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**Removal of Actinides from
Dissolved ORNL MVST Sludge
Using the TRUEX Process**

Barry B. Spencer
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C. W. Chase

MASTER 

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REMOVAL OF ACTINIDES FROM DISSOLVED ORNL MVST SLUDGE
USING THE TRUEX PROCESS

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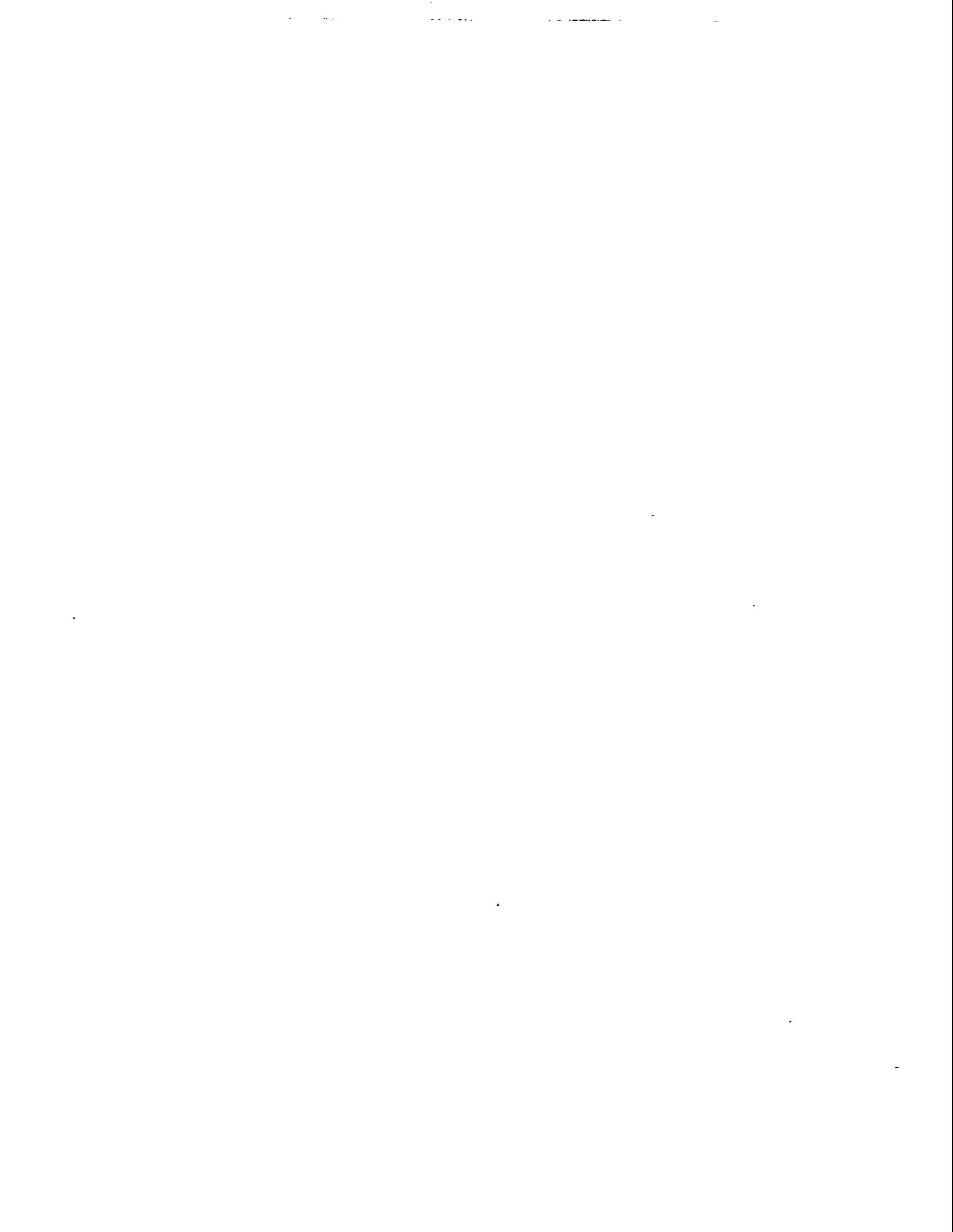
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Date Published—July 1997

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
managed by
LOCKHEED MARTIN ENERGY RESEARCH CORP.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-96OR22464

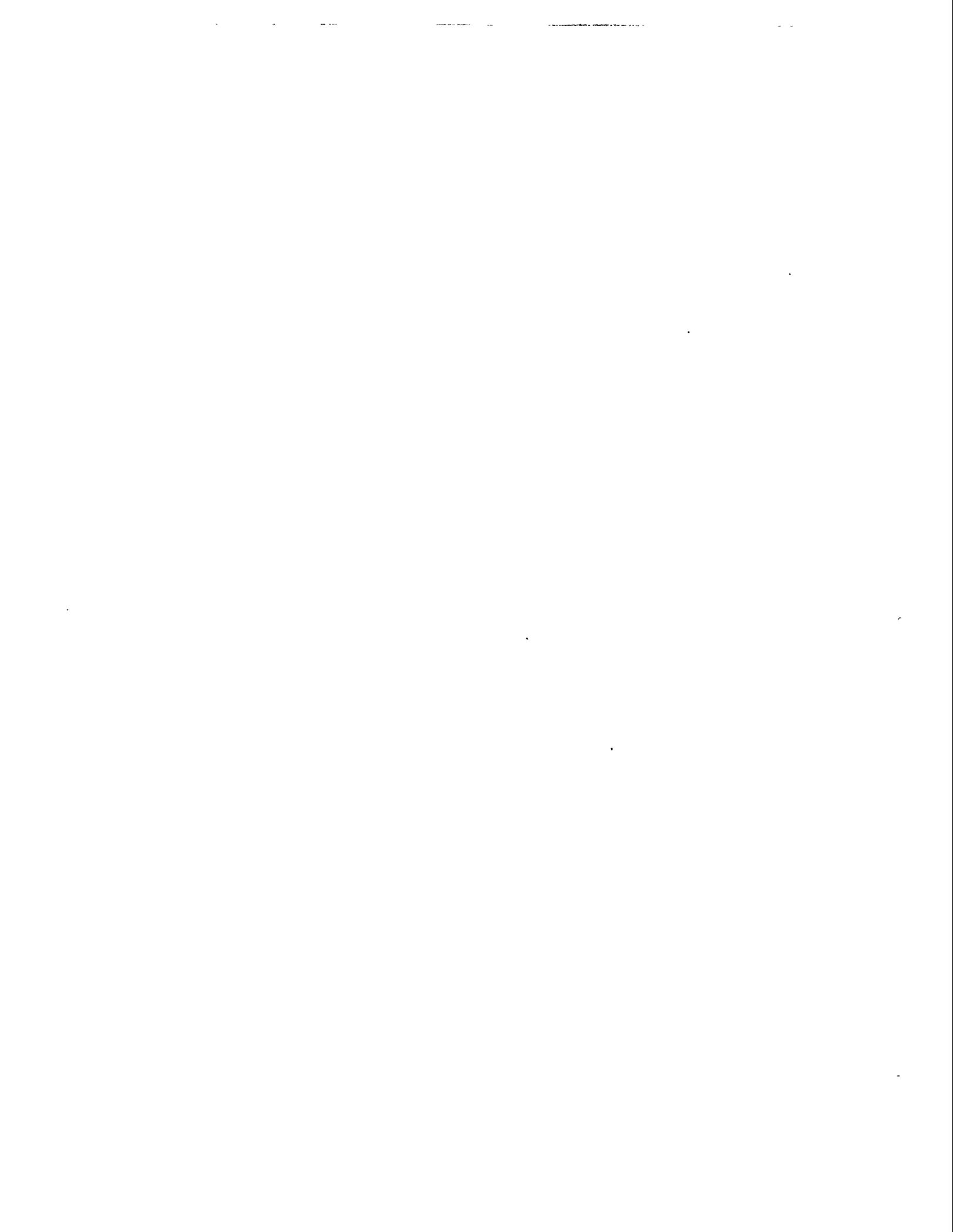
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LIST OF ACRONYMS

AES	atomic emission spectroscopy
ANL	Argonne National Laboratory
CMPO	octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide
DOE	Department of Energy
GTM	Generic TRUEX Model
HEDL	Hanford Engineering Development Laboratory
HLW	High-Level Radioactive Waste
HPLC	High-Performance Liquid Chromatograph
ICP	Inductively Coupled Plasma
INEEL	Idaho National Engineering and Environmental Laboratory
LANL	Los Alamos National Laboratory
MVST	Melton Valley Storage Tanks
NPH	Normal Paraffin Hydrocarbon
NTU	Nephelometric Turbidity Units
ORNL	Oak Ridge National Laboratory
RFP	Rocky Flats Plant
SRP	Savannah River Plant
TBP	tri- <i>n</i> -butylphosphate
TCE	tetrachloroethylene
TRU	Transuranium
TRUEX	Transuranium Extraction

ACKNOWLEDGMENTS

This work was sponsored by the U.S. Department of Energy's Office of Science and Technology-Tank Focus Area under U.S. Government contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. The work was performed at the Oak Ridge National Laboratory under the auspices of the Chemical Technology Division. The turbidity measurements on the aqueous samples were provided by E. C. Beahm and T. A. Dillow of the Chemical Technology Division. The Chemical and Analytical Services Division performed the chemical analyses of the samples.

ABSTRACT

Experiments were conducted to evaluate the transuranium extraction process for partitioning actinides from actual dissolved high-level radioactive waste sludge. All tests were performed at ambient temperature (24°C). Time and budget constraints permitted only two experimental campaigns. 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 dissolved in nitric acid to produce a solution containing total metal concentrations of ~1.8 M with a nitric acid concentration of ~2.9 M. About 50% of the dry mass of the sludge was dissolved. In the other campaign, the sludge was neutralized with nitric acid to destroy the carbonates, then leached with ~2.6 M NaOH for ~6 h before rinsing with the mild caustic. The sludge was then dissolved in nitric acid to produce a solution containing total metal concentrations of ~0.6 M with a nitric acid concentration of ~1.7 M. About 80% of the sludge dissolved. The dissolved sludge solution from the first campaign began gelling immediately, and a visible gel layer was observed after 8 days. In the second campaign, the solution became hazy after ~8 days, indicating gel formation, but did not display separated gel layers after aging for 20 days.

Batch liquid-liquid equilibrium tests of both the extraction and 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 species 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.

1. INTRODUCTION AND OBJECTIVES

Production operations at many Department of Energy (DOE) sites throughout the United States have resulted in enormous quantities of stored radioactive and hazardous wastes. Sites at which waste is stored include, but are not limited to, Hanford Engineering Development Laboratory (HEDL), Idaho National Engineering and Environmental Laboratory (INEEL), Oak Ridge National Laboratory (ORNL), Los Alamos National Laboratory (LANL), the Savannah River Plant (SRP), and the Rocky Flats Plant (RFP). The DOE is responsible for these wastes and their ultimate disposition.

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. Storage tank sludges contain most of the transuranium (TRU) elements, along with other radionuclides such as 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 greater than 100 nCi/g must be considered TRU waste and require expensive disposal methods—typically immobilization in deep geologic repositories (Moghissi et al., 1986). If these radioactive components could be removed and concentrated, then the bulk of the waste would become non-TRU and would be suitable for near-surface disposal. Large reductions in the amount of HLW could greatly reduce the cost of ultimate disposal of the stored wastes.

A number of processes that could partition specific components in the waste have been identified. In one concept, the supernatant and sludge phases are separated by centrifugation. The sludge is then washed with dilute caustic solution to remove any entrained supernatant and readily soluble radionuclides (particularly, cesium and strontium). Washed sludge is dissolved in nitric acid using additional reagents, such as hydrofluoric acid, as required. The TRU components would be removed from the acidic aqueous phase using a process appropriate for scaleup to industrial proportions, such as solvent extraction.

The focus of this experimental program was to evaluate the transuranium extraction (TRUEX) solvent extraction process for partitioning actinides from actual dissolved HLW sludge. A large sludge sample was previously removed from MVST W-25 and has been well characterized by Collins et al. (1994, 1995). This material has been used in various waste treatment tests, originally sponsored by the Underground Storage Tank Integrated Demonstration program but currently sponsored by the

Tank Focus Area task. Portions of this sludge were prepared and dissolved for use in the evaluation tests. Batch liquid-liquid equilibrium tests of both the extraction and 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). 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.

2. LITERATURE REVIEW AND ANALYSIS

2.1 TRUEX PROCESS

The TRUEX process is a solvent extraction process for recovering actinides from acidic nuclear waste streams (Horwitz and Schulz, 1990). Its development was dependent on the development of octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO), a bifunctional carbomoylphosphoryl extractant which is capable of extracting trivalent, as well as tetravalent and hexavalent, species. Horwitz et al. (1982) demonstrated that CMPO selectively extracts Am(III) from solutions containing Fe(III), a necessary characteristic for partitioning the trivalent actinides from wastes.

CMPO in pure form is a solid, so it must be dissolved in an organic solvent, such as *n*-dodecane or tetrachloroethylene, to be useful in liquid-liquid extraction systems. The solubility of CMPO-metal nitrate complexes in the above-mentioned solvents is limited, giving it a propensity to form a CMPO-rich, heavy organic phase (usually referred to as a third phase). A third phase is problematic in extraction systems because of the detrimental effects it has on the overall separation and recovery operations which normally take place in two phases. The addition of tri-*n*-butyl phosphate (TBP) ameliorates the formation of a third phase, permitting higher loadings of the organic solvent. Even though TBP is an extractant for tetravalent and hexavalent actinides, it is not as powerful an extractant as CMPO and is therefore considered to be a phase modifier in this system.

The TRUEX solvent is a mixture of CMPO and TBP in an organic diluent. Two types of diluent have been extensively tested and used for the TRUEX solvent: (1) a normal paraffin hydrocarbon (NPH) such as *n*-dodecane, where the concentrations of CMPO and TBP are typically 0.2 and 1.4 *M*, respectively, and (2) tetrachloroethylene (TCE), where the concentrations of CMPO

and TBP are typically 0.25 and 0.75 *M*, respectively. Because of the potential for introducing chloride into secondary waste streams, the use of chlorinated diluents is currently avoided in favor of paraffinic hydrocarbons, which can be completely incinerated.

In the TRUEX process, the actinides are extracted from a concentrated nitric acid solution into an organic phase. Some of the lanthanides, such as europium, are also effectively extracted. The trivalent actinides, primarily americium and curium, are readily stripped from the organic phase with weak, aqueous nitric acid solutions. Even at low concentrations of aqueous nitric acid, the distribution ratios for the tetravalent and hexavalent actinides, especially thorium and uranium, are quite high. This makes stripping of these elements difficult unless an aqueous-phase complexant such as oxalate (oxalic acid is an option) is added to the aqueous stripping solution. Plutonium may be stripped from the solvent at conditions between these extremes, making possible a configuration to partition the actinides into three fractions. However, separation of the actinides from one another is not required to downgrade TRU HLW.

Recent tests of the TRUEX process to demonstrate removal of actinides from waste streams have been reported by Ozawa et al. (1992), Mathur et al. (1993), Koma et al. (1993), and Lumetta et al. (1994).

2.2 GENERIC TRUEX MODEL

The GTM was developed at Argonne National Laboratory (ANL) and is well documented in reports by Vandegrift et al. (1992), Vandegrift et al. (1990), and Seefeldt et al. (1989). 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 (1972, 1973). The GTM is implemented as a computer program written in the macro language of Microsoft Excel™ and performs several types of calculations which can be selected by the user. As such, it is a computing tool to aid in the development of chemical process flowsheets and in estimating the size and cost of the processing facility. The model has evolved since the original program operating manual by Vandegrift et al. (1992) was published.

In the original GTM, an option for calculating the equilibration of an aqueous and organic batch was provided. Modeling sequential extraction or stripping operations was very inconvenient

and, for certain combinations, required that calculated equilibrium concentrations in a given phase be copied by hand to feed another calculation. However, beginning with GTM version 2.7, the means to reroute aqueous and organic streams between sections of a solvent extraction bank made it possible to use the stagewise modeling feature of the GTM to model sequential batchwise "crosscurrent" operations (Copple, 1993). The technique requires manual modifications to the export file, a spreadsheet prepared in Microsoft Excel™, which is generated by the front-end user interface of the GTM. Version 3.1.1 has a new front-end that permits the user to reroute streams to the desired sections (Copple, 1994), but phantom streams must be used to create the proper framework for the export file, and some editing of the file is required. Modeling of batch operations requires that one section be created for each equilibrium stage. For modeling a series of ideal equilibrium batch contacts, the fraction of each phase entrained in the other phase is set to zero and fractional efficiencies for each stage are set to unity.

2.3 ASSAY OF MVST W-25 SLUDGE

Detailed analytical data on MVST W-25 sludge solids and supernatant are available. Assay of the sludge solids is given in a report by Collins et al. (1994), and the analysis of the supernatant is given in a subsequent report by Collins et al. (1995). The data are shown in Table 2.1 (third and fourth columns). Data for the solids are measured in units of either becquerels per gram or milligrams per gram, and data for the supernatant are given in units of either becquerels per liter or milligrams per liter. Because the GTM requires all concentrations to be in units of g-mol per liter (M), it is convenient for subsequent calculations to first convert these base data to units of g-mol per kilogram for solids and g-mol per liter for liquid. Values of ^{99m}Tc concentration were computed from radioanalysis results assuming that all the technicium exists as ^{99m}Tc (half-life of ~6 years) because the long half-life of ^{99}Tc resulted in calculated concentrations greater than that given by chemical analysis. Calculated concentrations of $^{239/240}\text{Pu}$ were based on the half-life of ^{239}Pu , which gives the largest plutonium concentration. The results are given in the last two columns of Table 2.1.

Other data reported by Collins et al. (1994) that are essential to the calculations presented in this report are summarized as follows.

Air-dried solids content of centrifuged wet solids	0.590 g/g
Air-dried solids content of supernatant liquid	0.285 g/g

Table 2.1. Data on sludge solids and interstitial supernatant concentrations for Tank W-25

	Molecular weight	Sludge solids ^{a,b}	Supernatant solutes ^c	Sludge solids ^d	Supernatant solutes
Radionuclides		(Bq/g)	(Bq/L)	(g-mol/kg)	(g-mol/L)
⁶⁰ Co	60.	1.7×10^5	6.4×10^5	6.72×10^{-8}	2.53×10^{-10}
⁹⁰ Sr	90.	1.9×10^7	1.0×10^6	3.93×10^{-5}	2.07×10^{-9}
⁹⁹ Tc	99.	N.M. ^d	2.1×10^4	0.	1.09×10^{-15}
¹³⁴ Cs	134.	N.M.	6.5×10^5	0.	1.14×10^{-10}
¹³⁷ Cs	137.	1.4×10^6	2.5×10^8	3.20×10^{-6}	5.71×10^{-7}
¹⁵⁴ Eu	154.	1.4×10^5	1.1×10^5	1.68×10^{-7}	1.32×10^{-10}
²³⁸ Pu	238.	7.5×10^4	N.M.	5.13×10^{-7}	0.
^{239/240} Pu	239.	2.4×10^4	N.M.	4.43×10^{-5}	0.
²⁴¹ Am	241.	2.6×10^4	N.M.	9.17×10^{-7}	0.
²⁴⁴ Cm	244.	3.2×10^5	N.M.	4.43×10^{-7}	0.
Other metals		(mg/g)	(mg/L)	(g-mol/kg)	(g-mol/L)
Al	26.98	25.8	453.	0.956	0.017
Ba	137.33	0.4	1.2	0.0029	8.7×10^{-6}
Ca	40.08	96.0	9.5	2.395	0.00024
Cd	112.41	0.05	N.M.	0.00044	0.
Co	58.93	0.04	N.M.	0.00068	0.
Cr	52.00	0.6	51.	0.012	0.00098
Cu	63.55	0.3	N.M.	0.0047	0.
Cs	132.91	0.0026	0.19	1.96×10^{-5}	1.43×10^{-6}
Fe	55.85	8.6	N.M.	0.154	0.
Hg	200.59	0.2	B.D.L. ^e	0.0010	0.
K	39.10	14.4	14000.	0.368	0.358
Mg	24.31	13.5	N.M.	0.555	0.
Mn	54.94	0.8	N.M.	0.015	0.
Na	22.99	110.	89000.	4.785	3.871
Ni	58.70	0.4	B.D.L.	0.0068	0.
Pb	207.2	2.0	N.M.	0.0097	0.
Si	28.09	15.3	N.M.	0.545	0.
Sr	87.62	5.6	0.4	0.0064	4.57×10^{-6}
Tc	127.60	N.M.	0.032	0.	2.51×10^{-7}
Th	232.04	57.4	0.3	0.247	1.29×10^{-6}
Tl	204.37	0.8	N.M.	0.0039	0.
U	238.03	27.6	4.3	0.116	1.81×10^{-5}
Zn	65.38	0.8	9.5	0.012	0.000145
Anions		(mg/g)	(mg/L)	(g-mol/kg)	(g-mol/L)
Br ⁻	79.90	0.7	N.M.	0.0088	0.
Cl ⁻	35.45	3.7	3740.	0.104	0.106
F ⁻	19.00	1.9	371.	0.100	0.0195
CO ₃ ²⁻	60.00	115.	N.M.	1.917	0.
NO ₃ ⁻	62.00	179.	236000.	2.887	3.806
PO ₄ ³⁻	94.97	29.5	N.M.	0.311	0.
SO ₄ ²⁻	96.06	7.0	2370.	0.073	0.0247

^aAir-dried solids.

^bCollins et al. (1994).

^cCollins et al. (1995).

^dN.M. = not measured; values calculated from these are set to 0.

^eB.D.L. = below detectable limit; values calculated from these are set to 0.

Density of centrifuged wet solids	1.53 g/mL
Density of supernatant	1.206 g/mL
Volume ratio of decanted supernatant to wet solids	1:1
<u>pH of supernatant</u>	<u>13</u>

The mass of air-dried solids is 59% of the centrifuged wet solids. This implies that 1 kg of air-dried solids had an original wet mass of 1.69 kg. Consequently, 0.69 kg or 690 mL of water evaporated. The volume of supernatant from which this water evaporated can be estimated from a mass balance:

$$\rho V = \sum C_i V + m_{H_2O}, \quad (2-1)$$

where ρ = liquid density, g/mL;

V = volume, mL;

C_i = concentration of solutes, g/mL;

m_{H_2O} = mass of water, g; and

i = counter or identifier for solutes.

Using data from Table 2.1 (in the appropriate units), the volume of the supernatant associated with 1 kg of air-dried solids is 802 mL. Because the hydroxide concentration in the supernatant is not given in the data, it is necessary to assume that the concentration is low and that it contributes little to the total mass of the solute. This is probably a good assumption based on the measured pH of the supernatant. The fraction of solids associated with this liquid can be calculated by

$$\text{solids fraction} = \frac{\sum C_i V}{\sum C_i V + m_{H_2O}} \quad (2-2)$$

Substitution results in a value of 0.287 g/g, which compares very favorably with the measured value (0.285) reported by Collins et al. (1994).

Four different leaching and dissolution procedures have been tested by Collins et al. (1994) for treating MVST W-25 tank sludge. Two of these treatment regimens included leaching of the sludge with caustic solution prior to dissolution with strong nitric acid (~6.0 M). One treatment was

conducted with strong nitric acid (6.0 *M*) alone, and the other was conducted with strong nitric acid (5.8 *M*) mixed with hydrofluoric acid (1.0 *M*). Within 10 percentage points, the amount of solids dissolved in each case was 70% by mass. Regardless of the treatment scenario, almost all the americium and curium, and about half the plutonium, were leached from the solids. (One data point shows that ~90% of the uranium was leached from the solids 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 concentration of the nitric acid required to dissolve the solids depends on the equivalents of base stored in the solids, the base in the interstitial supernate, and the final acid concentration desired. Equivalents of base stored in the sludge may be estimated from data on an experiment reported by Collins et al. (1994). In that experiment, 78 mL of 6.0 *M* nitric acid was added to 39.48 g of centrifuged wet solids and resulted in a 3.4 *M* acid solution with about 63% of the solids dissolved. By the previous assumption that the hydroxide content of the interstitial supernatant is insignificant, the number of equivalents for air-dried solids is computed to be 5.98 mol/kg. If the difference in charge balance between the anions and cations in the sludge solids (from Table 2.1) is made up by hydroxide ion, the hydroxide content of the air-dried sludge is 5.5 mol/kg. These numbers are quite close and may be used in estimates of the amount of acid required to dissolve the sludge.

3. DESCRIPTION OF EXPERIMENTS

3.1 REAGENTS

Reagent-grade chemicals were purchased for use in purification of the CMPO extractant and as the working chemicals in the extraction tests. All chemicals except the CMPO were used as received. Water used in the experimental program was distilled and demineralized with an ion-exchange resin. The resulting "ultra pure" water had a measured resistance of ≥ 17.7 M Ω /cm.

CMPO was purchased from ATOCHEM North America, Philadelphia, Pennsylvania, with a purity of 95–97%. The CMPO was purified according to a procedure developed by Gatrone et al. (1987) and Tse and Vandegrift (1989), with modifications supplied by Vandegrift (1993). A detailed description of the purification as actually performed in the laboratory has been reported by Spencer (1994, 1995). The essential purification steps include (1) dissolving the CMPO in *n*-heptane, (2) filtering the resulting solution, (3) vigorously mixing Amberlyst A-26® (Rohm and Haas Company)

anionic resin that had been converted from the Cl^- to the OH^- form and Dowex AG MP-50® (Dow Chemical Company) cationic resin with the solution to remove charged particles, (4) filtering the solution to remove the resin particles, (5) washing the organic solution with aqueous sodium carbonate solution, (6) washing the organic again with mild aqueous nitric acid, (7) washing the organic with ultra pure water, (8) drying the organic with anhydrous sodium sulfate, (9) vacuum-evaporating about two-thirds of the *n*-heptane from the solution, (10) cooling the solution to allow the CMPO to crystallize, (11) grinding the crystals, and (12) drying the crystals under vacuum. Analysis of the purified CMPO using high-performance liquid chromatography (HPLC) at an absorbance wavelength of 222 nm, as recommended by Tse and Vandegrift (1989), showed that the purity was > 99.4%.

TRUEX solvent was prepared by dissolving weighed quantities of CMPO and TBP in *n*-dodecane to produce a solution of 0.2 M CMPO and 1.4 M TBP. Analytical-quality TBP manufactured by Eastman Kodak Company having a purity of > 99% and anhydrous *n*-dodecane from Aldrich Chemical Company having a purity of > 99% were used. Because the solvent was stored for a long time after it was prepared, it was treated with a carbonate wash to remove any degradation products (usually organic acids) before being used in the extraction tests. 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 ultra pure water.

Sludge wash solutions of 0.20 M NaOH were prepared from analyzed reagent by dilution with pure water. Nitric acid dissolution solutions were prepared from high-purity 6 M stock and titrated with 0.100 M NaOH analyzed reagent; a quantity of 5.44 M HNO_3 was prepared for the experiments. Various organic stripping solutions were prepared using reagent-grade nitric acid, sodium nitrate, and oxalic acid.

3.2 EXPERIMENTAL PROCEDURES

Only two TRUEX campaigns were performed. The sludge washing and dissolution and extraction and stripping procedures were all performed at ambient temperature (24°C). Because the treatment steps (acid concentration, volume ratios, etc.) between the two tests varied, the general procedures are given here. Details of each dissolution and TRUEX test are given in Sect. 4, Results and Discussion.

As part of an ongoing comprehensive sludge treatment program, approximately 5 L of sludge/supernatant was retrieved from MVST W-25 and stored in a stainless steel tank located in a

hot cell in Building 4501 (Collins et al., 1994). To prepare for TRUEX extraction tests, sludge samples were dispensed from the sludge storage tank into a 250-mL polypropylene centrifuge bottle. Using an International Equipment Company model Centra-GP8 centrifuge, the sludge was centrifuged at 4140g (where g is equal to the gravitational acceleration at the surface of the earth) for 20 min to separate the sludge solids and supernatant. The supernatant phase was decanted and saved. 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) that was equal to or exceeded the estimated interstitial supernatant volume remaining with the solids to remove these components without dissolving the actinides. The washing was repeated once or twice. Weighed quantities of sludge were then dissolved in strong nitric acid to produce solutions containing total metal concentrations of between 0.5 and 1.8 M and nitric acid concentrations between 1.6 and 3.0 M. Most of the sludge dissolved, leaving behind a small residue of undissolved solids which was dried at room temperature and weighed. Aliquots of the solution containing the dissolved sludge were taken for chemical analysis.

After the washing and dissolution operations, the dissolved sludge was less radioactive and could be handled in a chemical hood. The dissolved sludge solution was filtered with 0.45- μ m-porosity syringe filters; however, in one 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 coarse, fluted no. 588 filter paper. The filtered solution was contacted with TRUEX solvent in separatory flasks and shaken by hand for at least 60 s to obtain a good mixing of the phases. The aqueous and organic phases were then allowed to separate by gravity for 15 min. Samples of each phase were saved for chemical analysis. A similar procedure was used for a second extraction of the dissolved sludge and for aqueous stripping of the loaded organic phase. Samples of the aqueous dissolved sludge solutions and aqueous raffinate from the extraction steps were taken for nephelometry studies.

3.3 ANALYSIS OF SAMPLES

Chemical and radiochemical analyses of samples were performed by the Chemical and Analytical Services Division. Analyses included free acid concentration, cation concentrations, anion concentrations, and radiochemical measurements. Generally the analytical procedures used for the aqueous and organic samples were the same, but analysis of metals in the organic medium first required destruction of the organic matrix with a microwave acid digestion using a combination of

sulfuric and nitric acids to place the analytes in aqueous solution. Solids were dissolved in an aqueous medium prior to analysis. Turbidity measurements on the aqueous samples were performed in the laboratory. A brief summary of the analysis methods is provided as follows.

Potentiometric titration with 0.1 M NaOH solution was used to measure hydrogen ion concentration. The endpoint of the titration was elucidated by use of a Metrohm pH meter.

Metal analysis was accomplished by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). A Spectroflame-ICP Model FAO-05 analyzer simultaneously measured up to 22 metals at emission wavelengths of between 210 and 800 nm. All samples were fed to the analyzer through a Spectro cross-flow nebulizer.

The common ions, including fluoride, chloride, bromide, nitrate, phosphate, and sulfate, were analyzed using a Dionex series 4500i ion chromatograph. This unit was configured with a pulsed electrochemical detector operating in the conductivity mode.

Gross alpha analysis was accomplished on a Tennelec LB4000 low-level alpha/beta counter. Aqueous samples were prepared by dilution with aqueous nitric acid. Organic samples were prepared in one of two ways: the organic matrix in samples from the first TRUEX test was destroyed by acid digestion as described above, and those from the second TRUEX test were simply diluted in *n*-dodecane. Samples, in a liquid form, were pipetted onto a stainless steel planchet and evaporated to dryness. The radioactive materials were fixed to the planchet by heating over a Bunsen burner.

Following the gross alpha counting measurements, the planchets were analyzed using a Tennelec TC256 alpha spectrometer. Resolution of the energy peaks in the spectrograph was used to identify the alpha emitters and their relative abundance. Isotopes measured by this method included the actinides ²³⁹Pu, ²⁴¹Am, and ²⁴⁴Cm.

A method requiring heating of the sample could not be used for analysis of beta emitters because of the volatility of cesium. Gross beta analysis was performed using a Packard 2500 TR liquid scintillation counter. Gamma-emitting nuclides were counted with a high-purity germanium detector and a Canberra-Nuclear Data AccuSpec™ Genie-PC system that identifies the nuclides based on their associated gamma-ray energies. Strontium was isolated by extraction chromatography, placed on a stainless steel planchet, and counted with a Tennelec LB4000 gas flow proportional counter.

Turbidity in aqueous sludge leachates and extraction raffinates was measured with a Hach 2100 AN Turbidimeter, the same unit used in gelation studies conducted by Beahm et al. (1995). This instrument is capable of measuring in the range of 0–10,000 Nephelometric Turbidity Units (NTU). All samples in this test were acidic and were contained in glass vials.

4. RESULTS AND DISCUSSION

4.1 DISSOLUTION OF MVST SLUDGE

Representative actinide-bearing aqueous solutions prepared by dissolution of sludge by any of the methods tested by Collins et al. (1994) should be suitable for preliminary TRUEX tests. However, use of hydrofluoric acid is not recommended in the preliminary tests because (1) the major effect on dissolution is the release of more cesium, which is not extracted, and cesium is a source of radiation that can damage the solvent; (2) the fluoride suppresses the extraction of plutonium due to complex formation; and (3) hydrofluoric acid is potentially more difficult to handle.

The concentrations of the actinides in the sludge are quite low, so it is desirable to dissolve the sludge into as small a volume as possible to reduce dilution. On the other hand, simulations performed to plan the tests, using the GTM, did not converge when the total metal concentration exceeded 1.8 *M* in 3.0 *M* nitric acid solutions. The requirement to compare GTM calculations with measured results forces the use of conditions that the GTM can handle. The interstitial supernatant associated with the wet sludge contributes a large fraction of the total process metals, such as sodium, to the mass of dried sludge. For dissolved sludge solutions having a fixed total metal concentration (e.g., 1.8 *M*), washing of the sludge to reduce the metal contribution of interstitial supernatant will permit the sludge to be dissolved in a smaller volume than unwashed sludge. In turn, this will permit higher concentrations of the actinides in the final dissolvent. Collins et al. (1994) have shown that washing the sludge with mild caustic does not remove actinides from the sludge but does remove Na, Al, and some Cs and Sr.

Suitable dissolved sludge solutions can be prepared by first washing the sludge with mild caustic and then dissolving the sludge in strong nitric acid to produce a solution having a total metal concentration of ≤ 1.8 *M* in a nitric acid solution of 3.0 *M* or less. The dissolved sludge solution should be filtered prior to use in TRUEX extraction tests. Solutions with nitric acid concentrations around 3.0 *M*, and somewhat less, result in large distribution ratios during extraction, which is desirable.

Previous studies have shown that the sludge does not completely dissolve in nitric acid alone. The acid dissolves all the actinides except plutonium, which will be only about 50% dissolved. Silicates and aluminates are probably among the constituents that do not dissolve. Addition of hydrofluoric acid in the dissolution was tested and does improve overall dissolution, but it does not significantly affect the dissolution of plutonium (Collins et al., 1994). Presence of fluoride ion will,

on the other hand, detrimentally affect the TRUEX process by markedly suppressing the extraction of plutonium. General dissolution conditions were, therefore, adopted. The sludge was washed with mild caustic to remove the bulk of the interstitial nitrate-bearing solution. The caustic wash does not remove measurable quantities of the actinides, but it does remove much of the Na, Cs, Sr, and other solutes associated with the interstitial liquid by a dilution effect (Collins et al., 1994). Washing is followed by dissolution with moderate-strength nitric acid. The actinides report almost entirely to the dissolved sludge solution.

4.1.1 First Test

Two sludge samples (~125 mL each to accommodate using the centrifuge bottles as dissolution vessels) were removed from the storage reservoir and centrifuged, and the supernatant was decanted. The sludge was washed three times with 0.2 M NaOH solution, the mixture was centrifuged, and the supernatant was decanted after each washing. Washed sludge samples were dissolved using 5.5 M nitric acid. The resulting dissolved sludge solution had a cation concentration (not including H⁺) of ~1.8 M and a nitric acid concentration of ~2.9 M. Attempts were made to filter the solution with 0.45- μ m-porosity syringe filters, but the filters plugged almost immediately. This behavior was attributed to a rapidly forming gel. The solution was successfully filtered with coarse no. 588 filter paper; the collected residue appeared as a gel. A portion of the filtered solution was set aside for several days, during which time it gelled almost completely.

Given the assay of the sludge and supernatant provided by Collins et al. (1994, 1995), it is possible to estimate the solute concentrations in dissolved sludge. The concentrations of the solutes in the dissolved sludge solution were estimated as outlined in Appendix A. These calculations are based on the assumption that the sludge totally dissolves, leaving behind no residue. The estimated concentrations are compared with those actually measured in the dissolved sludge solution in Table 4.1. Only those components for which data are available for both the sludge and dissolved sludge are compared; all measurements made on the dissolved sludge solution are shown in Sect. 4.2. The ratio of the predicted (calculated) concentration to the measured concentration simplifies the comparison. Ratio values less than unity likely indicate analysis problems, and values greater than unity tend to indicate either those species that do not easily dissolve or analysis problems. Values much larger than unity are taken to indicate those species that do not readily dissolve. Small variations around unity, such as $\pm 20\%$, can be attributed to the many assumptions made to estimate the concentration in the dissolved sludge solution.

Table 4.1. Comparison of estimated and measured concentrations of species in dissolved sludge solution for the first test

	Calculated concentration (Bq/L)	TR01, measured concentration (Bq/L)	Ratio, calculated to measured
Radionuclides			
⁶⁰ Co	4.01×10^7	3.00×10^7	1.34
⁹⁰ AllSr	4.50×10^9	3.70×10^9	1.22
¹³⁴ Cs	1.12×10^4	$<1.30 \times 10^6$	>0.00865
¹³⁷ Cs	2.90×10^8	3.95×10^7	7.34
¹⁵⁴ Eu	3.31×10^7	2.90×10^7	1.14
²³⁸ Pu	1.77×10^7	7.25×10^6	2.45
^{239/240} Pu	5.67×10^6	3.85×10^6	1.47
²⁴¹ Am	6.15×10^6	$<1.10 \times 10^7$	>0.559
²⁴⁴ Cm	7.56×10^7	9.85×10^7	0.768
Other metals	(mg/L)	(mg/L)	
H ⁺	2960.	2850.	1.04
Al	6020.	6490.	0.928
Ba	94.4	116.	0.813
Ca	22700.	31600.	0.718
Cd	11.8	18.0	0.657
Co	9.46	8.13	1.16
Cr	133.	107.	1.24
Cu	70.9	53.0	1.34
Fe	2030.	1680.	1.21
Hg	47.3	467.	0.101
K	984.	1360.	0.724
Mg	3190.	3740.	0.853
Mn	189.	212.	0.892
Na	11400.	2090.	5.46
Ni	94.6	81.4	1.16
Pb	473.	555.	0.852
Si	3620.	149.	24.3
Sr	1320.	495.	2.67
Th	13600.	15600.	0.870
Tl	189.	<14.3	>13.2
U	6520.	7750.	0.842
Zn	188.	185.	1.01
Anions	(mg/L)	(mg/L)	
Br ⁻	166.	$<50.$	>3.31
Cl ⁻	228.	160.	1.43
F ⁻	385.	527.	0.731
NO ₃ ⁻	275000.	316000.	0.869
PO ₄ ³⁻	6970.	451.	15.5
SO ₄ ²⁻	1250.	346.	3.60

The data in Table 4.1 show that silicon, phosphate, and cesium (based on ^{137}Cs radiochemical analysis) are the primary constituents that do not dissolve in nitric acid. Ratios of predicted-to-measured concentrations are large enough for sodium and sulfate to indicate incomplete dissolution. The metals analysis indicates that strontium does not completely dissolve, but radiochemical analysis of ^{90}Sr does not corroborate this. Thallium and bromide concentrations in the dissolved sludge were below the detection limit, indicating that these species also do not readily dissolve. Radiochemical analysis of plutonium indicates that about half of the plutonium dissolved, which was expected based on the work of Collins et al. (1994).

The fraction of the sludge that did not dissolve can be calculated from the starting quantity of wet, centrifuged solids, the air-dried solids content of those solids (0.59 g/g, Sect. 2), and the air-dried mass of the residue. In this first test, ~46.5% of the sludge did not dissolve.

4.1.2 Second Test

Dissolution of the sludge for a second TRUEX experiment was carried out under less aggressive conditions and was designed to make a less concentrated solution to reduce the formation of gels. Preparation of the sludge consisted of (1) centrifuging and decanting the supernatant; (2) treating the sludge with nitric acid to neutralize all hydroxides and to destroy carbonates, thus liberating carbon dioxide; (3) treating the sludge with a strong caustic solution (~2.6 M) for ~6 h to reprecipitate any actinides that may have become soluble and to leach any caustic soluble species; (4) centrifuging and decanting the high-pH supernatant; (5) washing the remaining sludge with mild (0.2 M) caustic; (6) centrifuging and decanting the supernatant; and (7) dissolving the sludge in ~2.7 M HNO_3 . The final dissolution resulted in a solution containing cation concentrations (not including H^+) of ~0.6 M and a nitric acid concentration of ~1.7 M. Immediately following dissolution, the test specimen was centrifuged, and a sample of the acidic supernatant was filtered with a 0.45- μm -porosity syringe filter and taken for turbidity measurements. The supernatant and undissolved sludge solids were then remixed and placed on the rotator to agitate and age for about a week. Following this aging, the specimen was centrifuged and dissolved sludge solution was decanted for the extraction test. Before performing the TRUEX tests, the dissolved sludge solution was again filtered, with some difficulty, using 0.45- μm -porosity syringe filters. Gelation of the dissolved sludge was very much slower in this second test than it was in the first experiment.

Prediction of the solute concentrations in dissolved sludge from the sludge assay was also done for the second dissolution, as outlined in Appendix A. Because the sludge was first neutralized with acid and washed with strong caustic (essentially a caustic dissolution), the deviations from the

assumptions of ideality are expected to be greater than those for the first dissolution. However, some qualitative assessments may be made; the data are given in Table 4.2. Phosphate and cesium distinguish themselves as constituents that dissolve to a small extent. Fluoride and sulfate do not completely dissolve. Silicon and thallium appear to have more completely dissolved in the second test. Strontium behaves as before; the metals analysis indicates that it does not completely dissolve, but the radiochemical analysis does not corroborate this. Dissolution of plutonium is also not complete. Based on the analysis of $^{239/240}\text{Pu}$, about 25% of the plutonium dissolved. (The data on ^{238}Pu , which indicate that it is dissolved only sparingly, are probably in error.)

Again, the fraction of the sludge that did not dissolve can be calculated from the measured mass of the residue. In this second test, ~20.7% of the sludge did not dissolve. Compared with the first test, this a strong indication that the pretreatment of the sludge with strong caustic prior to dissolution removes some high-pH soluble species or changes the form of some species to make them more soluble. Additional work would need to be performed to ascertain the true mechanism.

4.2 TRUEX PARTITIONING OF DISSOLVED SLUDGE

Two different TRUEX tests were performed using the two different dissolved sludge solutions described above. The extraction and stripping operations were restricted to batch equilibrations. In each of the two tests, four separate equilibrations were performed to simulate four stages of a batch, cross-flow TRUEX process. TRUEX-NPH solvent, consisting of 0.2 M CMPO and 1.4 M TBP in a normal paraffin hydrocarbon (*n*-dodecane), was used in the tests. The temperature was maintained at a nearly constant 24°C.

The GTM (Vandegrift et al., 1992) was used to simulate the batch shake-out tests, and model predictions were compared with measured results. Equilibrium compositions in each phase, resulting from contacting the aqueous dissolved sludge solution with fresh organic TRUEX solvent, were estimated with the GTM. The GTM is capable of making the calculations for a temperature of 25°C for all species included in the model and can make corrections for other temperatures only for selected species included in the model. Because the test temperature was close to 25°C, the temperature at which the GTM data base is more complete, that value was used for all simulations.

Although the last release of the GTM [version 3.1.1 (Copple, 1993, 1994)] contains an improved user interface, it is still cumbersome to calculate multiple-batch contacts with fresh solvent in a single run of the code. Manual editing of the spreadsheet file containing the process description permits calculations that model sequential-batch contacts.

Table 4.2. Comparison of estimated and measured concentrations of species in dissolved sludge solution for the second test

	Calculated concentration	TRO2, measured concentration	Ratio, calculated to measured
Radionuclides	(Bq/L)	(Bq/L)	
⁶⁰ Co	1.34 × 10 ⁷	8.80 × 10 ⁶	1.53
^{90/111} Sr	1.50 × 10 ⁹	9.80 × 10 ⁸	1.54
¹³⁴ Cs	2.29 × 10 ³	<5.90 × 10 ⁴	>0.0388
¹³⁷ Cs	9.59 × 10 ⁷	1.50 × 10 ⁷	6.40
¹⁵⁴ Eu	1.11 × 10 ⁷	8.45 × 10 ⁶	1.31
²³⁸ Pu	5.94 × 10 ⁶	1.65 × 10 ⁴	360.
^{239/240} Pu	1.90 × 10 ⁶	4.59 × 10 ⁵	4.14
²⁴¹ Am	2.06 × 10 ⁶	1.95 × 10 ⁶	1.06
Other metals	(mg/L)	(mg/L)	
H ⁺	2080.	1660.	1.25
Al	2020.	1660.	1.22
Ba	31.6	30.1	1.05
Ca	7610.	7290.	1.04
Cd	3.96	4.00	0.991
Co	3.17	1.89	1.68
Cr	44.5	28.1	1.58
Cu	23.8	13.9	1.71
Fe	682.	501.	1.36
Hg	15.8	59.0	0.269
K	300.	190.	1.58
Mg	1070.	923.	1.16
Mn	63.4	51.9	1.22
Na	4470.	4290.	1.04
Ni	31.7	19.2	1.65
Pb	158.	127.	1.25
Si	1210.	742.	1.63
Sr	444.	43.7	10.2
Th	4550.	3970.	1.15
Tl	63.4	<50.0	>1.27
U	2190.	1990.	1.10
Zn	62.8	49.2	1.28
Anions	(mg/L)	(mg/L)	
Br ⁻	55.5	<50.	>1.11
Cl ⁻	68.6	67.	1.02
F ⁻	128.	48.	2.67
NO ₃ ⁻	134000.	130000.	1.03
PO ₄ ³⁻	2340.	63.	37.1
SO ₄ ²⁻	412.	114.	3.62

The dissolved sludge compositions were used to describe an aqueous feed stream in the GTM. Because the GTM does not include all species found in the sludge, similar species (those from the same periodic group) were assumed to behave in the same manner and were grouped together as follows: Tl with Al, Co and Ni with Fe, K with Na, Be with Mg, Mn with Tc, Zn and Hg with Cd, and Br and Cl with F. The elements Pb, Si, and V could not be as easily generalized, but because the concentrations were small and they should not extract appreciably, they were ignored. Carbonate was assumed to be evolved during the dissolution from the solutions as CO₂ and was set to zero in the GTM simulations. All plutonium was assumed to be in the +4 valence state.

4.2.1 First Test

Figure 4.1 illustrates the planned flow of material in the first test. Aqueous feed (dissolved sludge solution) is subjected to two extraction contacts with fresh organic; the separated aqueous from the first contact is contacted again with fresh organic. The figure also shows how the loaded organic from the first extraction (which is most heavily laden with actinides) is taken and subjected to two sequential aqueous strips. Such a diagram also illustrates the basis for setting up the GTM for a simulation.

In the laboratory, a 100-mL portion of the freshly filtered, dissolved sludge solution was contacted with an equal volume of TRUEX solvent. The contact resulted in the formation of a third phase at a temperature of ~24.0°C. Increasing the organic-to-aqueous volumetric phase ratio to 2.5:1 eliminated the third phase. A second equal-volume batch contact of the aqueous with fresh organic did not produce any phase separation problems. The loaded organic from the first batch extraction (in which the organic is most heavily loaded) was stripped with an equal volume of solution containing 0.5 M NaNO₃ and 0.01 M HNO₃ to remove nitric acid while attempting to keep the actinides in the organic phase. A second batch strip of the organic using an equal volume of aqueous solution containing 0.5 M H₂C₂O₄ and 0.01 M HNO₃, designed to remove the bulk of the actinides, resulted in a white precipitate in the aqueous phase; the organic remained clear. The organic phase was filtered to remove any stray particulates before analysis. The aqueous phase was homogenized so that the analysis of aliquots would include the precipitated species. Samples of each phase for each of the four separate contacts were submitted for analysis.

4.2.1.1 Evaluation of Data

Results of analyses of samples from the first TRUEX experiment on dissolved MVST sludge are shown in Tables 4.3 and 4.4. These data may be evaluated directly with calculations of the

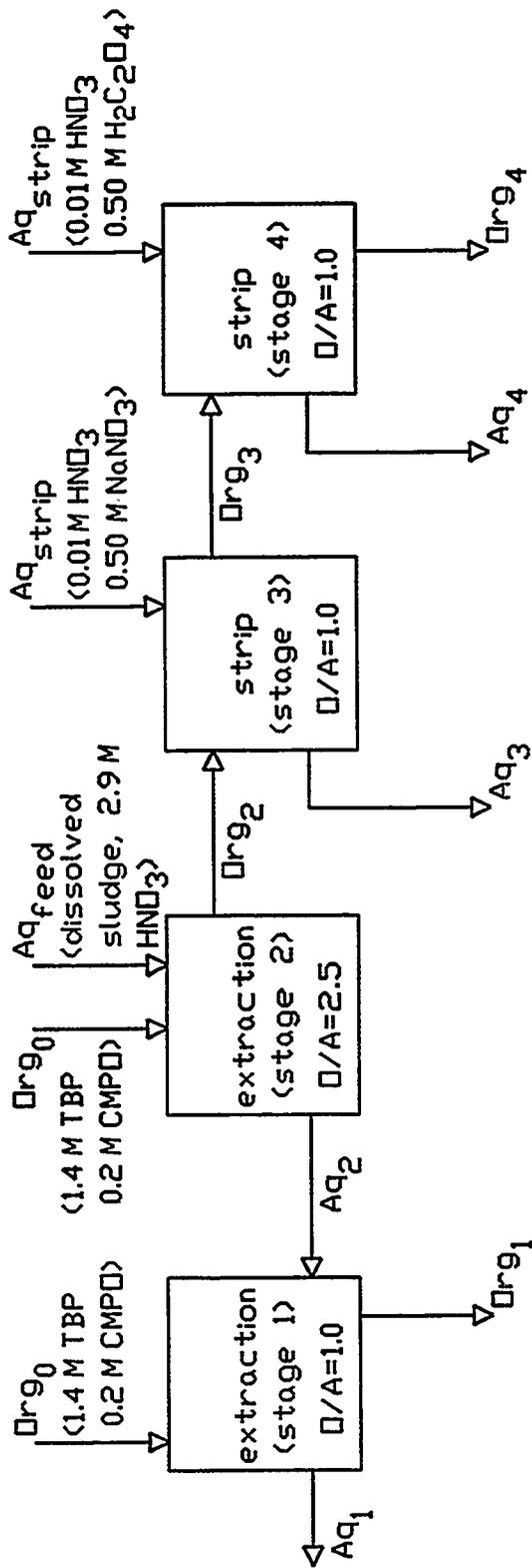


Fig. 4.1. Material flow paths for batchwise TRUEX test with two extraction and two strip stages.

Table 4.3. Composition of dissolved sludge solution and aqueous extraction and strip samples in first test^a

	Molecular weight	TR01, dissolved sludge (Bq/L)	TR01E1A, first extraction (Bq/L)	TR01E2A, second extraction (Bq/L)	TR01S1A, first strip (Bq/L)	TR01S2A, second strip ^b (Bq/L)
Radionuclides						
⁶⁰ Co	60.	3.00 × 10 ⁷	3.00 × 10 ⁷	2.95 × 10 ⁷	3.05 × 10 ⁵	<1.30 × 10 ⁵
^{90/107} Sr	90.	3.70 × 10 ⁹	3.75 × 10 ⁹	3.75 × 10 ⁹	2.70 × 10 ⁷	2.35 × 10 ⁵
¹³⁴ Cs	134.	<1.30 × 10 ⁶	<4.80 × 10 ⁵	<4.30 × 10 ⁵	<1.50 × 10 ⁵	<2.60 × 10 ⁵
¹³⁷ Cs	137.	3.95 × 10 ⁷	4.00 × 10 ⁷	3.95 × 10 ⁷	3.35 × 10 ⁵	<3.70 × 10 ⁵
¹⁵² Eu	152.	5.65 × 10 ⁷	<1.60 × 10 ⁶	<1.60 × 10 ⁶	2.55 × 10 ⁶	2.00 × 10 ⁷
¹⁵⁴ Eu	154.	2.90 × 10 ⁷	<1.10 × 10 ⁶	<8.40 × 10 ⁵	1.30 × 10 ⁶	1.05 × 10 ⁷
¹⁵⁵ Eu	155.	<5.50 × 10 ⁶	<2.40 × 10 ⁶	<2.40 × 10 ⁶	<5.10 × 10 ⁵	1.80 × 10 ⁶
²³⁸ Pu	238.	7.25 × 10 ⁶	8.10 × 10 ⁴	4.60 × 10 ⁴	3.80 × 10 ³	2.20 × 10 ⁶
²³⁸ Pu/ ²⁴¹ Am	238.	1.45 × 10 ⁷	5.45 × 10 ⁵	9.15 × 10 ⁵	3.00 × 10 ⁵	6.00 × 10 ⁶
^{239/240} Pu	239.	3.85 × 10 ⁶	4.05 × 10 ⁴	2.20 × 10 ⁴	2.05 × 10 ³	1.16 × 10 ⁶
²⁴² Pu	242.	3.00 × 10 ⁶	N.M. ^c	N.M.	N.M.	3.80 × 10 ⁵
²⁴¹ Pu	240.	1.11 × 10 ⁷	1.22 × 10 ⁵	6.80 × 10 ⁴	5.90 × 10 ³	3.30 × 10 ⁶
²⁴¹ Am	241.	<1.10 × 10 ⁷	<4.70 × 10 ⁶	<4.70 × 10 ⁶	<1.10 × 10 ⁶	2.95 × 10 ⁶
²⁴⁴ Cm	244.	9.85 × 10 ⁷	4.40 × 10 ⁶	2.20 × 10 ⁶	4.35 × 10 ⁶	3.75 × 10 ⁷
Gross α		1.20 × 10 ⁸	4.95 × 10 ⁶	3.75 × 10 ⁶	4.65 × 10 ⁶	4.55 × 10 ⁷
Gross β		1.05 × 10 ¹⁰	9.55 × 10 ⁹	9.35 × 10 ⁹	1.60 × 10 ⁸	1.80 × 10 ⁸
Other metals						
		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
H ⁺	1.00	2850.	1300.	1050.	365.	780.
Al	26.98	6490.	5840.	5940.	28.0	29.6
Ba	137.33	116.	118.	120.	0.684	<0.117
Be	9.01	7.59	7.61	8.07	<0.073	<0.091
Ca	40.08	31600.	29200.	28200.	920.	18.2
Cd	112.41	18.0	14.8	16.4	0.295	<0.136
Co	58.93	8.13	7.18	7.51	<0.121	<0.151
Cr	52.00	107.	103.	105.	0.581	<0.149
Cu	63.55	53.0	47.4	49.1	0.685	1.18
Cs	132.91	N.M.	N.M.	N.M.	N.M.	N.M.
Fe	55.85	1680.	1650.	1650.	33.7	4.92
Hg	200.59	467.	34.0	14.8	<5.0	87.1
K	39.10	1360.	1280.	1340.	26.3	21.1
Mg	24.31	3740.	4040.	4150.	19.3	1.81
Mn	54.94	212.	188.	190.	5.72	0.206
Na	22.99	2090.	2630.	2680.	3680.	9.37
Ni	58.70	81.4	71.8	79.4	0.486	<0.171
Pb	207.2	555.	457.	467.	19.4	<6.25
Si	28.09	149.	181.	247.	5.99	4.10
Sr	87.62	495.	283.	284.	114.	2.90
Th	232.04	15600.	180.	181.	5.23	6450.
Tl	204.37	<14.3	<1.49	<7.14	<1.19	<1.49
U	238.03	7750.	4.18	<3.69	7.27	607.
V	50.94	<1.54	1.42	1.15	0.217	<0.160
Zn	65.38	185.	194.	197.	1.71	<0.221
Anions						
		(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Br ⁻	79.90	<50.	<50.	<50.	<50.	<5.
Cl ⁻	35.45	160.	146.	146.	8.98	8.90
F ⁻	19.00	527.	621.	681.	<5.0	15.2
NO ₃ ⁻	62.00	316000.	224000.	201000.	59600.	18700.
PO ₄ ³⁻	94.97	451.	1340.	1660.	45.6	33.9
SO ₄ ²⁻	96.06	346.	300.	328.	<10.	14.0

^aSilver and antimony were below detectable limits in all samples.

^bThe oxalate precipitate particles were well mixed with the liquid before aliquots were taken for analysis. The analysis, therefore, includes the contribution from the precipitate.

^cN.M. = not measured.

Table 4.4. Composition of organic extraction and strip samples in first test^a

	TR01E1O, first extraction	TR01E2O, second extraction	TR01S1O, first strip	TR01S2O, second strip ^b
Radionuclides	(Bq/L)	(Bq/L)	(Bq/L)	(Bq/L)
⁶⁰ Co	<1.30 × 10 ⁵	2.45 × 10 ⁵	<7.40 × 10 ⁴	<2.70 × 10 ⁴
⁹⁰ / ^{all} Sr	2.15 × 10 ⁷	5.20 × 10 ⁷	3.50 × 10 ⁵	2.40 × 10 ⁴
¹³⁴ Cs	<1.60 × 10 ⁵	<3.30 × 10 ⁴	<1.60 × 10 ⁵	<2.20 × 10 ⁴
¹³⁷ Cs	2.00 × 10 ⁵	4.00 × 10 ⁴	<1.90 × 10 ⁵	3.50 × 10 ⁴
¹⁵² Eu	2.15 × 10 ⁷	6.65 × 10 ⁵	1.90 × 10 ⁷	<4.20 × 10 ⁴
¹⁵⁴ Eu	1.10 × 10 ⁷	3.80 × 10 ⁵	1.05 × 10 ⁷	<6.20 × 10 ⁴
¹⁵⁵ Eu	2.30 × 10 ⁶	<1.40 × 10 ⁵	2.50 × 10 ⁶	<4.30 × 10 ⁴
²³⁸ Pu	2.28 × 10 ⁶	1.25 × 10 ⁴	2.15 × 10 ⁶	9.40 × 10 ³
²³⁸ Pu/ ²⁴¹ Am	N.M. ^c	N.M.	N.M.	N.M.
^{239/240} Pu	1.16 × 10 ⁶	1.80 × 10 ⁴	1.12 × 10 ⁶	5.20 × 10 ³
²⁴² Pu	N.M.	N.M.	N.M.	N.M.
^{all} Pu	3.43 × 10 ⁶	3.05 × 10 ⁴	3.27 × 10 ⁶	1.40 × 10 ⁴
²⁴¹ Am	2.75 × 10 ⁶	<2.60 × 10 ⁵	2.30 × 10 ⁶	<9.90 × 10 ⁴
²⁴⁴ Cm	<i>d</i>	<i>d</i>	<i>d</i>	<i>d</i>
Gross α	4.40 × 10 ⁷	1.60 × 10 ⁶	4.10 × 10 ⁷	1.02 × 10 ⁶
Gross β	1.80 × 10 ⁸	1.25 × 10 ⁸	1.20 × 10 ⁸	2.00 × 10 ⁶
Other metals	(mg/L)	(mg/L)	(mg/L)	(mg/L)
H ⁺	615.	490.	575.	800.
Al	276.	12.8	290.	<9.21
Ba	<1.87	<1.87	<1.87	<1.87
Be	1.70	<1.45	1.80	<1.45
Ca	707.	1650.	64.8	57.7
Cd	<2.18	<2.18	<2.18	<2.18
Co	<2.42	<2.42	<2.42	<2.42
Cr	<2.39	<2.39	<2.39	<2.39
Cu	9.75	<2.56	9.90	<2.56
Cs	N.M.	N.M.	N.M.	N.M.
Fe	28.6	33.2	5.70	<1.80
Hg	<100.	<100.	<100.	<100.
K	<55.9	<55.9	<55.9	<55.9
Mg	<10.8	<10.8	<10.8	<10.8
Mn	4.20	9.95	<1.63	<1.63
Na	9.60	6.30	<4.44	<4.44
Ni	<2.73	<2.73	<2.73	<2.73
Pb	<109.	<109.	<109.	<109.
Si	98.8	61.9	112.	96.0
Sr	0.650	1.60	<0.14	<0.14
Th	4780.	11.6	5110.	53.9
Tl	28.8	<23.8	28.7	36.8
U	2490.	<59.1	2610.	2000.
V	<2.56	<2.56	<2.56	<2.56
Zn	<3.53	<3.53	<3.53	<3.53
Anions	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Br ⁻	<20.	<20.	<20.	<20.
Cl ⁻	<20.	<20.	<20.	<20.
F ⁻	<~500. ^e	<~500. ^e	<~500. ^e	<~500. ^e
NO ₃ ⁻	45100.	58200.	18100.	7030.
PO ₄ ³⁻	<100.	<100.	<100.	<100.
SO ₄ ²⁻	<100.	<100.	<100.	<100.

^aSilver and antimony were below detectable limits in all samples.

^bThe oxalate precipitate particles were filtered from the liquid before aliquots were taken for analysis. The analysis, therefore, does not include the contribution from the precipitate.

^cN.M. = not measured.

^dResidues left from destruction of the organic matrix interfered with alpha spectrometry analysis; no reliable result could be obtained.

^eLower limit of detection is unusually large due to organic sample matrix.

fraction of each metal species removed from the aqueous dissolved sludge solution, the fraction of the metals recovered in the aqueous strip solution, and the fraction of each species stripped from the organic solvent. The sample names shown in Tables 4.3 and 4.4 may be used as variable names for constructing the necessary equations. Based on the aqueous-phase measurements, the percentage of each species removed in the first extraction is

$$r_{i,1} = \left(\frac{TRO1 - TRO1E1A}{TRO1} \right)_i \times 100 , \quad (4-1)$$

where $r_{i,1}$ = percent of species i removed in the first stage.

The cumulative amount removed by both extraction stages is similarly based on the original aqueous feed and the final treated aqueous product,

$$r_{i,all} = \left(\frac{TRO1 - TRO1E2A}{TRO1} \right)_i \times 100 , \quad (4-2)$$

where $r_{i,all}$ = percent of species i removed by both extraction stages.

Similar equations could be constructed for the organic phase; however, there seems to be more noise in those data and no new information would be revealed.

The amount of each species recovered, based on the quantities introduced by the feed, can be calculated from the analysis of the aqueous stripping solutions. It was anticipated that the bulk of the actinides would be extracted in the first stage, so only the organic from the first extraction stage was subjected to the stripping operation. The percentage recovery by the first strip is given by

$$p_{i,1} = \left(\frac{2.5(TRO1S1A)}{TRO1} \right)_i \times 100 , \quad (4-3)$$

where $p_{i,1}$ = the percent of species i recovered by the first strip.

The factor 2.5 accounts for the 2.5:1 organic to aqueous-phase ratio used in the first extraction stage. The cumulative percentage recovery with both stripping stages is given by

$$p_{i,all} = \left(\frac{2.5(TRO1S1A + TRO1S2A)}{TRO1} \right)_i \times 100 , \quad (4-4)$$

where $p_{i,all}$ = the percent of species i recovered by both strip stages.

Another value of interest is the percentage of material stripped from the organic. The percentage stripped may be based on the concentrations in the loaded organic and the remaining concentrations in the organic after stripping. For the first strip stage, the value is given by

$$s_{i,1} = \left(\frac{TR01E1O - TR01S1O}{TR01E1O} \right)_i \times 100, \quad (4-5)$$

where $s_{i,1}$ = the percentage of species i stripped by the first stripping stage.

Similarly, the cumulative percentage stripped in both stripping stages is given by

$$s_{i,all} = \left(\frac{TR01E1O - TR01S2O}{TR01E1O} \right)_i \times 100, \quad (4-6)$$

where $s_{i,all}$ = the percentage of species i stripped by both stripping stages.

In this form, these last two equations pertain only to the effectiveness of removing solute from the organic and are independent of the amount originally extracted from the aqueous feed.

Results of the above calculations are given in Table 4.5. Europium, curium, plutonium, thorium, and uranium were all strongly extracted from the dissolved sludge solution. Concentrations of americium were below the reliable reporting limit. In the first-stage batch extraction, >97% of the europium, ~96% of the curium, ~99% of the plutonium, ~99% of the thorium, and >99% of the uranium were removed. The data indicated that mercury was strongly extracted. Cobalt, strontium, and cesium essentially did not extract. The second extraction was not as effective as the first, as might be expected. This is because (1) the organic- to aqueous-phase ratio was smaller in the second extraction, (2) the remaining concentrations were so low that discrimination in the analyses was difficult, and (3) it is likely that microscopic gelation sites formed that immobilized some of the constituents in the aqueous phase, thereby preventing their extraction. Given the large fraction of TRUs removed in only one stage, it appears that two or three ideal stages of extraction would render the dissolved sludge a non-TRU waste.

The percentages of the feed species recovered in the stripping solutions are also listed in Table 4.5. In the first stripping contact with mild nitric acid (0.01 M HNO₃) and sodium nitrate (0.5 M NaNO₃), little of the actinides or europium were recovered. Values of the percentages of components stripped from the organic verify this result (Table 4.5). Species that do not extract well, such as iron and calcium, were readily removed by the stripping solution. The actinides were not easily stripped because the high nitrate concentration in the aqueous provides a salting-out effect.

Table 4.5. Fraction of selected species removed from dissolved sludge, fraction recovered in aqueous strip, and fraction stripped from the organic in the first test

	Percent removed by extraction		Percent recovered by stripping		Percent stripped from organic	
	1st stage	Both stages	1st stage	Both stages	1st stage	Both stages
Radionuclides						
⁶⁰ Co	0.00	1.67	2.54	<3.63	<i>a</i>	<i>a</i>
^{90/111} Sr	-1.35	-1.35	1.82	1.84	98.37	99.89
¹³⁴ Cs	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
¹³⁷ Cs	-1.27	0.00	2.12	<4.46	>5.00	82.50
¹⁵² Eu	>97.17	>97.17	11.28	99.78	11.63	>99.80
¹⁵⁴ Eu	>96.21	>97.10	11.21	101.72	4.55	>99.44
¹⁵⁵ Eu	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	-8.70	>98.13
²³⁸ Pu	98.88	99.37	0.13	75.99	5.70	99.59
²³⁸ Pu/ ²⁴¹ Am	96.24	93.69	5.17	108.62	<i>a</i>	<i>a</i>
^{239/240} Pu	98.95	99.43	0.13	75.46	3.45	99.55
²⁴² Pu	<i>a</i>	<i>a</i>	<i>a</i>	31.67	<i>a</i>	<i>a</i>
²⁴¹ Pu	98.90	99.39	0.13	74.46	4.66	99.59
²⁴¹ Am	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	16.36	>96.40
²⁴⁴ Cm	95.53	97.77	11.04	106.22	<i>a</i>	<i>a</i>
Gross α	95.88	96.88	9.69	104.48	6.82	97.68
Gross β	9.05	10.95	3.81	8.10	33.33	98.89
Metals						
Al	10.02	8.47	1.08	2.22	-5.07	>96.66
Ba	-1.72	-3.45	1.47	<1.73	<i>a</i>	<i>a</i>
Be	-0.26	-6.32	<2.40	<5.40	-5.88	>14.71
Ca	7.59	10.76	7.28	7.42	90.83	91.84
Cd	17.78	8.89	4.10	<5.99	<i>a</i>	<i>a</i>
Co	11.69	7.63	<3.72	<8.36	<i>a</i>	<i>a</i>
Cr	3.74	1.87	1.36	<1.71	<i>a</i>	<i>a</i>
Cu	10.57	7.36	3.23	8.80	-1.54	>73.74
Cs	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
Fe	1.79	1.79	5.01	5.75	80.07	>93.71
Hg	92.72	96.83	<2.68	49.30	<i>a</i>	<i>a</i>
K	5.88	1.47	4.83	8.71	<i>a</i>	<i>a</i>
Mg	-8.02	-10.96	1.29	1.41	<i>a</i>	<i>a</i>
Mn	11.32	10.38	6.75	6.99	>61.19	>61.19
Ni	11.79	2.46	1.49	<2.02	<i>a</i>	<i>a</i>
Pb	17.66	15.86	8.74	<11.55	<i>a</i>	<i>a</i>
Si	-21.48	-65.77	10.05	16.93	-13.36	2.83
Sr	42.83	42.63	57.58	59.04	>78.46	>78.46
Th	98.85	98.84	0.08	103.45	-6.90	98.87
Tl	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	0.35	-27.78
U	99.95	>99.95	0.23	19.82	-4.82	19.68
V	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
Zn	-4.86	-6.49	2.31	<2.61	<i>a</i>	<i>a</i>

^aInsufficient data for calculation. Concentration before and after phase contact was either below the detectable limit or not measured.

In the second stripping stage, the aqueous strip solution contained oxalic acid ($0.5\text{ M H}_2\text{C}_2\text{O}_4$). A white precipitate was observed to form during the test. Presence of the precipitate indicated removal of substantial amounts of solute from the organic. Most of the actinides and europium are shown by both the values of the percentages recovered and the percentages stripped from the organic to be effectively isolated from the bulk of the dissolved sludge. Greater than 99% of the europium, ~96% of the americium, ~98% of the thorium, and only ~20% of the uranium were stripped from the organic. The low stripping and recovery factors for uranium indicate that either more stripping stages or a more effective stripping agent is required. It also makes separation of uranium from the other actinides appear to be an attractive option. Mercury was only moderately stripped from the organic under these conditions.

4.2.1.2 Comparison to Generic TRUEX Model

The GTM expects the concentrations of components in solution to be expressed in molar units. The measured concentrations of each species in the aqueous feed, that is, the dissolved sludge solution shown in Table 4.3, were converted to molar units. Species that were not included in the GTM but are similar to species that were included were grouped together, as described in Sect. 4.2. That is, their molar concentrations were summed. Similarly, the molar concentrations of all isotopes of a given element were added together to give the total concentration.

Given the feed streams indicated in Fig. 4.1 (i.e., those with descriptions), the GTM calculates the equilibrium distribution ratio in each stage, the concentration of each effluent stream (both aqueous and organic phases) associated with a stage, and the volume of each effluent. Because some effluent streams are feed streams to subsequent stages, any errors in the measured feed concentrations (provided as input to the model) propagate through each subsequent stage.

In modeling the first test, the iterative numerical methods of the GTM would not converge at the fourth stage, which is the second stripping stage where the aqueous strip solution contained $0.5\text{ M H}_2\text{C}_2\text{O}_4$ and 0.01 M HNO_3 . The model cannot handle cases where a precipitate forms, and a precipitate formed in this test, as previously described. To make the model converge, the concentration of the oxalic acid was set to 0.01 M ; higher values led to numerical instability. This means that results from only the first three stages may be compared with model calculations. Two techniques were chosen to compare the results with the model: (1) the fraction of selected species removed by the first extraction stage and (2) stage-to-stage concentration profiles.

The fraction of each metal removed from the aqueous phase in the first extraction stage, calculated from experimental data, is reported in Table 4.5. From that list, a shorter list of species, including chiefly the actinides, was selected and is shown in Table 4.6. The distribution ratios calculated with the GTM for these species are also listed in the table. The percentage of each species removed from the aqueous phase is readily calculated from the distribution ratio; thus,

$$r_{i,ext} = \left(\frac{2.5 D_i}{2.5 D_i + 1} \right) \times 100, \quad (4.7)$$

where $r_{i,ext}$ = the percentage of species i removed by the first extraction stage,

D_i = the distribution ratio for species i , and

2.5 = a factor accounting for an organic- to aqueous-phase volume ratio.

For each selected component, the calculated percentage removed from the aqueous phase is also listed in Table 4.6. The actinides are expected to be strongly extracted from the aqueous phase, and the data corroborate this prediction. More than 95% of the actinides are extracted in only one stage. Other metals such as Cs, Ca, and Fe, representing the alkali, alkaline earth, and transition metals, respectively, are predicted to be very weakly extracted. Within the error in the data, this prediction is also corroborated. In Table 4.6 it is also noted that mercury is found through experimentation to be strongly extracted, but it is not included in the GTM at present.

The predicted and measured concentration profiles of Eu, U, Pu, and Am are shown in Figs. 4.2 through 4.5. Errors in the concentrations, calculated from two replicate measurements, are depicted by error bars around the experimental data points. At first glance, agreement between the model and experiment appears poor for stages 1 and 4. However, stage 1 is the second extraction stage and the concentration in the aqueous phase has been reduced to near or below the detectable limit. In the case of stage 4, values of the oxalic acid concentration substituted into the model were set artificially low to make the model converge, and oxalate precipitates were noted to form during the experiment. Because of the precipitation, it should be expected that the organic-phase concentration would be low and the aqueous-phase concentration would be high. The figures show this effect. Comparisons between calculated and measured concentrations in stages 2 and 3 are fair. Considering the problems associated with forming gels and the initial low concentrations of actinides in the waste, these data verify the utility of the GTM for modeling extraction of actinides from acidic, multicomponent waste solutions. Strongly extracted components which are not included in the model,

Table 4.6. Fraction of selected species removed from dissolved sludge by first extraction stage of the first test and comparison of GTM predictions with measured values

Metal	GTM prediction		Measured value, percent removed
	Distribution ratio	Percent removed	
Cs	0.001	0.25	-1.3 ^a
Eu	36.97	98.9	>97.2 ^b
Pu	1415.	99.9+	98.9 ^c
Am	50.65	99.2	<i>d</i>
Cm	37.48	98.9	95.5
Ca	0.001	0.25	7.6
Fe	0.001	0.25	1.8
Th	4302.	99.9+	98.9
U	1349.	99.9+	99.9+
Hg	Not in GTM		92.7

^aBased on ¹³⁷Cs.

^bBased on ¹⁵²Eu and ¹⁵⁴Eu.

^cAverage of values for ²³⁸Pu, ^{239/240}Pu, and ^{all}Pu.

^dInsufficient data.

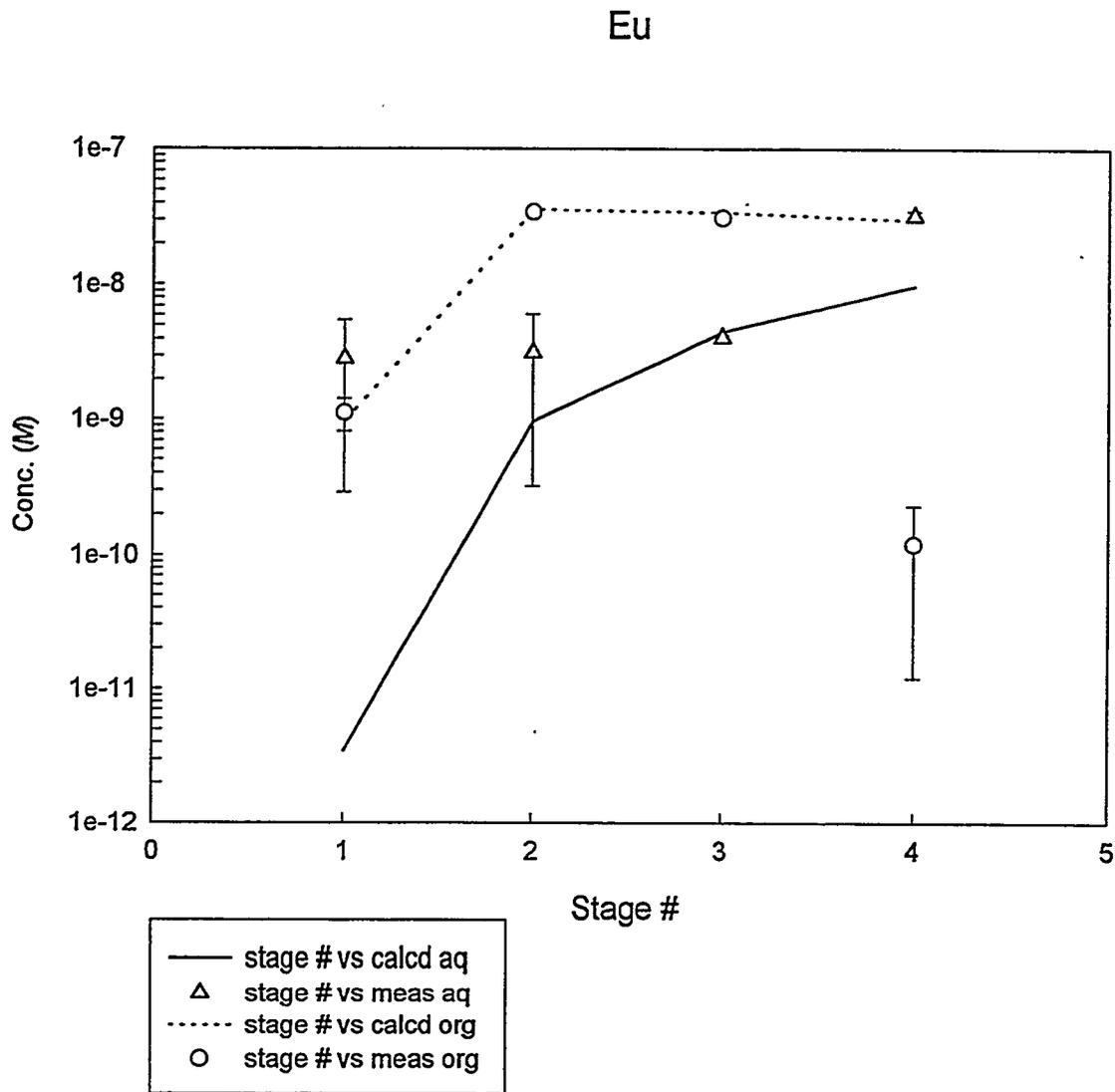


Fig. 4.2. Stagewise comparison of europium concentrations in the aqueous and organic phases for the first test.

U

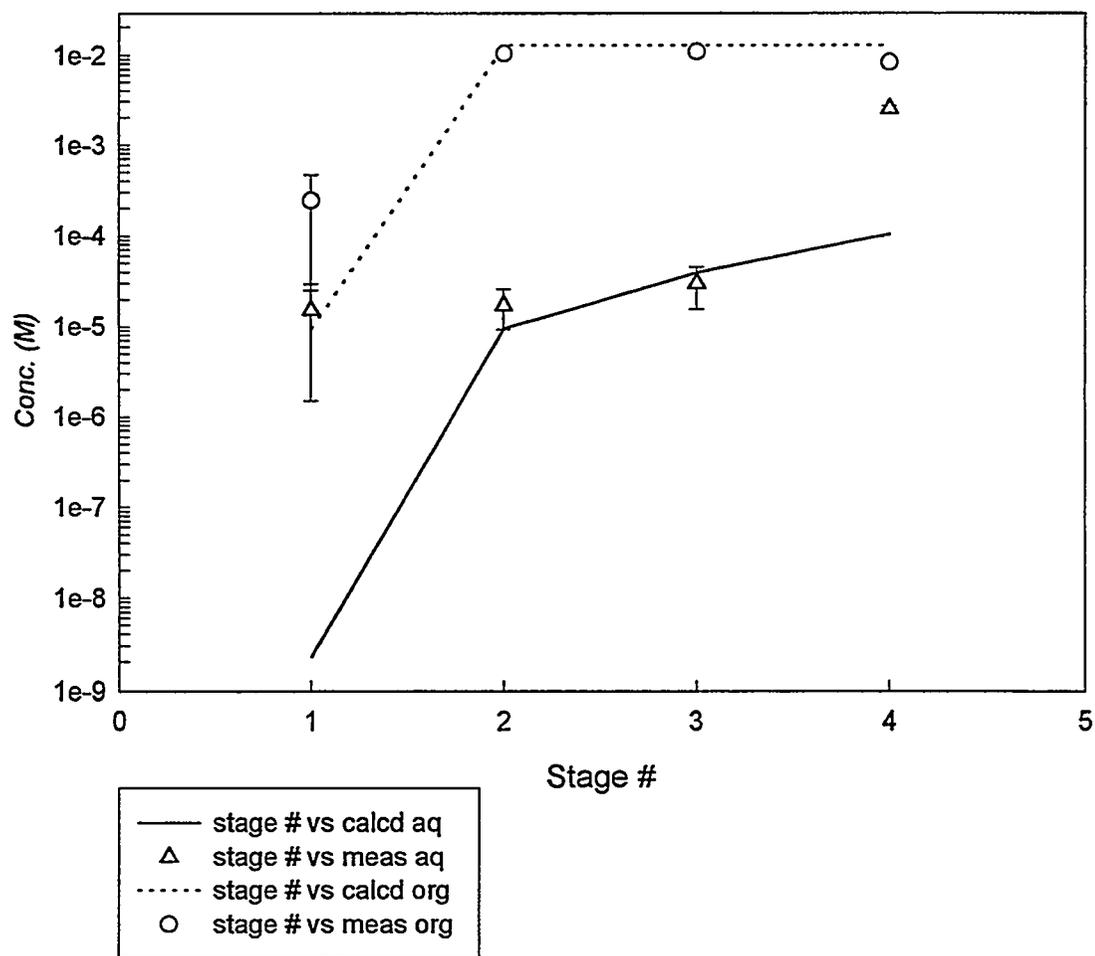


Fig. 4.3. Stagewise comparison of uranium concentrations in the aqueous and organic phases for the first test.

Pu

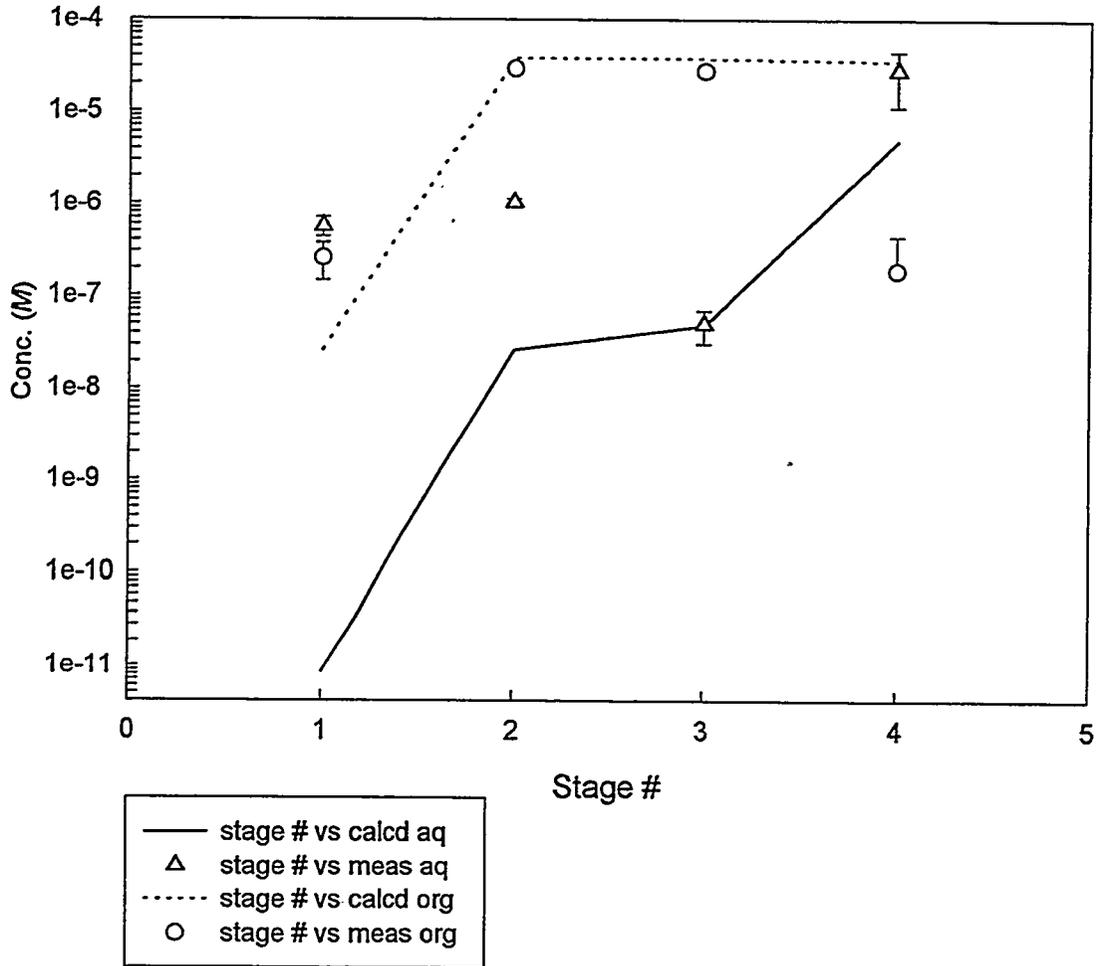


Fig. 4.4. Stagewise comparison of plutonium concentrations in the aqueous and organic phases for the first test.

Am

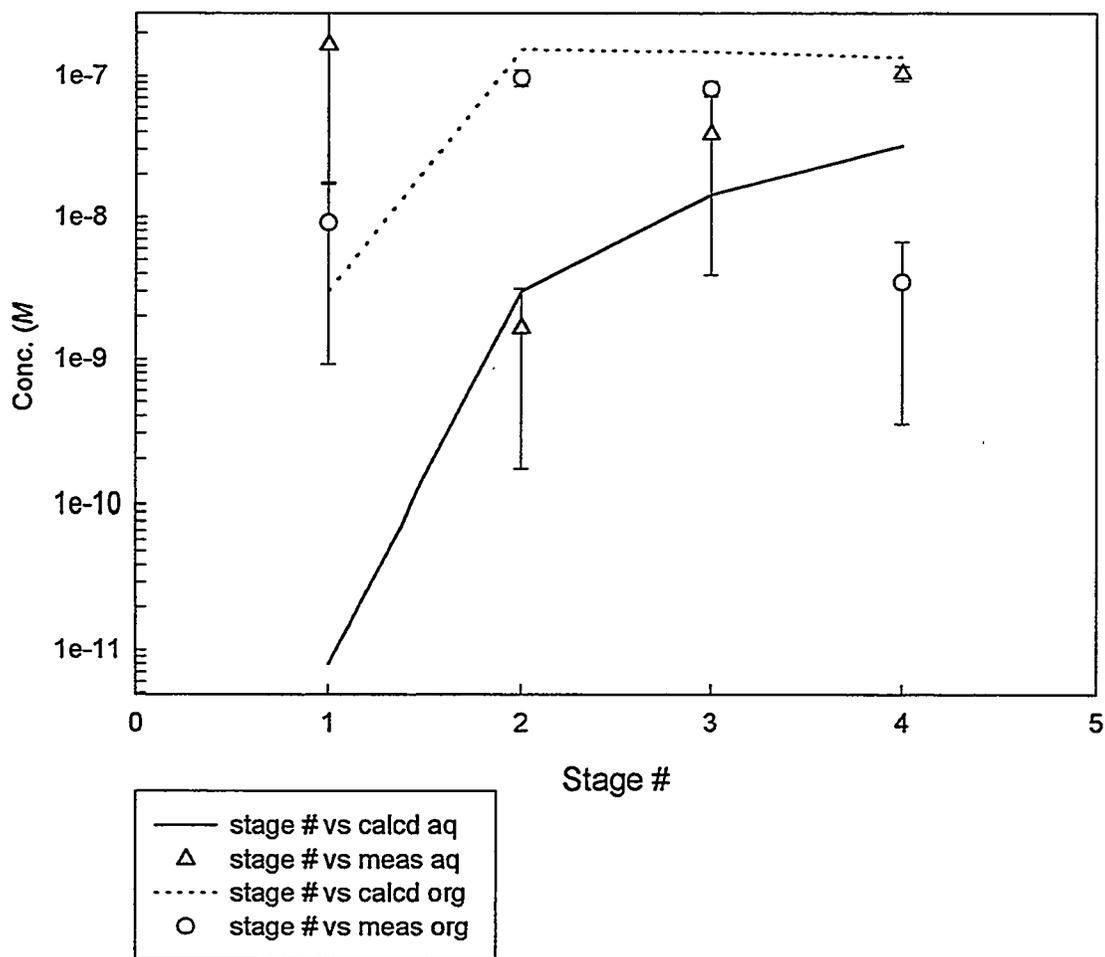


Fig. 4.5. Stagewise comparison of americium concentrations in the aqueous and organic phases for the first test.

such as mercury, can influence the concentration of CMPO available for extracting the actinides and cause the model to deviate from experimental measurements.

4.2.2 Second Test

In the second TRUEX experiment, the dissolved sludge solution was subjected to one batch extraction and three consecutive batch strips. Figure 4.6 illustrates the contacting pattern used in the experiment. The aqueous phase was initially slightly yellow in color. Following contact of equal volumes of dissolved sludge solution and fresh TRUEX solution at $\sim 24.0^\circ\text{C}$, the two phases separated well and no third phase was observed. After separation, the aqueous phase was nearly clear and the formerly clear organic phase had become slightly yellow. The organic was stripped three times with equal volumes of mild (0.01 *M*) nitric acid. 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 it was thought that stripping with mild nitric acid would not effectively recover a large fraction of the actinides unless the organic-phase acid concentration was first reduced, and there was some incentive to reduce analysis costs. No precipitates formed in any of the stages. All samples were submitted to the Analytical Services Organization for analysis.

4.2.2.1 Evaluation of Data

Results of analyses of the samples from the second TRUEX experiment are shown in Tables 4.7 and 4.8. Evaluation of the data proceeds along the same lines as that done for the first test. Based on aqueous-phase measurements, the percentage of each species removed by the single-stage extraction is

$$r_{i,1} = \left(\frac{TR02 - TR02E1A}{TR02} \right)_i \times 100, \quad (4.8)$$

where $r_{i,1}$ = percent of species i removed by the extraction stage.

Extracted species were recovered from the organic phase by stripping with mild nitric acid. With the data available from analysis of aqueous-phase samples, the percentage of each species recovered from the original dissolved sludge solution is readily calculated. The percentage recovered by the first strip is given by

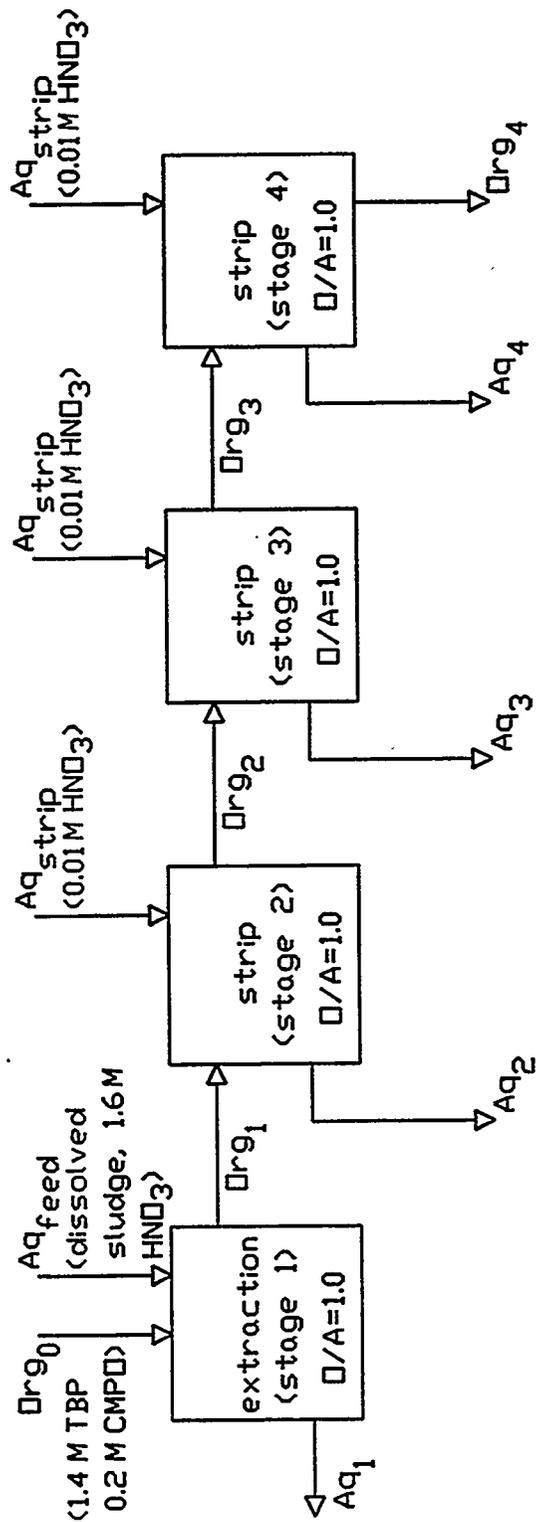


Fig. 4.6. Material flow paths for batchwise TRUEX test with one extraction and three strip stages.

Table 4.7. Composition of dissolved sludge solution and aqueous extraction and strip samples in second test^a

	TR02, dissolved sludge	TR02E1A, first extraction	TR02S1A, first strip	TR02S2A, second strip	TR02S3A, third strip ^b
Radionuclides	(Bq/L)	(Bq/L)	(Bq/L)	(Bq/L)	(Bq/L)
⁶⁰ Co	8.80 × 10 ⁶	9.20 × 10 ⁶	<1.55 × 10 ⁴	<1.10 × 10 ⁴	<8.10 × 10 ³
⁹⁰ AllSr	9.80 × 10 ⁸	9.60 × 10 ⁸	3.15 × 10 ⁶	8.80 × 10 ⁴	2.70 × 10 ⁴
¹³⁴ Cs	<5.90 × 10 ⁴	<4.40 × 10 ⁴	<2.20 × 10 ⁴	<2.90 × 10 ⁴	<1.50 × 10 ⁴
¹³⁷ Cs	1.50 × 10 ⁷	1.60 × 10 ⁷	<2.70 × 10 ⁴	<3.60 × 10 ⁴	<1.80 × 10 ⁴
¹⁵² Eu	1.55 × 10 ⁷	9.85 × 10 ⁵	4.60 × 10 ⁶	8.00 × 10 ⁶	1.85 × 10 ⁶
¹⁵⁴ Eu	8.45 × 10 ⁶	6.20 × 10 ⁵	2.45 × 10 ⁶	4.40 × 10 ⁶	1.00 × 10 ⁶
¹⁵⁵ Eu	1.90 × 10 ⁶	<2.30 × 10 ⁵	5.35 × 10 ⁵	7.70 × 10 ⁵	2.10 × 10 ⁵
²³⁸ Pu	1.65 × 10 ⁴	7.50 × 10 ³	3.25 × 10 ⁴	1.25 × 10 ⁵	4.40 × 10 ⁵
²³⁸ Pu/ ²⁴¹ Am	N.M. ^b	N.M.	N.M.	N.M.	N.M.
^{239/240} Pu	4.59 × 10 ⁵	3.40 × 10 ³	1.85 × 10 ⁴	5.90 × 10 ⁴	2.30 × 10 ⁵
²⁴² Pu	N.M.	N.M.	N.M.	N.M.	N.M.
²⁴¹ Pu	2.50 × 10 ⁶	1.09 × 10 ⁴	5.15 × 10 ⁴	1.80 × 10 ⁵	6.70 × 10 ⁵
²⁴¹ Am	1.95 × 10 ⁶	<4.40 × 10 ⁵	4.50 × 10 ⁵	1.10 × 10 ⁶	3.90 × 10 ⁵
²⁴⁴ Cm	N.M.	N.M.	N.M.	N.M.	N.M.
Gross α	2.12 × 10 ⁷	1.42 × 10 ⁶	3.81 × 10 ⁶	3.15 × 10 ⁶	1.15 × 10 ⁶
Gross β	3.00 × 10 ⁹	3.10 × 10 ⁹	3.50 × 10 ⁷	3.95 × 10 ⁷	1.70 × 10 ⁷
Other metals	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
H ⁺	1660.	1060.	345.	110.	40.
Al	1660.	1570.	1.23	7.43	44.5
Ba	30.1	31.1	0.280	0.260	<0.187
Be	<3.05	1.88	<0.145	<0.145	<0.145
Ca	7290.	7290.	125.	2.09	<0.312
Cd	4.00	4.07	<0.218	<0.218	<0.218
Co	1.89	1.90	<0.242	<0.242	<0.242
Cr	28.1	28.7	<0.239	<0.239	<0.239
Cu	13.9	14.0	<0.256	<0.256	1.28
Cs	N.M.	N.M.	N.M.	N.M.	N.M.
Fe	501.	491.	19.6	0.620	<0.180
Hg	59.0	2.88	<10.0	<10.0	<10.0
K	190.	194.	<5.59	<5.59	<5.59
Mg	923.	947.	<1.08	<1.08	<1.08
Mn	51.9	52.9	0.405	<0.163	<0.163
Na	4290.	4370.	3.94	1.10	0.565
Ni	19.2	19.7	<0.273	<0.273	<0.273
Pb	127.	124.	12.3	<10.0	<10.0
Si	742.	753.	2.87	1.16	<0.660
Sr	43.7	44.6	0.130	<0.014	<0.014
Th	3970.	5.54	13.2	135.	813.
Tl	<50.0	<2.38	<2.38	3.17	18.6
U	1990.	6.02	16.9	85.5	304.
V	0.460	0.265	<0.256	<0.256	<0.256
Zn	49.2	51.7	<0.353	<0.353	<0.353
Anions	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Br ⁻	<50.	<50.	<50.	<5.	<5.
Cl ⁻	67.	35.	9.0	7.0	7.0
F ⁻	48.	58.	<5.0	<5.0	<5.0
NO ₃ ⁻	130000.	101000.	21900.	5680.	2500.
PO ₄ ³⁻	63.	814.	<20.	<20.	<20.
SO ₄ ²⁻	114.	98.	<10.	<10.	<10.

^aSilver and antimony were below detectable limits in all samples.

^bN.M. = not measured.

Table 4.8. Composition of organic extraction and strip samples in second test^a

	TR02E1O, first extraction	TR02S3O, third strip
Radionuclides	(Bq/L)	(Bq/L)
⁶⁰ Co	<9.10 × 10 ⁵	<9.00 × 10 ⁴
^{90/111} Sr	1.30 × 10 ⁶	9.80 × 10 ⁴
¹³⁴ Cs	<8.60 × 10 ⁵	<9.70 × 10 ⁴
¹³⁷ Cs	<1.20 × 10 ⁶	2.60 × 10 ⁵
¹⁵² Eu	<5.00 × 10 ⁶	4.40 × 10 ⁵
¹⁵⁴ Eu	<2.40 × 10 ⁶	<3.30 × 10 ⁵
¹⁵⁵ Eu	<1.80 × 10 ⁶	<1.90 × 10 ⁵
²³⁸ Pu	1.60 × 10 ⁶	7.20 × 10 ⁵
²³⁸ Pu/ ²⁴¹ Am	N.M. ^b	N.M.
^{239/240} Pu	8.20 × 10 ⁵	3.20 × 10 ⁵
²⁴² Pu	N.M.	N.M.
²⁴¹ Pu	2.40 × 10 ⁶	1.00 × 10 ⁶
²⁴¹ Am	<3.30 × 10 ⁶	<3.60 × 10 ⁵
²⁴⁴ Cm	^c	^c
Gross α	9.10 × 10 ⁶	1.90 × 10 ⁵
Gross β	2.45 × 10 ⁷	7.05 × 10 ⁵
Other metals	(mg/L)	(mg/L)
H ⁺	390.	90.0
Al	200.	146.
Ba	<1.87	<1.87
Be	<1.45	<1.45
Ca	174.	46.0
Cd	<2.18	<2.18
Co	<2.42	<2.42
Cr	<2.39	<2.39
Cu	4.60	2.65
Cs	N.M.	N.M.
Fe	18.5	<1.80
Hg	139.	<100.
K	<55.9	<55.9
Mg	<10.8	<10.8
Mn	<1.63	<1.63
Na	8.80	4.60
Ni	<2.73	<2.73
Pb	<100.	<100.
Si	7.80	<6.60
Sr	<0.140	<0.140
Th	3600.	2690.
Tl	70.7	57.8
U	1820.	1420.
V	<2.56	<2.56
Zn	<3.53	<3.53
Anions	(mg/L)	(mg/L)
Br ⁻	<20.	<20.
Cl ⁻	<20.	<20.
F ⁻	<~500. ^d	<~500. ^d
NO ₃ ⁻	36900.	9340.
PO ₄ ³⁻	N.M.	N.M.
SO ₄ ²⁻	N.M.	N.M.

^aSilver and antimony were below detectable limits in all samples.

^bN.M. = not measured.

^cResidues left from destruction of the organic matrix interfered with alpha spectrometry analysis; no reliable result was obtained.

^dLower limit of detection is unusually large due to organic sample matrix.

$$p_{i,1} = \left(\frac{TR02S1A}{TR02} \right)_i \times 100 , \quad (4.9)$$

where $p_{i,1}$ = the percent of species i recovered by the aqueous phase in the first strip. Similarly, the percentage recovered by the second and third strip stages are given by

$$p_{i,2} = \left(\frac{TR02S2A}{TR02} \right)_i \times 100 \quad (4.10)$$

and

$$p_{i,3} = \left(\frac{TR02S3A}{TR02} \right)_i \times 100 , \quad (4.11)$$

respectively, where

$p_{i,2}$ = the percent of species i recovered by the second strip stage, and

$p_{i,3}$ = the percent of species i recovered by the third strip stage.

The total fraction of each species recovered by the three stripping stages is simply the sum of the individual stage effects; thus,

$$p_{i,all} = \left(\frac{TR02S1A + TR02S2A + TR02S3A}{TR02} \right)_i \times 100 , \quad (4.12)$$

where $p_{i,all}$ = the percent of species i recovered into the aqueous by all three strip stages.

Again, the percentage of material stripped from the organic is of interest because it indicates whether more stripping stages or a better stripping agent is required. The value here is based on the concentration in the loaded organic phase and the remaining concentration in the organic phase following the third strip stage because analyses are available only for these two organic samples. The cumulative fraction of each species stripped from the organic phase is given by

$$s_{i,all} = \left(\frac{TR02E1O - TR02S3O}{TR02E1O} \right)_i \times 100 , \quad (4.13)$$

where $s_{i,all}$ = the percentage of species i stripped from the organic phase by all three stages.

Results of the above calculations are given in Table 4.9. One stage of extraction removes, from the aqueous phase, ~93% of the europium, >99% of the thorium, and >99% of the uranium. The fractions of plutonium and americium extracted are ~99 and >77%, respectively. Discrepancies in the data for ²³⁸Pu are probably caused by the very low concentrations of this isotope and, therefore, relatively large errors in the measured concentration. Because of the small amounts of curium in the aqueous samples, its concentration was not measured. Metals including Ca, Co, Sr, Cs, Cr, Fe, and Ni were not extracted—a positive result since TRUEX does not target these metals. However, mercury is strongly extracted, to ~95%. Vanadium appears to be moderately extracted, and additional experiments should be made to verify this.

Stripping with mild nitric acid recovered ~93% of the europium and ~99% of the americium in three stages. Both of these metals were mostly recovered in the first two stripping stages, indicating that they were easily stripped. Plutonium was more difficult to strip and began to separate well from the organic in the third stripping stage. Thorium and uranium also began to transfer from the organic at the third stripping stage. The concentrations of mercury and vanadium, being at or below the detectable limit in the aqueous strip solution, did not permit definitive conclusions regarding their stripping behavior.

Examination of the amounts of each metal stripped from the organic, based on the concentration remaining in the organic after three stages, reveals that thorium and uranium are difficult to recover. Mercury appears to follow a similar pattern. Plutonium is not as difficult to recover. These results indicate that either more stripping stages are required or a stripping agent should be added to the mild nitric acid solution.

4.2.2.2 Comparison to Generic TRUEX Model

The calculation and methods used to compare the experimental results with the GTM simulations are similar to those used for the first test. No numerical stability problems with convergence of the GTM occurred in this case.

An abbreviated list of the metals extracted from the aqueous dissolved sludge solution and the fraction of those metals extracted in the first stage is given in Table 4.10. The distribution ratios calculated for each metal with the GTM is also listed in the table. Because a 1:1 organic- to aqueous-phase volume ratio was used in the experiment, the fraction removed is readily calculated from the distribution ratio by

Table 4.9. Fraction of selected species removed from dissolved sludge, fraction recovered in aqueous strip, and fraction stripped from the organic in the second test

	Percent removed by extraction, 1st stage	Percent recovered by stripping				Percent stripped from organic, three stages
		1st stage	2nd stage	3rd stage	Three stages	
Radionuclides						
⁶⁰ Co	-4.55	<0.18	<0.13	<0.09	<0.39	<i>a</i>
^{90/137} Sr	2.04	0.32	0.01	0.00	0.33	92.46
¹³⁴ Cs	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
¹³⁷ Cs	-6.67	<0.18	<0.24	<0.12	<0.54	<i>a</i>
¹⁵² Eu	93.65	29.68	51.61	11.94	93.23	<i>a</i>
¹⁵⁴ Eu	92.66	28.99	52.07	11.83	92.90	<i>a</i>
¹⁵⁵ Eu	>87.89	28.16	40.53	11.05	79.74	<i>a</i>
²³⁸ Pu	54.55	196.97	757.58	2666.67	3621.21	55.00
²³⁸ Pu/ ²⁴¹ Am	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
^{239/240} Pu	99.26	4.03	12.85	50.11	66.99	60.98
²⁴² Pu	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
²⁴¹ Pu	99.56	2.06	7.20	26.80	36.06	58.33
²⁴¹ Am	>77.44	23.08	56.41	20.00	99.49	<i>a</i>
²⁴⁴ Cm	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
Gross α	93.30	17.97	14.86	5.42	38.25	97.91
Gross β	-3.33	1.17	1.32	0.57	3.05	97.12
Metals						
Al	5.42	0.07	0.45	2.68	3.20	27.00
Ba	-3.32	0.93	0.86	<0.62	<2.42	<i>a</i>
Be	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
Ca	0.00	1.71	0.03	0.00	1.75	73.56
Cd	-1.75	<5.45	<5.45	<5.45	<16.35	<i>a</i>
Co	-0.53	<12.80	<12.80	<12.80	<38.41	<i>a</i>
Cr	-2.14	<0.85	<0.85	<0.85	<2.55	<i>a</i>
Cu	-0.72	<1.84	<1.84	9.21	<12.89	42.39
Cs	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>
Fe	2.00	3.91	0.12	<0.04	<4.07	>90.27
Hg	95.12	<16.95	<16.95	<16.95	<50.85	>28.06
K	-2.11	<2.94	<2.94	<2.94	<8.83	<i>a</i>
Mg	-2.60	<0.12	<0.12	<0.12	<0.35	<i>a</i>
Mn	-1.93	0.78	<0.31	<0.31	<1.41	<i>a</i>
Na	-1.86	0.09	0.03	0.01	0.13	47.73
Ni	-2.60	<1.42	<1.42	<1.42	<4.27	<i>a</i>
Pb	2.36	9.69	<7.87	<7.87	<25.43	<i>a</i>
Si	-1.48	0.39	0.16	<0.09	<0.63	>15.38
Sr	-2.06	0.30	<0.03	<0.03	<0.36	<i>a</i>
Th	99.86	0.33	3.40	20.48	24.21	25.28
Tl	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	18.25
U	99.70	0.85	4.30	15.28	20.42	21.98
V	42.39	<55.65	<55.65	<55.65	<166.96	<i>a</i>
Zn	-5.08	<0.72	<0.72	<0.72	<2.15	<i>a</i>

^aInsufficient data for calculation. Concentration before and after phase contact was either below the detectable limit or not measured.

Table 4.10. Fraction of selected species removed from dissolved sludge by extraction stage of the second test and comparison of GTM predictions with measured values

Metal	GTM Prediction		Measured value, percent removed
	Distribution ratio	Percent removed	
Cs	0.001	0.10	-6.67 ^a
Eu	18.66	94.9	93.2 ^b
Pu	1457.	99.9+	99.4 ^c
Am	25.56	96.2	> 77.4
Cm			<i>d</i>
Ca	0.001	0.10	0.0
Fe	0.001	0.10	2.0
Th	5916.	99.9+	99.9
U	679.7	99.9	99.7
Hg	Not in GTM		95.1

^aBased on ¹³⁷Cs.

^bBased on ¹⁵²Eu and ¹⁵⁴Eu.

^cAverage of values for ^{239/240}Pu and ^{all}Pu (specific activity of ²⁴²Pu used for ^{all}Pu).

^dInsufficient data.

$$r_{i,ext} = \left(\frac{D_i}{D_i+1} \right) \times 100 \quad . \quad (4.14)$$

These calculated values are also listed in Table 4.10. Good agreement between the data and model is indicated. Compared with the first test, europium is extracted to a slightly smaller extent (~93%) because of a lower concentration of aqueous nitric acid and, presumably, a lower salting-out power. As before, mercury is shown by the data to be strongly extracted. Adding mercury as one of the components modeled by the GTM should be considered.

The predicted concentration profiles of Eu, U, Pu, and Am are compared with the experimental data in Figs. 4.7 through 4.10. Error bars around the experimental data points are based on the variance between two replicate analyses. Large error bars appear 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. The predicted plutonium concentrations in the aqueous phase are uniformly lower than those for the experimental data. There are five reasons why this may occur: (1) the measured plutonium concentration in the starting dissolved sludge solution could be too low; (2) at the low concentrations in the test, the analysis method overestimates the plutonium concentration; (3) the model overestimates the distribution ratio; (4) microscopic gel particles may bind a fraction of the plutonium, thus preventing extraction; or (5) a small fraction of organic phase was entrained in the aqueous phase. The last two seem the most likely. Generally the agreement between the model and data is quite good.

4.3 GELATION OF DISSOLVED SLUDGE AND TRUEX RAFFINATE

4.3.1 First Test

As described in Sect. 4.1.1, the sludge was dissolved in strong nitric acid following a wash with 0.2 M NaOH solution. The resulting dissolved sludge solution had a cation concentration (not including H⁺) of ~1.8 M and a nitric acid concentration of ~2.9 M. The solution could not be filtered with 0.45- μ m-porosity syringe filters because these filters plugged almost immediately. Filtering with no. 588 coarse filter paper removed a small amount of gel-like residue and provided a slightly hazy solution that was used in the extraction tests. Following the first extraction, the aqueous raffinate remained slightly hazy and was similar in appearance to the original aqueous solution. Turbidity measurements were taken on samples of both solutions over a period of several days.

Eu

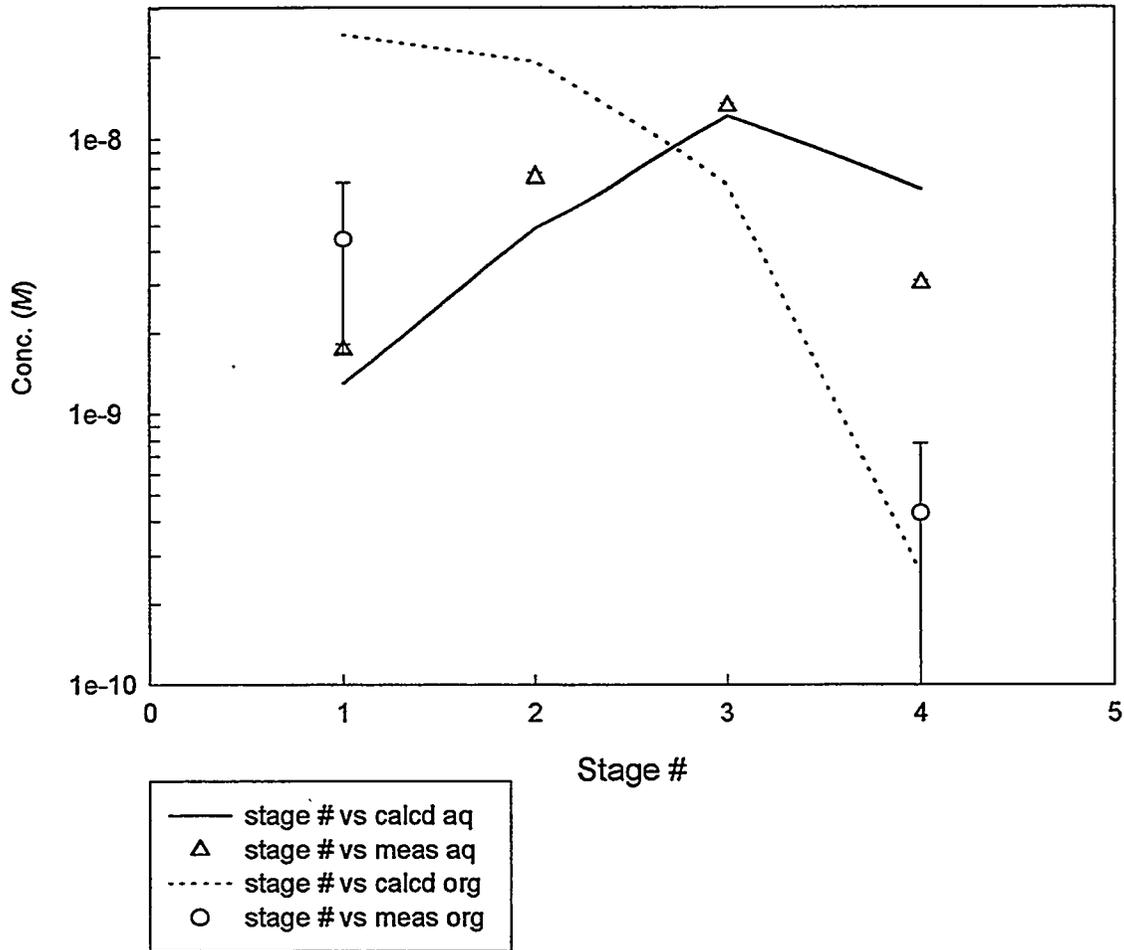


Fig. 4.7. Stagewise comparison of europium concentrations in the aqueous and organic phases for the second test.

U

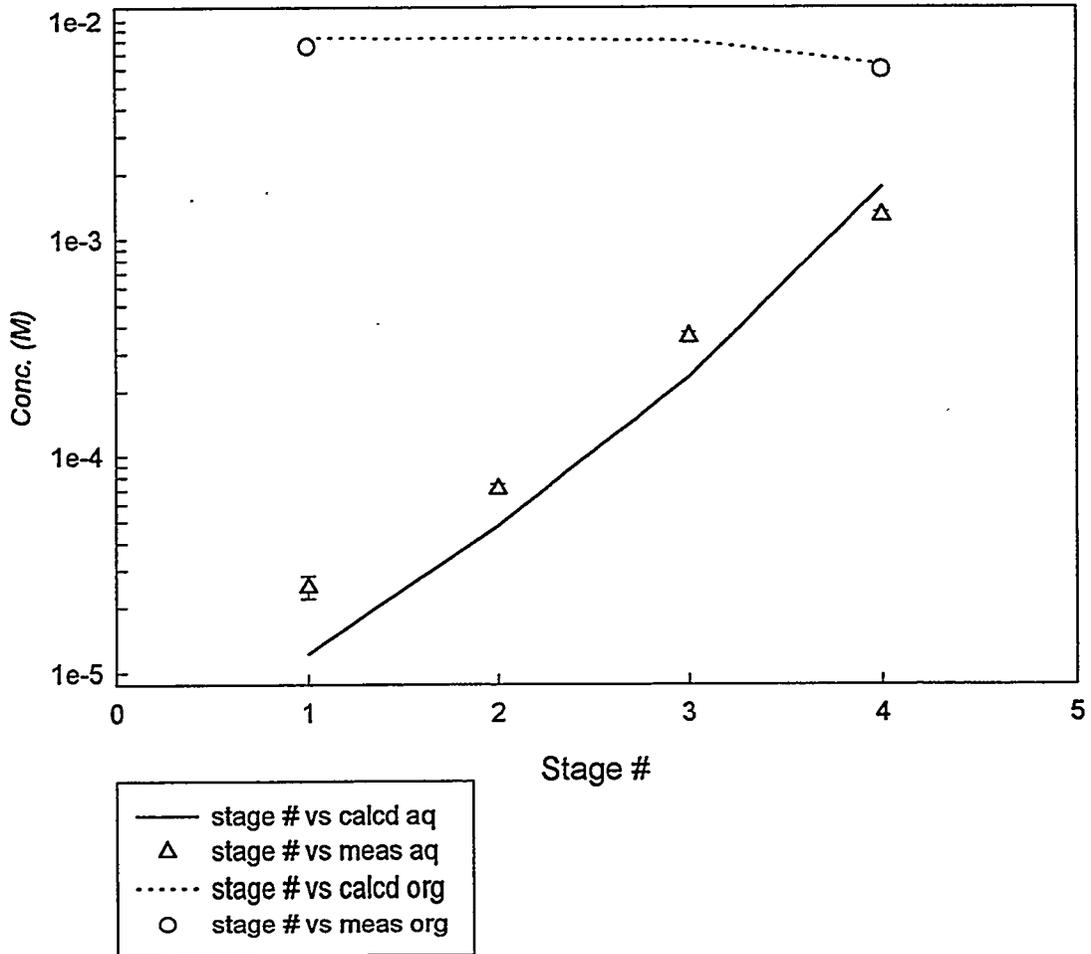


Fig. 4.8. Stagewise comparison of uranium concentrations in the aqueous and organic phases for the second test.

Pu

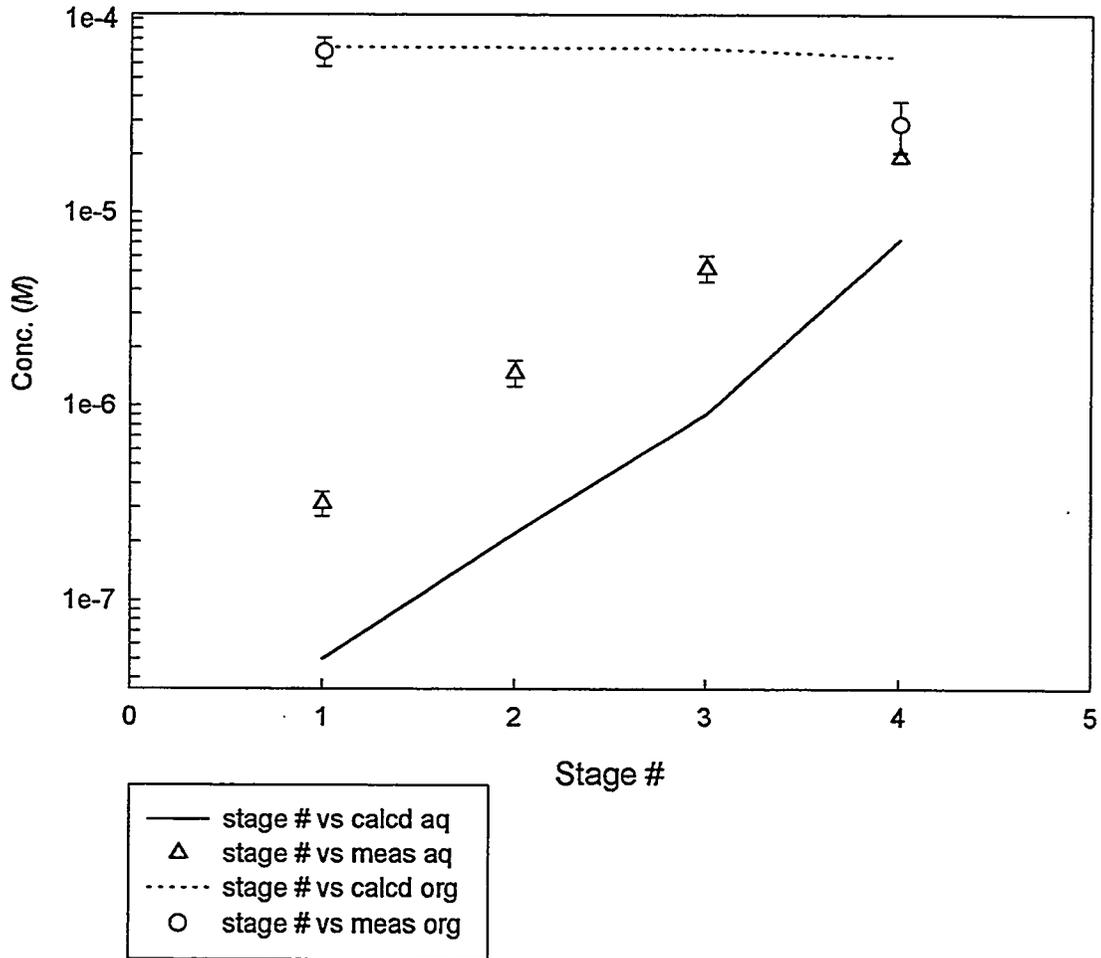


Fig. 4.9. Stagewise comparison of plutonium concentrations in the aqueous and organic phases for the second test.

Am

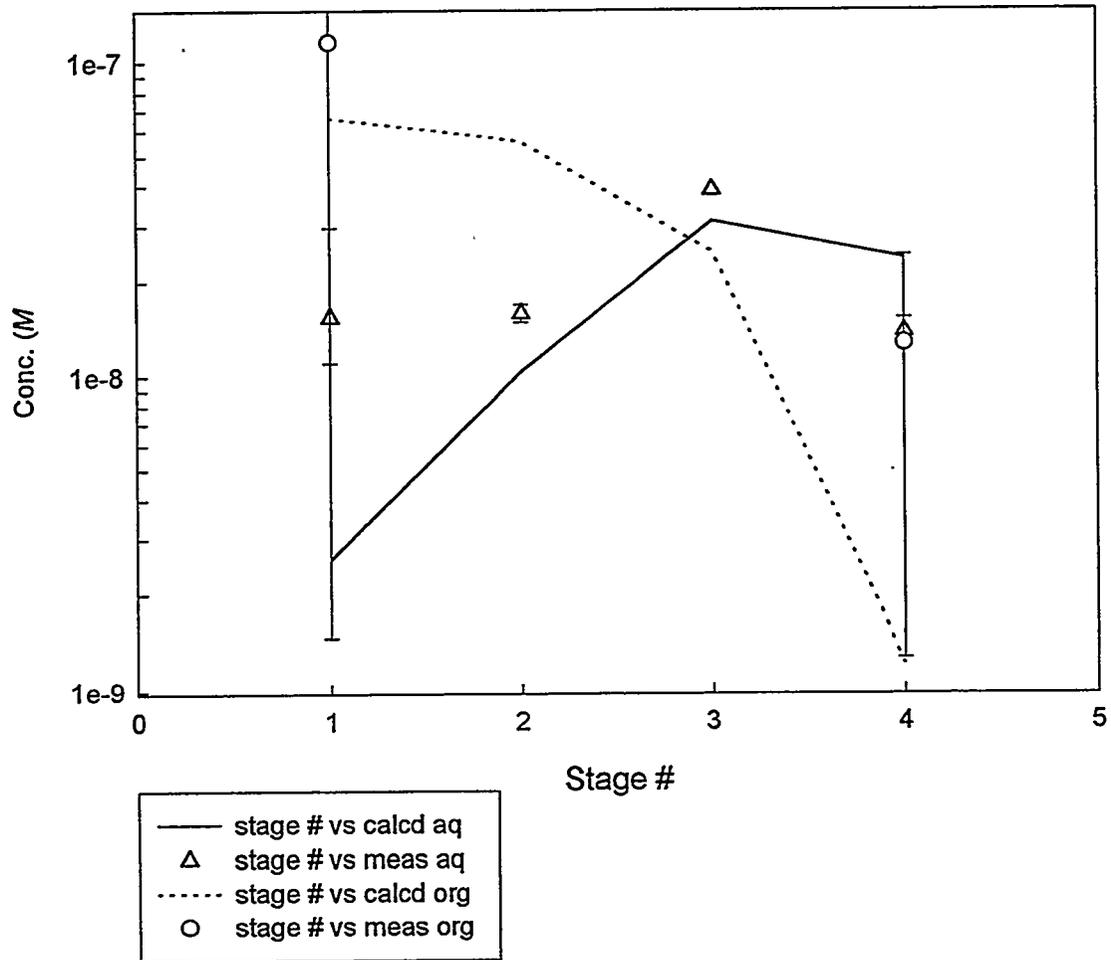


Fig. 4.10. Stagewise comparison of americium concentrations in the aqueous and organic phases for the second test.

Figure 4.11(a) and (b) shows the measured turbidity of the aqueous feed solution and the aqueous raffinate from the first extraction stage, respectively. In both cases, the initial turbidity is high, as might be expected due to the slightly hazy character of the liquids. It was presumed that the haziness was due to microscopic gel globules forming throughout the liquid. The turbidity of the raffinate from the extraction was initially higher than the feed, indicating that the forming gel may have interfered with complete aqueous/organic-phase separation. A visible layer of gel formed in both samples at around 8 days, and both samples were almost completely gelled in 20 days. The untreated (before TRUEX) and treated (after one stage of TRUEX) aqueous solutions formed the gels shown in Figs. 4.12 and 4.13, respectively, after aging for ~20 days. Gels of this type cause operational difficulties with most fluid delivery systems and processing equipment.

4.3.2 Second Test

The sludge was dissolved by a different procedure from that used in the first test and is described in Sect. 4.1.2. In essence, the sludge was neutralized with nitric acid (i.e., metal hydroxides and carbonates destroyed), leached with ~2.6 *M* caustic for ~6 h (accomplished by adding strong caustic to the neutralized mixture), and then dissolved in nitric acid. The resulting dissolved sludge solution had a cation concentration (not including H⁺) of ~0.6 *M* and a nitric acid concentration of ~1.7 *M*. This solution was, with some difficulty, filtered with 0.45- μ m-porosity syringe filters. Samples of this solution and the raffinate from the extraction stage were set aside for turbidity measurements.

Figure 4.14(a) and (b) shows the measured turbidity over a period of several days. The data are plotted on the same scale as the data from the first test to facilitate comparisons. As shown by examining the figures, the measured turbidity was very much lower for samples from this second test. Both samples were initially clear and became hazy in ~8 days for the original solution and ~1 day for the treated solution. Neither sample gelled after aging for 20 days. Either the caustic leaching prior to acid dissolution removed some components that contribute to gelation or the lower acid and "sludge" concentrations do not readily promote gelation. The mechanism should be investigated further.

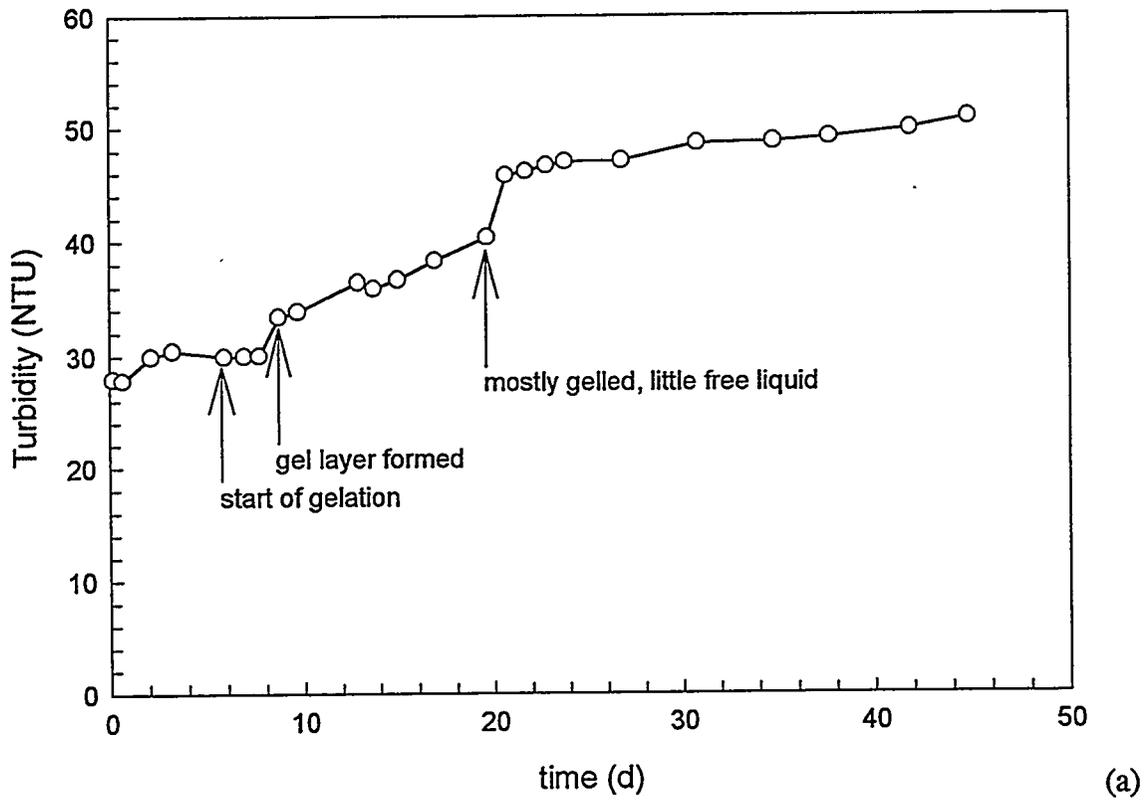
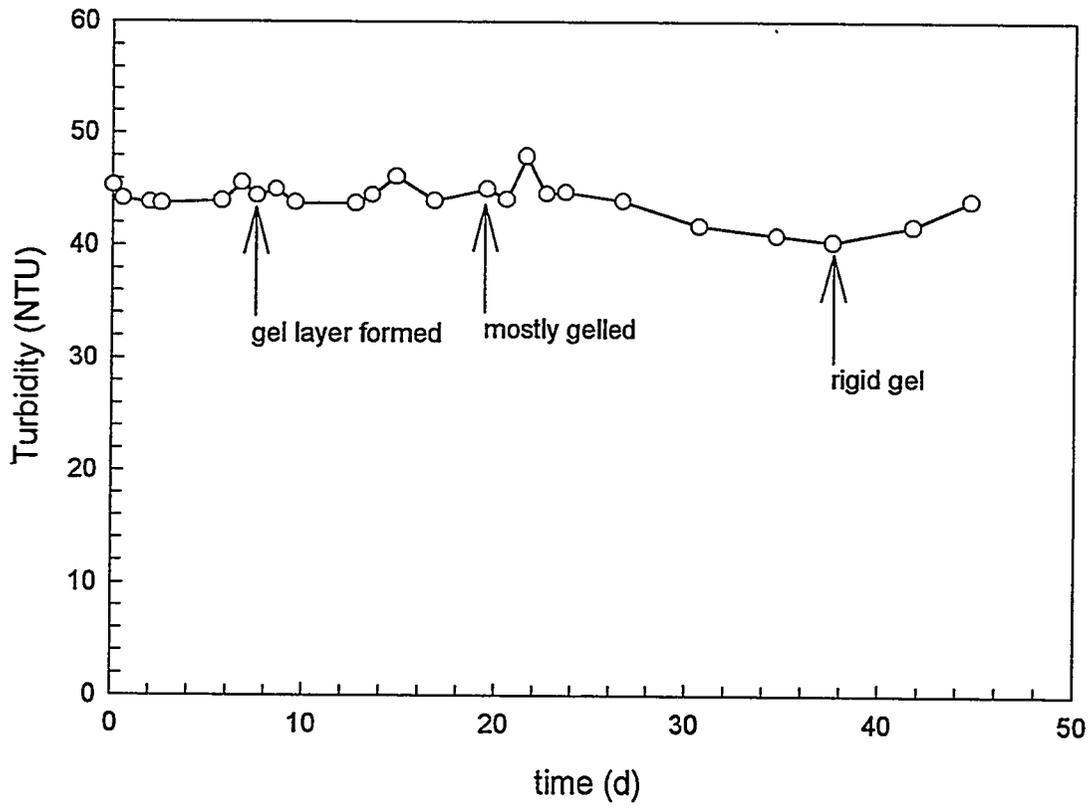


Fig. 4.11. Turbidity of dissolved sludge solution in the first test (a) before the extraction process and (b) after one stage of extraction.



(b)

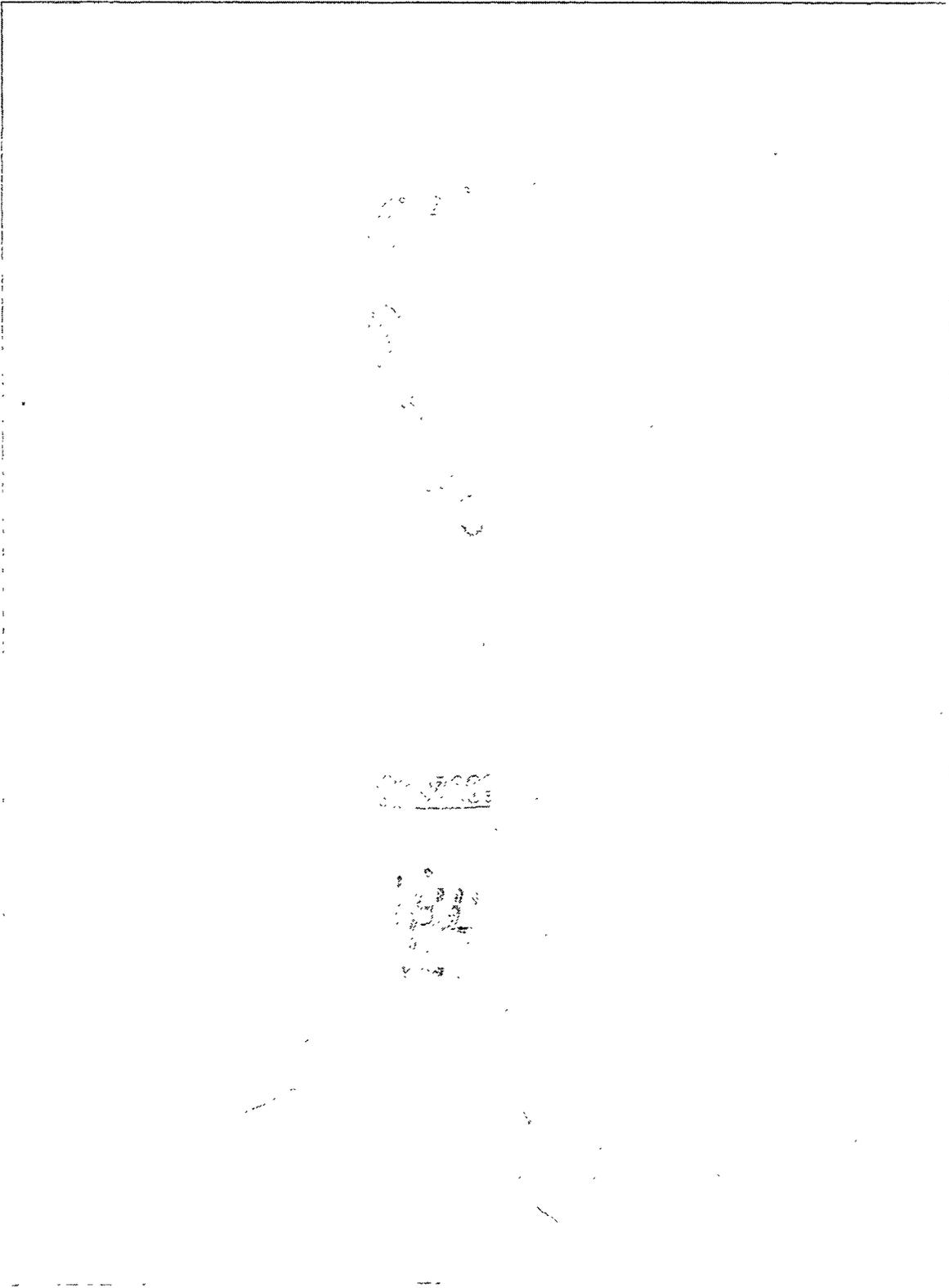


Fig. 4.12. Gelled sample of untreated dissolved sludge.



Fig. 4.13. Gelled sample of treated dissolved sludge (one stage of extraction).

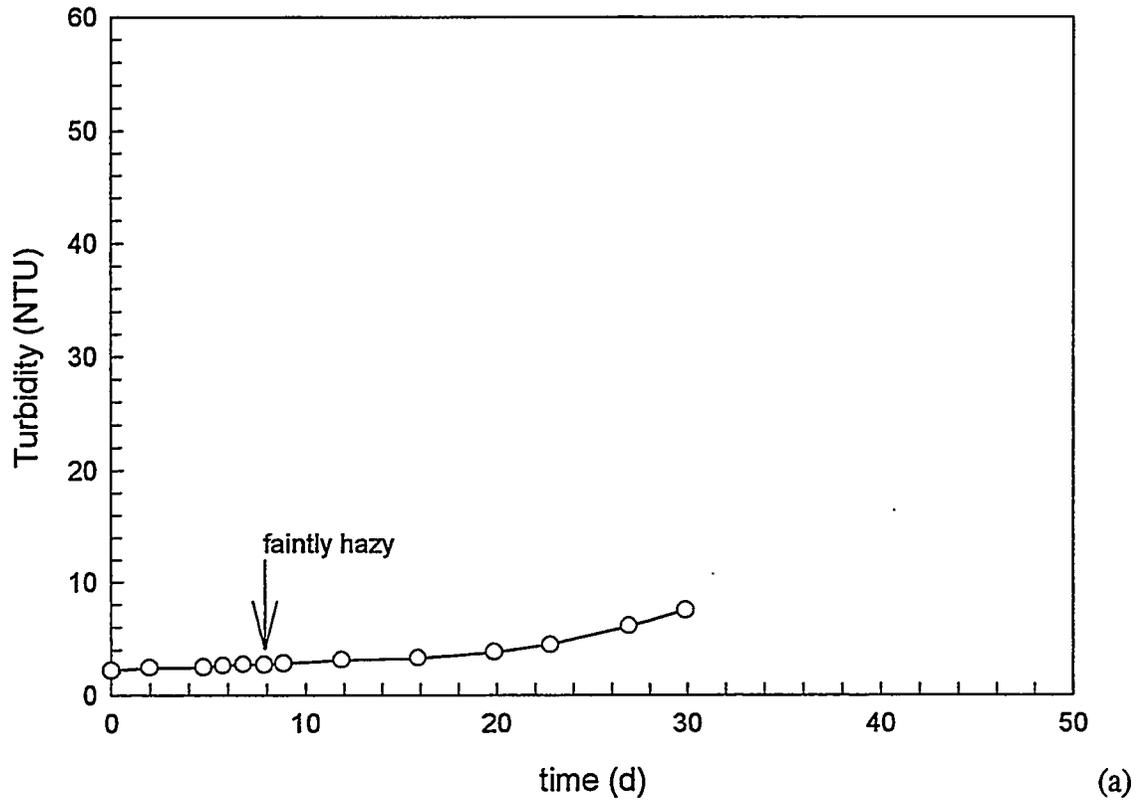
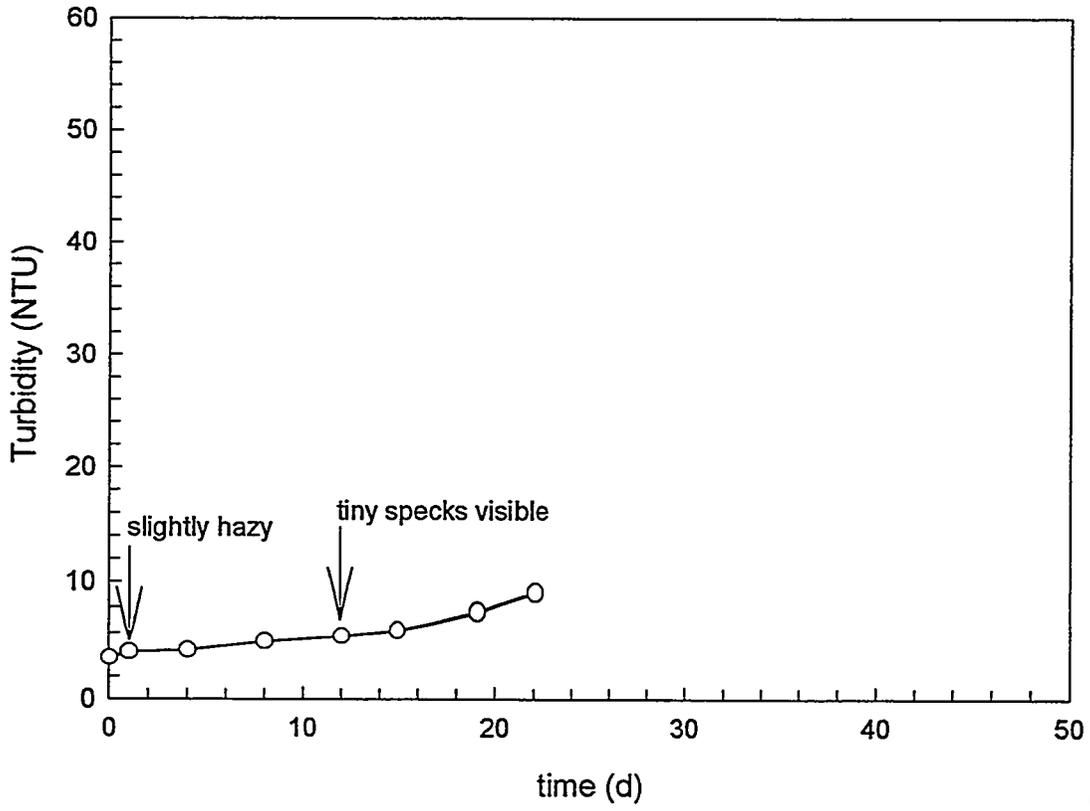


Fig. 4.14. Turbidity of dissolved sludge solution in the second test (a) before the extraction process and (b) after one stage of extraction.



(b)

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The following conclusions are drawn from this study.

1. On a dry weight basis, about half of the sludge from MVST Tank W-25 dissolves in 5.5 *M* nitric acid. Silicon, phosphate, and cesium are the primary constituents that do not dissolve. About half of the plutonium dissolves, but the other actinides dissolve more readily.
2. Neutralizing the sludge with nitric acid (which destroys hydroxides and carbonates) followed by leaching with 2.6 *M* caustic prior to final acid dissolution results in ~80% of the sludge being dissolved.
3. Large increases in the rate of gel formation and the quantities of gel formed are observed when the sludge is not preleached with caustic and when the total cation and acid concentrations are increased.
4. The bulk of the actinides are readily extracted from dissolved sludge solutions with the TRUEX process, even at low acidity (~0.6 *M*). However, formation of gels appears to raise the lower limits of concentration that can be achieved in the aqueous phase.
5. In spite of difficult process conditions (e.g., gels), the Generic TRUEX Model does a good job in predicting the removal and recovery of the actinides.

5.2 RECOMMENDATIONS

The following recommendations are made.

1. The effects of caustic leaching prior to acidic dissolution should be investigated further to (a) ascertain and quantify the reduction in gel formation and (b) evaluate the reduction such a two-step process achieves in the ultimate quantities of HLW requiring vitrification.
2. 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.
3. To inhibit gel formation, additives, such as fluoride, should be evaluated with respect to both gel formation and the effect on the TRUEX process.

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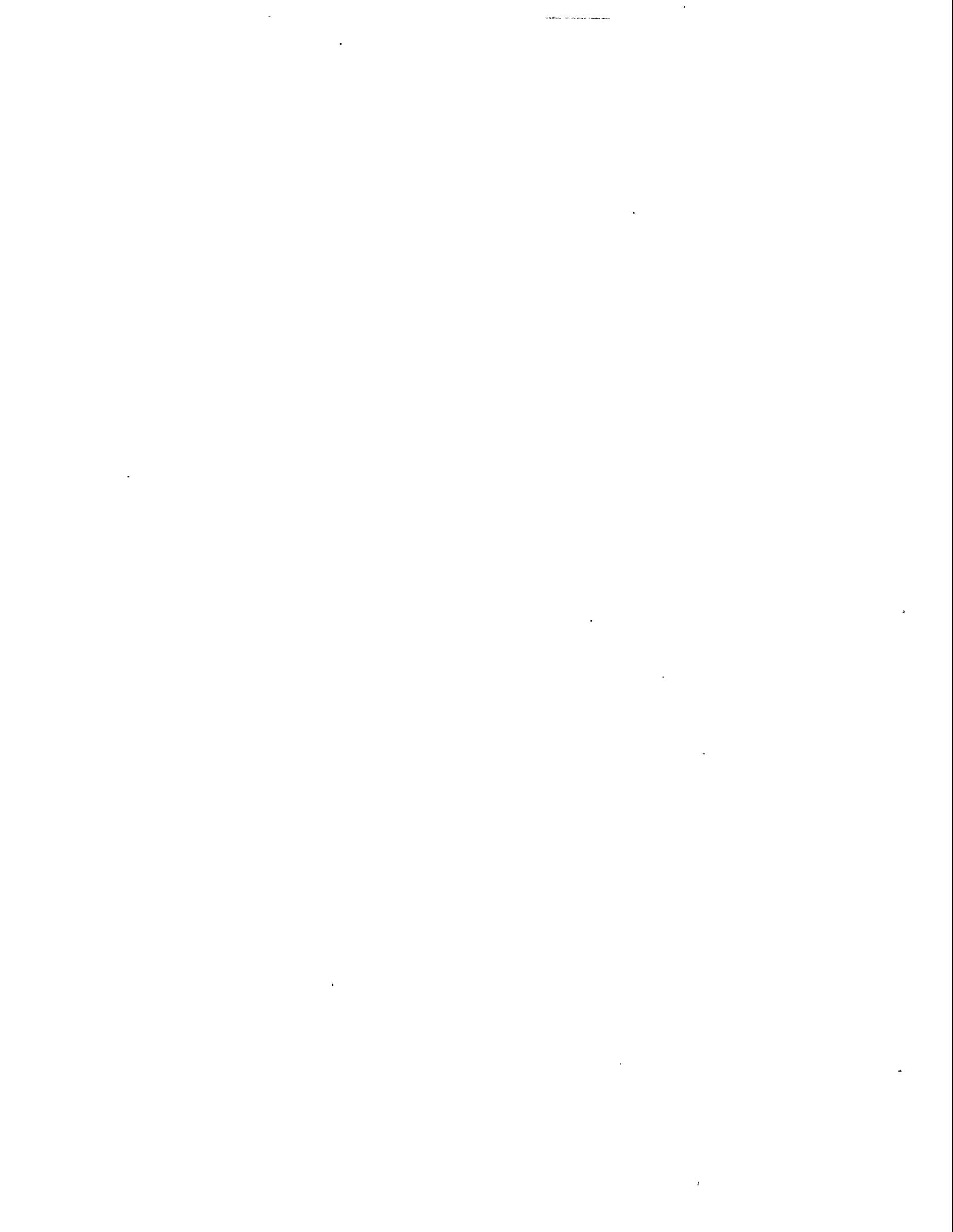
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APPENDIX A

APPENDIX A. ESTIMATION OF SOLUTE CONCENTRATIONS IN DISSOLVED SLUDGE SOLUTIONS

Using the data given in Table 2.1, the composition of a dissolved sludge solution resulting from a specific dissolution procedure can be estimated. The methods and assumptions used to estimate the composition of the dissolved sludge solution are described as follows for each of the two tests performed.

Washing and Dissolution for First Test

In the first test, the sludge aliquot to be dissolved was split into two nearly equal portions, as described in Sect. 2, so that existing centrifuge bottles could be used as process vessels. The quantities of reagent used to treat each portion were equal on a volume-per-unit mass basis. At the end of the dissolution, the dissolved sludge solution from each centrifuge bottle was placed in one container and thoroughly mixed. For purposes of estimating the dissolved sludge composition, it seems acceptable to treat the two portions as though they were one sample and add quantities of materials together.

A sludge aliquot was withdrawn from the storage reservoir. It was centrifuged and the supernatant was decanted to provide a sample of 179.1 g of centrifuged wet solids. The work of Collins et al. (1994) indicates that a mild caustic washing of the sludge essentially reduces the concentrations of solutes in the interstitial liquid. Mild caustic is used rather than plain water because plain water could lower the pH, thus causing dissolution of some actinide species. The centrifuged wet solids were then washed three times with 104 mL of 0.2 M NaOH solution. The three sequential washes consisted of (1) adding the wash solution to the wet sludge, (2) mixing the phases very well, (3) centrifuging the mixture, and (4) decanting the supernatant liquid.

The amount of solids contributed by the supernatant to centrifuged, air-dried solids is readily calculated by the product of the liquid-phase concentration of each solute and the volume of interstitial liquid. The volume of interstitial liquid is calculated as shown in Eq. (2-1); the result is 802 mL/kg (on a dry solids basis). For the sludge sample at hand, the interstitial volume is

$$V_{interstitial} = 179.1 \text{ g} \left(0.59 \frac{\text{g}(dry)}{\text{g}(wet)} \right) \left(\frac{802 \text{ mL}}{1000 \text{ g}(dry)} \right) \approx 85 \text{ mL} \quad (A-1)$$

The effects of washing the sludge may be modeled by assuming (1) the mild caustic mixes thoroughly with the interstitial liquid, (2) the mild caustic does not dissolve any of the solid-phase materials,

(3) the interstitial volume of the centrifuged solid does not change, and (4) the liquids are ideal, so the volumes are additive. The resulting interstitial supernatant concentrations for all solutes, except Na^+ and OH^- , are then given by

$$C_i = \left(\frac{85}{85+104} \right)^3 C_{i,0} = 0.09096 C_{i,0} \quad (\text{A-2})$$

where

$C_{i,0}$ = initial interstitial solute concentration, mg/L, and

C_i = interstitial solute concentration after washing, mg/L.

For Na^+ and OH^- , the calculated concentrations may be reduced as shown by Eq. (A-2), followed by the addition of

$$C_{\text{Na,OH}} = \left[\frac{85^2(104)}{(85+104)^3} + \frac{85(104)}{(85+104)^2} + \frac{104}{(85+104)} \right] 0.2 = 0.1818M \text{ or } 4182 \text{ mgNa/L} \quad (\text{A-3})$$

to the result. The remaining sludge solids, on a dry basis, are calculated by

$$\begin{aligned} \text{remaining solids} &= \text{untreated air dried solids} \\ &\quad - \text{interstitial supernate solids contribution} \\ &\quad + \text{interstitial supernate contribution after washing} \end{aligned} \quad (\text{A-4})$$

Before proceeding with the calculation of the solute concentrations in the dissolved sludge, the amount of acid added to the sludge to dissolve it must be considered. At this point, the base equivalents of washed sludge solids must be assumed to be the same as those for unwashed sludge, for which a value of ~ 5.98 mol/kg (dry basis) is known. The starting amount of sludge, on a dry basis, is 179.1 g (0.59 g/g) = 105.67 g . In this particular instance, the sludge was dissolved with 362 mL of 5.44 M HNO_3 . The final liquid volume is assumed to be equal to the sum of the acid volume added and the interstitial liquid volume. Furthermore, dissolution of the solids is assumed to cause no liquid volume change. The final acid concentration in the solution is then approximately

$$H_{\text{final}} = \frac{0.362(5.44) - \frac{105.67}{1000}(5.98) - 0.085(0.1818)}{(0.085 + 0.362)} = 2.96 \text{ M} \quad (\text{A-5})$$

Assuming the sludge solids totally dissolve, and with the foregoing assumptions, the concentrations of all solutes contributed by the sludge will be equal to the remaining solids, described by Eq. (A-4), divided by the liquid volume. Expressed in symbols,

$$R_i = 105.67S_i - 0.085C_{i,0} + 0.085C_i, \quad (\text{A-6})$$

where R_i = amount of solute, mg.

For all except NO_3^- , the final concentration of each solute in the dissolved sludge solution is derived by dividing R_i by the solution volume,

$$C_{fi} = \frac{R_i}{(0.085+0.362)} \quad [\text{mg/L}] \quad (\text{A-7})$$

For nitrate, a value of

$$C_{\text{NO}_3^-} = 0.362(5.44)(62)(1000) = 122,000 \text{ mg/L} \quad (\text{A-8})$$

must be added to the value calculated by Eq. (A-7).

Washing and Dissolution for Second Test

In the second test, a smaller sludge sample was used and could be processed in one centrifuge bottle. The quantity of sludge removed from the reservoir yielded 30.84 g of centrifuged wet solids, which had a calculated interstitial volume of 14.6 mL. The calculation methods and assumptions to estimate the solute concentrations in the dissolved sludge are similar to those used above. Variations in the details occur because the washing treatment and volumes of reagents used were different. The centrifuged wet solids were first "neutralized" by adding 20 mL of 5.44 M nitric acid to destroy hydroxides and carbonates. The acid balance is

$$30.48(0.59) \left(\frac{5.96}{1000} \right) = 0.109 = 0.020(5.44) = 0.109 \quad (\text{A-9})$$

Following the "neutralization," 25 mL of 6.27 M NaOH was added (resulting in a caustic concentration of ~2.6 M) to ensure that the actinides would remain as precipitates. The mixture was centrifuged and the supernatant was decanted. Then the solids were washed with 50 mL of 0.20 M NaOH solution and centrifuged and the supernatant was decanted. Even though the "neutralization," in all likelihood, changed the interstitial volume significantly, lack of information again forces the assumption that the

interstitial volume did not change. For all components except Na^+ , OH^- , and NO_3^- , the resulting interstitial supernatant concentrations are given by

$$C_i = \frac{(14.6)^2}{(50 + 14.6)(20 + 25 + 14.6)} C_{i,0} \approx 0.05536 C_0 \quad (\text{A-10})$$

For Na^+ , OH^- , and NO_3^- , the calculated concentrations may be reduced as shown by Eq. (A-10), followed by the addition of

$$C_{\text{Na}^+} = \frac{(14.6)(25)(6.27)}{(50 + 14.6)(20 + 25 + 14.6)} + \frac{(50)(0.2)}{(50 + 14.6)} \approx 0.749M \text{ or } 17200\text{mg/L} \quad (\text{A-11})$$

$$C_{\text{OH}^-} = C_{\text{Na}^+} \approx 0.749M \text{ or } 12700\text{mg/L} \quad (\text{A-12})$$

and

$$C_{\text{NO}_3^-} = \frac{(14.6)(20)(5.44)}{(50 + 14.6)(20 + 25 + 14.6)} \approx 0.413M \text{ or } 25600\text{mg/L} \quad (\text{A-13})$$

respectively.

Because the sludge was already "neutralized," it could be dissolved under milder conditions. A 125-mL volume of water was added to the sludge, followed by the addition of 90 mL of 5.44 M HNO_3 . This resulted in a final acid concentration of about

$$H_{\text{final}} = \frac{(90)(5.44) - (14.6)(0.749)}{(125 + 90 + 14.6)} \approx 2.08M \quad (\text{A-14})$$

The remaining sludge solids composition is estimated by

$$R_i = 30.84(0.59)S_i - 0.0146C_0 + 0.0146C_i \quad (\text{A-15})$$

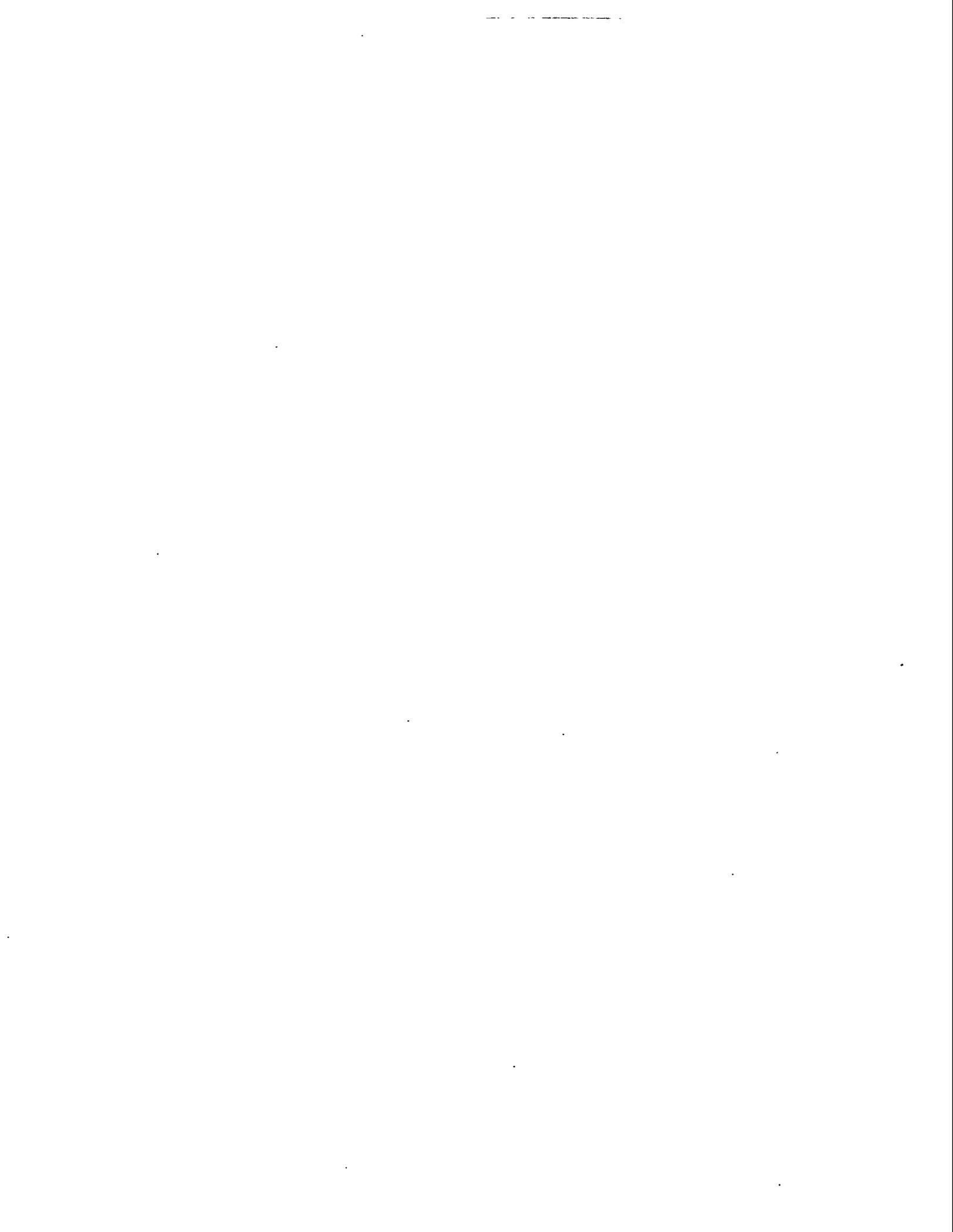
For all except NO_3^- , the final concentration of each solute in the dissolved sludge solution is given by

$$C_{fi} = \frac{R_i}{(0.125 + 0.090 + 0.0146)} \quad [\text{mg/L}] \quad (\text{A-16})$$

For nitrate, a value of

$$C_{NO_3^-} = 0.090(5.44)(62)(1000) \approx 30400 \text{ mg/L} \quad (\text{A-17})$$

must be added to the value calculated by Eq. (A-16).



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