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Pacific Northwest National Laboratory
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Alternative TRUEX-Based Pretreatment Processing of INEEL Sodium Bearing Waste

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September 2000

Prepared for the U.S. Department of Energy
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Radiochemical Processing Group
Pacific Northwest National Laboratory
Richland, Washington 99352

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Summary

The major goals of this study were to demonstrate a selective mercury complexant for separating mercury from the transuranic (TRU) elements in the transuranic extraction (TRUEX) process and to demonstrate alternative stripping methods to eliminate phosphorus-containing, actinide-stripping agents during TRUEX processing. The work described in this report provides the basis for implementing an improved TRUEX-based flowsheet for processing INEEL sodium-bearing waste using only minor modifications to the current Idaho National Engineering and Environmental Laboratory (INEEL) flowsheet design. Specifically, it has been shown that:

- The presence of cysteine in concentrations up to 10 mM is effective at inhibiting mercury extraction by the TRUEX solvent.
- The use of 0.5 M oxalic acid prevents substantial Zr extraction from INEEL simulant while still allowing for effective actinide extraction.
- Preliminary tests using the Sr•Spec® resin (Eichrom Industries) indicate that the presence of 10 mM cysteine will also prevent mercury extraction during the strontium extraction (SREX) cycle of tank waste pretreatment.
- A 0.1 M solution of ammonium bioxalate was found to effectively strip both uranium and transuranic elements (americium and plutonium) from TRUEX solvent.
- Americium and plutonium also can be selectively removed from the TRUEX solvent through contact with 0.1 M ascorbic acid/0.04 M nitric acid strip solution.

As a result of the testing described in this report, an improved TRUEX flowsheet can be recommended. This improved flowsheet is illustrated below in Figure S1.

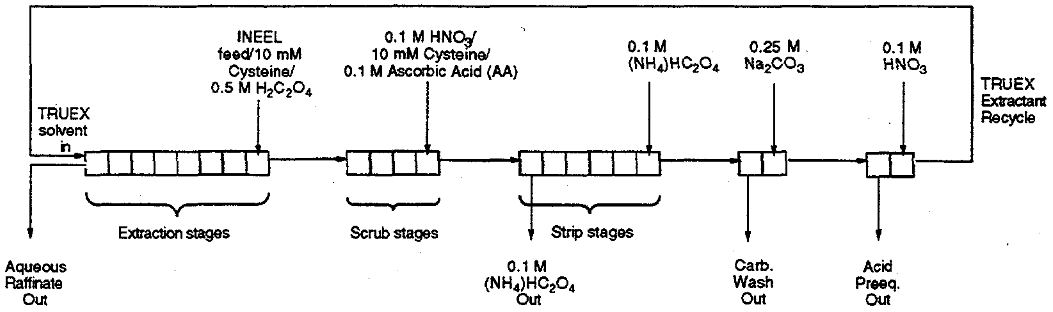


Figure S1. Schematic Illustration of the Final Recommended TRUEX Flowsheet

Contents

Figures

Tables

1.0 Introduction

INEEL staff have had an ongoing effort to evaluate radionuclide separation processes to minimize the amount of high level radioactive waste requiring disposal in a geological repository. One process that has received much attention is the transuranic extraction (TRUEX) process for selectively separating actinides out of acidic waste solutions (Herbst et al. 2000; Law et al. 1996; Law et al. 1998a and 1998b).

A TRUEX process flowsheet as recently tested at Idaho National Engineering and Environmental Laboratory (INEEL) is outlined in Figure 1.1. Contact of the dissolved acidic high level tank waste with the TRUEX solvent, composed of 0.2 M CMPO (octyl, phenyl-N, N-diisobutylcarbamoylmethyl phosphine oxide), 1.4 M tributyl phosphate (TBP) in a aliphatic hydrocarbon diluent, is performed in the extraction stages to selectively partition the actinides to the organic phase. The loaded organic phase is transferred to the scrub stages where the organic phase is contacted with 0.1 M nitric acid to reduce the amount of nitric acid co-extracted into the organic phase. The organic phase is transferred to the strip stages, where the organic phase is contacted with an aqueous solution 0.04 M in nitric acid and 0.04 M in HEDPA (1—hydroxyethane 1,1-diphosphonic acid). Contact of the organic phase with this low acid/HEDPA solution effectively partitions the actinides back to the aqueous phase, and generates a transuranic (TRU) waste stream containing the bulk of the actinides designated for long term immobilization through vitrification. A 0.25 M carbonate wash of the organic phase is next performed to remove any TRUEX degradation products followed by a 0.1 M nitric acid rinse to condition the extractant before it is recycled back to the extraction stages.

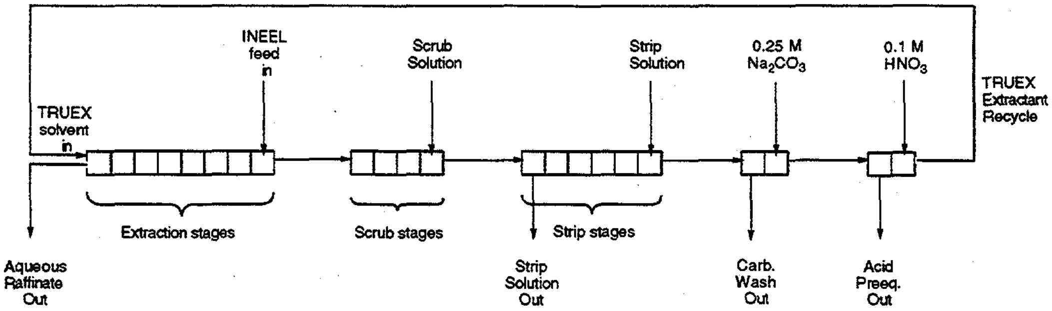


Figure 1.1. Outline of Generic TRUEX Flowsheet for INEEL Tank Waste

Previous studies with INEEL tank waste and tank waste simulants (Herbst et al. 2000; Law et al. 1996; Law et al. 1998a and 1998b) indicate that the TRUEX process performs effectively and much as expected, allowing for the extraction of actinides and lanthanides from the feed solution and their transfer to the targeted aqueous strip solution. However, there are still some aspects of the current flowsheet that could stand improvement.

The first improvement derives from the choice of 0.04 M HEDPA as the agent to induce actinide stripping. The presence of this diphosphonic acid introduces a substantial amount of phosphorus into the high level waste stream and is the limiting factor in determining how much of the high level waste can be introduced into a given amount of glass. To reduce or even eliminate the amount of phosphorus present in the high level waste stream would improve the attractiveness of the TRUEX process at treating INEEL tank waste by minimizing the amount of vitrified high level material.

Second, the co-extraction of mercury by the TRUEX solvent introduces some processing problems. Recent test results (Herbst 2000) indicate that some of the mercury can precipitate (presumably as HgO) during the carbonate wash stages. This precipitation can probably be avoided by keeping the organic to aqueous ratios low enough so that the solubility of HgO in the carbonate wash is not exceeded, but it does currently exist as a processing problem that deserves attention.

It should be noted that when proposing alternatives to the current flowsheet, there are two attractive aspects to the current flowsheet that should be maintained. First, having the uranium follow the TRUs in the process flowsheet is desirable. Second, preventing the extraction of zirconium is also an attractive feature.

To summarize, these are the goals directing this investigation of alternatives to the current TRUEX flowsheet for treating INEEL tank waste:

- Prevent the extraction of or allow for the highly selective stripping of mercury.
- Provide for the uranium to strip along with the TRUs.
- Prevent the extraction of zirconium.
- Demonstrate a workable flowsheet through a series of linked, batch contacts.

2.0 Experimental

With the exception of Isopar L® (Exxon Chemical, Houston Texas), a commercial mixture of branched paraffinic hydrocarbons, and tributyl phosphate (in-house stocks), all bulk chemicals were of reagent grade or better. Sr•Spec® resin, 20–50 micron particle size, was purchased from Eichrom Industries (Darien, Illinois) and used as received.

The INEEL simulant was prepared by adding the solid chemicals listed in Table 2.1, with the exception of aluminum nitrate, in the indicated amounts, followed by a small amount of deionized water sufficient to generate a free flowing solution/mixture. In the meantime, a suspension of nominally 2.2 M aluminum nitrate was prepared. The designated volume of 2.2 M aluminum nitrate was then added to the container with the other metal-containing components. Next, with vigorous stirring, the designated amounts of nitric acid, hydrochloric acid, sulfuric acid, and hydrofluoric acid were added using either a graduated cylinder (nitric acid) or with a calibrated pipette. The suspension was stirred for 3 days at room temperature and filtered through a 0.45-micron nylon membrane filter into a plastic receiving vessel. A relatively small amount of colorless solid was left on the filter. No precipitation from the light blue-violet filtered solution was observed during the ensuing months of experimental work.

The concentrations of the nitric acid stock solutions were measured by potentiometric titration using a standardized NaOH solution. To obtain the acid concentration of the INEEL simulant, where determining the titration breakpoint can be complicated by concomitant base-consuming metal hydrolysis, the measurement was made either by 1) adding an aliquot of INEEL simulant to DI water and using only the first observed break point during the potentiometric titration to determine the free acid concentration or 2) performing the measurement by adding an aliquot of INEEL simulant into a 0.5 M sodium oxalate solution and then performing the potentiometric titration.

Solutions of ^{203}Hg (in 1 M hydrochloric acid) and ^{95}Zr (in 0.5 M oxalic acid) were obtained from Isotope Products Laboratories. Strontium-85 (initially in 0.5 M hydrochloric acid, diluted to 1 mM hydrochloric acid before use) was obtained from NEN Life Science Products. Before use, the oxalic acid in the ^{95}Zr solution was destroyed by evaporation of the solution, followed by repeated contacts with either concentrated nitric acid or 30% hydrogen peroxide as previously described (Brewer et al. 1998). The final ^{95}Zr residue was dissolved in a small amount of 2 M nitric acid and passed through a 0.2-micron syringe filter into a glass receiving vial. The reaction vessel was rinsed thrice with additional portions of 2 M nitric acid, and these rinsings also passed through the syringe filter. Other tracers, uranium (^{233}U) in 0.155 M nitric acid, ^{239}Pu in 7 M nitric acid, and ^{241}Am in 0.01 M nitric acid, were obtained from in-house stocks.

Table 2.1. Composition of INEEL Simulant

Component	**Reagent**	**Target conc. M**	**Calc. Conc. M, 1st batch**	**Calc. Conc. M, 2nd batch**
Al	$Al(NO_3)_3 \bullet 9H_2O$	6.52E-01	6.52E-01	6.52E-01
B	H_3BO_3	2.04E-02	2.04E-02	2.04E-02
Ca	$Ca(NO_3)_3 \bullet 4H_2O$	5.65E-02	5.63E-02	5.63E-02
Ce	$Ce(NO_3)_3 \bullet 6H_2O$	2.28E-05	2.35E-05	2.42E-05
Cr	$Cr(NO_3)_3 \bullet 9H_2O$	5.77E-03	5.80E-03	5.79E-03
Cs	$CsNO_3$	9.11E-06	1.85E-05	1.15E-05
Fe	$Fe(NO_3)_3 \bullet 9H_2O$	2.40E-02	2.40E-02	2.40E-02
Hg	$HgCl_2$	1.82E-03	1.83E-03	1.82E-03
K	KNO_3	1.95E-01	1.95E-01	1.95E-01
Mn	$Mn(NO_3)_2$	1.45E-02	1.46E-02	1.45E-02
Mo	Na_2MoO_4	7.42E-04	7.58E-04	7.53E-04
Na	$NaNO_3$	1.68E+00	1.68E+00	1.68E+00
Nd	$Nd(NO_3)_3 \bullet 6H_2O$	3.81E-05	3.86E-05	4.29E-05
Ni	$Ni(NO_3)_2 \bullet 6H_2O$	2.39E-03	2.43E-03	2.41E-03
Pb	$Pb(NO_3)_2$	1.15E-03	1.17E-03	1.15E-03
PO_4	KH_2PO_4	7.72E-03	7.72E-03	7.75E-03
Pr	$Pr(NO_3)_3 \bullet 6H_2O$	1.06E-05	1.38E-05	1.21E-05
Zr	$ZrO(NO_3)_2 \bullet 2H_2O$	1.43E-02	1.43E-02	1.44E-02
HNO_3	HNO_3	1.90E+00	1.90E+00	1.90E+00
HCl	HCl	3.15E-02	3.16E-02	3.18E-02
HF	HF	9.81E-02	9.80E-02	9.83E-02
H_2SO_4	H_2SO_4	4.41E-02	4.41E-02	4.41E-02
Total $[H^+]$**		2.14E+00*	2.14E+00*	2.14E+00*
Total $[NO_3^-]$		5.99E+00	6.00E+00	6.00E+00
Total $[Cl^-]$		3.15E-02	3.52E-02	3.91E-02

* Defined here as the sum of [HF] + [HCl] +$[HNO_3]$ + 2*$[H_2SO_4]$ + 2*$[KH_2PO_4]$

** Measured total $[H^+]$ = 1.93 M.

The TRUEX extractant solution was prepared by adding 40.8 g of octyl(phenyl)-N,N-diisobutylcarbamoylphosphine oxide (CMPO) (Strem Chemicals) and 184 g of tributyl phosphate (in-house stock) in a 500-mL volumetric flask and filling it to the mark with Isopar L® (Exxon Chemical). A stir bar was added, the flask was capped, and the contents were stirred for 3 days. This organic solution then was contacted thrice with 0.25 M sodium carbonate at an organic to aqueous phase ratio (O/A) of 2 and filtered through a medium sintered glass fritte. The clear filtrate was tested by measuring the D(Am) values following contact of a 1-mL pre-equilibrated TRUEX solution with 1 mL of 0.01, 0.04, 0.2, and 2 M nitric acid solutions, respectively, with each solution containing an additional 5 microliters of the ^{241}Am stock solution. Two batches of TRUEX were prepared and tested in this way; the results are shown in Table 2.2.

Liquid-liquid distribution values were measured by pre-equilibrating the organic phase with fresh aqueous phase (O/A = 1) three times and then contacting the pre-equilibrated organic phase with an aqueous phase containing the tracer of interest. The phases were agitated by vortex mixing for 1 min and separated by centrifugation for at least 1 min. Aliquots of each phase were removed for activity measurements. The gamma activity of an aliquot was measured by gamma energy analysis (GEA) of the sample in a 2-dram vial containing 1 mL of ethanol. For ^{203}Hg, the photopeak at 279.2 keV was used, for ^{85}Sr, the photopeak at 514 keV was used, and for ^{95}Zr, both photopeaks at 724.2 and 756.7 keV were used. The alpha activity of an aliquot was measured for the ^{239}Pu, ^{241}Am, and ^{233}U isotopes by liquid scintillation counting of the aliquot in 10 to 15 mL of Ultima Gold AB liquid scintillation cocktail containing an equal volume of the opposite phase. This other phase was added to ensure that each phase was counted in an identical matrix to minimize potential variable quenching effects. Since the samples used to calculate distribution values were counted within minutes to hours in all instances, decay corrections were not employed. All sample activities were corrected for background activity.

Solid-liquid distribution values for Sr•Spec® resin were obtained by adding a known amount of resin to a known volume of liquid containing ^{85}Sr, ^{203}Hg, and stable Sr corresponding to 20% of the resin's reported capacity. Sample slurries were shaken overnight, filtered through a 0.2-micron syringe filter, aliquots removed, and the aliquot's activity determined by GEA. Distribution values were obtained by comparing the activity of the sample after resin contact with the activity measured from an aliquot taken before resin contact and using the relationship:

$$K_d = [(A_0-A_{eq})/A_{eq}] * (V/m) \tag{1}$$

where A_0 refers to the aqueous solution activity before resin addition, A_{eq} refers to the aqueous solution activity after resin contact, V refers to the volume of the aqueous solution in mL, and m refers to the resin's dry mass in grams.

Table 2.2. D(Am) as f(HNO_3)

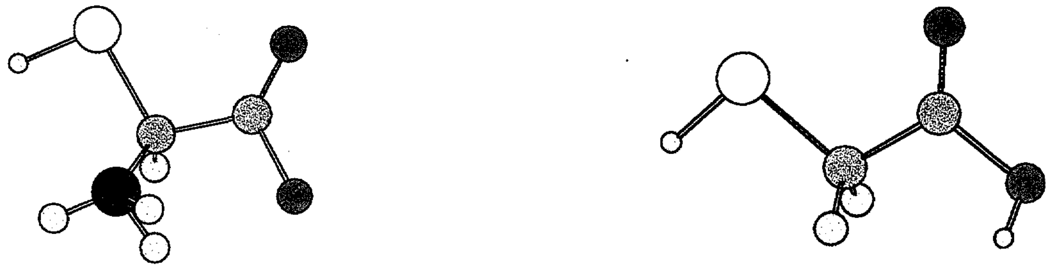
Eq. (HNO_3)	Found D(Am) - 1st batch of TRUEX	Found D(Am) – 2nd batch of TRUEX	Expected[(a)] D(Am)
1.89	24.3	23.1	> 20
0.19	2.50	2.31	1.9 to 2.2
0.038	0.112	0.266	0.08 to 0.4
0.01	0.045	0.02	0.008 to 0.03
(a) INEEL staff, private communication.			

3.0 Results

3.1 Selection of Candidate Molecules for Selective Mercury Complexation

A search of an electronic version of the IUPAC stability constants database (Pettit and Powell 1993–1997) was performed to identify potential candidate agents for the selective complexation of mercury in the presence of actinides. To be selected as a potential candidate, the compound needed a large absolute affinity for mercury as well as a substantial difference in the affinity of mercury compared to the other metals (and especially the radionuclides) present in INEEL tank waste. Other considerations included high aqueous solubility, commercial availability, low cost, and low toxicity. As might be expected, all of the molecules with the strongest affinity for mercury shared the common characteristic of a thiol (RSH), thiocarboxylate (RC(O)SH) or dithiocarboxylate (RC(S)SH) functionality. Two candidates were judged to best meet the criteria mentioned above, cysteine [$(NH_3)(SH)CHCO_2$] and mercaptoethanolic acid (thioglycolic acid) [$HSCH_2CO_2H$]. Figure 3.1 shows the structure of these molecules and summarizes some key properties. Table 3.1 summarizes some key binding constant information.

Both of these molecules show similar binding characteristics to a variety of metals. Both complex strongly to Hg(II), with both molecules exhibiting a β_2 of over 40. Both molecules appear, to the extent data are available, to be selective for Hg(II) over lanthanide and actinide (III) and (IV) ions and even uranyl ion, where a greater than 30 orders of magnitude preference for Hg(II) exists. The high water solubility reported for these candidate molecules bodes well for partitioning of the mercury complexes to the aqueous phase if used in a TRUEX process flowsheet. However, the thioglycolic acid is reported also to be soluble in organic liquids, such as chloroform, benzene, and ether. It seems likely that, under the acidic conditions present in TRUEX processing, the neutral thioglycolic acid might partition substantially to the organic phase, whereas the cysteine, which always is present in an ionic form, will be less likely to partition to the organic phase. For this reason, cysteine was chosen as the ligand most suitable for testing.



Cysteine (Zwitterionic form)
FW: 121.16 (157.61 as hydrochloric acid salt)
Highly water soluble
pK_as: 1.71, 8.33, 10.78
Cost: 100g/$37 (hydrochloric acid salt, Aldrich)
Naturally occurring non-essential amino acid

Thioglycolic acid (TGA)
FW: 92.12 (114.1 as Na salt)
Highly water soluble
pK_as: 3.68, 10.68
Cost: 2.39 kg/$472 (Aldrich)
LD50 (oral in rats): 0.15 mL/kg

Figure 3.1. Candidate Molecules for Selective Mercury Complexation

Table 3.1. Summary of Binding Constant Measurement of Cysteine and Thioglycolic Acid to Selected Metal Ions

Metal	Log K_1 (Cysteine)	Log K_2 (Cysteine)	Log K_1 (TGA)	Log K_2 (TGA)
Hg(II)	37.8 (I = 1.0)(a)	6.2 (I = 1.0)(a)	34.5 (I = 0.1)(a)	6.0 (I = 0.1)(a)
Pb(II)	12.21 (I = 1.0)(b)	6.36 (I = 1.0)(b)	8.5 (I = 0.002)(c)	-
UO_2(II)	5.84 (I = 0.1)(d)	6.01 (I = 0.1)(d)	2.88 (I = 0.1)(e)	2.40 (I = 0.1)(e)
Am(III)	4.2 (I = 1.0)(f)	-	1.55 (I = 0.5)(g)	1.05 (I = 0.5)(g)
Ce(III)	-	-	1.43 (I = 2.0)(h)	0.7 (I = 2.0)(h)
Th(IV)	7.56 (I = 0.1)(i)	7.29 (I = 0.1)(i)	-	-

(a) Basinger et. al. 1981
(b) Corrie et al. 1976
(c) Li and Manning 1955
(d) Nourmand and Meissami 1982
(e) Cefola et al. 1962
(f) Rogosina et al. 1974
(g) Grenthe 1962
(h) Bear et al. 1962
(i) Nourmand and Meissami 1983

3.2 Batch Contact Testing

3.2.1 Background

3.2.1.1 Mercury Distribution Behavior in the Presence of Cysteine

The following experiments evaluated the effectiveness of cysteine at enhancing the partitioning of mercury to the aqueous phase under TRUEX processing conditions:

3.2.1.1.1 D(Hg) as f[L-cysteine HCl] and f[HNO_3]

Fifteen mL of TRUEX solvent was pre-equilibrated with 2 M nitric acid. The TRUEX solvent was next contacted with an aqueous solution containing ^{203}Hg with an approximate bulk composition of 0.1 mM in mercuric chloride, 2 M in nitric acid, and ca. 0.0067 M in hydrochloric acid. The aqueous phase was removed, and the organic phase was contacted three times with a fresh aqueous phase 0.01 M in nitric acid and 1 mM in sodium chloride. The purpose of these contacts was to reduce the amount of nitric acid co-extracted in the organic phase while sodium chloride was introduced to minimize the partitioning of mercury to the aqueous phase during these scrub steps (Herbst 1995). The distribution values for mercury D(Hg) were measured for each step and are reported in Table 3.2.

One-mL samples of this mercury-loaded TRUEX solvent were then contacted with 1-mL samples of nitric acid solutions containing varying amounts of nitric acid and L-cysteine hydrochloric acid. The impact of changing nitric acid and cysteine concentrations is summarized in Figure 3.2.

Several aspects of the results illustrated in Figure 3.2 are noteworthy. First, the trends in D(Hg) as a function of nitric acid concentration generally agree well with a previous literature report on TRUEX extraction of mercury, especially the decrease in D(Hg) observed at ca. 0.5 M or greater (nitric acid) (Herbst et al. 1995). The magnitude of the D(Hg) values found here also agrees fairly well with this previous study.

Table 3.2. D(Hg) for TRUEX Extraction and 0.01 M Nitric Acid Scrub Steps

Stage	D(Hg)
Extraction	5.3
1st scrub	6.5
2nd scrub	8.8
3rd scrub	5.1

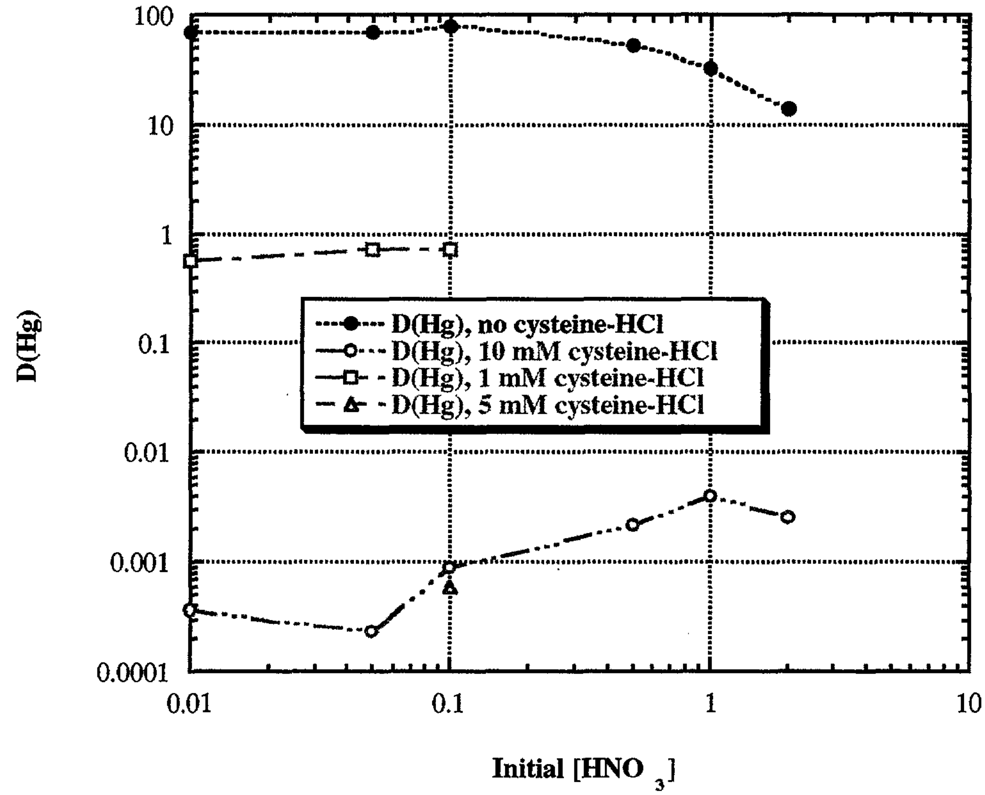


Figure 3.2. Log-Log Plot Illustrating the Effect of L-Cysteine as f[HNO_3] on D(Hg) from Mercury-Loaded TRUEX Solvent

The impact of having the L-cysteine hydrochloric acid salt present in the aqueous phase is impressive, with the partitioning of mercury to the aqueous phase increasing by up to 5 orders of magnitude. Even concentrations of cysteine as low as 1 mM (which is still an order of magnitude or more greater than the total mercury concentration) have a marked inhibition on mercury extraction by the TRUEX solvent. Based on the very limited amount of data obtained, it appears that cysteine concentrations greater than 5 mM have little additional impact on D(Hg). Finally, it appears that the effectiveness of cysteine at inhibiting mercury extraction by TRUEX solvent may have some acid dependence, with its effectiveness beginning to decrease in solutions more acidic than 0.1 M nitric acid. Fortunately, the observed decrease in effectiveness is small and to some extent may be an experimental artifact as the uncertainty in the very low distribution measurements obtained with 5 and 10 mM cysteine is typically 20% or greater for each data point. The decreasing effectiveness of cysteine at inhibiting mercury extraction by TRUEX is mitigated to a minor extent by the decrease in D(Hg) that occurs in the absence of cysteine at these higher nitric acid concentrations. In any event, the capability of cysteine to suppress mercury extraction by TRUEX from simple nitric acid/chloride solutions is striking and promising for its potential application throughout the TRUEX process flowsheet.

3.2.1.1.2 Kinetics of D(Hg) at a Given (nitric acid) and (L-cysteine hydrochloric acid)

One-mL portions of a mercury-loaded TRUEX solution prepared as described above were contacted with 1-mL portions of an aqueous phase 0.1 M in nitric acid and 10 mM in L-cysteine hydrochloric acid. The samples were agitated by vortex stirring for various lengths of time. The vortex stirring was stopped, the phases were separated by centrifugation, and the distribution of mercury was measured. The results are illustrated in Figure 3.3.

The system appears to reach equilibrium rapidly in the stripping of mercury, with D(Hg) requiring between 30 and 60 sec to reach a constant value. This experiment, which looks at the stripping of mercury from a loaded TRUEX solvent after contact with a fresh 0.1 M nitric acid solution, reaches a similar conclusion as a previously described experiment that looked at the rate of mercury extraction from 1 M nitric acid after contact with fresh TRUEX solvent (Herbst et al. 1995). In that previous study, equilibrium in the mercury extraction by TRUEX occurred rapidly, requiring no more than 15 sec of contact time.

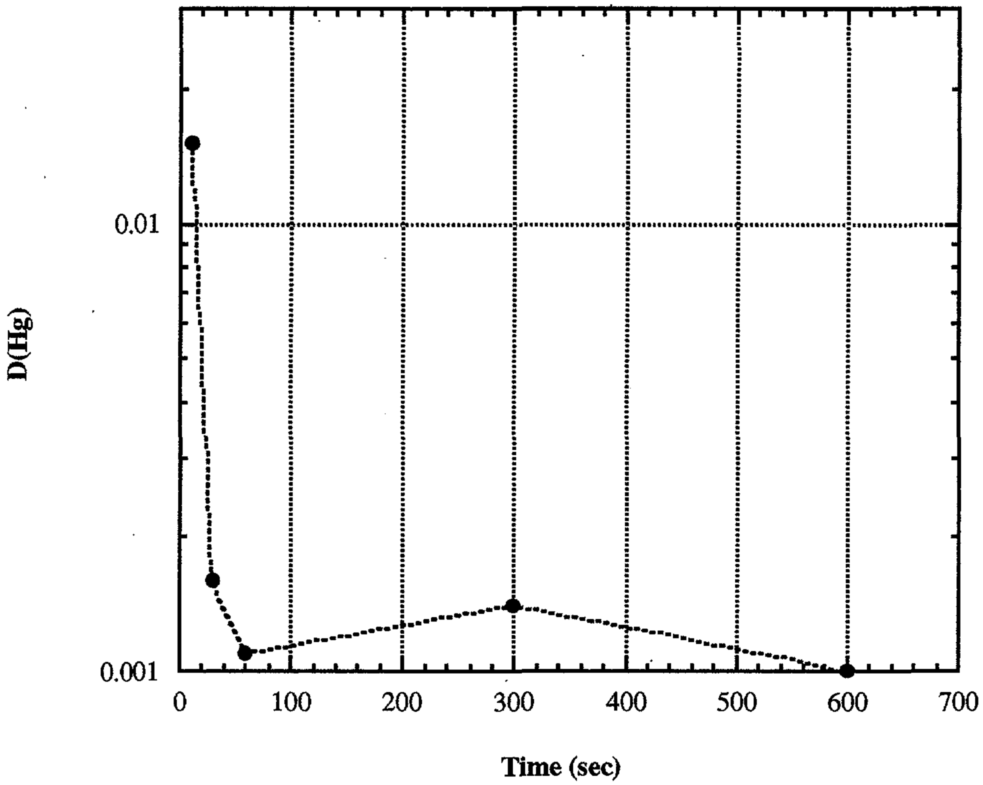


Figure 3.3. Kinetics of Hg(II) Stripping from TRUEX Solvent by 0.1 M Nitric Acid/10 mM L-Cysteine Hydrochloric Acid

3.1.1.1.3 L-Cysteine Hydrochloric Acid Solution Stability

The stability of nitric acid solutions containing L-cysteine hydrochloric acid was tested by measuring D(Hg) from a mercury-loaded TRUEX solution 3 weeks after an initial measurement. The results, shown in Table 3.3, indicate that only a modest decrease in efficacy occurs in L-cysteine hydrochloric acid's capability to compete with the TRUEX solvent for mercury complexation in acidic solutions.

Table 3.3. Changes in D(Hg) After 3 Weeks After Contact of Mercury-Loaded TRUEX Solution by 1 and 0.01 M Nitric Acid/10 mM L-Cysteine Hydrochloric Acid Solutions

Initial Nitric Acid Concentration, M	D(Hg) – Freshly Prepared Aqueous Solution	D(Hg) – 3-Week Old Aqueous Solution
0.01	0.00037	0.00091
1	0.0040	0.0053

3.2.1.1.4 The Impact of L-Cysteine Hydrochloric Acid on D(Hg) from INEEL Simulant Solutions

The above tests seem to indicate that in the absence of other, potentially competing metals, cysteine can be quite effective at inhibiting the extraction of mercury by TRUEX solvent. However, actual waste solutions contain a variety of other metals. Under these conditions, a sufficient amount of cysteine might be sequestered by other metal ions so that the capability of cysteine to inhibit mercury extraction could be compromised. To test this possibility, a sample of TRUEX solvent pre-equilibrated with 2 M nitric acid (the approximate free acid concentration of the INEEL simulant) was contacted with INEEL simulant (O/A = 1) that had been spiked with ^{203}Hg tracer. D(Hg) was measured for this contact and for a similar contact where the INEEL simulant was also made 10 mM in L-cysteine hydrochloric acid. The results, shown in Table 3.4, indicate that addition of L-cysteine hydrochloric acid to a high nitrate, high total metal-ion solution such as the INEEL simulant is still capable of effectively inhibiting mercury extraction by the TRUEX solvent. It is worth noting that the D(Hg) values here in the absence of L-cysteine hydrochloric acid agree well with similar D(Hg) values on actual (Herbst et al. 2000; Law et al. 1996; Law et al. 1998a and 1998b) and simulated (Brewer et al. 1995) INEEL waste during the initial extraction stages of the TRUEX process.

Table 3.4. The Effect of 10 mM L-Cysteine Hydrochloric Acid on Mercury Extraction by TRUEX

Aqueous Phase Composition	D(Hg)
INEEL simulant	1.92
INEEL simulant/10 mM L-cysteine hydrochloric acid	0.0007

3.2.1.2 Am Distribution Behavior in the Presence of Cysteine

TRUEX solutions pre-equilibrated with nitric acid were contacted with ^{241}Am-spiked aqueous solutions containing varying amounts of nitric acid in the presence or absence of 10 mM L-cysteine hydrochloric acid in the aqueous phase. The results are shown in Figure 3.4.

Clearly, for nitric acid concentrations of 0.1 M or above, the influence of cysteine on D(Am) is insignificant. This is the most important range from a TRUEX processing standpoint since most TRUEX flowsheets generally require at least a 0.1 M or greater nitrate concentration in the extraction and scrub stages. At the lower nitric acid concentrations examined, from 0.01 to 0.1 M, D(Am) appears to decrease slightly in the presence of cysteine, but the impact on cysteine overall on D(Am) appears to be minor to non-existent.

A second test was performed where the TRUEX solvent was pre-equilibrated with 2 M nitric acid (approximately the amount of nitric acid present in the INEEL simulant) and then was contacted with an INEEL simulant simultaneously spiked with ^{203}Hg and ^{241}Am. The organic phase was then contacted with either a 0.01 or 0.1 M nitric acid solution or a 0.01 or 0.1 M nitric acid solution containing 10-mM L-cysteine hydrochloric acid. The results are shown in Table 3.5.

This test verifies the conclusions from previous measurements, namely, that the presence of cysteine has no impact on D(Am), but dramatically reduces D(Hg). The lack of influence on the initial aqueous

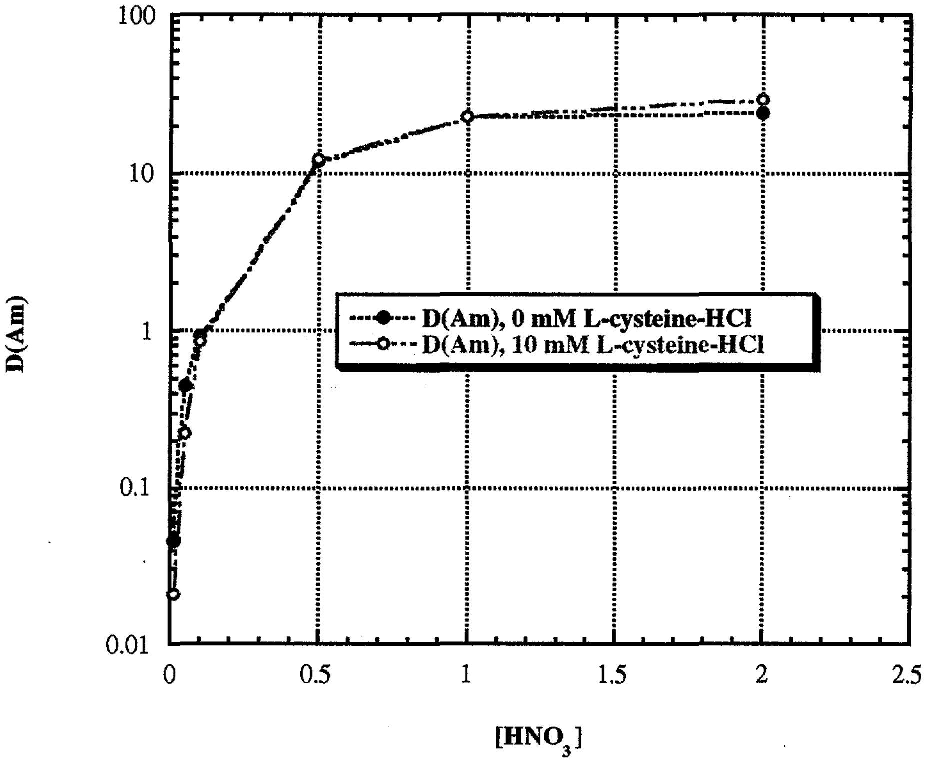


Figure 3.4. D(Am) as f(HNO$_3$) for TRUEX Solvent in the Presence or Absence of 10 mM L-Cysteine Hydrochloric Acid

(nitric acid) upon D(Am) and D(Hg) comes from the fact that the total amount of nitric acid in the system is dominated by the amount of nitric acid initially present in the aqueous phase (making the final equilibrium aqueous nitric acid concentration in both cases about 0.5 M).

Table 3.5. The Effect of 10 mM L-Cysteine HCl on D(Am) and D(Hg) from TRUEX Extractant Following Contact with Mercury and Am-Spiked INEEL Simulant

Initial (HNO$_3$)	D(Am)	D(Hg)
0.1 M Nitric Acid/10 mM L-Cysteine Hydrochloric Acid	15	0.002
0.1 M Nitric Acid	15	23
0.01 M Nitric Acid/10 mM L-Cysteine Hydrochloric Acid	15	0.002
0.01 M Nitric Acid	15	23

3.2.1.3 Pu^{4+} Distribution Behavior in the Presence of Cysteine

Samples of TRUEX solutions pre-equilibrated with nitric acid were contacted with ^{239}Pu-spiked aqueous solutions containing varying amounts of nitric acid in the presence or absence of 10-mM L-cysteine hydrochloric acid in the aqueous phase. The results are shown in Figure 3.5.

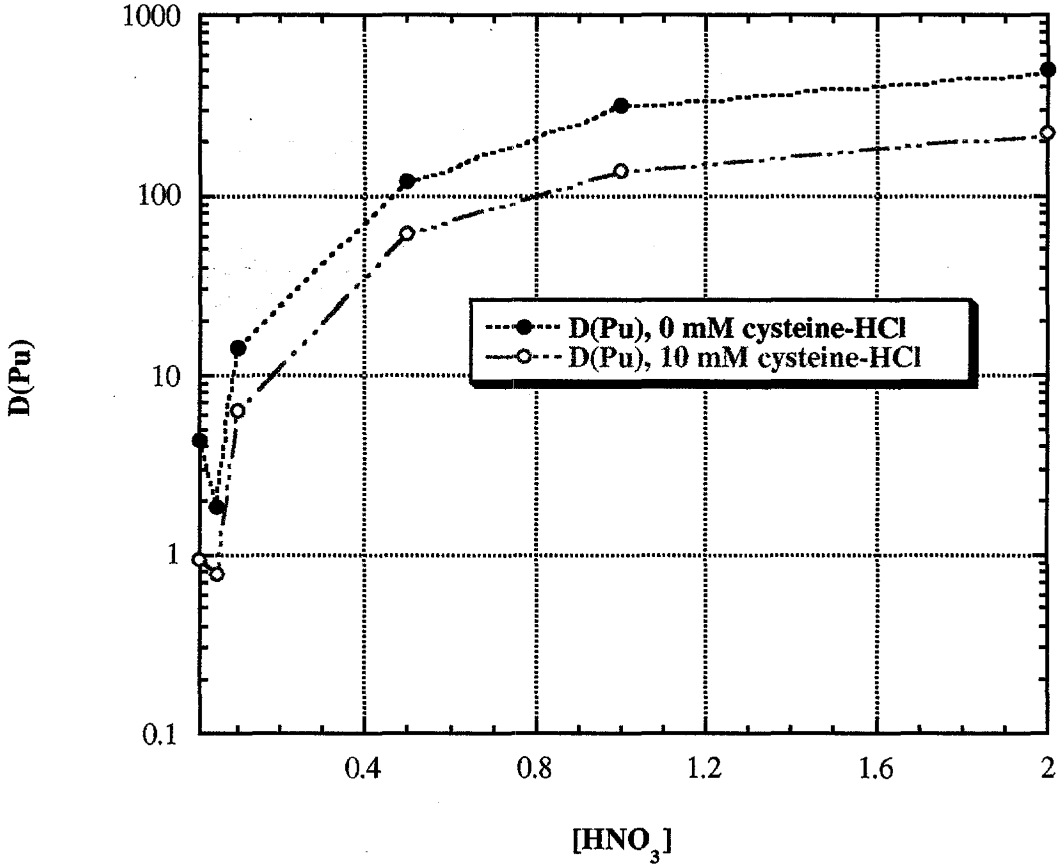


Figure 3.5. D(Pu) as f(HNO$_3$) for TRUEX Solvent in the Presence or Absence of 10 mM L-Cysteine Hydrochloric Acid

As was observed with Am, the presence of L-cysteine hydrochloric acid causes no significant change in D(Pu) at high nitric acid concentrations. Again like Am, a small decrease in the observed distribution value is found at low nitric acid concentrations. This could be caused by complexation of the Pu by cysteine at these lower acid concentrations, an explanation also applicable to Am. Another possibility, especially at higher acid concentrations, is that the cysteine acts as a reductant and reduces some of the Pu^{4+} to Pu^{3+}, with the corresponding observed decrease in D(Pu). The increase in D(Pu) at the lowest (0.01 M) nitric acid concentration examined is probably due to trace amounts of acidic impurities present in the TRUEX solvent.

3.2.1.4 UO_2^{2+} Distribution Behavior in the Presence of Cysteine

Samples of TRUEX solutions pre-equilibrated with nitric acid were contacted with ^{233}U-spiked aqueous solutions containing varying amounts of nitric acid in the presence or absence of 10 mM L-cysteine hydrochloric acid in the aqueous phase. The results are shown in Figure 3.6.

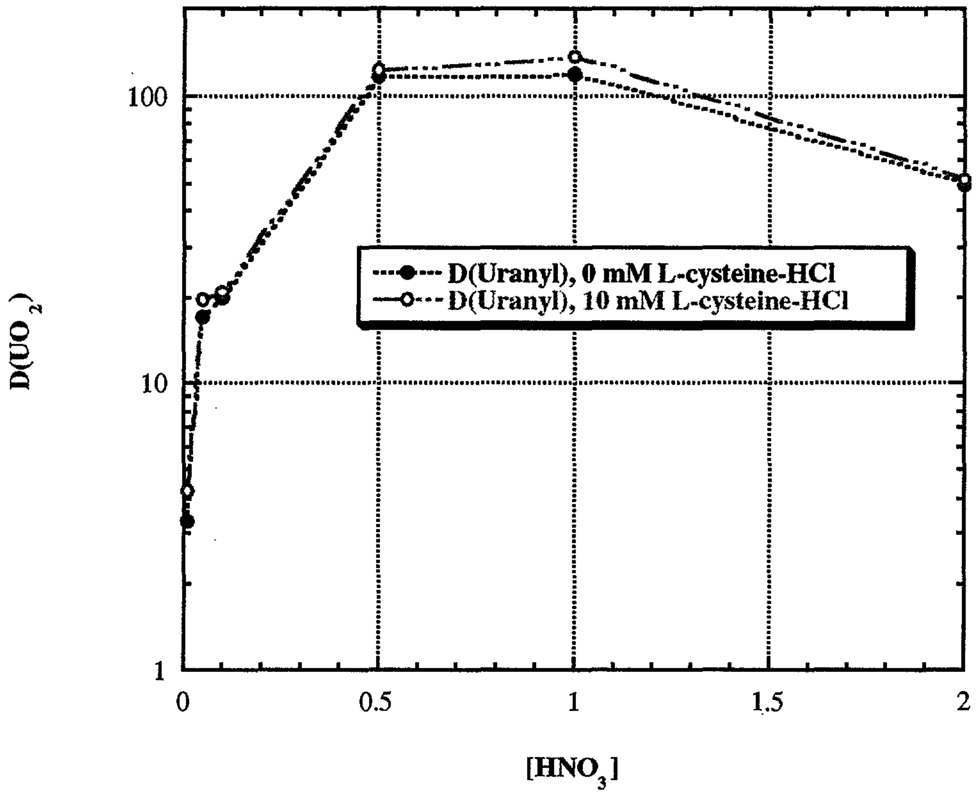


Figure 3.6. $D(UO_2^{2+})$ as $f(HNO_3)$ for TRUEX Solvent in the Presence or Absence of 10 mM L-Cysteine Hydrochloric Acid

The behavior of D(uranyl) parallels that of D(Am) and D(Pu) as a function on nitric acid concentration, although the decrease in D(uranyl) at low nitric acid concentrations is very small; indeed, it is found only at the lowest nitric acid concentration observed, 0.01 M.

3.2.1.5 Zr Distribution Behavior in the Presence of Cysteine

Samples of TRUEX solutions pre-equilibrated with nitric acid were contacted with ^{95}Zr-spiked aqueous solutions containing varying amounts of nitric acid in the presence or absence of 10 mM L-cysteine hydrochloric acid and in the presence of added non-radioactive Zr in the aqueous phase. The results are shown in Figure 3.7. In addition, ^{95}Zr-spiked INEEL simulant (both in the presence and absence of 10 mM L-cysteine hydrochloric acid) was contacted with TRUEX solvent that had been pre-equilibrated by three previous contacts (O/A = 1) with fresh, unspiked INEEL simulant. The results are shown in Table 3.6. These experiments indicate that 1) the presence of L-cysteine hydrochloric acid has little impact of D(Zr), 2) the increase in D(Zr) found when non-radioactive Zr is present suggests that some amounts of oxalic acid remain in the radioactive Zr stock solution in sufficient quantities to depress zirconium extraction, and 3) L-cysteine hydrochloric acid by itself will not prevent zirconium extraction during the TRUEX extraction stages.

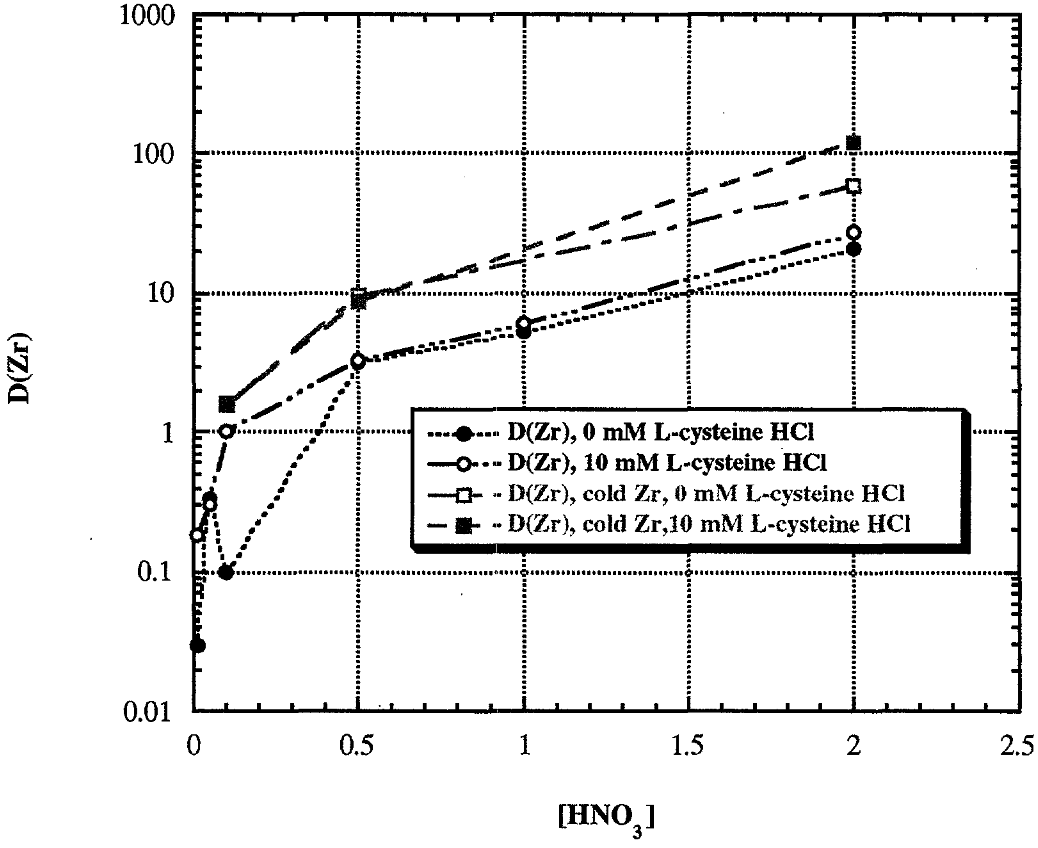


Figure 3.7. D(Zr) as f(HNO$_3$) for TRUEX Solvent in the Presence or Absence of 10 mM L-Cysteine Hydrochloric Acid

Table 3.6. The Effect of 10 mM L-Cysteine HCl on D(Zr) from Pre-Equilibrated TRUEX Extractant Following Contact with Zr-Spiked INEEL Simulant

Aqueous Phase	D(Zr)
INEEL Simulant	56
INEEL Simulant/10 mM L-Cysteine hydrochloric acid	31

3.2.1.6 Am Distribution Behavior in the Presence of Ammonium Bioxalate

The impact of two potential stripping agents, ammonium bioxalate (the use of ammonium oxalate and bioxalate for the stripping of actinides from TRUEX-containing organic phases has been previously demonstrated – Horwitz et al. 1990; Yamaura and Matsuda 1999) and ascorbic acid on important INEEL waste constituents was next examined. The tests were performed by generating a radionuclide-loaded TRUEX stock solution, prepared by first contacting an INEEL simulant solution with TRUEX at a 2:1 (O/A) ratio. The organic phase was then contacted three times with fresh 0.1 M nitric acid at an O/A of 1 to scrub excess acid from the TRUEX solvent. Samples of this organic phase were then contacted with the aqueous solutions described below. Because of their envisioned use in the strip stages, distribution measurements were made only at low nitric acid concentrations.

Two acid concentrations (0.04 M nitric acid and DI water for ammonium bioxalate and 0.04 M and 0.01 M nitric acid for ascorbic acid) and two stripping-agent concentrations (0.1 and 0.01 M) were tested. Am is an exception in that only ammonium bioxalate was tested as a stripping agent. The results of this test are shown in Figure 3.8 and indicate that ammonium bioxalate does indeed act as an effective Am stripping agent.

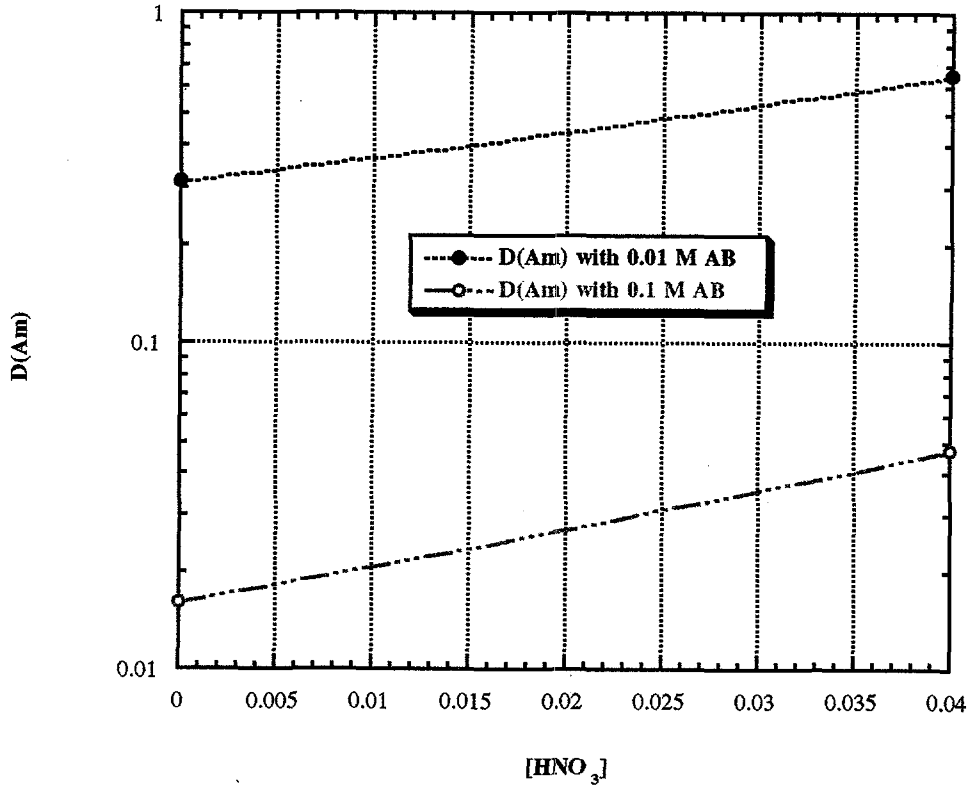


Figure 3.8. D(Am) for TRUEX Contacts at 0 and 0.04 M Nitric Acid and 0.01 and 0.1 M Ammonium Bioxalate

3.2.1.7 Pu^{4+} Distribution Behavior in the Presence of Ammonium Bioxalate and Ascorbic Acid Stripping Agents

The effect of ammonium bioxalate and ascorbic acid solutions on D(Pu^{4+}) were investigated. The results of these experiments are summarized graphically in Figure 3.9. Several features are noteworthy. First, although in nitric acid itself, the D(Pu^{4+}) from 0.04 to 0.1 M nitric acid remains far too high (> 1) for stripping, the addition of either a reducing agent (0.1 M ascorbic acid) or a complexant, ammonium bioxalate generates adequate stripping agents). Second, the ammonium bioxalate, even at 0.01 M, is more effective than 0.1 M ascorbic acid at a comparable nitric acid concentration. Third, the 0.1 M ascorbic acid/0.04 M nitric acid contacts yielded almost identical results whether or not the scrubbed Pu-loaded TRUEX solvent was used or whether a TRUEX solvent simply pre-equilibrated with nitric acid/0.1 M ascorbic acid solution was contacted with the Pu-spiked aqueous phase. This indicates both that the scrub steps were effective at stripping out excess nitric acid from the INEEL simulant contact and that the amount of nitric acid remaining in the organic phase after these scrubs is, as expected, insufficient to perturb the total nitric acid introduced initially by the aqueous phase.

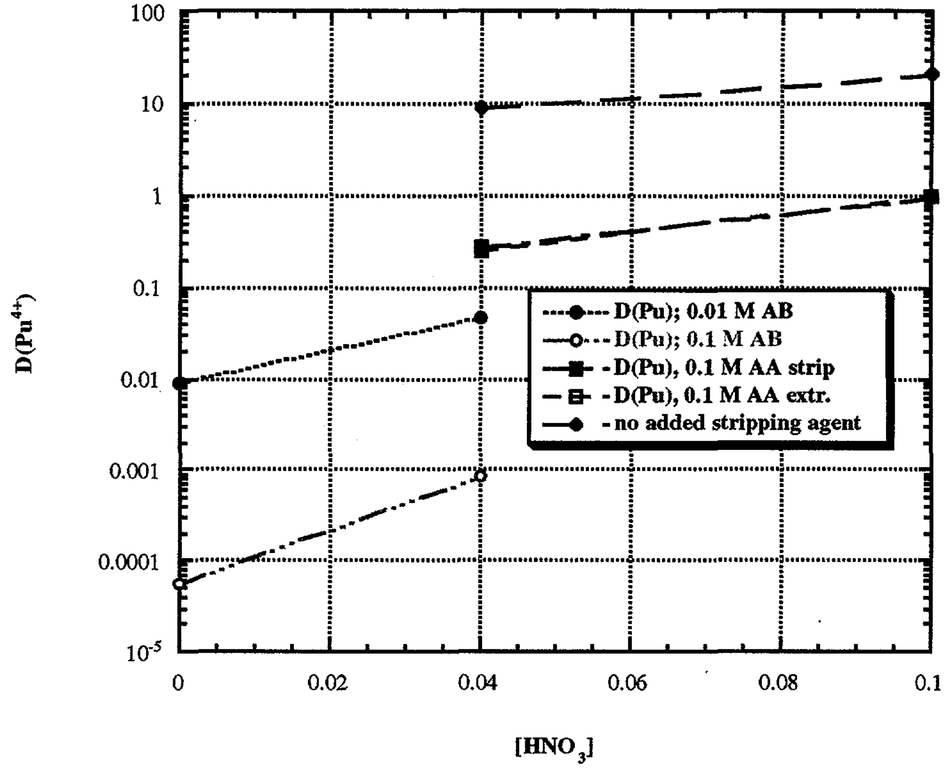


Figure 3.9. $D(Pu^{4+})$ for TRUEX Contacts as $f(HNO_3)$ with no Added Stripping Agent (0.04 and 0.1 M nitric acid), 0.01 and 0.1 M Ammonium Bioxalate (DI water and 0.04 M nitric acid) or 0.1 M Ascorbic Acid (at 0.04 and 0.1 M nitric acid)

3.2.1.8 Uranyl Distribution Behavior in the Presence of Ammonium Bioxalate and Ascorbic Acid Stripping Agents

The effect of ammonium bioxalate and ascorbic acid solutions on $D(UO_2^{2+})$ as a function of nitric acid were investigated. The results of these experiments are summarized graphically in Figure 3.10.

Unlike with Pu, only one of the stripping agents has an appreciable impact on the distribution of uranium. Ascorbic acid has no discernable impact on $D(UO_2^{2+})$ while ammonium bioxalate suppresses $D(UO_2^{2+})$ at low ($\geq$ 0.04 M) nitric acid concentrations. As might be expected, the suppression of $D(UO_2^{2+})$ increases as the concentration of ammonium bioxalate increases and requires a fairly concentrated solution, such as 0.1 M, to act as an effective stripping agent under TRUEX processing conditions.

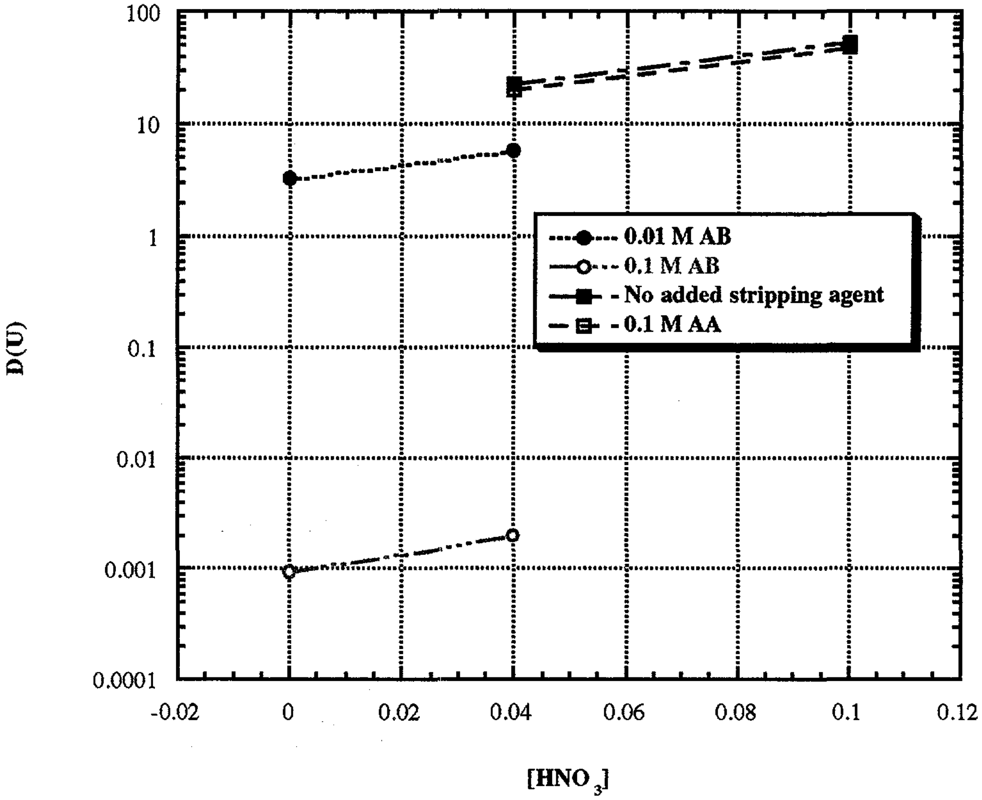


Figure 3.10. D(UO_2^{2+}) for TRUEX Contacts as f(HNO_3) with no Added Stripping Agent (0.04 and 0.1 M Nitric Acid), 0.01 and 0.1 M Ammonium Bioxalate (DI Water and 0.04 M Nitric Acid) or 0.1 M Ascorbic Acid (at 0.04 and 0.1 M Nitric Acid)

3.2.1.9 Mercury Distribution Behavior in the Presence of Ammonium Bioxalate and Ascorbic Acid Stripping Agents

The effect of ammonium bioxalate and ascorbic acid solutions on D(Hg^{2+}) as a function of nitric acid were investigated. The results of these experiments are summarized graphically below in Figure 3.11.

The key result illustrated in Figure 3.11 is that, like nitric acid itself, neither ammonium oxalate nor ascorbic acid are effective stripping agents for mercury at low nitric acid concentrations.

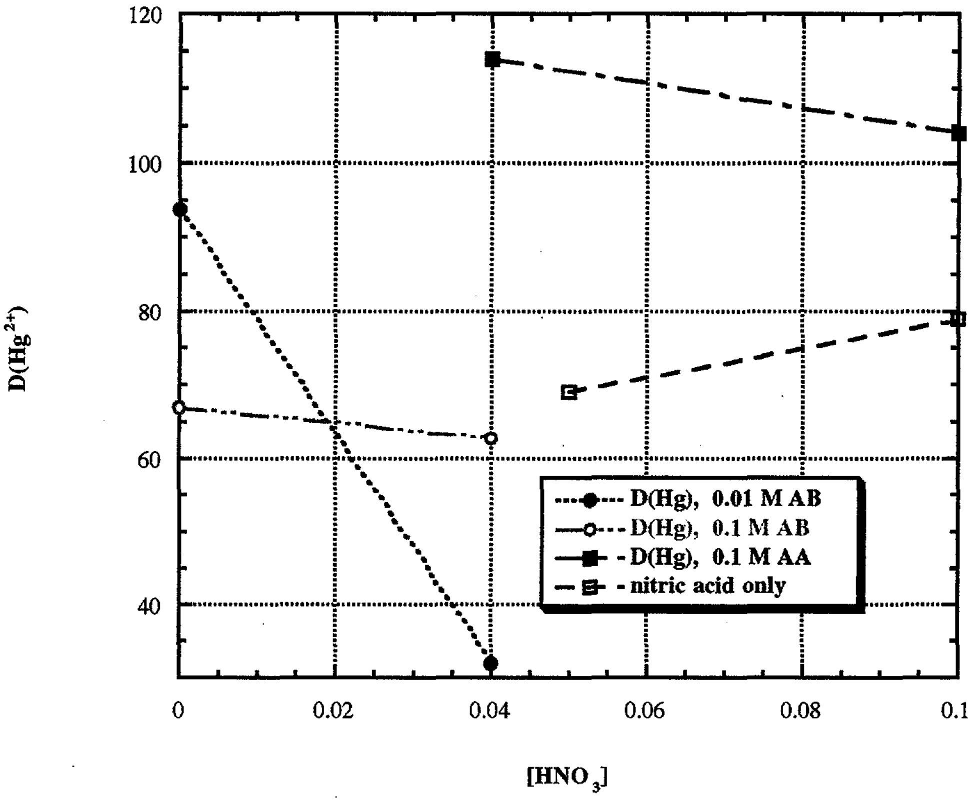


Figure 3.11. D(Hg^{2+}) for TRUEX Contacts as f(HNO_3) with no Added Stripping Agent (0.05 and 0.1 M Nitric Acid), 0.01 and 0.1 M Ammonium Bioxalate (DI Water and 0.04 M Nitric Acid) or 0.1 M Ascorbic Acid (at 0.04 and 0.1 M Nitric Acid)

3.2.1.10 Zirconium Distribution Behavior in the Presence of Ammonium Bioxalate and Ascorbic Acid Stripping Agents

The effect of ammonium bioxalate and ascorbic acid solutions on D(Zr) as a function of nitric acid were investigated. The results of these experiments are summarized graphically below in Figure 3.12.

Like uranyl ion, the choice of stripping agent has a marked effect on zirconium distribution. The effect of 0.1 M ascorbic acid at low nitric acid concentration, as might be expected, is negligible. However, the presence of ammonium oxalate markedly depresses the partitioning of zirconium to the organic phase, with even 0.01 M ammonium oxalate solutions acting as a highly effective stripping agent at low nitric acid concentrations.

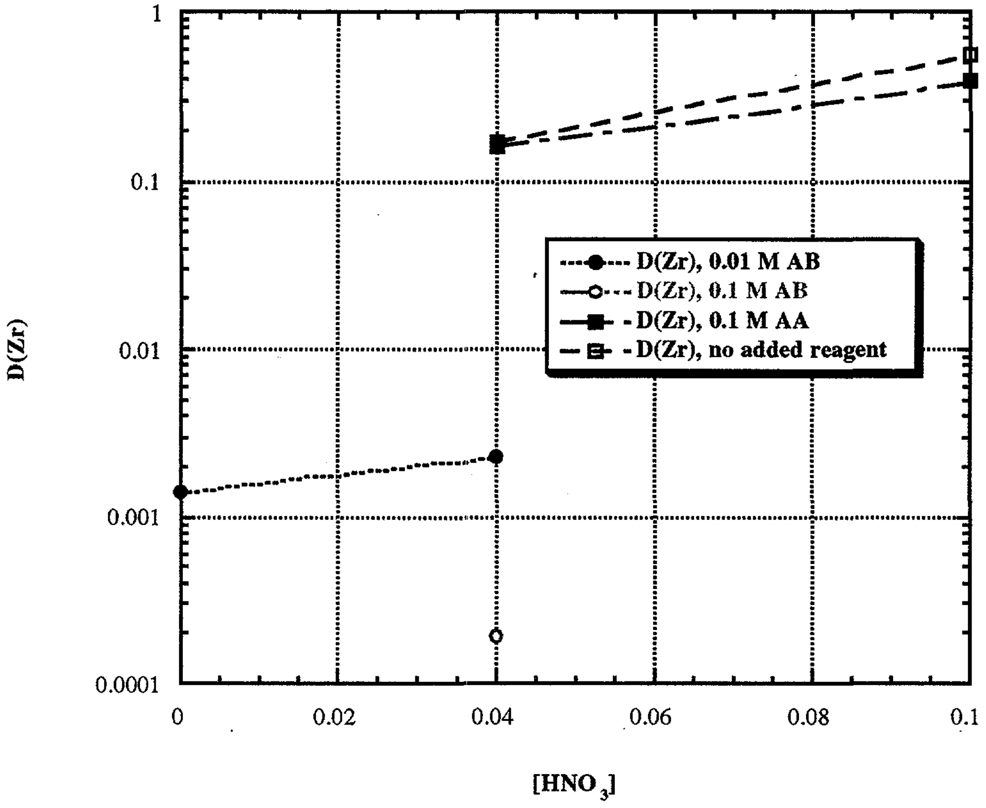


Figure 3.12. D(Zr) for TRUEX Contacts as f(HNO_3) with no Added Stripping Agent (0.05 and 0.1 M Nitric Acid), 0.01 and 0.1 M Ammonium Bioxalate (DI Water and 0.04 M Nitric Acid) or 0.1 M Ascorbic Acid (at 0.04 and 0.1 M Nitric Acid)

3.2.1.11 The Impact of Oxalic Acid and Hydrofluoric Acid on Metal Distribution from INEEL Simulant

Oxalic acid and hydrofluoric acid were investigated for their effectiveness at selectively inhibiting Zr extraction by TRUEX from an INEEL simulant solution. March and Yarbro (1988) have shown that the presence of fluoride has little impact on the distribution values of Am(III) by TRUEX-like extractant, although it markedly suppresses Pu(IV) distribution values. Zr(IV) is known to strongly bind to fluoride, so one potential approach to prevent Zr extraction by TRUEX would be to add fluoride to the feed. Given the large amount of other metals, such as Al, that also strongly complex F, it was decided to add sufficient fluoride to generate at least 0.1 M free fluoride even if three equivalents of fluoride were sequestered by aluminum complexation and four equivalents of fluoride were sequestered by zirconium complexation. Concentrated HF, therefore, was added to INEEL simulant to generate a solution 2.1 M in fluoride. This solution was stirred overnight and sufficient ascorbic acid was then added to make the solution 0.1 M in ascorbic acid. The solution was filtered and centrifuged to remove some gel that had formed. To 1 mL of the filtrate, 1 mL of TRUEX solvent was added followed by ^{95}Zr and ^{239}Pu spikes. The solutions were mixed and centrifuged, and each phase was sampled. Table 3.7 shows the results of this contact.

Table 3.7. Distribution Values for Zr and Pu from an INEEL Simulant Solution after HF and Ascorbic Acid Addition

Metal	D
Zr	0.28
Pu	137

So it appears that HF and ascorbic acid addition would provide an effective means to prevent Zr extraction while allowing for effective actinide extraction by TRUEX. Unfortunately, this treatment also generates a gel. A series of qualitative experiments examined gel formation as a function of HF addition. The gel formed immediately upon mixing, and the amount did not appear to change even while the total added fluoride to the simulant was varied between 2 and 3 M. The gel also did not appear to either increase or decrease in amount, even after stirring for several days or further standing for several weeks.

An XRD analysis was performed on the gel that formed from both the lowest (2 M) and highest (3 M) HF additions to try and ascertain its composition. Identical results were obtained in both cases. The results of the XRD as well as the results from an attempted computer match of the measured spectrum are shown in Figure 3.13.

As can be seen in Figure 3.13, the peaks are quite narrow, which suggests that the precipitated material is microcrystalline. A match of the intensity positions indicates that the most likely candidate for the solid is zirconium hydrogen fluoride hydrate, ZrH_2F_6-$0.7H_2O$, card number 19-1485, with a second potential contributor being sodium calcium aluminum fluoride, $NaCaAlF_6$, card number 42-1149. The zirconium compound clearly provides the best match with both peak positions and peak intensities and appears also to be chemically reasonable.

Because of the precipitation initiated by HF addition, an alternative source to selectively inhibit Zr extraction by TRUEX was investigated. The extraction of Pu^{4+}, Am^{3+}, UO_2^{2+}, and Zr^{4+} from the INEEL simulant in the presence of various concentrations of oxalic acid was investigated. The results are shown in Table 3.8.

Clearly, these results indicate that oxalic acid concentrations greater than 0.1 M are sufficient to suppress zirconium extraction with negligible impact on uranyl or americium extraction and still exhibit more than sufficient TRUEX affinity for Pu^{4+}. It should be noted that these results are in keeping with previous studies on the affinity of oxalic acid for +4 ions over +3 ions (Horwitz 1985 and 1993).

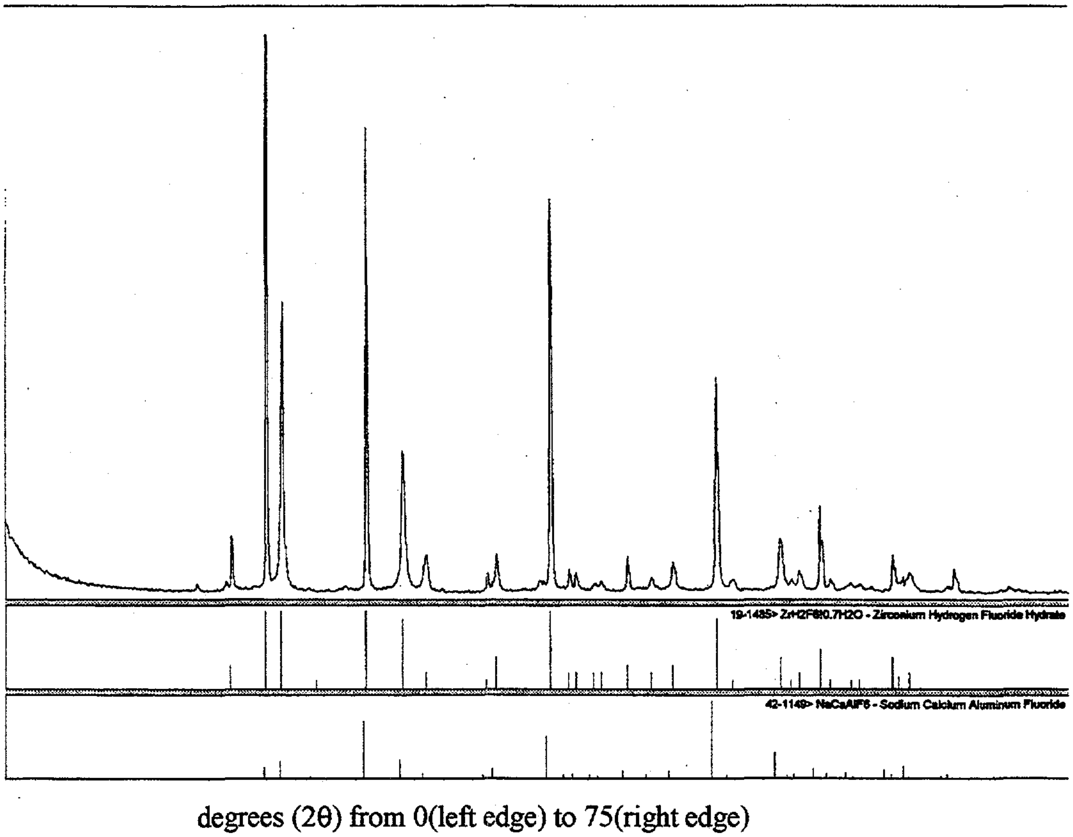


Figure 3.13. XRD from HF/INEEL Simulant Precipitate. The measured spectrum is on top while the spectra of potential candidate matches appear below.

Table 3.8. TRUEX Distribution Values for Extraction of Selective Components from INEEL Simulant

$[H_2C_2O_4]$,M	D(Pu^{4+})	D(Am^{3+})	D(UO_2^{2+})	D(Zr^{4+})
0	610	26	190*	56
0.05	517	14	70	1.41
0.1	456	18	74	0.34
0.5	237	20	80	0.0057

* Measured with an Aqueous Phase Composition of Simulant/10 mM L-cysteine Hydrochloric Acid

3.2.2 First Flowsheet Test

A series of linked, batch contacts was performed to verify the results of the individual measurements described above. In this flowsheet test, the organic phase was subjected to a series of contacts, with the phases from each contact being mixed, separated, and sampled. A set of contacts was performed for each investigated component, with the phase ratios and number and type of stages designed to mimic as closely as possible previous flowsheet testing at INEEL. The initial TRUEX extraction solution first was pre-equilibrated by three contacts with unspiked INEEL simulant at an O/A of 2. A summary of the stages examined in this flowsheet test is provided in Table 3.9, a summary of the flowsheet design targeted for simulation by these batch contacts is shown in Figure 3.14, and a graphical summary of the results of the flowsheet tests is shown in Figure 3.15.

In general, the results of the first flowsheet test are highly encouraging. With only a few exceptions, the worst being the final two uranium strip solutions, the mass balances for all radionuclides were excellent, with recoveries generally around 100 ± 5%. All actinide distribution values are high in the extraction stage, remain substantially above 1 throughout the scrub stages, and reduce to substantially below 1 in each strip stage. The phase ratios used only enhanced the partitioning behaviors described by the distribution value measurements in retaining the actinides in the organic phase during the extraction and scrub stages and transferring the actinides to the aqueous phase during the strip stages.

Table 3.9. Summary of Batch Contacts Performed in the First Flowsheet Test

Stage #	Stage Type	Volume org. (mL)	Volume aq. (mL)[(a)]	Phase Ratio
0	Extraction	16.4	38.2	0.43
1	Scrub	14	9.3	1.5
2	Scrub	12	8	1.5
3	Scrub	10	6.67	1.5
4	Scrub	8	5.28	1.52
5	Strip	6	8.01	0.75
6	Strip	4	5.28	0.76

(a) In the extraction stage, the organic phase was pre-equilibrated TRUEX, and the aqueous phase was 29% by volume scrub solution (0.1 M nitric acid/10 mM L-cysteine hydrochloric acid) and 71% by volume feed solution (INEEL simulant/10 mM L-cysteine hydrochloric acid). In the scrub stages, the aqueous phase was 0.1 M nitric acid/10 mM L-cysteine hydrochloric acid. In the strip stages, the aqueous phase was 0.1 M ammonium bioxalate/water.

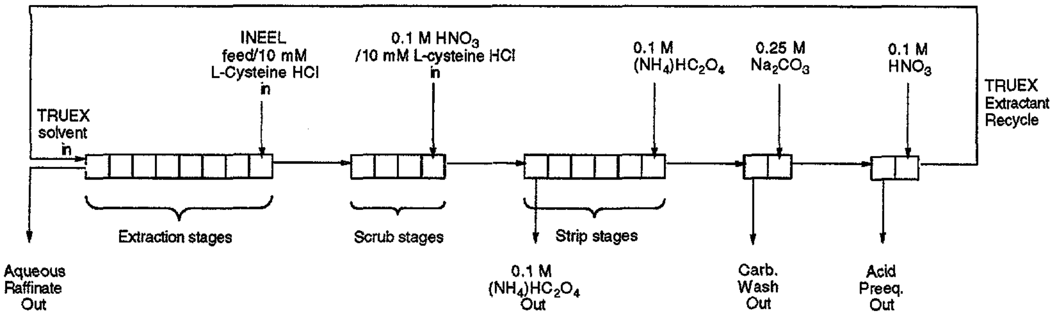


Figure 3.14. Schematic Illustration of the First Flowsheet Test

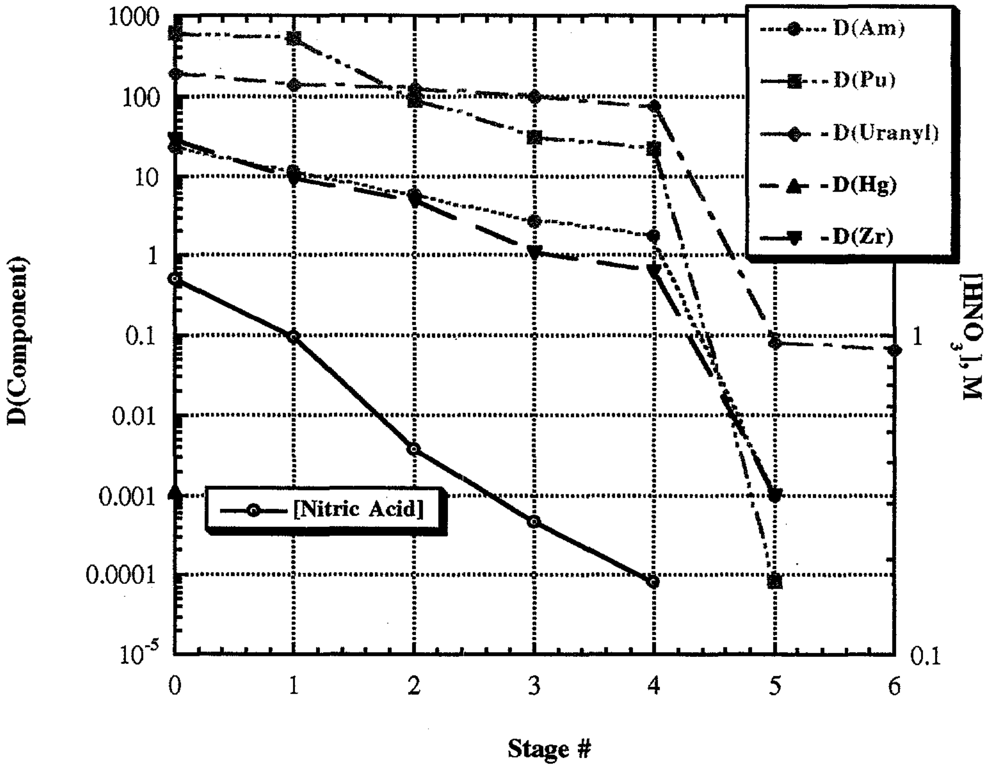


Figure 3.15. Summary of Distribution Behavior for Key Components in the First Flowsheet Test Using Batch Contacts. All distribution coefficients are reported using the left-side Y-scale, and the equilibrium nitric acid concentration is reported using the right-side Y-scale. Stage 0 refers to the extraction stage, stages 1–4 refer to scrub stages, and stages 5–6 refer to strip stages.

The highest actinide distribution values in the strip contacts are found for uranyl ion, but even here the distribution values are less than 0.1. This implies that with six strip stages and an O/A of less than 1 in each strip stage, effectively all of the uranium should be readily removed, with the transuranic elements being even more effectively stripped from the TRUEX solvent into the high level TRU waste stream.

The use of 10 mM L-cysteine hydrochloric acid in the extraction and scrub stages had the desired effect of inhibiting mercury transfer to the organic phase from the feed solution. Indeed, the number of counts in the organic phase even during extraction stage was so low that no discernable ^{203}Hg activity could be detected even in the first scrub stage.

The only potential troublesome element examined was zirconium. Zirconium appears to be well extracted, with a D of ca. 30 in the extraction stage, but by the final scrub step, the distribution value dropped appreciably below 1 (0.63). Even with a phase ratio of 1.5, the extraction ratio increases only to 0.95, which suggests that the possibility of significant buildup of zirconium may exist. It should be noted that although no problems with respect to zirconium precipitation have been noted during previous INEEL flowsheet testing, the stage-wise measurement of zirconium has not been reported.

The dispersion values for each examined stage were measured, and the results are summarized in Table 3.10. It should be noted that these tests were not made using the recommended standard conditions (Leonard 1995 and 1999). With this caveat in mind, the measured dispersion values seem acceptable, except for the last two scrub stages, where the dispersion values of slightly less than 3E-04 are only fair.

In summary, the first flowsheet test shows that 10 mM L-cysteine hydrochloric acid works well at preventing mercury extraction by TRUEX from INEEL simulants and that 0.1 M ammonium bioxalate is an effective, phosphorus-free replacement for 0.04 M HEDPA as an actinide stripping agent.

Table 3.10. Measured Dispersion Values from the First Flowsheet Test

Stage #	Stage type	Container Type	Solution Height (m)	Dispersion Time (sec)	Dispersion #
0	Extraction	A	0.0395	32	1.98E-03
1	Scrub 1	B	0.071	126	6.75E-04
2	Scrub 2	B	0.063	158	5.07E-04
3	Scrub 3	B	0.055	255	2.94E-04
4	Scrub 4	B	0.049	307	2.30E-04
5	Strip 1	B	0.053	113	6.50E-04
6	Strip 2	B	0.044	73	9.17E-04
7	Strip 3	B	0.033	42	1.38E-03
8	Strip 4	B	0.026	30	1.72E-03

* A = 120 mL bottle, 5 cm in diameter. B = 50 mL centrifuge tube, 2.7 cm in diameter with the bottom 1.5 cm in height tapering from 2.7 to 0 cm in diameter.

3.2.3 Second Flowsheet Test

In the first flowsheet test, the capability of cysteine to inhibit mercury extraction by the TRUEX solvent and the capability of 0.1 M ammonium bioxalate to effectively strip actinides and extracted zirconium was demonstrated. The main drawback to the first flowsheet design was the extraction of zirconium, which is carried along with the actinides into the high level waste stream. The second flowsheet test was designed to prevent zirconium extraction through the addition of oxalic acid to the feed solution. In addition, a reductive strip step was tested as an alternative to 0.1 M ammonium bioxalate. A schematic illustration of the second flowsheet test is provided in Figure 3.16.

There were two changes from the first flowsheet test: first, the adjustment of the feed solution to be 0.5 M in oxalic acid as well as 10 mM in L-cysteine hydrochloric acid and second, the use of 0.1 M ascorbic acid/0.04 M nitric acid as the stripping agent. The phase ratios used in the second flowsheet test are identical to those used in the first flowsheet test.

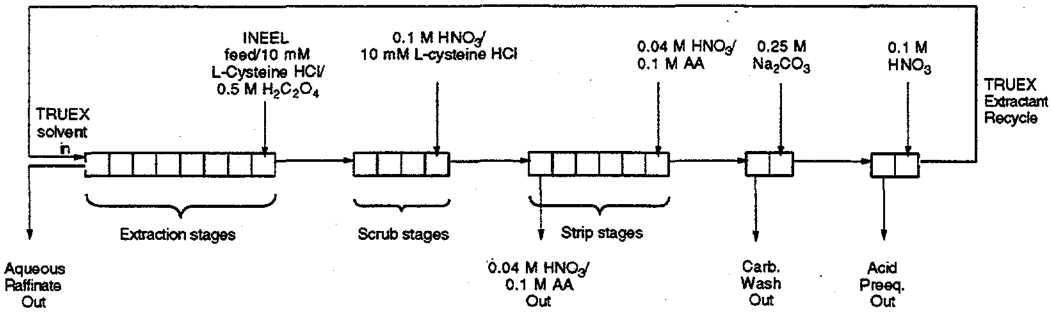


Figure 3.16. Schematic Illustration of the Second Flowsheet Test

Only the distribution behavior of Am, Pu, and Hg were examined. Again, the mass balances were excellent. Because of the lack of change from the first extraction flowsheet in the extraction and scrub (nitric acid), stage-by-stage measurements of equilibrium nitric acid concentrations were not performed. A graphical presentation of the Am and Pu distribution results is shown in Figure 3.17.

Flowsheet testing was stopped at this point, based on the Am and Pu results. Two problems are apparent. First, the distribution value for Pu drops significantly (0.56) below 1 during the final scrub step. Second, in the latter strip steps, the distribution values for both Am and Pu begin to increase, reaching a value significantly greater than 1 in the third strip stage.

A probable reason for this low D(Pu) in the final scrub step lies in the use of oxalic acid to inhibit zirconium extraction. Oxalic acid is known to be extracted by TRUEX solvent and to act as a stripping agent for Pu, especially at lower aqueous nitrate concentrations (March and Yarbro 1988; Clark et al. 1987). It seems likely that sufficient oxalic acid was carried along with the organic phase to adversely impact D(Pu) in the final scrub stage.

The increase in D(Pu) and D(Am) in the latter strip stages is also well known in the TRUEX extraction literature and is assigned to acidic impurities in the TRUEX solvent (Chiarizia and Horwitz 1990; Tse et al. 1990). This increase in distribution values is usually seen under conditions of low

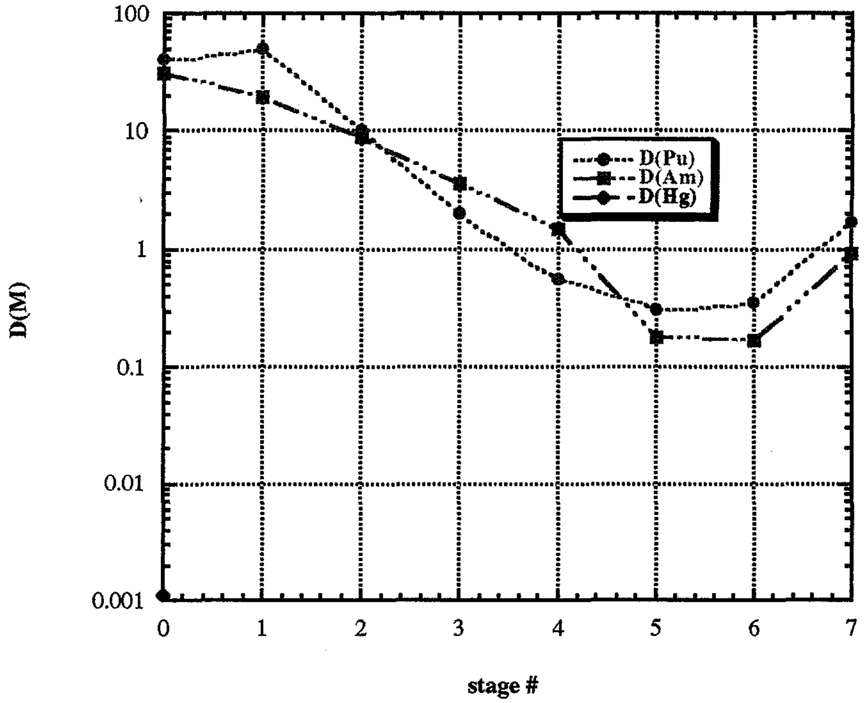


Figure 3.17. Summary of Distribution Behavior for Am and Pu in the Second Flowsheet Test Using Batch Contacts. Stage 0 Refers to the Extraction Stage, Stages 1–4 Refer to Scrub Stages, and Stages 5–7 Refer to Strip Stages.

aqueous acidity and low total concentrations of extractable metals. Both conditions are found in the latter strip stages of this flowsheet test. Indeed, the behavior is so well known that it was decided not to purify the TRUEX solvent, but to leave the solvent unaltered to facilitate comparisons between various flowsheet designs.

The measurement of D(Hg) again shows how highly effective cysteine is at preventing TRUEX extraction of mercury. Attempts to measure distribution values in the first scrub stage were frustrated by an inability to detect any ^{203}Hg activity in the organic phase.

3.2.4 Third Flowsheet Test

The third flowsheet test was designed to avoid the problem of low D(Pu) in the final scrub stage (again, presumably due to the influence of co-extracted oxalic acid). This was done by introducing ascorbic acid into the scrub stage to reduce Pu(IV) to Pu(III). Pu(III) should show similar behavior to Am(III), and Am(III) distribution values appear to be less affected than Pu(IV) by the presence of oxalic acid (Table 3.8).

A schematic illustration of the third flowsheet test is provided in Figure 3.18, and a graphical illustration of the test results is shown in Figure 3.19. As noted above, it differs from the second flowsheet test only in the composition of the scrub solution, which has been made 0.1 M in ascorbic acid as well as 0.1 M in nitric acid and 10 mM in L-cysteine hydrochloric acid. Again, because of the lack of change from the first extraction flowsheet in the extraction and scrub (nitric acid), stage-by-stage measurements of equilibrium nitric acid concentrations were not performed.

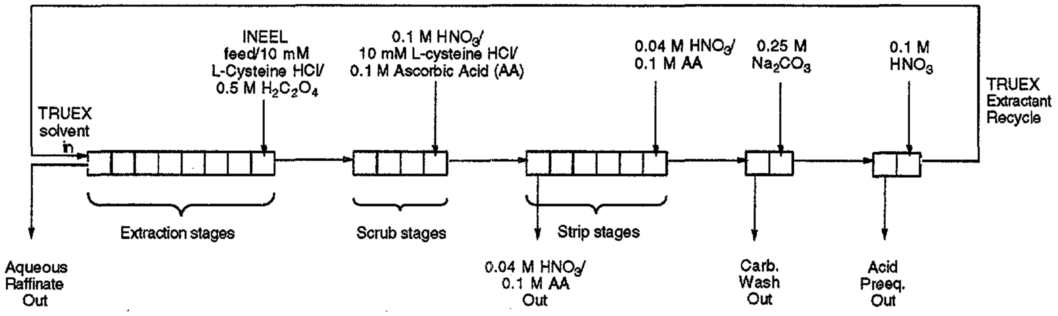


Figure 3.18. Schematic Illustration of the Third Flowsheet Test

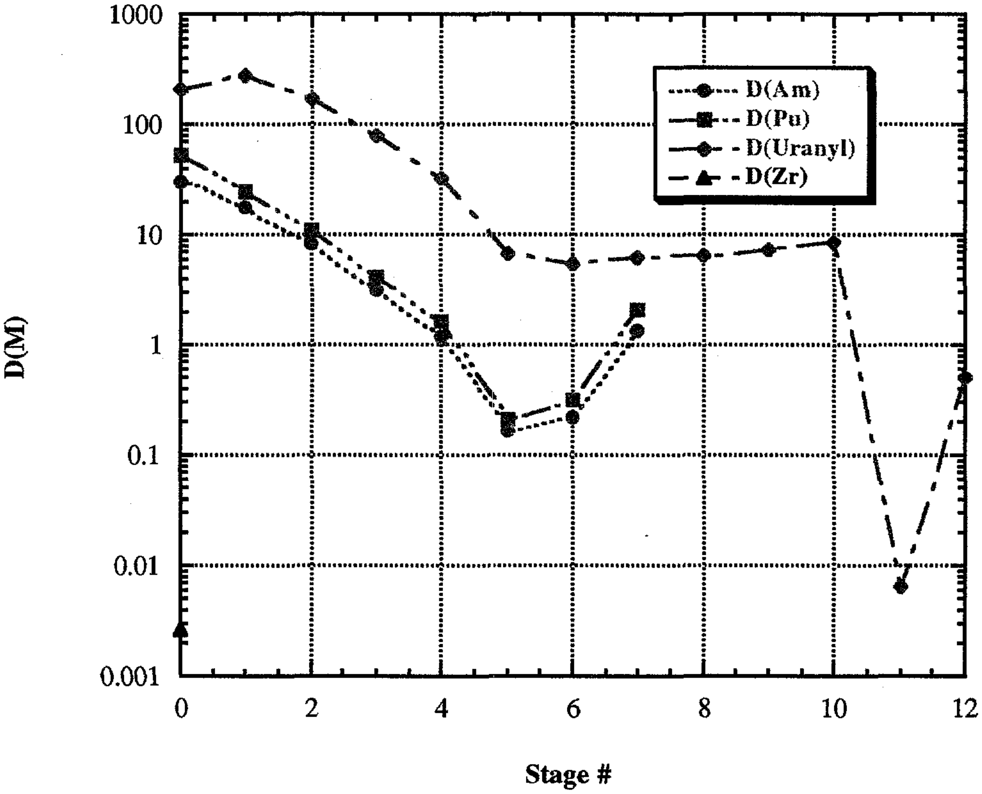


Figure 3.19. Summary of Distribution Behavior for Am and Pu in the Third Flowsheet Test Using Batch Contacts. Stage 0 Refers to the Extraction Stage, Stages 1–4 Refer to Scrub Stages, Stages 5–10 Refer to Strip Stages, and Stages 11–12 Refer to 0.25 M Carbonate Washes.

The dispersion values for each examined stage were measured, and the results were summarized in Table 3.11. The dispersion values measured for the third flowsheet are, as expected, very similar to those measured during the first flowsheet test.

The results of this flowsheet test met expectations. Again, the mass balances for the radionuclides from stage-to-stage were excellent. The D(Pu) and D(Am) values track each other well throughout the flowsheet and remain high during the extraction step, above 1 during the scrub steps and below 1 during the first two strip steps. The D(Pu) and D(Am) values again rise to above 1 in the third strip stage, presumably because of the presence of acidic impurities in the TRUEX solvent as mentioned above. The uranyl distribution values are very high in the extraction stage and decrease but remain well over 1 throughout the scrub and strip stages. They decrease very low (<<1) in the carbonate wash stages, as expected (March and Yarbro 1988; Schultz and Horwitz 1988; Horwitz and Schultz 1991). Finally, the presence of 0.5 M oxalic acid does an excellent job of preventing zirconium extraction by the TRUEX solvent in the extraction stage, with insufficient activity being carried over even to the first scrub stage to measure an activity above background in the organic phase.

Table 3.11. Measured Dispersion Values from the Third Flowsheet Test

Stage #	Container Type	Solution Height (m)	Dispersion Time (sec)	Dispersion #
0	A	0.04	21	3.04E-03
1	B	0.046	120	5.71E-04
2	B	0.041	125	5.17E-04
3	B	0.038	140	4.45E-04
4	B	0.035	140	4.27E-04
5	B	0.044	160	4.19E-04
6	B	0.04	165	3.87E-04
7	B	0.035	170	3.51E-04
8	C	0.073	155	5.57E-04
9	C	0.064	138	5.85E-04
10	C	0.053	127	5.79E-04
11	C	0.044	60	1.12E-03
12	C	0.036	25	2.42E-03

A = 250-mL bottle, 6 cm in diameter. B = 60-mL bottle, 3.8 cm in diameter. C = 50-mL centrifuge tube, 2.7 cm in diameter with the bottom 1.5 cm in height, tapering from 2.7 to 0 cm in diameter.

3.2.5. The Impact of Cysteine on Hg Extraction by Sr•Spec® Resin

A test was set up to investigate whether the Hg(II) that, in the presence of cysteine, will no longer be extracted from the aqueous phase by the TRUEX solvent, would adversely impact the downstream SREX process. The SREX process will also extract Hg(II), and the presence of the bulk of the mercury in the INEEL tank waste could cause loading problems and so interfere with the efficiency of ^{90}Sr removal. Lacking the reagents needed to generate the SREX process solvent, a test was instead designed using Sr•Spec® resin, which uses the same Sr-specific complexing agent and exhibits similar extraction performance to the SREX liquid-liquid extraction process (Horwitz et al. 1992).

Two sets of tests were performed. In one set of tests, the distribution values were measured for mercury and Sr from 2 M nitric acid made ca. 0.13 mM in cold Sr and spiked with ^{203}Hg and ^{85}Sr in the presence and absence of 10 mM L-cysteine hydrochloric acid. Under these test conditions, the amount of added cold Sr was approximately 20% of the reported resin capacity (Horwitz et al. 1992). In the second set of tests, the distribution values were measured for mercury and Sr from the INEEL simulant solution spiked with ^{203}Hg and ^{85}Sr in the presence and absence of 10 mM L-cysteine hydrochloric acid. Again, the ratio of resin used to volume of simulant was such that the total amount of Pb + Hg + Sr + Ba initially present was approximately 20% of the resin's capacity. The results of these tests are summarized in Table 3.12.

Table 3.12. D(Hg) and D(Sr) Using Sr•Spec Resin from Acidic Nitrate Solution in the Presence or Absence of 10 mM L-Cysteine Hydrochloric Acid

Aqueous Matrix	**K_d(Sr)**	**K_d(Hg)**
INEEL Simulant	32	32
INEEL Simulant/10 mM L-Cysteine Hydrochloric Acid	36	~ 0*
2 M Nitric Acid/0.13 mM Strontium	48	1010
2 M Hydrochloric Acid/0.13 mM Strontium/10 mM L-Cysteine Hydrochloric Acid	51	~ 0*

* Counts in aqueous phase after resin contact slightly greater than counts before resin contact.

Like with the TRUEX complexing agent, the strong complexing capability of cysteine prevents extraction of mercury by the Sr complexant into the organic phase while having no discernable impact on Sr complexation.

4.0 Conclusions

The major goals of this study were to develop a method for separating mercury from the TRU stream in the TRUEX process and to demonstrate alternative stripping methods to eliminate phosphorus-containing actinide stripping agents from the TRU stream. The work described in this report provides the basis for implementing an improved TRUEX-based flowsheet using only minor modifications to the current INEEL flowsheet design. Specifically, it has been shown that:

- The presence of cysteine in concentrations up to 10 mM is effective at inhibiting mercury extraction by the TRUEX process solvent. It should be noted that, although for the purposes of convenience testing, this was done with the hydrochloric acid salt, the compound is commercially available as a liquid as an overall neutral form, and this form could be used. This would eliminate the need to add corrosive hydrochloric acid to the system.
- Preliminary tests using the Sr•Spec® resin indicate that the presence of 10 mM cysteine will also prevent mercury extraction during the SREX cycle of tank waste pretreatment. The implication of this test is that the SREX stages of the pretreatment flowsheet could be performed before the TRUEX stages without compromising SREX performance because of mercury loading of the organic phase.
- The use of 0.5 M oxalic acid prevents substantial Zr extraction from INEEL simulant while still allowing for effective actinide extraction. However, extraction of oxalic acid by the TRUEX solvent causes low Pu(IV) distribution values in the scrub stages, requiring the presence of a Pu(IV) to Pu(III) reductant, such as 0.1 M ascorbic acid, to obtain satisfactory flowsheet performance. The choice of 0.5 M oxalic acid is somewhat arbitrary; use of the Generic TRUEX Model (GTM) (Nunez and Vandegrift 1995) may allow for a more targeted concentration to be chosen as well as suggesting modifications that may remove the need for the presence of a reductant in the scrub stages.
- The addition of HF to the INEEL feed simulant to a nominal concentration of 2 M or greater, was found to generate insoluble solids. Preliminary identification of the solids by XRD indicates that the majority of the material is zirconium hydrogen fluoride hydrate, with possible minor amounts of calcium aluminum fluoride.
- A 0.1 M solution of ammonium bioxalate was found to effectively strip both uranium and transuranic elements (Am and Pu) from TRUEX solvent under TRUEX processing conditions. Alternatively, it was shown that the transuranic elements Am and Pu can be selectively removed from the TRUEX solvent under TRUEX processing conditions through contact with 0.1 M ascorbic acid/0.04 M nitric acid strip solution. In this instance, it is estimated that only about 20% [=1/(Extraction Constant)] of the extracted uranium will report along with the TRUs; the other 80% of the uranium will be transferred to the aqueous phase during the carbonate wash step. An advantage of the ammonium bioxalate strip solution is that the distribution values appear to be less sensitive to the presence of acidic impurities in the TRUEX solvent than is the case with the ascorbic acid strip solution.

As a result of the testing described in this report, an improved TRUEX flowsheet can be recommended. This improved flowsheet is described in Figure 4.1.

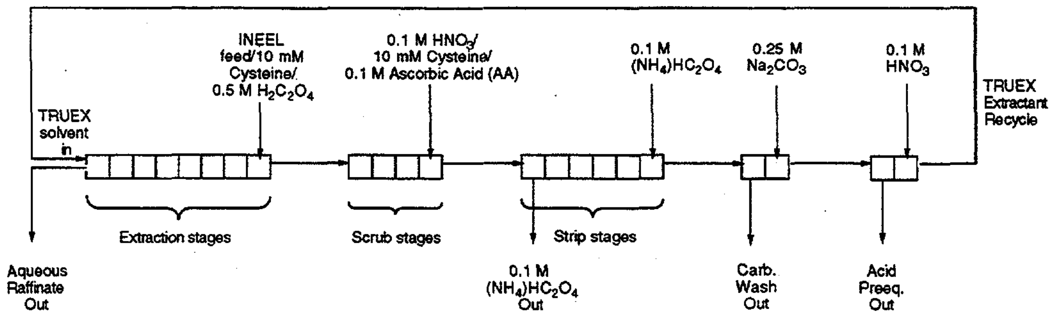


Figure 4.1. Schematic Illustration of the Final Recommended TRUEX Flowsheet

This flowsheet meets the objectives for an improved TRUEX flowsheet for the pretreatment of INEEL tank waste while minimizing changes in the current flowsheet design. The feed solution is adjusted with 10 mM cysteine to prevent mercury extraction and 0.5 M in oxalic acid to prevent zirconium extraction. To avoid the adverse impact of co-extracted oxalic acid on D(Pu), 0.1 M ascorbic acid is added the scrub stages to reduce Pu(IV) to Pu(III) along with 10 mM cysteine to remove any trace extracted amounts of mercury. The co-extracted oxalic acid should further inhibit any potential zirconium extraction in the scrub stages. Finally, the use of 0.1 M ammonium bioxalate in the strip stages will effectively strip any extracted actinides and lanthanides in the strip stages.

It is worthwhile noting that the use of cysteine to inhibit mercury extraction by TRUEX is perhaps the only novel processing aspect in this work. The use of oxalic acid to selectively prevent zirconium extraction while allowing for actinide extraction by TRUEX from tank wastes has been previously reported (Lumetta et al. 1995), and the use both of ascorbic acid in dilute nitric acid as a TRU stripping agent (Lumetta et al. 1994) and, as noted above, the use of ammomium oxalate and bioxalate as an actinide stripping agent have been reported previously. A test of the revised TRUEX flowsheet in a continuous process, and further testing of the impact of mercury, lead, and strontium extraction by SREX under real processing conditions would be a recommended next step.

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P.O. Box 2008
Oak Ridge, Tennessee 37831-6223

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