the United States have resulted in large inventories of stored radioactive and hazardous wastes. High-level radioactive waste (HLW) sludges, such as those stored in the Melton Valley Storage Tanks (MVSTs) at ORNL, were formed when acidic waste streams were concentrated by evaporation of water, neutralized with caustic to precipitate many of the metals from solution, and further concentrated by additional evaporation of the water. These processes resulted in stored wastes comprised of two distinct phases: a high-pH, nitrate-bearing supernatant; and a precipitated, actinides-bearing sludge (or, in some cases, saltcake). Sludges contain most of the transuranium (TRU) elements, along with other radionuclides such as those of the rare earths, cobalt, cesium, and strontium. The radioactive components represent only a small fraction of the sludge. However, wastes containing TRU components that contribute ionizing radiation of more than 100 nCi/g must be considered TRU waste, requiring expensive disposal methods (typically immobilization in deep geologic repositories[1]). If these radioactive components could be removed and concentrated, then the bulk of the waste would become non-TRU material suitable for near-surface disposal. Large reductions in the amount of high level waste could greatly decrease the cost of ultimate disposal of the stored wastes.

The focus of this experimental program was to evaluate the transuranium extraction (TRUEX) process for partitioning actinides from actual dissolved HLW sludge. A large sludge sample that was removed from MVST W-25 has been well-characterized by Collins et al.[2,3] Portions of this sludge were dissolved for use in the evaluation tests. Batch liquid-liquid equilibrium tests of both the extraction and the stripping operations were conducted. Chemical and radiochemical analyses of both the aqueous and organic phases were used to evaluate the distribution of selected components. Additional information on the dissolution of MVST sludge and on the gelation of the resulting solutions was obtained as part of the preparation for the extraction tests.

## LITERATURE REVIEW

### TRUEX Process

The TRUEX process is a solvent extraction process for recovering actinides from acidic nuclear waste streams.[4] TRUEX solvent is a mixture of octyl(phenyl)-N,Ndiisobutylcarbamoylmethylphosphine oxide (CMPO) and tri-*n*-butyl phosphate (TBP) in an organic diluent. When the diluent is a normal paraffin hydrocarbon (NPH), such as *n*-dodecane, the concentrations of CMPO and TBP are typically 0.2 and 1.4 *M*, respectively. CMPO is capable of extracting trivalent, as well as tetravalent and hexavalent, species[5]. Even though TBP is an extractant for tetravalent and hexavalent actinides, it is not as powerful an extractant as CMPO. Because it ameliorates the formation of a second, heavy organic phase, TBP is considered a phase modifier in this system.

Dissolution of tank-stored wastes in nitric acid produces a solution similar to those for which TRUEX was developed. Differences occur because some stored wastes were produced by processes other than the plutonium-uranium extraction (PUREX) process and because various materials were added to precipitate the waste components. Although the sludges dissolve in acid, Collins et al.[3] have shown that the solutions may gel. This is potentially a serious problem for any liquid-liquid extraction process. Recent tests of the TRUEX process to demonstrate removal of actinides from PUREX raffinate streams have been reported by Ozawa et al.,[6] Mathur et al.,[7] and Koma et al.[8] In these studies the distribution ratios of selected waste components were measured to demonstrate the effectiveness of the TRUEX process. Lumetta et al.[9,10] tested the acid dissolution of, and the removal of actinides from, Hanford tank sludge. Their studies showed that TRUEX could be used to separate the actinides from the waste, and that uranium could be separated from the transuranics. Gelation of the dissolved sludge was noted when the solution was allowed to stand for more than two weeks. Law et al.[11] tested TRUEX for partitioning the actinides from Idaho Chemical Processing Plant waste sludges. No process difficulties were observed and an overall actinide removal efficiency of 99.9% was measured across eight extraction stages.

## Generic TRUEX Model

The Generic TRUEX Model (GTM) was developed at Argonne National Laboratory (ANL) as a design tool to develop TRUEX flowsheets[12,13]. It is a thermodynamic model based on mass action equations that describe the equilibrium between ionic species in the aqueous phase and neutral complexed species in the organic phase. The thermodynamic equilibrium constants for the mass action equations are based on equilibrium distribution measurements made on pure-component systems. The multicomponent aqueous phase is quite nonideal, and the activity of each species in solution is modeled by the ion interaction approach of

Bromley.[14,15] The GTM, which is implemented as a computer program written in the macro language of Microsoft Excel™, performs several types of calculations that can be selected by the user. It is a computing tool to aid in the development of chemical process flowsheets and in the estimation of the size and cost of a processing facility. In this work it was used to model a series of ideal equilibrium batch contacts.

### Data on MVST W-25 Sludge Used in These Tests

Detailed analytical data on MVST W-25 sludge solids and supernatant are available in reports by Collins et al.[2,3] Overall properties of the sludge and entrained supernatant include (1) air-dried solids content of centrifuged wet solids, 0.590 g/g; (2) air-dried solids content of supernatant liquid, 0.285 g/g; (3) density of centrifuged wet solids, 1.53 g/mL; (4) density of supernatant, 1.206 g/mL; (5) volume ratio of decanted supernatant to wet solids, 1:1; and (6) pH of supernatant, 13. Available data also include the concentrations of the primary cations and anions (except $O^{2-}$ and $OH^-$) in both the supernatant and sludge phases. From these data and mass balances, it is easy to estimate that 1 kg of centrifuged wet solids contains 475 mL of interstitial supernatant and that water comprises 408 g of that liquid.

Selection of a dissolution procedure to prepare MVST W-25 sludge for the TRUEX tests was based on four different leaching and dissolution tests reported by Collins et al.[3] The tests were conducted at temperatures ranging from ambient (~22 °C) to 95 °C. Two of these tests included leaching the sludge with caustic solution prior to dissolution with strong nitric acid (~6.0 *M*), one treatment was performed with strong nitric acid (6.0 *M*) alone, and one treatment was done with strong nitric acid (5.8 *M*) mixed with hydrofluoric acid (1.0 *M*). The amount of solids dissolved in each case was 70 ± 10 %, by mass. Additionally, almost all the americium and curium and about half the plutonium were dissolved. In one test ~90% of the uranium was dissolved with 3.0 *M* nitric acid. Pretreatment with caustic or addition of hydrofluoric acid to the nitric acid dissolution primarily increased the cumulative amounts of cesium removed from the sludge.

The amount of nitric acid required to dissolve the solids depends on the equivalents of base stored in the solids, the base in the interstitial supernatant, and the final acid concentration desired. Using two independent methods, Spencer et al.[16] estimated the equivalents of base stored in the sludge from experimental data reported by Collins et al.[3] First, from overall dissolution data and with the assumption that the hydroxide content of the interstitial supernatant was insignificant (reasonable since the pH is 13), the number of equivalents for air-dried solids was computed to be 5.98 mol/kg. Second, under the assumption that the difference in charge balance between the measured anions and cations in the sludge solids was made up by the unmeasured hydroxide ion, the hydroxide content of the air-dried sludge was estimated at 5.5 mol/kg. These numbers, which are quite close, may be used in estimates of the amount of acid required to dissolve the sludge.

## Description of Experiments

### Reagents

Reagent-grade nitric acid, sodium hydroxide, sodium nitrate, sodium carbonate, and oxalic acid were purchased from VWR Scientific Products Corporation (Oak Ridge, Tennessee) and were used as received. Washing, leaching, stripping, and other aqueous solutions were prepared by dilution with deionized water and were titrated as required to verify concentration. CMPO was purchased from ATOCHEM North America (Philadelphia, Pa.) and was purified as previously reported by Spencer et al.[17] TRUEX solvent was prepared by dissolving weighed quantities of CMPO and TBP (purchased from Eastman Kodak Company, Rochester, New York) in anhydrous *n*-dodecane (purchased from Aldrich Chemical Company, Milwaukee, Wisconsin) to produce a solution of 0.2 $M$ CMPO and 1.4 $M$ TBP. The solvent was washed twice with 0.25 $M$ $NaCO_3$ solution using an organic:aqueous phase ratio of 2:1, each time discarding the aqueous phase. Then, using the same procedure, the TRUEX solvent was washed twice with 0.1 $M$ $HNO_3$, followed by two washes with deionized water (measured resistance $\geq 17.7$ MΩ/cm).

### Procedures

In previously reported work by Collins et al.,[2] approximately 5 L of sludge/supernatant was retrieved from MVST W-25 and stored until needed in a stainless steel mixing tank. Sludge aliquots were dispensed from the tank and were centrifuged at $4140\times g$ (where $g$ is equal to the gravitational acceleration at the surface of the earth) for 20 min to separate the sludge solids and the supernatant. The supernatant phase was then decanted and saved, and the sludge solids were weighed. This mechanical separation and all subsequent chemical processing that followed were performed at a temperature of ~24°C. Because the supernatant contains a high nitrate concentration and a significant fraction of the radioactive cesium, the sludge was washed with a volume of mild caustic solution (0.20 *M* NaOH) equal to or exceeding the estimated interstitial supernatant volume remaining with the solids to remove these components without dissolving the actinides. At this point, the dissolution procedure for the two test campaigns varied.

In the first campaign 179.1 g of sludge was washed with 104 mL of mild caustic, the mixture centrifuged, and the liquid decanted. This washing step was repeated twice. The sludge was then dissolved using 362 mL of 5.44 *M* $HNO_3$. Immediately after dissolution, the solution was filtered in preparation for the TRUEX tests.

In the second campaign, 30.8 g of sludge was "neutralized" by adding 20 mL of 5.44 *M* $HNO_3$ to destroy hydroxides and carbonates. To this mixture was added 25 mL of 6.27 *M* NaOH, resulting in an ~2.6 *M* NaOH leaching solution, which was mixed for 6 h. The mixture was centrifuged and the strong caustic solution decanted. The sludge was washed twice with 50 mL of mild caustic. Finally, the sludge was dissolved using 215 mL of 2.7 *M* $HNO_3$ and allowed to age for about 1 week prior to further processing.

In each campaign, the undissolved solids were dried at room temperature and weighed. Aliquots of the solution containing the dissolved sludge were then taken for chemical analysis. Following the washing and dissolution operations, the radiation emitted by the sample was less intense, permitting it to be moved from the hot cell to a chemical hood to simplify handling. Dissolved sludge solution was filtered with 0.45-μm-porosity syringe filters; however, in the first test the syringe filter plugged almost immediately, presumably due to a rapidly forming gel. Solutions that could not be filtered with the syringe filter were successfully filtered with No. 588 coarse, fluted filter paper. In each of the two test campaigns, four separate equivolume equilibrations were performed to simulate four stages of a batch, cross-flow TRUEX process. The temperature was maintained at 24 °C. Filtered solution was contacted with TRUEX solvent in separatory flasks and shaken by hand for at least 60 s. The aqueous and organic phases were then allowed to separate by gravity for 15 min. Each phase was sampled for chemical analysis. Similar procedures were used for any subsequent extraction steps and for aqueous stripping of the loaded organic phase. In the second extraction stage of the first test, a third phase formed. However, the addition of fresh solvent to increase the organic:aqueous phase ratio to 2.5:1 eliminated the third phase. Figures 1 and 2 illustrate the contacting patterns and reagents used at each equilibrium stage.

## Analyses of Samples

Generally, the analytical procedures used for the aqueous and organic samples were the same; however analyses of metals in the organic medium first required destruction of the organic

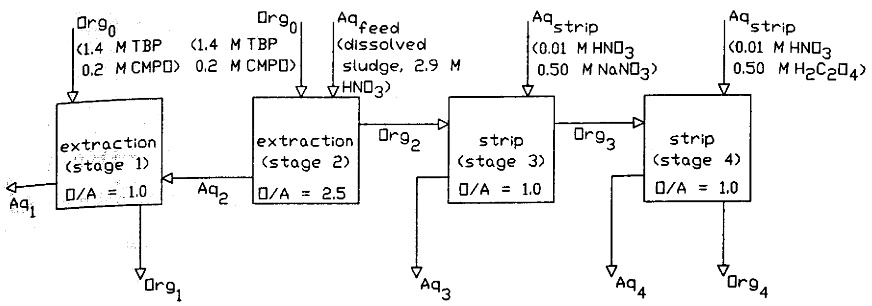

FIGURE 1. Material flow paths for first TRUEX test campaign.

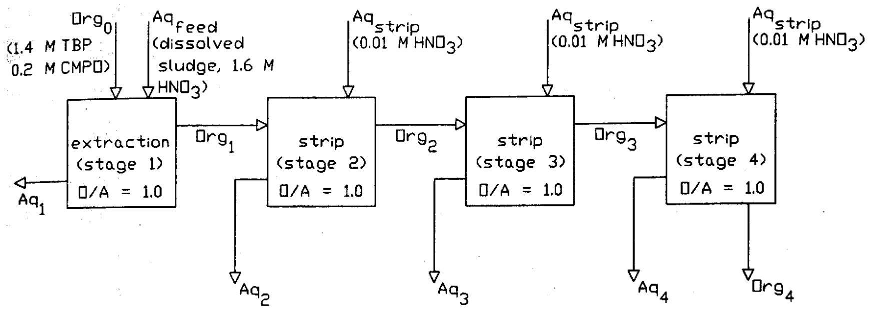

FIGURE 2. Material flow paths for second TRUEX test campaign.

matrix with a microwave acid digestion using a combination of sulfuric and nitric acids to place the analytes in aqueous solution. Details of the analytical methods that were used are found in a report by Keller et al.[18] Acid concentration was measured using potentiometric titration with 0.100 *M* NaOH solution. Metals were analyzed with inductively coupled plasma—atomic emission spectroscopy. Ion chromatography was used to measure the concentrations of the common ions (e.g., F$^-$, Cl$^-$, Br$^-$, NO$_3^-$, PO$_4^{3-}$, and SO$_4^{2-}$). Alpha spectroscopy was used to measure the amounts of the transuranium elements $^{239}$Pu, $^{241}$Am, and $^{244}$Cm in a sample. Gamma-emitting nuclides, such as $^{137}$Cs and $^{154}$Eu, were measured with gamma spectroscopy. Strontium was isolated by extraction to reduce interferences prior to radiocounting. Turbidity in aqueous sludge leachates and extraction raffinates was measured with a Hach 2100 AN turbidimeter as described previously by Beahm et al.[19]

## RESULTS AND DISCUSSION

### Dissolution of MVST Sludge

Dissolution of the sludge in the first campaign resulted in a solution having a cation concentration (not including $H^+$) of ~ 1.8 *M* and an $HNO_3$ concentration of 2.9 *M*. On the basis of air-dried sludge and residue, only 54.4% of the sludge dissolved. Because the objective was to test the TRUEX process, the residue was not analyzed. However, the dissolved sludge solution was well characterized. A calculation was made based on the sludge characterization data of Collins et al.[3] to estimate the concentration of each species in dissolved sludge under the assumptions that all the sludge dissolved and the volume of the acid solution did not change during dissolution. The calculated concentrations are compared with those actually measured in the solution in Table 1. The ratio of the calculated concentration to the measured concentration simplifies comparison of the data. Values of the ratio near unity indicate those species that dissolved completely. Small variations around unity (say, ±0.20) are attributed to the assumptions on which the calculations were made. The larger values are taken to indicate those species that dissolved sparingly. From these results the undissolved solids are inferred to contain large fractions of the initial Cs, Pu, Na, Si, Sr, Tl, $PO_4^{3-}$, and $SO_4^{2-}$. Most of the other metals, including the rare earths and actinides, dissolved almost completely.

In the second campaign, the dissolution procedure resulted in a solution having a cation concentration (not including $H^+$) of ~0.6 *M* and a $HNO_3$ concentration of 1.7 *M*. On the basis of air-dried solids, 79.3% of the sludge dissolved even though weaker nitric acid was used. The improved dissolution is thought to be the result of a combination of preleaching the solids with 2.6 *M* caustic and using a larger liquid-to-solids ratio. The effect of neutralizing the sludge with nitric acid to destroy the carbonates may have improved the effectiveness of the caustic preleach. Again, a calculation was made to estimate the concentration of each species in the solution by assuming that the sludge completely dissolved in the nitric acid. No credit was taken in the calculation for species that may have been removed by the caustic leaching. The calculated and actual concentrations in the dissolved sludge solution, as well as the ratio of the two, are shown in Table 2. The ratios are significantly greater than unity for those species that were either removed by the caustic preleaching or undissolved. Species fitting this description include Cs, Pu, Sr, $PO_4^{3-}$, and $SO_4^{2-}$. In the second test, the concentrations of species that originate from the sludge should be, assuming that all the sludge dissolved in the nitric acid, about one-third of those obtained in the first test. A comparison of the measured concentration

TABLE 1. COMPARISON OF CALCULATED[a] AND MEASURED CONCENTRATIONS OF SELECTED SPECIES IN DISSOLVED SLUDGE SOLUTION FOR THE FIRST TEST

| | Calculated concentration[a] | Measured concentration | Ratio, calculated to measured |
|---|---|---|---|
| **Radionuclides** | (Bq/L) | (Bq/L) | |
| $^{60}$Co | $4.01 \times 10^7$ | $3.00 \times 10^7$ | 1.34 |
| $^{90/\mathrm{all}}$Sr | $4.50 \times 10^9$ | $3.70 \times 10^9$ | 1.22 |
| $^{137}$Cs | $2.90 \times 10^8$ | $3.95 \times 10^7$ | 7.34[b] |
| $^{154}$Eu | $3.31 \times 10^7$ | $2.90 \times 10^7$ | 1.14 |
| $^{239,240}$Pu | $5.67 \times 10^6$ | $3.85 \times 10^6$ | 1.47[b] |
| $^{244}$Cm | $7.56 \times 10^7$ | $9.85 \times 10^7$ | 0.768 |
| **Other Metals** | (mg/L) | (mg/L) | |
| $H^+$ | 2,960. | 2,850. | 1.04 |
| Al | 6,020. | 6,490. | 0.928 |
| Ca | 22,700. | 31,600. | 0.718 |
| Fe | 2,030. | 1,680. | 1.21 |
| Mg | 3,190. | 3,740. | 0.853 |
| Mn | 189. | 212. | 0.892 |
| Na | 11,400. | 2,090. | 5.46[b] |
| Si | 3,620. | 149. | 24.3[b] |
| Sr | 1,320. | 495. | 2.67[b] |
| Th | 13,600. | 15,600. | 0.870 |
| Tl | 189. | <14.3 | >13.2[b] |
| U | 6,520. | 7,750. | 0.842 |
| **Anions** | (mg/L) | (mg/L) | |
| $Cl^-$ | 228. | 160. | 1.43 |
| $NO_3^-$ | 275,000. | 316,000. | 0.869 |
| $PO_4^{3-}$ | 6,970. | 451. | 15.5[b] |
| $SO_4^{2-}$ | 1,250. | 346. | 3.60[b] |

[a] Ideal solutions and total solids dissolution were assumed.

[b] Components were inferred to dissolve incompletely.

### TABLE 2. COMPARISON OF CALCULATED[a] AND MEASURED CONCENTRATIONS OF SELECTED SPECIES IN DISSOLVED SLUDGE SOLUTION FOR THE SECOND TEST

| | Calculated concentration[a] | Measured concentration | Ratio, calculated to measured |
|---|---|---|---|
| **Radionuclides** | (Bq/L) | (Bq/L) | |
| $^{60}$Co | $1.34 \times 10^7$ | $8.80 \times 10^6$ | 1.53 |
| $^{90/\text{all}}$Sr | $1.50 \times 10^9$ | $9.80 \times 10^8$ | 1.54 |
| $^{137}$Cs | $9.59 \times 10^7$ | $1.50 \times 10^7$ | 6.40[b] |
| $^{154}$Eu | $1.11 \times 10^7$ | $8.45 \times 10^6$ | 1.31 |
| $^{239,240}$Pu | $1.90 \times 10^6$ | $4.59 \times 10^5$ | 4.14[b] |
| $^{241}$Am | $2.06 \times 10^6$ | $1.95 \times 10^6$ | 1.06 |
| **Other Metals** | (mg/L) | (mg/L) | |
| $H^+$ | 2080. | 1,660. | 1.25 |
| Al | 2,020. | 1,660. | 1.22 |
| Ca | 7,610. | 7,290. | 1.04 |
| Fe | 682. | 501. | 1.36 |
| Mg | 1,070. | 923. | 1.16 |
| Mn | 63.4 | 51.9 | 1.22 |
| Na | 4,470. | 4,290. | 1.04 |
| Si | 1,210. | 742. | 1.63 |
| Sr | 444. | 43.7 | 10.2[b] |
| Th | 4,550. | 3,970. | 1.15 |
| Tl | 63.4 | <50.0 | >1.27 |
| U | 2,190. | 1,990. | 1.10 |
| **Anions** | (mg/L) | (mg/L) | |
| $Cl^-$ | 68.6 | 67. | 1.02 |
| $NO_3^-$ | 134,000. | 130,000. | 1.03 |
| $PO_4^{3-}$ | 2,340. | 63. | 37.1[b] |
| $SO_4^{2-}$ | 412. | 114. | 3.62[b] |

[a] Ideal solutions and total solids dissolution were assumed.

[b] Components were inferred to dissolve incompletely or removed by caustic leaching.

of silicon and phosphate between Tables 1 and 2 indicates that silicon was made much more soluble in the second dissolution procedure and that phosphate was likely removed by the caustic preleach. Similarly, strontium was removed by the pretreatment. Previous work[3] has shown that caustic leaching does not significantly remove strontium, so the results may indicate an effect of the initial acidification. The caustic in the preleach was not strong enough to solubilize plutonium, so the data indicate that much of it remains with the undissolved residue.

## Gelation of Dissolved Sludge

After the sludge had dissolved, the solution was filtered. Dissolved-sludge solution from the first campaign could not be filtered with 0.45-$\mu$m-porosity syringe filters because the filters plugged almost immediately. The solution was filtered with No. 588 coarse filter paper, and a small amount of gel-like residue could be observed on the filter. Following filtration, the solution was hazy. Turbidity measurements were made over a period of several days (see data in Figure 3). In 8 days a visible layer of gel formed, and after 20 days the sample was almost completely gelled, as shown in Figure 4. Beahm et al.[19] theorize that gels occur in acidified sludge because of the formation of silicic acid.

Solution from the second campaign was successfully filtered with the syringe filters, although some difficulty was encountered. The sample was initially clear, but became hazy in 8 days. Gelation did not occur after 20 days. Measured values of turbidity are shown in Figure 3 to permit direct comparison with the results from the first campaign. The difference is quite marked. Table 3 summarizes the dissolution and gel formation characteristics observed in the two campaigns.

Aqueous raffinate samples from the dissolved sludge feed stage of each campaign were also set aside for observation. Both visual observations and measured turbidity followed the same pattern as was observed for the dissolved sludge solution.

## TRUEX Partitioning of Dissolved Sludge

The generic TRUEX model (GTM) was used to simulate the batch shake-out tests, and model predictions were compared with measured results. Because the test temperature of 24 °C was close to 25 °C (the temperature at which the GTM data base is more complete), that value was used for all simulations. Measured dissolved sludge compositions were used to describe the aqueous feed stream. Because the GTM does not include all species found in the sludge, species from the same periodic group were assumed to behave similarly and were lumped as follows: (1) Tl with Al, (2) Co and Ni with Fe, (3) K with Na, (4) Be with Mg, (5) Mn with Tc,

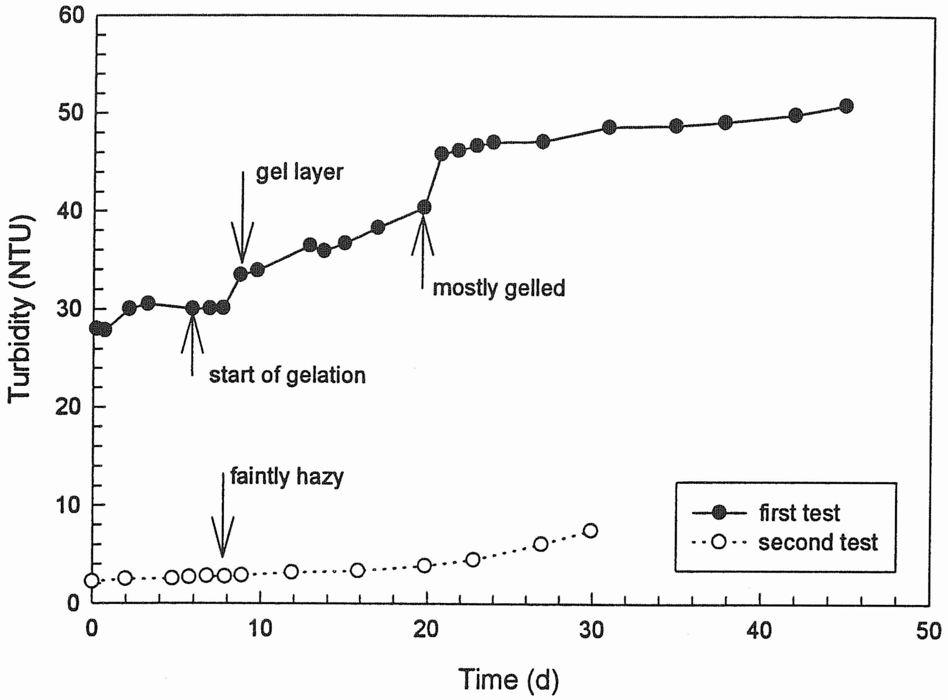

FIGURE 3. Comparison of turbidities of dissolved sludge solutions in the two tests.

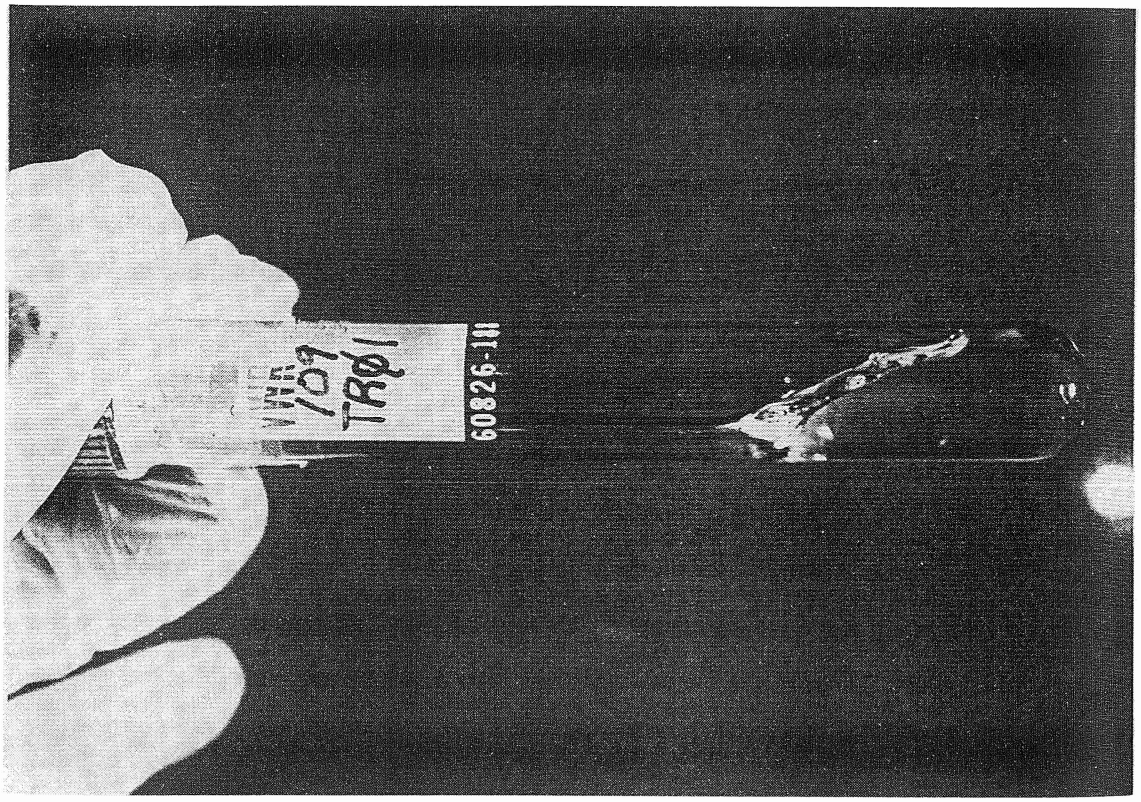

FIGURE 4. Sample of gelled dissolved sludge from first test campaign.

TABLE 3. SUMMARY OF DISSOLUTION RESULTS AND EFFECT ON GEL FORMATION CHARACTERISTICS IN THE TWO CAMPAIGNS

| | First test | Second test |
|---|---|---|
| Acid neutralization | No | Yes |
| Caustic preleach | No | 2.6 *M* |
| Acid dissolution | | |
| Final $HNO_3$ | 2.9 *M* | 1.7 *M* |
| Final metal | 1.8 *M* | 0.6 *M* |
| Solid residue | 46.5% | 20.7% |
| Main undissolved species | | |
| Actinides | Pu | Pu |
| Fission products | Cs, Sr, Tl | Cs, Sr |
| Process chemicals | Na, Si, $PO_4^{3-}$ | $PO_4^{3-}$ |
| Gel formation | | |
| Rate | Rapid | Slow |
| Condition at several minutes | Hazy | Clear |
| Condition at 8 days | Gel layer | Hazy |
| Condition at 20 days | Rigid gel | Hazy |

(6) Zn and Hg with Cd, and (7) Br and Cl with F. This allowed the model to estimate the appropriate total anion concentrations. The elements Pb, Si, and V were not as easily generalized; however, because the concentrations were small and they should not extract appreciably, they were ignored. Carbonate was assumed to be evolved from the solutions as $CO_2$ during the dissolution and was set to zero in the simulations. All of the plutonium was assumed to be in the quadrivalent state. The fractions of each phase entrained in the other phase were set to zero, and fractional efficiencies for each stage were set to unity. The GTM uses the composition and volume of each of the aqueous and organic feed solutions to calculate the distribution ratios and equilibrium concentrations of the various species in both phases. When the effluent from one stage becomes the feed to another stage, the computed concentrations are passed on as input to the subsequent calculation.

First Campaign. As illustrated in Figure 1, the first TRUEX campaign consisted of two extraction and two strip steps. Experimental values of the percentage of each component extracted from the dissolved sludge solution were calculated from the aqueous concentrations measured before and after extraction. Results of the GTM simulation were converted to predicted values by combining the calculated distribution ratios with the organic-to-aqueous phase ratio. That is,

$$r_{i,ext} = \left( \frac{(V_{org}/V_{aq})\, D_i}{(V_{org}/V_{aq})\, D_i + 1} \right) \times 100 \quad , \tag{1}$$

where $r_{i,\,ext}$ is the percentage of species $i$ removed by the second extraction (feed) stage, $D_i$ is the distribution ratio for species $i$, $V_{org}$ is the organic-phase volume, and $V_{aq}$ is the aqueous-phase volume. The predicted and measured values for the second extraction stage are compared in Table 4 for selected components. The extent of extraction was 97% for Eu, 99% for Th, 99+% for U, 99% for Pu, and 96% for Cm. Concentrations of americium were below the reliable reporting limit. The Fe, Ca, Sr, and Cs essentially did not extract. Model predictions are consistent with these results. Although cadmium was not expected to extract, the data indicate that a small quantity was extracted. The data also indicate that mercury was strongly extracted, with 93% removal. Similar reductions in the aqueous-phase concentrations of the actinides in the first extraction stage could not be verified experimentally because (1) the remaining concentrations were so low as to make discrimination in the analyses difficult, and (2) it is likely that the microscopic gelation sites were instrumental in immobilizing some of the constituents in the aqueous phase, thereby preventing their extraction.

The loaded organic from the second extraction stage was subjected to two sequential aqueous strips. Stripping with mild nitric acid (0.01 *M* $HNO_3$) and sodium nitrate (0.5 *M* $NaNO_3$) removed some of the nitric acid from the organic phase, but only very small quantities of the actinides or europium were recovered. The GTM accurately predicted this result. The second strip was done with an aqueous solution of mild nitric acid and oxalic acid (0.5 *M* $H_2C_2O_4$). A white precipitate was observed to form in the aqueous phase. Analysis of the filtered organic samples indicated that stripping from the organic occurred as follows: Eu, >99%; Am, 96%; Th, 98%; Hg, 50%; and U, only 20%. The low stripping and recovery factors for uranium indicate that either more stripping stages or a more effective stripping agent would be required. They also make separation of uranium from the other actinides feasible, as expected of the standard TRUEX process. The iterative numerical methods of the GTM would not converge at the second stripping stage where the precipitate formed.

### TABLE 4. FRACTION OF SELECTED SPECIES REMOVED FROM DISSOLVED SLUDGE BY SECOND EXTRACTION STAGE OF THE FIRST TEST, AND COMPARISON OF GTM PREDICTIONS WITH MEASURED VALUES

| | GTM prediction | | Measured value, percent removed |
|---|---|---|---|
| Metal | Distribution ratio | Percent removed | |
| Ca | 0.001 | 0.25 | 7.6 |
| Cr | 0.001 | 0.25 | 3.7 |
| Fe | 0.001 | 0.25 | 1.8 |
| Sr | 0.001 | 0.25 | ~0.[a] |
| Cd | 0.003 | 0.30 | 17.8 |
| Cs | 0.001 | 0.25 | ~0.[b] |
| Hg | Not in GTM | | 92.7 |
| Eu | 36.97 | 98.9 | >97.2[c] |
| Th | 4,302. | 99.9+ | 98.9 |
| U | 1,349. | 99.9+ | 99.9+ |
| Pu | 1,415. | 99.9+ | 98.9[d] |
| Am | 50.65 | 99.2 | *e* |
| Cm | 37.48 | 98.9 | 95.5 |

[a] Based on $^{90}$Sr.
[b] Based on $^{137}$Cs.
[c] Based on $^{152}$Eu and $^{154}$Eu.
[d] Average of values for $^{238}$Pu, $^{239}$Pu, and $^{242}$Pu.
[e] Insufficient data.

Second Campaign. The second TRUEX campaign included one extraction and three consecutive strip steps (see Figure 2). Aqueous-phase samples were taken from each of the four individual contacts. Organic- phase samples were taken from the extraction stage (stage 1) and the last strip stage (stage 4). The organic phases from stages 2 and 3 were not sampled because stripping with mild nitric acid (0.01 *M*) would not effectively recover a large fraction of the actinides unless the organic-phase acid concentration was first reduced. No precipitates formed in any of the stages, and gelation was not as evident as in the first campaign.

The experimentally measured percentages of selected species extracted from the aqueous dissolved sludge solution are compared with values predicted by the GTM in Table 5. One stage of extraction removed 93% of the Eu, >99% of the Th, >99% of the U, 99% of the Pu, and >77% of the Am. The Ca, Sr, Cs, Cr, and Fe were not extracted — a positive result since

### TABLE 5. FRACTION OF SELECTED SPECIES REMOVED FROM DISSOLVED SLUDGE BY EXTRACTION STAGE OF THE SECOND TEST, AND COMPARISON OF GTM PREDICTIONS WITH MEASURED VALUES

| | GTM prediction | | Measured value, percent removed |
|---|---|---|---|
| Metal | Distribution ratio | Percent removed | |
| Ca | 0.001 | 0.10 | 0.0 |
| V | Not in GTM | | 42.4 |
| Cr | 0.001 | 0.10 | ~0. |
| Fe | 0.001 | 0.10 | 2.0 |
| Sr | 0.001 | 0.10 | 2.0[a] |
| Cd | 0.004 | 0.43 | ~0. |
| Cs | 0.001 | 0.10 | ~0.[b] |
| Hg | Not in GTM | | 95.1 |
| Eu | 18.66 | 94.9 | 93.2[c] |
| Th | 5,916. | 99.9+ | 99.9 |
| U | 679.7 | 99.9 | 99.7 |
| Pu | 1,457. | 99.9+ | 99.4[d] |
| Am | 25.56 | 96.2 | >77.4 |
| Cm | | | [e] |

[a] Based on $^{90}$Sr.

[b] Based on $^{137}$Cs.

[c] Based on $^{152}$Eu and $^{154}$Eu.

[d] Average of values for $^{239}$Pu and $^{242}$Pu.

[e] Insufficient data.

TRUEX does not target these metals. The model indicates that Cd is not extracted, and the data corroborate this; however, 95% of the Hg and 42% of the V were extracted.

Based on measured aqueous-phase concentrations, stripping with mild nitric acid recovered 93% of the Eu and 99% of the Am in three stages. Both Eu and Am were primarily recovered in the first two stripping stages, 81% and 80%, respectively, indicating that they were easily stripped. Plutonium was more difficult to strip, with little being recovered until the third stripping stage where 50% was recovered. Thorium and uranium also began to transfer from the organic at the third stripping stage. The concentrations of Hg and V, being at or below the detectable limit in the aqueous strip solution, did not permit definitive conclusions regarding their stripping behavior.

The predicted concentration profiles of Eu, U, Pu and Am are compared with the experimental data in Figures 5 through 8. Error bars around the experimental data points are based on the variance between two replicate analyses. Large error bars occur where the measured concentration is at or below the detectable limit, and the model may be expected to vary from the data at these points. In many instances, the error bars do not extend beyond the data markers. Concentrations of Eu and Am were higher in the second strip (third stage) than in the third strip (fourth stage), indicating the relative ease of recovery as described above. Uranium and plutonium are more difficult to strip, as indicated by the high concentrations remaining in the organic phase after the third strip. The predicted plutonium concentrations in the aqueous phase are uniformly lower than the experimental data. There are five reasons why this might occur: (1) the measured plutonium concentration in the starting dissolved sludge solution (used as an input parameter to the model) could be too low, which would cascade through the calculations to subsequent stages; (2) at the low concentrations of the test, the analysis method overestimates the plutonium concentration; (3) the model overestimates the distribution ratio; (4) microscopic gel particles may trap a fraction of the plutonium, thus preventing extraction; or (5) a small fraction of organic phase may be entrained in the aqueous phase. The last two explanations seem the most likely. In general, the agreement between the model and data is quite good.

## SUMMARY

On a dry-weight basis, about half of the sludge from MVST Tank W-25 dissolved in 5.5 *M* nitric acid. Silicon, phosphate, and cesium were the primary constituents that do not dissolve. About half of the plutonium dissolved, but the other actinides dissolved more readily. Neutralizing the sludge with nitric acid (which destroys hydroxides and carbonates) followed by leaching with 2.6 *M* caustic prior to final acid treatment resulted in dissolution of ~80% of the sludge. The second dissolution, where the sludge was preleached with caustic and the total cation and acid concentrations were lower (0.6 *M* vs 1.8 *M* and 1.7 *M* vs 2.9 *M*, respectively), resulted in large decreases in the rate of gel formation and the quantities of gel formed. Additional work needs to be performed to ascertain the causal mechanism.

Most of the actinides are readily extracted from dissolved sludge solutions with the TRUEX process, even at low acidity (~0.6 *M*). However, the formation of gels appears to raise the lower limits of concentration that can be achieved in the aqueous phase. In spite of difficult

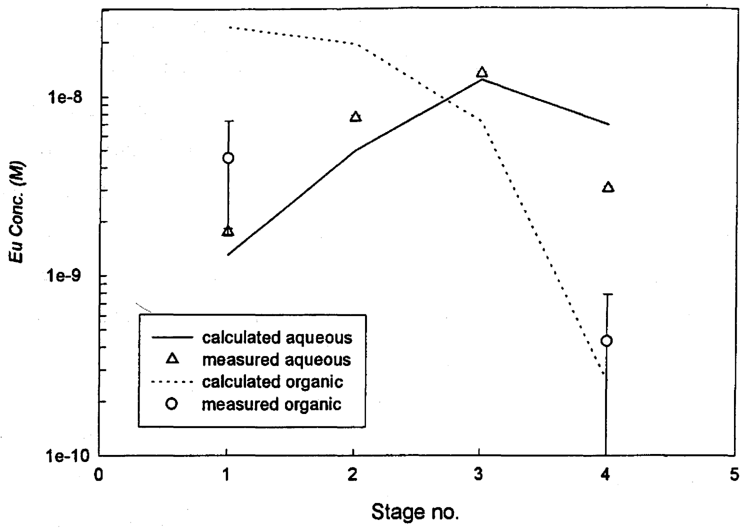

FIGURE 5. Comparison of measured and calculated stagewise concentration profiles for europium ($2^{nd}$ campaign).

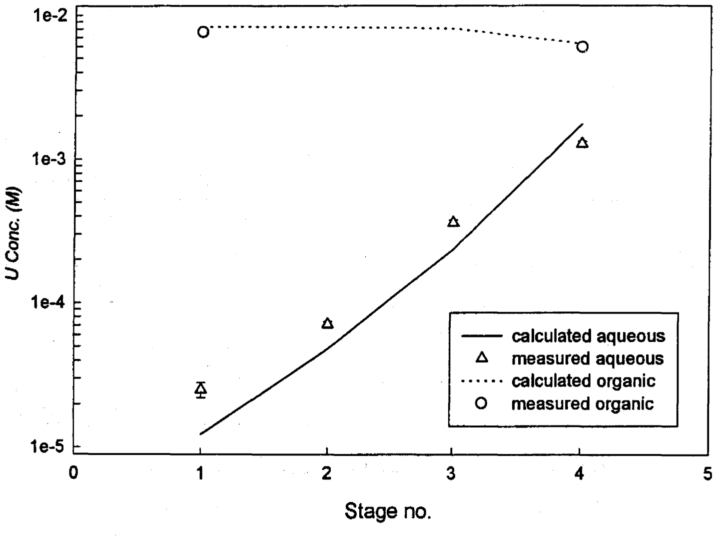

FIGURE 6. Comparison of measured and calculated stagewise concentration profiles for uranium ($2^{nd}$ campaign).

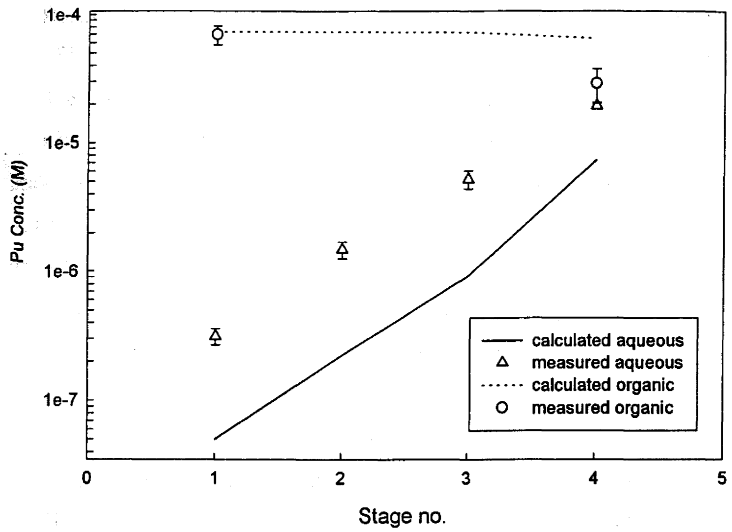

FIGURE 7. Comparison of measured and calculated stagewise concentration profiles for plutonium (2nd campaign).

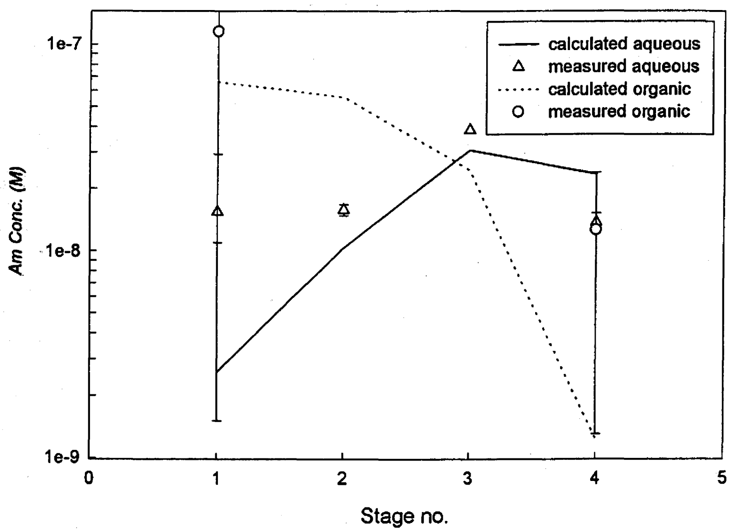

FIGURE 8. Comparison of measured and calculated stagewise concentration profiles for americium (2nd campaign).

process conditions (e.g., gels), the GTM can accurately predict the removal and recovery of the actinides.

Caustic leaching prior to acidic dissolution should be investigated further to (1) ascertain and quantify the effects on gel formation and (2) evaluate the reduction such a two-step process achieves in the ultimate quantities of HLW requiring vitrification. Cation concentrations may also affect gel formation. The quantities of mercury and vanadium in the waste should be evaluated to ascertain whether the extraction characteristics of these metals should be quantified and added to the GTM. Additives, such as fluoride, to inhibit gel formation should be evaluated with respect to both gel formation and the effect on the TRUEX process.

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