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Validation of the Generic TRUEX Model Using Data from TRUEX Demonstrations with Actual High-Level Waste

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ABSTRACT

The main objective of the Generic TRUEX Model (GTM) is to calculate TRUEX solvent extraction flowsheets based on input of a specific feed and a specific set of process goals and constraints. The output will be (1) the compositions of all effluent streams, (2) the compositions of both phases (organic and aqueous) in each stage of the contacting equipment at steady state, and (3) estimates of the space and cost requirements for installing the flowsheet in a plant situation. Other options are available to calculate aqueous-phase speciation and thermodynamic activities, distribution ratios of extractable species, and solvent radiolytic and hydrolytic degradation. Calculation of these options is based on initial aqueous- and organic-phase compositions and other important variables supplied by the user.

Three demonstrations of the TRUEX process have been run by Power Reactor and Nuclear Fuel Development Corp. (PNC) researchers at the Tokai Works using actual PUREX raffinates. A 19-stage mixer settler was used for the extraction and scrub sections, and a 16-to-19-stage unit for stripping. Stagewise data were collected on the behavior of nitric acid and several fission-product and actinide radioisotopes during these runs; Run 2 was the best documented and the one with which most comparisons were made. These data are important tools for validating predictions made by the GTM and understanding the intricacies of the TRUEX process. In this paper, results of the GTM calculations will be compared to the actual data published by PNC researchers. Differences between model predictions and experimental data were analyzed in terms of the process chemistry and demonstration conditions.

INTRODUCTION

The TRUEX solvent extraction process is capable of separating, with very high efficiency, small quantities of transuranic elements (e.g., Np, Am, Pu, Cm) from aqueous nitrate or chloride solutions that are typically generated in reprocessing plant operations or in plutonium production and purification operations. The resulting solutions can be sufficiently separated from TRU elements to warrant disposal as a nonTRU, low-level waste. If the TRU content of a waste stream can be lowered to below 100 nCi/g of solid, the waste can be classified as nonTRU, and, if ^{137}Cs and ^{90}Sr levels are acceptable or are reduced, it will be eligible for near-surface or greater-confinement disposal. In the case of PUREX high-level waste, this would mean that only the TRU concentrate product (< 1 wt% of the initial mass) may need to be placed in deep geologic disposal. The largest effort associated with developing this process at Argonne National Laboratory is the Generic TRUEX Model (GTM).

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The GTM was developed for use in designing site- and feed-specific TRUEX flowsheets and in estimating the space and cost requirements for installing a TRUEX process [VANDEGRIFT]. The GTM continues to be enhanced through collection of laboratory and pilot-plant data and through improvements in the thermodynamic modeling and computer codes. User friendliness, accuracy of predictions, and compatibility with both Macintosh and IBM PCs are keys to its usefulness. The GTM's equilibrium calculations for the extraction behaviors of waste components are based on experimental data. These data were used to develop distribution ratio models that are mechanistically correct and based on thermodynamic activities of important aqueous-phase species; therefore, the GTM is accurate for all nitrate solutions--whether containing high or low acid concentrations or high or low salt concentrations. Flowsheet calculations can be performed for processes using centrifugal contactors, mixer settlers, or pulsed columns. At every process stage, one can specify: (1) an external feed for both phases (organic and aqueous), (2) a fractional external effluent for both phases, (3) side-stream sampling for both phases, (4) other-phase carryover (backmixing) in both phases, and (5) an extraction efficiency.

The GTM is a useful tool for (1) designing and simulating a TRUEX process, (2) performing sensitivity analyses on process flowsheets, (3) designing and simulating any given multistage solvent extraction process by giving the user the ability to incorporate appropriate equilibrium data (distribution ratios), and (4) calculating and predicting aqueous-based chemistry in equilibrium, including speciation and complexation, for over 44 feed components.

The Power Reactor and Nuclear Fuel Development Corp. (PNC) of Japan has been promoting actinide partitioning studies as part of advanced reprocessing system development efforts. In the last four decades, PNC has recovered uranium and plutonium from spent fuel using the PUREX process. The PUREX process allows minor actinides (americium, curium, and a fraction of the neptunium) to remain in the high-level liquid waste, which will be vitrified in the current PNC program. In recent studies [OZAWA-1992A, OZAWA-1993B, OZAWA-1992C], Ozawa et al. evaluated the option of separating all actinides from high-level liquid waste (HLLW) by using the TRUEX process. The main purpose of their study was to verify the ability of the TRUEX process to treat actual highly active raffinate (HAR), originated from reprocessing experiments using fast breeder reactor (FBR) spent fuel. At the Chemical Tokai-works Processing Facility, five countercurrent flowsheet tests were conducted in which the TRUEX solvent was composed of $0.2\underline{M}$ CMPO and $1.0\underline{M}$ TBP in n-dodecane. The HAR feed was generated from PUREX reprocessing experiments of FBR-Joyo MK-II spent fuel burned up to 54,000 MWD/T (megawatt-days per ton) and cooled for 2 to 4 years. The HAR was used without adjusting acidity, but small amounts of plutonium and oxalic acid were added. Oxalic acid was added to inhibit zirconium and molybdenum from co-extraction with the actinides. The countercurrent experiments were conducted in mixer settlers. The mixer settlers had 19 stages for extraction-scrubbing and 16 to 19 stages for stripping and solvent regeneration. The volume holdup of one stage of the mixer settler was 23 mL.

Prior to 1993, researchers at PNC conducted three countercurrent mixer-settler runs. Table 1 shows the flowsheet conditions for each run [OZAWA-1992A]. For Run 2, $0.02\underline{M}$ $H_2C_2O_4$ was added to the feed, and ^{238}Pu was added as a tracer. The composition of the HAR feed solution is given in Table 2 [OZAWA-1992B]. The values reported by PNC for uranium, neptunium, americium, curium, and cesium were estimated with the ORIGEN-II code. The three countercurrent flowsheets tested at PNC were simulated using the GTM in order to compare the results predicted with those measured in the experimental runs. The experimental concentration profiles for all three runs were compared to the predictions made by the GTM for given flowsheet conditions. For Run 1, only a concentration profile for HNO_3 was reported in the literature [OZAWA-1992B]. Profiles for Run 2 were obtained from the literature [OZAWA-1992B, OZAWA-1992C] and personal communication. For Run 3, information was obtained in [OZAWA-1992A].

Table 1. Operating Conditions for PNC's Mixer-Settler Demonstration Runs

Run	Feed (HAR)	Solvent	Scrub - 1	Scrub - 2	Am strip	Np strip	Pu strip	U strip
1st	Joyo MK - II 54100 MWD/T 1500 d cooling $H^+ = 4.0\underline{M}$ 196 mL/h	0.2 $\underline{M}$ CMPO 1. $\underline{M}$ TBP in n-dodecane 87 mL/h 8 stages	---	0.3 $\underline{M}$ HNO_3 0.1 $\underline{M}$ $H_2C_2O_4$ 40 mL/h 11 stages	---	---	0.01 $\underline{M}$ HNO_3 106 mL/h 16 stages	---
2nd	Joyo MK-II 54100 MWD/T 1500 d cooling $H^+ = 4.5\underline{M}$ 0.02 $\underline{M}$ $H_2C_2O_4$ ^{238}Pu addition 196 mL/h	0.2 $\underline{M}$ CMPO 1.0 $\underline{M}$ TBP in n-dodecane 119 mL/h 8 stages	7.7 $\underline{M}$ HNO_3 0.03 $\underline{M}$ $H_2C_2O_4$ 12 mL/h 6 stages	0.3 $\underline{M}$ HNO_3 16 mL/h 5 stages	---	---	0.01 $\underline{M}$ HNO_3 79 mL/h 16 stages	---
3rd	Joyo MK-II 54100 MWD/T 1500 d cooling + Joyo MK-II 54700 MWD/T 700 d cooling $H^+ = 7.0\underline{M}$ 200 mL/h	0.2 $\underline{M}$ CMPO 1.0 $\underline{M}$ TBP in n-dodecane 100 mL/h 8 stages	7.7 $\underline{M}$ HNO_3 0.03 $\underline{M}$ $H_2C_2O_4$ 30 mL/h 6 stages	0.3 $\underline{M}$ HNO_3 30 mL/h 5 stages	0.01 $\underline{M}$ HNO_3 100 mL/h 5 stages	0.3 $\underline{M}$ HNO_3 0.1 $\underline{M}$ HAN 50 mL/h 5 stages	0.5 $\underline{M}$ HNO_3 0.1 $\underline{M}$ $H_2C_2O_4$ 50 mL/h 5 stages	0.1 $\underline{M}$ Na_2CO_3 50 mL/h 4 stages

Table 2. Composition of the HAR[a]

Species	Concentration, $\underline{M}$	Species	Concentration, $\underline{M}$
U(VI)	7.1E-04[b]	Sm	4.5E-04
Np(V)	4.2E-05[c]	Eu	6.0E-05
Pu(IV)	6.7E-05[d]	Cs	2.3E-03
Am	5.0E-04[c]	Sr	5.1E-04
Cm	1.2E-06[c]	Zr	<3.3E-05[e]
Y	3.9E-04	Mo	1.2E-03
La	6.1E-04	Ru	3.1E-03
Ce	1.0E-03	Rh	2.5E-04
Pr	3.0E-04	Pd	<1.9E-05[e]
Nd	1.7E-03	Tc	2.1E-04

[a] Hydrogen ion concentration and additions are shown in Table 1 for each run.

[b] Estimated value corresponds to 0.5% leakage.

[c] Estimated value corresponds to 100% leakage.

[d] Artificially added.

[e] Value lower than detection limit.

RESULTS

Flowsheet conditions for the PNC countercurrent tests were simulated using the GTM versions 3.0.2 and 3.1. The primary difference between these two versions is that in version 3.1 we have added nitrate complexes of metal ions to our speciation calculations. The importance of that addition will be shown later in this section. Variations in stage efficiency, process temperature, and oxidation state of the actinides are also evaluated. Predictions were compared to the results reported by PNC researchers. In general, the GTM predictions correlated well with experimental results for the runs, especially for the rare earth fission products, americium, and curium. Species measured by PNC in the three runs were HNO_3, ^{242}Cm, ^{244}Cm, ^{241}Am plus ^{238}Pu, ^{239}Pu plus ^{240}Pu, ^{237}Np, ^{144}Ce, ^{155}Eu, ^{137}Cs, ^{125}Sb, ^{95}Zr, and ^{106}Ru. The concentration of ^{95}Zr was always under the detection limits. To validate the accuracy of the GTM for designing and simulating TRUEX processes, we compared the stagewise concentration profiles reported by PNC researchers to those predicted by the GTM. (Results reported here are typical; in the future, an Argonne National Laboratory topical report will be published showing all results of this study.) We focus the discussion here on the behavior of Ce(III) because it is indicative of all the rare-earth fission products, americium, and curium. Typical results for nitric acid, cesium, ruthenium, plutonium, and neptunium are also discussed.

During our simulation, we encountered convergence problems in the modeling of the PNC demonstrations. These problems were traced to unrealistic zirconium concentrations being calculated for some of the stages due to PNC having added inappropriate amounts of oxalic acid to the extraction and scrub sections. In general, oxalic acid is added to the feed to minimize the extraction of zirconium, molybdenum, and ruthenium. Although the concentration of ^{95}Zr was under the detection limits in the PNC simulations, it is very likely that in the actual demonstrations, zirconium and perhaps other metal salts were "pinched" in the scrub and strip sections. Pinching means that the extraction factor is >1 in the first stage of a section and <1 in the last stage of the same section. Therefore, the concentration of these metals increased in both phases in all stages of the given section. Precipitation of oxalate was noted in the first PNC run [OZAWA-1992A]. Also, it is highly likely, especially because PNC researchers used 1.0$\underline{M}$ TBP rather than the suggested 1.4$\underline{M}$ [VANDEGRIFT], that third-phase formation occurred in the scrub section due to the buildup of zirconium. In our effort to model the PNC runs, we lowered the concentration of zirconium in the feed, when necessary, to avoid convergence problems in the GTM. With 100% stage efficiency, the reduction in zirconium concentration was as high as eleven orders of magnitude for run 1, three orders of magnitude in run 2, and two orders of magnitude in run 3. Lowering the stage efficiency made these reductions less severe. At 90% stage efficiency, run 2 could be modeled with no reduction in zirconium feed concentration, but run 1 still required a nine orders of magnitude reduction, and run 3 still required a reduction by two orders of magnitude. Figure 1 shows the calculated pinching of zirconium in the scrub section of run 1 and in the strip section of run 2. Note that in run 1 the zirconium concentration is being increased by three orders of magnitude above its feed concentration in the scrub section.

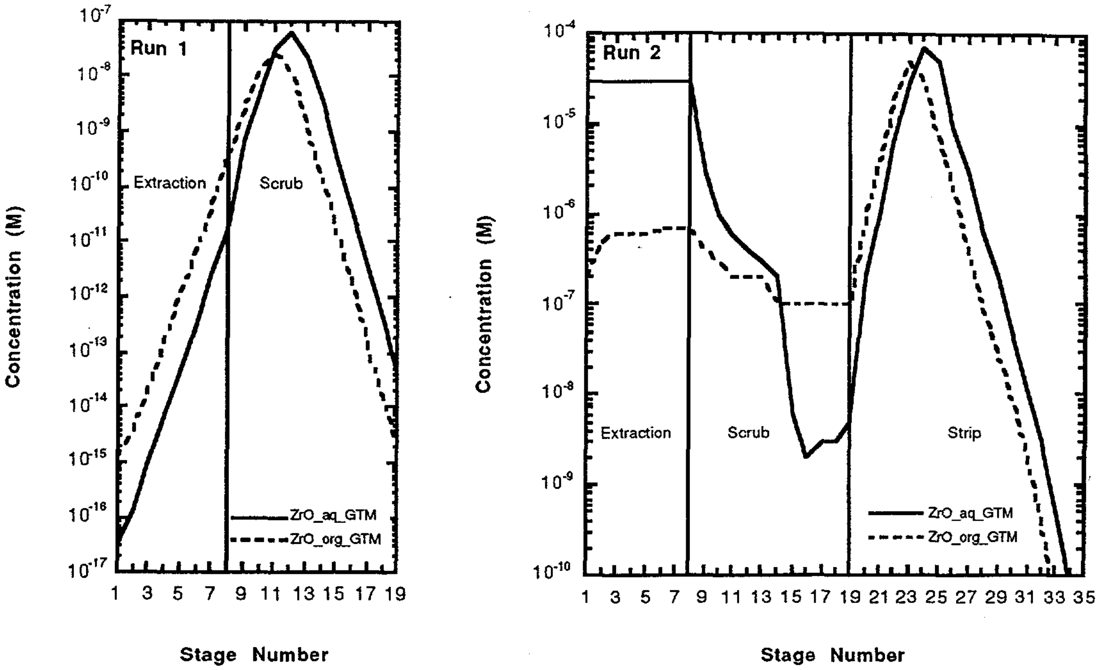

Fig. 1. Aqueous- and Organic-Phase Concentration Profile for Zirconium in the Extraction/Scrub and Strip Sections. These figures show the GTM simulations for 90% stage efficiency for PNC Run 1 (left) and Run 2 (right).

Four stage efficiencies (100%, 90%, 80%, and 70%) were simulated, and we concluded that the extraction/scrub section could best be simulated by 90% and the strip section by 100% stage efficiency. Figure 2 shows the aqueous-phase concentration profile for Ce(III) at different stage efficiencies in the extraction/scrub and strip sections for run 2; clearly, the best fit is for 90% stage efficiency for the extraction/scrub section. Fitting of the strip section data was less accurate. To be consistent, all flowsheet calculations were done using 90% stage efficiency for all stages.

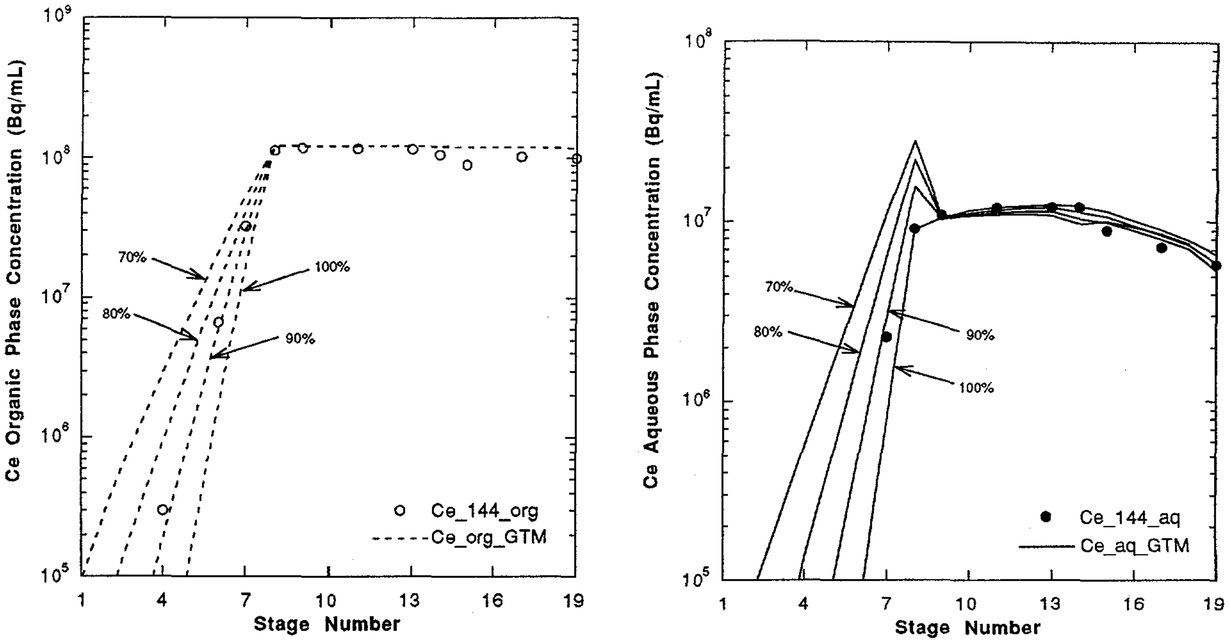

Fig. 2. Organic- and Aqueous-Phase Concentration Profile for Cerium as a Function of Stage Efficiency for the Extraction/Scrub Section. Shown in these figures are the GTM simulations for 70%, 80%, 90%, and 100% stage efficiency for Run 2 for the organic phase (left) and aqueous phase (right) and the experimental results obtained for this run.

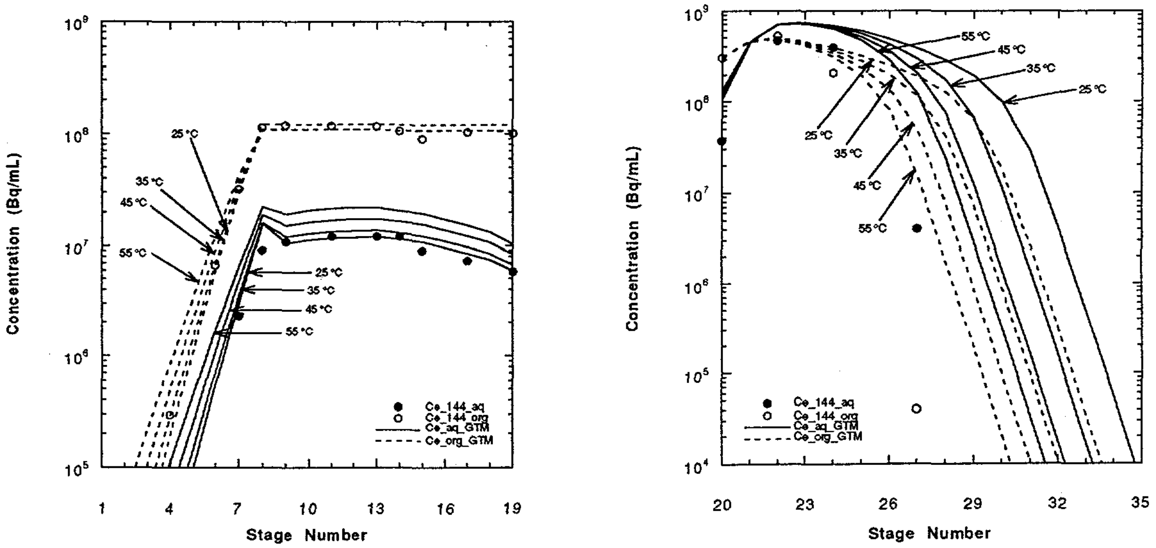

Fig. 3. Aqueous- and Organic-Phase Concentration Profile for Cerium as a Function of Temperature for the Extraction/Scrub (left) and Strip Section (right). Shown in this figure are the GTM simulations for 25°C, 35°C, 45°C, and 55°C at 90% stage efficiency for Run 2 and the experimental results obtained for this run.

The effects of process temperature were also included as part of the GTM simulation. Figure 3 shows the calculated and measured effect of temperature on the behavior of Ce(III) in run 2. These results are also typical of the predicted and measured stripping behavior of the rare earths, americium, and curium. Increasing the temperature has an adverse effect on the extraction section for americium, curium, and the rare earths because it decreases their distribution ratios, thus increasing their concentrations in the aqueous phase. For the strip section, an increase in temperature also decreases the distribution ratio, but, in this case, a lower distribution ratio increases the effectiveness of the strip section, lowering the organic-phase concentrations of those components that exit the strip section. Because the process temperature was not controlled in the PNC runs, we looked at the effect that process temperatures would have on the flowsheets. Results presented in Fig. 3 show that 25°C gives the best fit for the extraction/scrub sections and ≥55°C gives the best fit for the strip section. Although we don't know the conditions of the experimental setup, it is difficult to believe that the ambient temperature varied this much between the two sections.

In GTM versions 3.01 and earlier, nitrate complexes of metal ions [e.g., $Eu(NO_3)^{2+}$, $Pu(NO_3)_2^{2+}$] were not included in the speciation calculations. Recently, we designed a TRUEX process flowsheet for recovering two product streams from the processing of Mark 42 targets at Oak Ridge National Laboratory (ORNL). These targets contained highly irradiated ^{239}Pu [BATTLES]. The product streams were (1) an americium, curium, rare-earth product that should be ≥99.9% free of plutonium and (2) a plutonium product that should be ≥99.9% free of americium, curium, and rare-earth elements. Comparing the results of the run made at ORNL [FELKER] with our simulation showed that these complexes could not be ignored for the high concentrations of rare-earth fission products in the feed. Neglecting them would predict far more free nitrate ion available than there actually is--causing much higher distribution ratios to be calculated. (Distribution ratios for the tripositive actinides and rare-earth elements are approximately proportional to the nitrate activity to the third power.) Nitrate complexes of metal ions were added to the GTM in version 3.1. The effects of including nitrate complexation can be seen in Fig. 4, where the ORNL data for curium stripping are compared with the predicted behavior by GTM versions 3.01 and 3.1. The PNC runs were also fit by both GTM versions, and as expected, the best fit was obtained for GTM version 3.1.

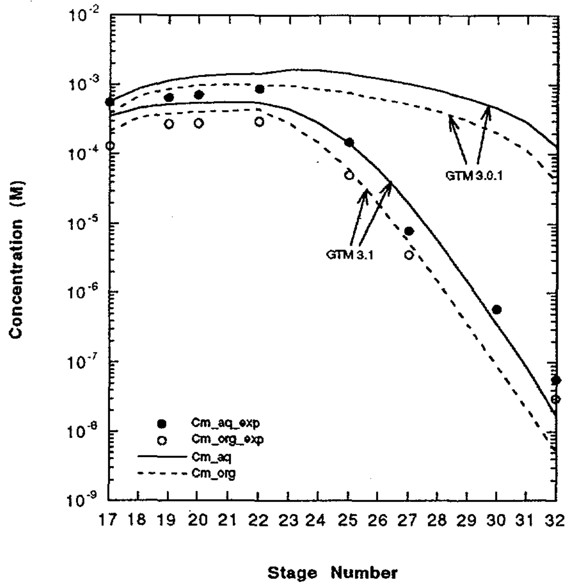

Fig. 4. Aqueous- and Organic-Phase Concentration Profile for Curium in the Strip Section. Shown is the GTM simulation for the basic TRUEX flowsheet for processing Mark 42 targets calculated using GTM version 3.0.1 and 3.1 and the experimental results obtained by ORNL.

Calculational and experimental results for plutonium and neptunium showed less agreement than the rare earths. The GTM assumes specific oxidation states for its calculations [Pu(III) or (IV) and Np(IV) or (V)]; the PNC data are reported as specific isotope concentrations only. Figure 5 shows the GTM simulation for stripping of Pu(IV) in run 3 and the experimental results. The shape of the Pu(III) simulation is much like that of Ce(III), shown in Fig. 3 (right). Comparison of the experimental results and the GTM simulation for Pu(III) and Pu(IV) shows that experimental results are in better agreement with the Pu(IV) simulation. Figure 6 shows the experimental stagewise aqueous-phase concentrations of neptunium and the two GTM predictions that assumed all the neptunium was in either the (IV) or (V) oxidation state. Neptunium stripping results in run 3 are much better fit by the GTM by assuming Np(IV) rather than Np(V). For the case of americium, predicted and experimental results were hard to compare. The americium experimental results were reported as ^{241}Am and ^{238}Pu since their alpha particle energies are very similar. In the case of the GTM, results are given for americium.

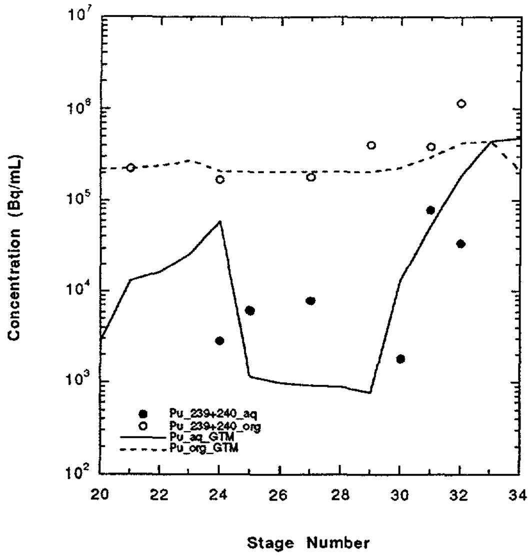

Fig. 5. Aqueous- and Organic-Phase Concentration Profile for Plutonium(IV) in the Strip Section. Shown are the GTM simulation for the stagewise aqueous- and organic-phase profiles at 90% stage efficiency for Run 3 and the experimental results obtained for plutonium-239 plus plutonium-240 for this run.

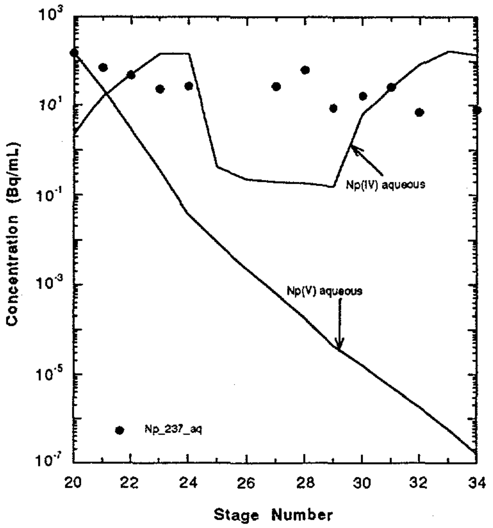

Fig. 6. Aqueous-Phase Concentration Profile for Neptunium(IV) and (V) in the Strip Section. Shown are the GTM simulation for 90% stage efficiency for Run 3 and the experimental results obtained for this run.

The hydrogen-ion profile was well predicted by the GTM in the extraction section for run 2. The predicted concentrations are generally lower in the scrub and strip sections. Small differences from the stated flow rates could account for this effect. The comparison is shown in Fig. 7.

Researchers at PNC collected data for two more HAR feed components that are modeled by the GTM--cesium and ruthenium. In the case of cesium, which doesn't extract, the GTM predicts a distribution ratio of 1×10^{-3}, based on our assumption that distribution ratios of less than that would never be seen. According to the PNC experimental data, this value should be 1×10^{-4}. In the case of ruthenium, comparison to the PNC experimental results indicated that the GTM is inaccurate if we assume that the ruthenium species are equilibrated. In calculating the distribution ratio of ruthenium in a stage, the GTM takes into account the type of contact equipment used by assuming that the contact time is a matter of a few seconds (a centrifugal contactor) or a minute or more (pulsed columns and mixer settlers). The difference in modeling these types of contacting equipment is that we assume that (1) in a pulsed column or mixer settler, the contact time between the organic and aqueous phases is long enough that ruthenium species have time to equilibrate, and (2) in the centrifugal contactor, no reequilibration can occur, and the speciation that is present in the feed remains constant throughout the flowsheet. As seen by Fig. 8, the stripping behavior of ruthenium was better fit by assuming that the organic phase is not reequilibrating with the aqueous strip solution.

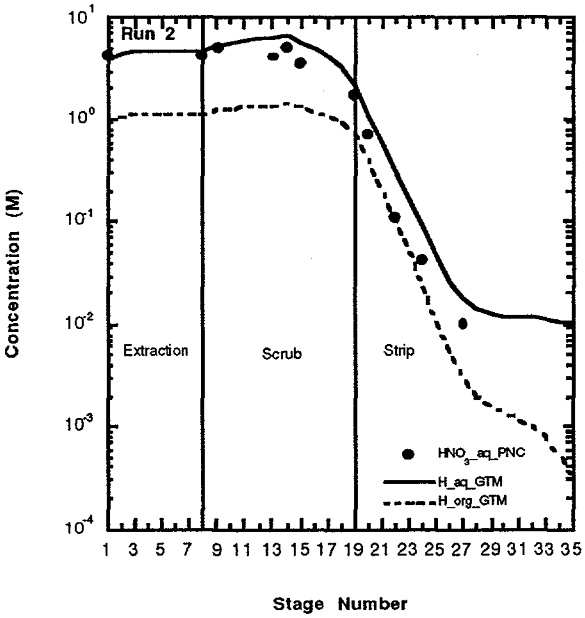

Fig. 7. Aqueous- and Organic-Phase Concentration Profile for Hydrogen Ion in the Extraction/Scrub and Strip Sections for Run 2 Using 90% Stage Efficiency. Measured aqueous-phase nitric acid concentrations are also shown.

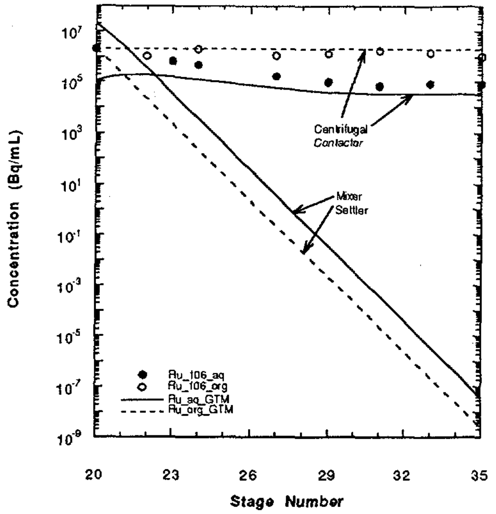

Fig. 8. Aqueous- and Organic-Phase Concentration Profile for Ruthenium in the Strip Section for a Mixer Settler and a Centrifugal Contactor. Shown in this figure are the GTM simulations for a mixer settler and a centrifugal contactor at 90% stage efficiency for Run 2 and the experimental results obtained for this run.

CONCLUSIONS

The GTM was used to predict concentration profiles for the three flowsheet demonstrations of the TRUEX process run at the Tokai Works prior to 1993, using actual PUREX raffinate. The predictions agreed well with experimental results for the runs, especially for the rare earth fission products, americium, and curium. Comparison of the predictive and experimental results proves the capability of the GTM as a computational tool for designing and simulating TRUEX process flowsheets. The algorithms used by the GTM could still be improved, but can be used with a high degree of confidence for the design of TRUEX solvent extraction flowsheets. The differences between simulated and experimental behavior of the species should be analyzed and used to improve the model's predictions. The GTM can also be used to perform a sensitivity analysis on the flowsheets to determine how variabilities in aqueous-feed compositions, TRUEX-solvent composition, and feed flow rates affect the concentration profiles of the waste components.

These results also point out the importance of the GTM as a tool for designing flowsheets and performing sensitivity analyses. It is very likely that if the PNC researchers had been given access to the GTM in the planning stage, the flowsheets would have differed from those reported. Certainly, the amount of oxalic acid added to the process and its point of entry would have been modified to prevent zirconium and ruthenium from being extracted--thus avoiding the precipitation problems.

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