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NUCLEAR TECHNOLOGY PROGRAMS
SEMIANNUAL PROGRESS REPORT

April-September 1988

Chemical Technology Division

M. J. Steindler, Director
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MASTER

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ABSTRACT

This document reports on the work done by the Nuclear Technology Programs of the Chemical Technology Division, Argonne National Laboratory, in the period April-September 1988. These programs involve R&D in three areas: applied physical chemistry, separation science and technology, and nuclear waste management. The work in applied physical chemistry includes investigations into the processes that control the release and transport of fission products under accident-like conditions, the thermophysical properties of metal fuel and blanket materials of the Integral Fast Reactor, and the properties of selected materials in environments simulating those of fusion energy systems. In the area of separation science and technology, the bulk of the effort is concerned with developing and implementing processes for the removal and concentration of actinides from waste streams contaminated by transuranic elements. Another effort is concerned with examining the feasibility of substituting low-enriched for high-enriched uranium in the production of fission-product ^{99}Mo . In the area of waste management, investigations are underway on the performance of materials in projected nuclear repository conditions to provide input to the licensing of the nation's high-level waste repositories.

SUMMARY

Applied Physical Chemistry

Calculational and experimental efforts are underway to investigate fission product release and transport from a light water reactor (LWR) under accident conditions. These efforts are concentrated on determining the release of refractory fission products from the molten core-concrete mixtures that would form if a molten core penetrated the bottom of a reactor vessel in a severe accident. In the experimental effort, the vaporization of core-concrete mixtures is being measured by the transpiration method, in which mixtures of stainless steel, concrete, and urania (doped with La_2O_3 , SrO , BaO , and ZrO_2) are vaporized at 2150 K into flowing He -6% H_2 -0.06% H_2O . Calculations of fission product release are also being done with the SOLGASMIX computer code. The results indicate that the release of the refractory fission products (La, Ba, and Sr) from core-concrete mixtures at 2150 K is much less than is predicted by simple models that employ ideal solutions of strontia, baria, and lanthana. The results are being used to test the thermodynamic data base and the underlying assumptions of computer codes used for prediction of release during a severe accident.

Measurements are being performed to provide needed thermodynamic and transport property data for Integral Fast Reactor (IFR) fuels. Experiments were completed to determine the thermal expansion and thermal conductivity of two cladding materials (the austenitic alloy D9 and the ferritic alloy HT9) at temperatures of 400-1300 K. The thermal conductivity and thermal expansion data for D9 were typical of 316 stainless steel, whereas those for HT9 showed a phase transition at about 1030 K and were typical of 410 stainless steel. A calculated phase diagram for the U-Zr alloy was derived and found to be in good agreement with literature data. These data will be used in determining the U-Pu-Zr phase diagram.

Use of the IFR has been proposed for breeding tritium from lithium oxide. For safety and efficiency, tritium loss to the sodium coolant by permeation through the cladding must be less than 1% per year. An effort is therefore underway to test methods for limiting tritium loss. In this report period, an unlined tungsten capsule, a nickel-lined tungsten capsule, and a silver capsule were loaded with Li_2O and tritiated water to test their tritium permeation rates between 300 and 450 °C (573 and 723 K). The lined tungsten capsule showed the lowest tritium loss, $0.085 \pm 0.048\%$ per year. Tests were initiated to evaluate yttrium as a getter material.

A critical element in the development of a fusion reactor is the blanket for breeding tritium fuel. Several studies are underway with the objective of determining the feasibility of using lithium-containing ceramics as breeder material. In one such study, measured thermodynamic and kinetic data are being related to tritium retention and release from ceramic tritium breeder materials. Adsorption of $\text{H}_2\text{O}(\text{g})$, dissolution of OH^- , and evolution of $\text{H}_2\text{O}(\text{g})$ are being measured at high temperature (573-873 K) for the $\text{LiAlO}_2\text{-H}_2\text{O}(\text{g})$ system to provide thermodynamic and kinetic data for these processes for LiAlO_2 , a candidate tritium breeder material. The adsorption isotherms for the $\text{LiAlO}_2\text{-H}_2\text{O}$ system indicated that physisorption occurs at lower temperatures (< 773 K), but chemisorption is the dominant process at higher temperatures. The surface adsorption curves for both processes were of the Freundlich type, indicating surface heterogeneity such as the presence of more than one kind of surface site for adsorption. The implications of these results for future tritium release studies are discussed.

In another effort, we have developed a computer model to predict tritium release from a ceramic breeder. Initially, it was assumed in this model that diffusion and desorption are the rate-controlling mechanisms. But the model was unable to account for the observed tritium release in the CRITIC experiment for temperature increases of 50-100 °C with a 0.1% hydrogen concentration in the helium purge gas. Predictable tritium release was obtained for identical temperature changes but a purge gas containing 1.0% H_2 . This suggested that the desorption activation energy was changing with surface coverage by adsorbed hydrogen. The model was thus revised so that the desorption activation energy varied with surface coverage. The revised model accounts for the unusual release observed in the CRITIC experiment and is consistent with recent work that suggests the presence of multiple desorption sites on materials of interest as ceramic breeders.

The ASPIRE (Advanced Safe Pool Immersed Reactor) concept involves the use of a pool of molten LiF-BeF_2 (FLIBE) as the breeder blanket and shield. The feasibility of this concept depends upon the ability to control the FLIBE chemistry with respect to TF/T_2 ratio and corrosion. We have designed and constructed an experimental apparatus for testing the FLIBE chemistry. A series of experiments to demonstrate the critical assumptions on FLIBE chemistry is planned.

An experimental effort is underway to assess the usefulness of tritium oxidation at the surface of 316 stainless steel as a means of minimizing permeation of molecular tritium in fusion reactor systems. The experiments were run with double-walled steel tubes at 400-550 °C (673-823 K) for up to 265 h. A tritium/helium mixture was circulated through the inner tube, and an oxygen/helium mixture through the outer tube. The maximum yield of tritiated water ($< 99\%$) occurred at oxygen levels > 550 ppm in the presence of an iron oxide formed at 400 °C (673 K); Fe_3O_4 is assumed to be the iron species present.

In fusion-related design studies for the international thermonuclear experimental reactor (ITER) project, we are assessing radiolysis that would be produced in an aqueous salt solution (2M LiNO_3 or LiOH), a blanket design concept. Calculations indicated that this blanket will require pressurization (about 2.1 MPa for LiNO_3 and 2.5 MPa for LiOH) to keep the evolved gas in solution. The implications of these results for the ITER design effort are discussed.

In neutron dosimetry and damage analysis, neutron facilities are being characterized in terms of neutron flux and energy spectrum, which can be used to calculate atomic displacements and transmutations. These damage parameters can also be used to correlate properties changes and to predict materials performance in fusion reactors. Data obtained in this report period included neutron fluences for helium production measurements near 14 MeV neutron energies, neutron yields and energy spectra for 113 and 256 MeV protons, and neutron activation cross sections near 14 MeV for two long-lived isotopes (^{93}Mo and $^{93\text{m}}\text{Nb}$).

Separation Science and Technology

The Division's work in separation science and technology is mainly concerned with removing and concentrating actinides from waste streams contaminated with transuranic (TRU) elements by use of the TRUEX solvent extraction process. The extractant found most satisfactory for the TRUEX process is octyl (phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is abbreviated CMPO. This extractant is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX process solvent. The diluent is typically a normal paraffinic hydrocarbon (NPH) or a nonflammable chlorocarbon such as tetrachloroethylene (TCE). Another project is concerned with examining the feasibility of substituting low-enriched uranium for the high-enriched uranium currently used in the production of ^{99}Mo .

The major effort involves development of a generic data base and modeling capability for the TRUEX solvent extraction process. The Generic TRUEX Model (GTM) will be directly useful for site-specific flowsheet development directed to (1) establishing a TRUEX process for specific waste streams, (2) assessing the economic and facility requirements for installing the process, and (3) improving, monitoring, and controlling on-line TRUEX processes. The GTM is composed of three sections that are linked together and executed by HyperCard and Excel software. The heart of the model is the SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) code, which calculates multistaged, countercurrent flowsheets based on distribution ratios calculated in the SASPE (Spreadsheet Algorithms for Speciation and Partitioning Equilibria) section. The third section of the GTM, SPACE (Size of Plant and Cost Estimation), estimates the space and cost requirements for installing a specific TRUEX process in a glove box, shielded-cell, or canyon facility. Refinements to all three sections continue to be made. Most of the distribution coefficient data generated at CMT through September 1988 have been entered into a data base. Additions will be made as further data are generated.

Mathematical models of extraction data for the GTM continue to be improved as more data are collected. In this report period, models were developed to estimate the activity coefficients for the electrolytes $\text{Al}(\text{NO}_3)_3$ and $\text{Fe}(\text{NO}_3)_3$, major components in a number of TRU and high-level waste streams. Models were also improved for determining (1) extraction constants for TBP-dodecane, CMPO-dodecane, and TRUEX-NPH, (2) distribution coefficients for TRUEX-NPH and TRUEX-TCE extraction of yttrium, lanthanum, and lanthanides, (3) stability constants for americium nitrate, plutonium nitrate, and americium sulfate, (4) distribution coefficients for TRUEX-TCE extraction of Pu(IV), and (5) activity coefficients and osmotic coefficients for sulfuric acid under TRUEX conditions (i.e., where H_2SO_4 behaves as a 1:1 electrolyte, yielding H^+ and HSO_4^- upon dissociation).

In laboratory studies to obtain data for the GTM, we determined the effects of (1) 0.001M neodymium on the distribution ratios for Am(III) between 0.25M CMPO-TCE and HNO_3 , (2) nitric acid/aluminum nitrate concentration on the extraction of ^{241}Am by 0.25M CMPO-TCE, and (3) concentration of nitric acid, oxalic acid, hydrofluoric acid, and nitrate salts on the extraction of ^{88}Zr and ^{88}Y by TRUEX-NPH. The distribution of Np(IV), (V), and (VI) between TRUEX solvents and acidic aqueous solutions was also studied. For each oxidation state, the distribution ratios increased as the nitric

acid concentration was increased from 0.05 to 5M, except that with Np(IV) the ratio appeared to level off, or decrease slightly, from 3 to 5M. The Np(V) species extracted poorly, as expected for the singly charged ion, NpO_2^+ , while the other two species were well extracted. Distribution ratios in nitric acid solutions containing sulfuric, oxalic, or hydrofluoric acid were also measured. The presence of these acids, which form complexes with Np(IV), lowered the distribution ratios substantially and gave more reproducible results than was the case with nitric acid alone.

Efforts have been initiated to improve the TRUEX process for generic applications by testing new stripping and scrubbing reagents. In this period, we determined the effects of sulfate, oxalate, fluoride, and phosphate on the partitioning of americium between TRUEX-NPH and acidic nitrate solutions (NO_3^- between 0.1M and 10M). The results showed that all four acids depress the americium distribution ratios, but to different extents. Sulfuric acid uniformly depressed the distribution ratios for all HNO_3 concentrations, while the three weak acids generally depressed the distribution ratios more at low NO_3^- concentrations.

During contact with PUREX raffinates from the reprocessing of irradiated fuel, a fraction of the TRUEX-NPH solvent will be degraded, through radiolysis and hydrolysis, to other chemical species. Laboratory studies were therefore undertaken to measure the americium distribution coefficients between samples of solvent that had been previously subjected to radiolysis or hydrolysis and 0.01-2.0M HNO_3 . The distribution coefficient was shown to be dependent on received dose and hydrolysis time and temperature. The effects of radiolysis and hydrolysis were found to be partially reversed by washing the solvent with water or sodium carbonate solution.

The technique of supercritical fluid chromatography was adapted for quantitating the purity of commercially available CMPO and the compositions of the TRUEX-TCE and TRUEX-NPH solvents under plant conditions. This technique yields a good separation of the components in the TRUEX solvent and is useful at temperatures below the CMPO decomposition temperature (about 180°C).

A project is underway to modify the Argonne centrifugal contactor to work with specific extraction processes. To evaluate processes involving high alpha/beta activity levels (in a glove box) and/or high gamma radiation (in a shielded cell facility), we designed and built a 4-cm contactor that can be used where remote handling is required. This contactor has been evaluated under typical operating conditions in both a glovebox and a shielded cell mockup area with good success. The basic design for remote handling is now being used in a sixteen-stage 2-cm contactor, which minimizes the feed needed for testing solvent extraction flowsheets.

A series of laboratory verification studies has been initiated to develop a better understanding of the chemistry of the TRUEX process, test and verify process modifications, and verify the results from GTM predictions. Two nonradioactive verification runs were completed in this period, both with the TRUEX-TCE solvent. The measured data are being compared with calculated results from the GTM. Data collected in the nonradioactive tests will be used to analyze data from radioactive-tracer experiments.

Another project in separation science and technology is concerned with examining the feasibility of substituting low-enriched uranium for the high-enriched uranium now used in the production of fission product ^{99}Mo . Technetium-99m, the daughter of ^{99}Mo , is used widely in medical applications. This period, targets of U_3Si_2 and U metal were irradiated at low burnup and processed by basic dissolution. After dissolution, alumina column separation was used to obtain molybdenum. Test results indicated that ^{99}Mo loss for the fuel particles into the aluminum matrix due to fission recoil is substantial, and that the present two-step dissolution must be modified to recover the molybdenum loss to the decladding solution.

High Level Waste/Repository Interactions

The volcanic tuff beds of Yucca Mountain, Nevada, are being studied as a potential repository site for the isolation of spent reactor fuel and high-level defense and commercial waste. The reprocessed high-level wastes will be incorporated into a borosilicate glass matrix prior to the emplacement in the repository. The behavior of this waste in the host environment must be sufficiently well understood to project its stability over very long time periods. As part of the waste package study group of the Yucca Mountain Project, CMT has been studying the corrosion behavior of simulated nuclear waste glass and spent fuel in aqueous environments relevant to the Yucca Mountain site.

In an ongoing study, simulated waste glasses (SRL 165 and ATM-10) have been intermittently contacted with dripping well water (J-13) using an unsaturated test method developed in CMT. In tests with the SRL 165 glass through 130 weeks, results indicated that the greatest effects on glass reaction are due to spallation of the reacted glass layer and interaction between the solution, glass, and sensitized metal components of the waste package assemblage. In tests with ATM-10 glass through 80 weeks, the releases from this glass were about three times larger than those for SRL 165 glass under similar conditions; also, there was no evidence of strong reaction between the sensitized metal components and the glass.

From hydration tests of Hawaiian basalt glass exposed to 100% relative humidity at 175-200°C for 150 days, the activation energy for the hydration process was estimated to be 9 kcal/mol (38 kJ/mol), which is in good agreement with literature data. An investigation was initiated to measure the intrinsic water contents of obsidian and nuclear waste glasses.

Experiments are underway to determine the influence of penetrating gamma radiation on the chemistry of tuff groundwater and the reaction of simulated nuclear waste glass with tuff groundwater. Preliminary experiments were completed to determine the behavior of the radionuclides U, Np, Pu, and Am during the reaction of SRL 165 glass without complications due to radiation. These results will be used for comparing results obtained with the waste glass in different gamma radiation fields.

In spent fuel studies, tests have been initiated to determine the radionuclide release rates from spent reactor fuels immersed in J-13 water at ambient hot cell temperatures and to examine the dissolution of enriched UO_2 powder in J-13 water under steady-state conditions. In other spent fuel studies, a set of experiments, in which Zircaloy clad- UO_2 pellets have been contacted by dripping J-13 water, has been in progress for 3.5 years. Results showed that a pulse of uranium release from the UO_2 solid, combined with the formation of schoepite and dehydrated schoepite on the sample surface, characterizes reactions between 25 and 100 weeks. Thereafter, the uranium pulse subsided, and another set of secondary phases was observed to form on the top of the UO_2 surfaces. Continued observations will be made as to any additional phases that form as the reaction progresses.

A program has been initiated to investigate the effect of radiation on the performance of candidate waste canister materials in an irradiated environment. The emphasis of this program is establishing the extent and nature of radiolytic products generated under repository-relevant conditions, experimentally addressing questionable or unusual results relevant to this task reported in the literature, and performing atmospheric corrosion studies in an irradiated environment.

I. APPLIED PHYSICAL CHEMISTRY (C. E. Johnson)

The program in applied physical chemistry involves studies of the thermochemical, thermophysical, and transport behavior of selected materials in environments simulating those of fission and fusion energy systems.

A. Fission Product Release from Core-Concrete Mixtures (M. F. Roche, J. Settle, and L. Leibowitz)

In a severe nuclear reactor accident, the core could melt, penetrate the bottom of the reactor vessel, and react with the concrete basemat beneath the vessel. The objective of our work is to measure and calculate the vaporization of certain refractory fission products--strontium, barium, and lanthanum--from the molten core-concrete mixtures that would form under these conditions. The vaporization measurements are being done using a transpiration method; the calculations employ the SOLGASMIX computer code.¹ Our version of the code calculates equilibrium conditions for 17 elements in the gas, liquid, and solid phases. One hundred gas-phase species (elements, oxides, hydroxides) are included in the calculations; there are also 74 solid or liquid species included in the metal and oxide phases. The thermodynamic data for these species were obtained from a variety of sources.²⁻⁷

1. Experiments

Experiments were conducted with either zirconia or molybdenum crucibles. The amounts of materials employed in the experiments with zirconia crucibles were: limestone-aggregate concrete, 3 g; stainless steel, 3 g; and UO_2 (doped with 1 mol% La_2O_3 , 0.4 mol% BaO , 1 mol% SrO , and 2 mol% ZrO_2), 3 g. The same amounts were employed in the experiments with molybdenum crucibles except that the steel (which forms a separate phase) was omitted. The materials were heated at 2150 K within a Mo-30W furnace tube (46-cm long x 2.9-cm OD x 2.4-cm ID). The gas flowing over the materials was He-6% H_2 -0.06% H_2O ; this H_2 -to- H_2O ratio is equivalent to a partial molar free energy of -420 kJ per mole of O_2 . The flow rate of the gas was either 100 or 200 cm^3/min (measured at 25 °C), and about 0.6 mol of gas was used. The water concentration in the gas was measured with a thin-film alumina hygrometer (Model 550 Panametrics, Inc.).

Materials vaporized from the core-concrete sample were collected in a molybdenum condenser tube (54-cm long x 0.8-cm OD x 0.5-cm ID) whose entrance lay within the crucible a few centimeters above the sample surface. Following a run, the condensate was extracted from the condenser tube with acid washes (HCl , HNO_3), and the solutions were analyzed by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) or fluorescence spectroscopy (for uranium). In addition, the starting materials were all assayed by the same techniques.

The sample from one of the runs employing a zirconia crucible was cross sectioned, mounted, polished, and examined by electron probe microanalysis (EPM).

2. Results and Discussion

a. Post-Test Analysis

The zirconia crucible from a 146-min run (100 cm^3/min gas flow rate) was examined after cross-sectioning. The solidified mass of concrete, urania, and steel, which occupied the bottom third of the crucible, had evidently been at least partially liquid during the run. The concrete-urania phase,

which had wet the zirconia crucible, had a pronounced meniscus. In addition, the thickness of the zirconia-crucible wall had been reduced by roughly 40% in the wetted area (the bottom third of the crucible). The steel phase (approximately spherical) was embedded within the solidified concrete-urania mixture; evidently, the steel phase could not readily equilibrate with the gas phase in this geometry.

The EPM results for two areas of this sample are shown in Figs. I-1 and -2. A secondary electron image and maps of the distribution of the major elements (U, Zr, Ca, Mg, and Si) are shown for each area. Also detected by EPM in spot analyses were the elements Al, La, Ba, Sr, Cr, and Fe. The La and Sr distributions tended to parallel the Ca distribution. The signal for Ba was too weak to draw any general conclusions about its distribution, but it was detectable in several regions high in uranium.

The major phases present in the mixture were deduced from the overlap of the elemental images in the photomicrographs. The phases were determined to be urania containing calcia and zirconia, calcium zirconate, a calcium-magnesium silicate, and magnesia associated with the calcium-magnesium silicate. About 10% of the zirconia crucible was dissolved by the concrete-urania mixture during the experiment; this accounts for the presence of zirconia-containing major phases. The urania and calcium-zirconate phases seen in the sample have melting points above 2500 K and were probably solids during the experiment. The calcium-magnesium silicate and magnesia phases probably crystallized from

Fig. I-1. Electron Probe Microanalysis of 100 x 80 μm Area in Sample from 146-min Run at 2150 K. The sample contained limestone-aggregate concrete, doped urania, and stainless steel.

Fig. I-2. Electron Probe Microanalysis of Another 100 x 80 μm Area in Sample from 146-min Run at 2150 K. The sample contained limestone-aggregate concrete, doped urania, and stainless steel.

a liquid phase. This phase had a composition near a eutectic (mp, 2070 K) on the calcium orthosilicate-magnesia tie line in the CaO-MgO-SiO_2 phase diagram,⁸ according to SOLGASMIX calculations (Sec. I.A.2.c.).

b. Measured Transport

The analytical data from the runs in the zirconia crucibles have been presented elsewhere,⁹ but the detailed EPM results on system phases were not available at that time. In the runs, the amount of material transported in the zirconia crucible at a gas flow rate of 100 and 200 cm^3/min was nearly the same (98 and 129 mg, respectively), indicating that gas saturation had been achieved. The analytical chemistry data from the two runs are shown in Table I-1. The "Amounts Added" column in this table includes our estimate of zirconia dissolution from the beaker and is a factor of 100 higher than the amount incorporated as a dopant in the urania.

The analytical data in Table I-1 suggest that the major limestone-concrete components, Mg and Ca, had achieved saturation because the amount of transport was independent of gas flow rate. However, we know that the major steel components (Fe, Cr, and Ni) did not saturate the gas

Table I-1. Calculated and Measured Vapor Transport in Zirconia Crucibles with Stainless Steel, Limestone-Aggregate Concrete, and Doped Urania at 2150 K

Element	Amount Added, mg	Calculated Transport, mg	Measured Transport, mg	
			200 cm ³ /min	100 cm ³ /min
La	33	0.015	<0.002	<0.005
Ba	6	0.019	0.018	0.028
Sr	12	0.010	0.006	0.012
U	2648	0.087	0.047 (0.005)*	0.028 (0.014)
Fe	2470	44	1.26 (1.00)	1.52 (0.51)
Cr	628	33	1.64 (0.97)	1.36 (0.54)
Ni	277	3	0.08 (0.06)	0.04 (0.02)
Mn	50	38	15.4 (3.4)	9.7 (3.6)
Zr	2056	0	0.009	<0.005
Ca	974	0.6	0.2	0.22
Mg	143	67	40	39
Si	118	1.8	2.9	---
Al	32	31	0	0.2

*Values in parentheses are analyses on the second, more severe HNO₃ etch of the molybdenum condenser tubes. Note diffusion of some elements (mainly Cr, Fe, Ni, Mn, but also U) into the Mo surface.

phase. They exhibited much less transport in these runs than in earlier runs with the steel alone, in which gas saturation by the steel components was indicated by both analytical data and SOLGASMIX calculations.⁹ The lack of saturation in the present runs is attributed to the steel phase being embedded in the concrete-uranium phase.

The data from the molybdenum crucible runs are given in Table I-2. Again, the masses transpired, 86 and 91 mg, respectively, at 100 and 200 cm³/min gas flow rate were nearly identical. Also, the amount of magnesium (the major element in the deposits) being transported is nearly the same in both runs.

Note that the major differences in the "Amount Added" column between Tables I-1 and I-2 are in the amounts of the steel components and the zirconium. The measured transport of the alkaline earths is generally higher with the steel and zirconia at low levels (Table I-2). It is about a factor of two higher for barium and about a factor of four higher for strontium. The lanthanum also is higher in that it is at least detectable in the vapor condensates for the runs reported in Table I-2. Clearly, these differences are not due to the steel, which forms a separate phase, but to the zirconia, which suppresses vaporization of the alkaline earth oxides by reaction with them to form a mixed zirconate. The decrease in lanthanum vaporization can also be explained by zirconate formation; the compound La₂Zr₂O₇ (mp, 2573 K) is known to exist.¹⁰

c. Calculated Transport

The calculated transport shown in Tables I-1 and -2 is based on the phase information obtained from the EPM analysis. Previously, we had assumed that all the solid oxides (including the zirconates of the alkaline earths) formed an ideal solid solution.⁹ Using the EPM phase data as a guide, we split the solid oxides into a uranium solid solution, an alkaline earth zirconate solid solution

Table I-2. Calculated and Measured Vapor Transport in Molybdenum Crucibles with Limestone-Aggregate Concrete, and Doped Urania at 2150 K

Element	Amount Added, mg	Calculated Transport, mg	Measured Transport, mg	
			200 cm ³ /min	100 cm ³ /min
La	32	0.016	0.005	0.003
Ba	6	0.348	0.065	0.033
Sr	12	0.199	0.040	0.031
U	2542	0.100	0.170 (0.015) ^a	---
Fe	18	18	4.8 (2.4)	10.8 (8.1)
Cr	0.13	0.13	0.02	0.11 (0.10)
Ni	0	0	0.0	0.02 (0.01)
Mn	0.35	0.33	2.3 (0.5)	1.7
Zr	20	0	0.0	0.0
Ca	988	1.5	4.6 (0.1)	1.8 (0.2)
Mg	144	70	58 (0.1)	57 (2.5)
Si	107	0.34	---	---
Al	32	32	0	0.0

^aValues in parentheses are analyses on the second, more severe HNO₃ etch of the molybdenum condenser tube. Note that a manufacturing error led to some iron and manganese contamination in the two molybdenum tubes used in these runs.

(unfortunately, no thermodynamic data are available for lanthanum zirconate), and a "silicate" solid solution. As a result of these changes in SOLGASMIX, the data and the calculations in Table I-1 agree reasonably well. If we repeat the calculations for Table I-1, but with the species SrZrO₃ and BaZrO₃ omitted, then the calculated transports of Sr and Ba are 0.167 and 0.292 mg, respectively. From the ratio of the calculated transports with and without the zirconates, we derive an apparent activity coefficient of about 0.06 for both strontia and baria in the high-zirconia system.

The calculations are less satisfactory for the case where the zirconia concentration is small (Table I-2). Here, the calculated values for the alkaline earths (which are based on an ideal solution of strontia, baria, lanthana, and urania) are too high by a factor of about five. The problem is that thermodynamic data for the silicates of strontia, baria, and lanthana are not available. Including these silicates in the data base would improve the calculations. The silicate data for magnesia and calcia are included in SOLGASMIX, and their release is predicted quite well. From the ratio of the calculated and measured transport in Table I-2, we derived apparent activity coefficients for strontia, baria, and lanthana of about 0.2 in the low-zirconia system.

A continuing problem with the SOLGASMIX calculation is the prediction of a solid silicate slag rather than a liquid. We will need to improve the treatment of the liquid oxides to model the region near the melting point of these complex silicate mixtures. For example, the calculated silicate phase for the cases presented in both Tables I-1 and -2 is a nearly equimolar solid solution of calcium orthosilicate and magnesia. However, according to the MgO-CaO-SiO₂ phase diagram,⁸ a mixture of these solids does not form a solid solution and, in fact, is some 75 K above the melting point. Except for these problems with the silicate phase, the phases derived from the SOLGASMIX code are now in good agreement with experiments.

3. Conclusions

The release of the refractory fission products strontium, barium, and lanthanum from core-concrete mixtures at 2150 K is much less than is predicted by simple models that employ ideal solutions of strontia, baria, and lanthana. Those simple models yield release fractions that are a factor of sixteen too high. It is necessary to include the thermodynamics of the zirconates of the alkaline earths and the rare earths to reflect the actual phases in a core-concrete mixture. Even in the absence of the zirconates, the amount of vaporization is less than predicted by the ideal-solution model. We believe that thermodynamic data for the silicates of the alkaline earths and rare earths must be included to correctly predict the release under these conditions.

The transpiration method provides an effective test of the thermodynamic data base and the model assumptions used in the computer codes. If the experiments are extended to other types of concrete, other oxygen potentials, and other temperatures, then reliable predictions can be made for a variety of reactors.

B. Thermophysical Properties of Metal Fuels

Recently, increased interest¹¹ in metallic (U-Pu-Zr) fuel for liquid-metal fast breeder reactors has prompted a reassessment of the available thermodynamic and transport property data for materials of interest. The two primary cladding alloys under consideration are the stainless steels D9 (an austenitic alloy similar to 316 stainless steel) and HT9 (a ferritic alloy similar to 400 series steels).

1. Thermal Conductivity and Expansion (L. Leibowitz and R. A. Blomquist)

Modeling of fuel performance and reactor behavior depends, in part, on the thermodynamic and transport properties of the cladding. Because of a lack of reliable literature data for D9 and HT9, we undertook measurements of their thermal expansion and thermal conductivity. The composition for D9 is 15.5 wt % Ni, 13.5 wt % Cr, 2.0 wt % Mn, 2.0 wt % Mo, 0.75 wt % Si, 0.25 wt % Ti, and 0.04 wt % C; the composition for HT9 is 0.5 wt % Ni, 12.0 wt % Cr, 0.2 wt % Mn, 1.0 wt % Mo, 0.25 wt % Si, 0.5 wt % W, 0.5 wt % V, and 0.2 wt % C, with the balance Fe. The alloys were used in the as-received condition. The D9 was solution annealed at 1322 K and 20% cold worked; the HT9, which had a martensitic structure, was tempered by heat treating at 1033 and 1311 K. Our experimental methods and results are reported below.

a. Experimental

(1) Thermal Expansion

The thermal expansion of the alloys was measured with a Netzsch Inc. Model 402 dilatometer containing a horizontal, single push rod and a rhodium furnace. Because it was used for measurements on plutonium-containing materials, the instrument was located in a helium-atmosphere glove box and connected to a Kinetic Systems Corp. computer automatic measurement and control (CAMAC) data acquisition system, which was interfaced to a Digital Equipment Corp. (DEC) PDP-11/34 computer. The sample was held in an alumina support tube, closed at one end, and positioned in the center of the constant temperature zone of the furnace. A vacuum-tight protective tube allowed control of the atmosphere to which the sample was exposed. An alumina rod in a low-friction support transferred the change in length of the sample to an inductive displacement transducer. Sample temperatures were measured with a Type S (Pt vs. Pt-10% Rh) thermocouple.

In a typical measurement, a 50-mm long sample was prepared with flat, parallel end faces and installed in the instrument. The furnace was evacuated and flushed with high purity helium several times and finally filled with high purity helium to a pressure slightly above ambient. The desired set of temperature cycles was entered in the temperature controller and the test series begun. The dilatometer was periodically calibrated with a National Bureau of Standards (NBS) tungsten thermal expansion standard (SRM 737). Several heating and cooling rates were tested, and 1 K/min was chosen as the standard rate. A few measurements made on HT9 at 0.5 and 2 K/min are discussed below. Length changes measured with the dilatometer depend on the differences between expansion of the sample and its holder. From the known thermal expansion of the NBS standard, a correction due to expansion of the sample holder was calculated and applied to subsequent measurements. Separate temperature calibrations were performed with NBS aluminum (SRM 44f) and high purity gold (reported to be 99.99% pure). These calibrations were performed by using a foil of the metal between two 25.4 mm-long alumina rods in place of the normal thermal expansion sample. The temperature at which a sharp change in length was observed was taken as the melting point of the metal. In all cases, our indicated temperatures were within ± 2 K of the expected melting point. We estimated the accuracy of our thermal expansion data to be about $\pm 2\%$, although the precision is significantly better (discussed later).

(2) Thermal Conductivity

The thermal conductivity was measured with a Dynatech Corp. Model TCFCM-N20 thermal conductivity instrument. The instrument was located in the same helium-atmosphere glove box as the thermal expansion system. The hot zone of the instrument was further protected from gaseous impurities by enclosing it in a large aluminum bell jar, secured to the base plate through a rubber gasket. The bell jar could be evacuated and filled with high-purity helium. The apparatus is based on the comparative thermal conductivity method.¹² An unknown cylindrical sample was positioned under spring tension between two identical, calibrated reference cylinders of thermal conductivity, thereby forming a vertically stacked column. Longitudinal heat flow was established by heaters placed above and below the column. The bottom heater rested on a water-cooled block and served as a heat sink. Radial heat losses were minimized by surrounding the column with guard furnaces in which the thermal gradient was matched to that of the column and by filling the annular space with alumina granules.

Six ungrounded Chromel-Alumel thermocouples sheathed in Inconel were used for temperature measurements. Each of the three cylinders comprising the experimental stack held two thermocouples in wells that were a known distance apart (Δx). No thermocouple calibrations were made because only the differences in temperature were of consequence in calculating thermal conductivities and because all thermocouples were derived from the same batch. In earlier work with this instrument, thermocouple calibrations were performed, and corrections were found to be negligible.

In a typical experiment, the column was assembled and the thermocouples were inserted into their designated wells. After the guard furnace had been lowered, the annular space was filled with alumina granules and covered with quartz wool. After the bell jar had been lowered on the base plate, the assembly was evacuated, degassed for several hours at 572 K, flushed several times with ultra-high purity helium, and then backfilled with helium to a pressure of ~ 80 kPa. The top and bottom heaters were programmed for the desired temperature gradient (~ 80 K), and the system was allowed to come to steady state. At the end of equilibration, thermocouple outputs were measured with a digital voltmeter to within ± 5 μ V, and the heaters were re-programmed for the next temperature.

Our experience indicated that a slight flux (q_r) difference, noticeable between the top and bottom references, is a function of the temperature gradient (ΔT) imposed on the column

between the top and bottom thermocouples. In earlier measurements, we attempted to improve the accuracy of our data by obtaining at least two values of ΔT selected in such a way that the condition $q_{\text{top}} > q_{\text{bottom}}$ existed at the lower ΔT value, and $q_{\text{top}} < q_{\text{bottom}}$ at the higher value. Linear interpolations (or, in some cases, extrapolations) were then used to establish a value of ΔT at which there was an identical heat flux (q_{ref}) in both references and also to determine the corresponding average value of the sample temperature centered between the thermocouples in the unknown. Thermal conductivity of the unknown sample (λ_{sample}) was then calculated from the following equation:

$$\lambda_{\text{sample}} = \left(\frac{\Delta x}{\Delta T} \right)_{\text{sample}} \lambda_{\text{ref}} \left(\frac{\Delta T}{\Delta x} \right)_{\text{ref}} \quad (\text{I-1})$$

Subsequent measurements showed that no improvement in reliability was gained by using this procedure. In the work described here, we used only a single gradient at which differences in heat fluxes in the top and bottom references were insignificant.

The primary reference standard used for the thermal conductivity measurement was an austenitic stainless steel (SRM 1462) supplied by the NBS. Its chemical composition is 62.0 wt % Fe, 20.2 wt % Ni, 16.2 wt % Cr, 1.2 wt % Mn, 0.28 wt % Si, and <0.01 wt % C.

Cylindrical samples (25.4 mm in diameter and 25.4 mm high) were machined from available stock, and thermocouple wells (12.7 mm long and 1.7 mm in diameter) were drilled 6.35 mm from the top and bottom of each sample. The faces of the samples were carefully polished to provide good thermal contact.

Thermal expansion corrections were made to the interwell distances of all alloys used. Our own thermal expansion values were used for the cladding alloys D9 and HT9. For the NBS reference, data were taken from the compilation of Touloukian et al.,¹³ by substituting Fe + 24-26 wt % Ni + 15-20 wt % Cr + Σx_i for the NBS standard. Thermal expansion corrections between room temperature and 1200 K were 1.4% for the NBS reference, 1.8% for D9, and 1.1% for HT9.

Test measurements were performed in which all three cylinders were NBS reference steel; that is, we measured the thermal conductivity of the NBS standard in the same way that we would measure our unknown alloys. These measurements were within the NBS stated uncertainty of 5%. We estimated the accuracy of our measurements on cladding alloys to be about $\pm 10\%$, although the precision is significantly better (discussed later).

b. Results

(1) Thermal Expansion

D9: Figure I-3 shows thermal expansion data for D9 as well as data for 316 stainless steel of similar composition reported by Lucks et al.¹⁴ and data given by Touloukian et al.¹³ for 300 series stainless steels, including 316. No data are available in the literature for the thermal expansion of D9. The composition of the steel used by Lucks et al.¹⁴ was 11.6 wt% Ni, 16.82 wt% Cr, 1.59 wt% Mn, 2.18 wt% Mo, 0.26 wt% Si, 0.108 wt% C, 0.023 wt% S, and 0.018 wt% P, with the balance Fe. (One point tabulated at 1123 K in Ref. 14, which appears to have been a typographical error, was omitted from the plot.) As can be seen in Fig. I-3, the agreement between the three sets of data is good, and in contrast with HT9 (as will be discussed below), no phase transitions are apparent. The key

Fig. I-3.

Measured Thermal Expansion of D9
Compared with Data of Lucks et al.¹⁴ and
Touloukian et al.¹⁵ (TPRC) for 316 Stainless
Steel

features of present interest in these steel alloys are the existence of a face-centered cubic (fcc) γ -phase (austenite) and a body-centered cubic (bcc) α -phase (ferrite). An inspection of the Fe-Cr-Ni phase diagram¹⁵ suggests no transitions from the γ -phase in D9. Our thermal expansion results for the heating and cooling cycles agreed very well for this alloy. The pooled results of six heating and cooling cycles at 1 K min^{-1} are described by

$$\Delta L/L_0 = -0.4247 + 1.282 \times 10^{-3}T + 7.362 \times 10^{-7}T^2 - 2.069 \times 10^{-10}T^3 \quad (\text{I-2})$$

with a percent standard deviation (σ) of 0.17. In this equation and the next one, the temperature, T , is in K, and the relative change in length referenced to 293 K is given in percent. That is, $\Delta L/L_0 = 100 \times [L(T) - L(293)]/L(293)$.

HT9: Thermal expansion data for HT9 are shown in Fig. I-4. It is evident that a transition occurs at about 1100 K on heating and about 1050 K on cooling. Inspection of the Fe-Cr-Ni¹⁵ and the Fe-Cr phase diagrams¹⁶ indicate a $\alpha \rightarrow \gamma$ transition at roughly 1100 K. On cooling, however, the transition is substantially delayed, even at 1 K min^{-1} . A few measurements performed at 0.5 K min^{-1} were essentially the same as those at 1 K min^{-1} , whereas markedly increased hysteresis was found at 2 K min^{-1} .

With regard to the Fe-Cr-Ni phase diagram, Ref. 15 states that "The outstanding feature, however, is the pronounced reluctance of metastable austenite to transform when once established at high temperatures." The hysteresis shown in Fig. I-4 clearly demonstrates this effect. Also shown are data for the thermal expansion of HT9 taken from an industrial data sheet and from values given by Touloukian et al.¹³ for 400 series stainless steels (including 410, which is similar to HT9).

Fig. I-4.

Measured Thermal Expansion of HT9 Compared with Data Given for HT9 by SANDVIK¹⁷ and for 410 Stainless Steel by Touloukian et al.¹³ (TPRC). ("Heating" and "Cooling" designate data obtained by us for heating and cooling cycles.)

The agreement of Refs. 17 and 13 with our results at low temperatures is very good. The following equation ($\sigma = 0.17$) represents the data below the transition temperature:

$$\Delta L/L_0 = -0.2191 + 5.678 \times 10^{-4}T + 8.111 \times 10^{-7}T^2 - 2.576 \times 10^{-10}T^3 \quad (I-3)$$

(2) Thermal Conductivity

D9: There are no literature values for the thermal conductivity of D9. Thus, our measured thermal conductivity data for D9 are compared in Fig. I-5 with literature values for 316 stainless steel.^{14,18,19} As can be seen, agreement is quite good with the data of Lucks et al.¹⁴ At higher temperatures, our data differ somewhat with the data of Matolich¹⁸ and Chu and Ho.¹⁹ The composition of Matolich's sample of 316 stainless steel (his designation 3A) was 12.60 wt% Ni, 17.45 wt% Cr, 1.59 wt% Mn, 2.55 wt% Mo, 0.6 wt% Si, 0.063 wt% C, 0.01 wt% S, 0.023 wt% P, 0.09 wt% Cu, and 0.19 wt% Co, with the balance Fe. The values of Chu and Ho arose from an assessment of a great many measurements on 316 stainless steel. Considering the accuracy of the measurement plotted in Fig. I-5, the differences are of marginal significance.

Our data for D9 were taken in random temperature order to minimize any influence of instrument drift or other sources of systematic error. There seems to be a change in our data at about 1030 K, which we believe to be real. We have, consequently, represented the values to 1030 K by Eq. I-4 ($\sigma = 0.47$) and values about 1030 K by Eq. I-5 ($\sigma = 0.51$):

$$\lambda = 7.598 + 2.391 \times 10^{-2}T - 8.899 \times 10^{-6}T^2 \quad (I-4)$$

$$\lambda = 7.260 + 1.509 \times 10^{-2}T \quad (I-5)$$

The thermal conductivity, λ , is in $\text{W m}^{-1}\text{K}^{-1}$ and the temperature, T , is in K.

Fig. I-5.

Measured Thermal Conductivity of D9 Compared with Data for 316 Stainless Steel of Matolich,¹⁸ Lucks et al.,¹⁴ and Chu and Ho¹⁹

HT9: Figure I-6 shows our data for the thermal conductivity of HT9 along with values taken from an industrial data sheet for HT9¹⁷ and the values recommended by Chu and Ho¹⁹ for 410 stainless steel. Agreement is reasonably good with the smoothed curve obtained from the SANDVIK¹⁷ values; however, these values are quite sparse. Agreement with the Chu and Ho values is also fairly good, considering that they apply to different steels. Chu and Ho comment that there are no data for temperatures above 1000 K, and their recommended values above that temperature are based on extrapolations. Our experience has shown that it is extremely difficult to obtain reproducible data much above that temperature. Reproducible values could be obtained in random temperature order either entirely below or entirely above the transition temperature. It was very difficult, however, to move from above to below the transition temperature and reproduce the lower temperature data. This could only be done by changing the temperature in very small steps and waiting for long times before measuring the conductivity. Obtaining reproducible results by moving from below to above the transition was simpler, in accord with expectations for the ferritic-to-austenitic transformation. Equation I-6 ($\lambda = 0.57$) represents our data below the transition at 1030 K, and Eq. I-7 reproduces the data ($\sigma = 0.30$) above 1030 K:

$$\lambda = 17.622 + 2.428 \times 10^{-2}T - 1.696 \times 10^{-5}T^2 \quad (I-6)$$

$$\lambda = 12.027 + 1.218 \times 10^{-2}T \quad (I-7)$$

The thermal conductivity, λ , is in $\text{W m}^{-1} \text{K}^{-1}$ and the temperature, T , is in K.

Fig. I-6.

Measured Conductivity of HT9 Compared with Data Given for HT9 by SANDVIK¹⁷ and for 410 Stainless Steel by Chu and Ho¹⁹

c. Discussion

The thermal expansion results for D9 and HT9 are in reasonable accord with expectations from the relevant phase diagrams.^{14,15} No transitions that would influence thermal expansion are expected in the austenitic alloy, D9. In contrast, the ferritic steel, HT9, is expected to show a ferritic-to-austenitic transition in the neighborhood of 1100 K. Curie transitions would not influence thermal expansion. The hysteresis shown by the thermal expansion data for HT9 is a reflection of the difficulty of reversing the phase transition.

The thermal conductivity results are somewhat more difficult to interpret. It is expected that a Curie transition influences the thermal conductivity at high temperatures. In the ferritic alloys, one would be expected at a temperature of about 1040 K, slightly below that of the $\alpha \rightarrow \gamma$ transitions. Indeed, we found a marked break in the thermal conductivity curve for HT9 at about 1030 K rather than at the 1100 K seen in the expansion curve. Only one thermal conductivity measurement was obtained between these temperatures (at 1071 K), and we cannot distinguish between the effects of the $\alpha \rightarrow \gamma$ and the Curie transitions on thermal conductivity. It is possible that the thermal expansion transition at 1100 K was slightly delayed. Thermal expansion measurements at lower heating rates than 0.5 K min^{-1} , which could elucidate this possibility, could not be performed. However, because virtually identical results were obtained at 0.5 and 1 K min^{-1} , work at even lower rates does not seem promising. The observation of a transition in the D9 thermal conductivity data at 1030 K, exactly the same temperature as seen in HT9, leads us to speculate that a small amount of a ferritic phase had been formed in that alloy, possibly as a consequence of the heat treatment it received during the thermal conductivity measurements. Because the sample used is now contaminated with plutonium, further examination will

be very difficult. A similar effect may be responsible for the differences between the data of Lucks et al.¹⁴ and Matolich.¹⁸

d. Summary

Data have been presented for thermal expansion and thermal conductivity of the steel alloys D9 and HT9. The austenitic alloy, D9, shows values for both thermal expansion and thermal conductivity typical of 316 stainless steel. The ferritic alloy, HT9, however, shows a phase transition in the neighborhood of 1030 K and is similar to 410 stainless steel in these properties. Although 1030 K is far above the recommended service temperature of HT9, assessments of its behavior under severe, unexpected conditions, such as hypothetical nuclear reactor accidents, must take this transition into account.

2. Thermodynamics of U-Zr System (L. Leibowitz)

Increased interest in metallic fuels for liquid-metal fast breeder reactors has prompted a reassessment of the available thermodynamic and transport property data of the proposed fuel alloys. Current interest is centered on U-Pu-Zr alloys, with particular importance being given to the phase diagram and thermodynamic properties of that system. Although some work has appeared in the literature,²⁰ the previously available data are inadequate in scope and reliability for present purposes. We are employing a dual approach of phase diagram calculations and experimental determination of transition temperatures for selected alloys.²¹ Calculation of the ternary phase diagram requires thermodynamic functions for the three binary sub-systems, and we have begun with an analysis of the U-Zr system.

Relatively little thermodynamic data exist for the U-Zr system. Fedorov and Smimov reported emf data in the temperature range 1030-1184 K,²² from which they calculated thermodynamic properties of the system. The same authors²³ later reported heat capacity data to about 1273 K. A careful review of the thermodynamic data for the U-Zr system,²⁴ however, pointed out serious discrepancies in the emf data. More recently, a critical assessment of the U-Zr phase diagram was performed by Sheldon and Peterson.²⁵ The present analysis has relied, to a great extent, on the Sheldon and Peterson work. Finally, thermodynamic data were obtained by Knudsen effusion mass-spectrometric methods²⁶ over the temperature range 170-2060 K.

The techniques involved in our thermodynamic phase diagram analysis have been well documented.^{27,28} When applied to the computation of an unknown ternary phase diagram, these techniques involve the critical evaluation and analysis of all relevant phase diagram and thermodynamic data for the three binary sub-systems with a view of obtaining mathematical expressions for the thermodynamic properties of all binary phases as functions of composition and temperature. Following this, interpolation techniques based upon solution models are used to estimate the thermodynamic properties of the ternary phases from the properties of the binary phases. The ternary phase diagram is then calculated from the estimated ternary Gibbs energy surfaces. In the work described here, expressions for the thermodynamic properties of all phases in the U-Zr system have been derived. All calculations are performed with programs of the F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) computer system based in Montreal.²⁷

a. Gibbs Energies of Transition

The Gibbs energies of transition for both components of the U-Zr alloy are required in the present analysis. In the equations which follow, the Gibbs energies of transition, ΔG^* (transition),

are in cal/mol, and the temperatures, T, are in K. Equations for Gibbs energies of melting of U and Zr used in the present work are identical with those presented earlier²¹ and only a brief discussion of the values selected will be given here.

The data for U were reviewed by Oetting et al.²⁹ There are three solid phases: orthorhombic U(α), tetragonal U(β), and bcc U(γ). The temperatures and enthalpies of transition as given by Oetting et al.²⁹ are 942 K and 667 cal/mol for U($\alpha \rightarrow \beta$) and 1049 K and 1137 cal/mol for U($\beta \rightarrow \gamma$). Heat capacity values (ΔC_p) were also taken from Oetting et al.²⁹ The resulting equations for Gibbs energies of transition are:

$$\Delta G^\circ (\text{U}, \alpha \rightarrow \beta) = 1816.7 - 10.29T + 1.221T \ln T \quad (\text{I-8})$$

$$\Delta G^\circ (\text{U}, \beta \rightarrow \gamma) = 2301.8 - 9.915T + 1.11T \ln T \quad (\text{I-9})$$

Some additional discussion is needed regarding the melting transition for uranium. Oetting et al.²⁹ discussed two determinations of the enthalpy of fusion of uranium,^{30,31} and selected the more recent calorimetric value, 2185 cal/mol. However, our earlier work²¹ indicated that the value of 2185 cal/mol gives poor agreement with the U-Pu phase diagram. Other values of 2900 cal/mol,³² 3250 cal/mol,³³ and 2500 cal/mol³⁴ have also been published. The Savage and Seibel³² value of 2900 cal/mol gives much better agreement with the U-Pu phase diagram. This problem was resolved earlier²¹ in favor of the enthalpy of fusion of uranium in Ref. 30 as recommended by Ref. 29. In future work on the U-Pu system, we will expand on this complication. The melting point was taken as 1405 K, and ΔC_p as 2.48 cal/(mol·K). The resulting equation used for the Gibbs energy of melting of uranium is:

$$\Delta G^\circ (\text{U}, \gamma \rightarrow \ell) = -1299 + 18.899T - 2.48T \ln T \quad (\text{I-10})$$

With regard to the other component of the binary alloy, zirconium, it has two solid phases: hexagonal Zr(α) and bcc Zr(β). Values for the solid-state transition of Zr were taken from Hultgren,³⁵ who gives 1136 K as the transition temperature and 941 cal/mol as the enthalpy of transition. The resulting equation for the Gibbs energy of transition is

$$\Delta G^\circ (\text{Zr}, \alpha \rightarrow \beta) = 1738.4 - 6.455T + 0.7T \ln T \quad (\text{I-11})$$

Melting data for zirconium were taken from JANAF,³⁵ which gives the melting point as 2125 K and the enthalpy of fusion as 5000 cal/mol. Solid and liquid heat capacities were also taken from JANAF.³⁶ The resulting Gibbs energy of melting is

$$\Delta G^\circ (\text{Zr}, \beta \rightarrow \ell) = 2308 + 16.474T + 5.550 \times 10^{-4}T^2 - 2.446T \ln T \quad (\text{I-12})$$

b. Condensed Phases

The U-Zr phase diagram of Sheldon and Peterson²⁵ as reported by Massalski³⁷ is shown in Fig. I-7. As can be seen from the diagram, solubility of Zr in U(α) or U(β) is very low, as is the solubility of U in Zr(α). These three phases have been treated by us as Henrian solid solutions. The two bcc phases, U(γ) and Zr(β), form a solid solution phase (which will be referred to as the γ -phase) in which a miscibility gap exists. The γ -phase was taken as the reference state. An intermediate phase (δ) is also shown in Fig. I-7. This phase has been treated by a quasi-chemical model.³⁸

Fig. I-7. Uranium-Zirconium Phase Diagram of Massalski.^{2,39}
(Reproduced with permission.)

Henry's law coefficients were calculated for the U(α), U(β), and Zr (α) phases from the appropriate phase boundaries taken from the work of Sheldon and Peterson.²⁵ For each of these phases, the solvent was considered ideal. Values of $RT \ln \gamma_i^\circ$ (where γ_i° is the activity coefficient of species i) for the solute with respect to Zr(α) and U(α) as standard states were:

$$U(\alpha): RT \ln \gamma_{Zr}^\circ = 9232 \text{ cal/mol} \quad (I-13)$$

$$U(\beta): RT \ln \gamma_{Zr}^\circ = 8029 \text{ cal/mol} \quad (I-14)$$

$$Zr(\alpha): RT \ln \gamma_u^\circ = 9365 \text{ cal/mol} \quad (I-15)$$

Sub-solidus boundaries of the γ -phase were taken from the diagram of Sheldon and Peterson.²⁵ Assuming that the terminal solutions are Henrian as discussed above and taking into account the γ -phase miscibility gap, we derived the following equation for the excess Gibbs energy (G^E) of the γ -phase:

$$G_\gamma^E = X_U X_{Zr} (10470 - 5.25T - 5279X_{Zr} + 3078X_{Zr}^2) \quad (I-16)$$

where X_i is the mole fraction of the subscript element. Differentiation of Eq. I-16 yields the following equations for activity coefficients in the γ -phase:

$$G_{U(\gamma)}^E = RT \ln \gamma_{U(\gamma)} = X_{Zr}^2 (15749 - 5.25T - 16714X_{Zr} + 9234X_{Zr}^2) \quad (I-17)$$

$$G_{Zr(\gamma)}^E = RT \ln \gamma_{Zr(\gamma)} = X_U^2(10470 - 5.25T - 10558X_{Zr} + 9234X_{Zr}^2) \quad (I-18)$$

Equation I-16 differs from the one proposed earlier by us²¹ and better represents the U-Zr system over the whole composition range. Both equations represent the γ -phase miscibility gap reasonably well. In that temperature range, the results obtained from two equations for G^E do not differ greatly except at low values of X_U . Because of the entropy term in Eq. I-16, the differences increase at higher temperatures.

The U-Zr phase diagrams given by IAEA²⁴ and by Massalski³⁷ and Sheldon and Peterson²⁵ differ somewhat in the extent of existence of the δ -phase. The IAEA report gives a composition range of 67-73.1 at.%, whereas the other authors give 66-78 at.%. The experimental evidence for the wider extent of the Zr-rich boundary of the latter authors is quite limited, and we have accepted the IAEA boundaries in our analysis of the δ -phase. This phase was treated by us with a quasi-chemical model³⁸ that is appropriate for ordered phases. We consider the δ -phase to be effectively UZr_2 with some solubility for Zr. This model was developed many years ago³⁹ and was expanded by Pelton and Blander.³⁸ A difficulty arises in trying to treat ordered systems with simple polynomial expansions for excess enthalpy and entropy in that the shapes of these functions are not readily represented by such expansions. The quasi-chemical model is used to fix a composition of maximum ordering (in this case, $X_U = 1/3$ and $X_{Zr} = 2/3$) at which the Gibbs energy function will have a sharp minimum. The minimum can be made more or less sharp by adjusting an ordering parameter, $\omega - \eta T$. As this parameter becomes more negative, the minimum becomes deeper and sharper. In the present case,

$$\omega - \eta T = -3675 + 5.0T \text{ cal/mol} \quad (I-19)$$

and the Gibbs energies (relative to the γ -phase) of the δ -phase were taken as varying from

$$G_{U(\delta)}^* = -2400 + 20.205T - 2.331T \ln T \text{ (at } X_U = 1) \quad (I-20)$$

to

$$G_{Zr(\delta)}^* = -1300 + 6.455T - 0.7T \ln T \text{ (at } X_{Zr} = 1) \quad (I-21)$$

c. Solidus-Liquidus Temperatures

The solidus and liquidus temperatures for U-Zr were measured by Summers-Smith.⁴⁰ Data for solidus and liquidus temperatures for a single alloy (U-19.3 at. % Zr) were reported by us in an earlier paper.²¹ Our experimental values were in reasonable agreement with the Summers-Smith data. In conjunction with the Gibbs energy equation for the γ -phase, an equation that would reasonably reproduce the available experimental values was derived for the liquid:

$$G_L^E = X_U X_{Zr} (9835 - 5.25T - 3956X_{Zr} + 3078X_{Zr}^2) \quad (I-22)$$

Differentiation of Eq. I-22 yields the following equations for activity coefficients in the liquid phase:

$$G_{U(l)}^E = RT \ln \delta_{U(l)} = X_{Zr}^2 (13791 - 5.25T - 14068X_{Zr} + 9234X_{Zr}^2) \quad (I-23)$$

$$G_{Zr(l)}^E = RT \ln \delta_{Zr(l)} = X_U^2 (9835 - 5.25T - 7912X_{Zr} + 9234X_{Zr}^2) \quad (I-24)$$

While Eqs. I-16 and I-22 are different from those published previously,²¹ agreement with the experimental values is about the same as shown previously.²¹ In contrast, the recent results of Kanno et al.²⁶ yield a solidus-liquidus which does not agree well with the Summers-Smith experimental values. The solidus-liquidus curves given by Massalski^{25,37} were based on the Summers-Smith data.

d. Discussion

Our calculated sub-solidus diagram and that of Massalski^{25,37} are shown in Fig. I-8. As can be seen, agreement is reasonably good. Our calculated solidus-liquidus diagram is shown in Fig. I-9 along with the available experimental values. The solidus-liquidus of Massalski was essentially drawn through the Summers-Smith data. There are several areas of difference shown in Fig. I-7, one of which, the extent of the δ -phase, has already been discussed. Other areas of disagreement have to do with the limiting slopes of the phase boundaries. For example, it is known²⁹ that, for a melting transition, as the composition approaches a pure component, the difference between the slopes of the liquidus and solidus curves is determined by just the enthalpy of fusion, ΔH_f , and the melting point, T_f , of that component. That is,

$$\lim_{X_B \rightarrow 1} \left(\frac{dX_B^l}{dT} - \frac{dX_B^s}{dT} \right) = \frac{\Delta H_f}{RT_f^2} \quad (\text{I-25})$$

This result is independent of any model. Our calculated diagram shows the correct limiting slopes.

Fig. I-8. Calculated U-Zr Phase Diagram (broken line) and that of Massalski^{25,37} (solid line). (Calculated temperatures and composition are indicated in the diagram.)

As indicated in Fig. I-8, the major temperatures and compositions calculated by us agree very well with those of Sheldon and Peterson.²⁵ In some other cases, agreement is not as good. As pure Zr is approached, for example, our curve shows the correct limiting slope, and the calculated boundary between the γ -phase and the two-phase region is probably reasonably correct. This is an area, however, in which there are essentially no data.²⁵ Another area of disagreement exists between our Zr-rich boundary for the δ -phase and that of Sheldon and Peterson.²⁵ There are also no data

Fig. I-9. Calculated U-Zr Solidus-Liquidus Diagram and Literature Data.
(The mean of Summers-Smith solidus values is shown.)

here to allow a clear decision to be made. As mentioned above, our boundaries for the δ -phase agree with those recommended by IAEA.²⁴ Less significant differences exist along the boundary between the multiphase region and the δ -phase. This is another region in which no data are available.²⁵ Differences between the miscibility gaps are difficult to assess. This is a region in which both calculations and measurements are subject to significant uncertainty, and we believe that the differences shown are acceptable. The final region to consider is that near pure uranium. Our curve shows the correct limiting slope as required by Eq. I-23. A rough estimate of the limiting slope of the Sheldon and Peterson²⁵ curve from the available information indicates that it may be incorrect. Nevertheless, both curves are in reasonably good agreement with the available data. Overall, we believe that the calculated diagram is a good representation of the U-Zr phase diagram.

The source of the differences between our excess Gibbs energies and those of other authors^{22,26} is not clear. The values of Fedorov and Smirnov were criticized in an IAEA²⁴ review because they do not yield the correct relative partial molar Gibbs energies. We previously discounted those data,²¹ which appear to be much too negative for the γ -phase. Our excess Gibbs energies near the same temperatures (~ 1000 K) are slightly positive and agree remarkably well with the estimates of Rand and Kubaschewski,³⁴ which were based on the Cr-Mo system.

The solidus-liquidus diagram shown in Fig. I-9 is quite similar to that published previously.²¹ Agreement with the Summers-Smith data is reasonably good. Differences between our excess Gibbs energies and those of Kanno et al.²⁶ are difficult to resolve. Our values for the γ -phase were derived from phase diagram information at the sub-solidus boundaries. Extrapolation to the solidus temperatures is bound to introduce additional uncertainty, particularly in view of the relatively large entropy term in Eq. I-16. Nevertheless, our excess Gibbs energies are slightly negative near the solidus, while those of Kanno et al. at 1773 K are even more negative than those of Fedorov and Smirnov at 1100 K (see Ref. 26). It is expected that the γ -phase would become more nearly ideal at the higher

temperatures, not less so. It is also disturbing that the Kanno et al. solidus-liquidus diagram is at such variance with the Summers-Smith data.⁴⁹ Judging from the Ta-Zr phase diagram,³⁷ the choice of tantalum for the IR Knudsen cell is questionable. In addition, the oxygen content of their alloys, 300-600 ppm, could have influenced their results. We previously found a Zr-rich crust at the surface of our samples with one-tenth the oxygen content.²¹ Post-test examination of the Kanno samples would be very desirable. The narrowness of our calculated solidus-liquidus diagram near pure Zr is a consequence of the enthalpy of fusion of Zr, as expressed in Eq. I-23. Any thermodynamically correct diagram must conform to the constraints of that equation. Given the present state of understanding, however, this disagreement remains unresolved. We are performing solidus-liquidus temperature measurements which should help clarify this matter.

3. Redistribution of Fuel Components during Irradiation

Several models have been proposed to account for redistribution of IFR fuel components during irradiation. None, however, seems as satisfactory as that proposed several years ago by A. D. Pelton.⁴¹ This model appears to correctly present the conceptual framework within which to view alloy redistribution. The central argument is summarized below.

Figure I-10 shows a binary phase diagram (A-B) which contains, in simplified form, the essential elements of the U-Zr system. There is a phase (α) which is nearly pure A and a solid solution phase (γ). Let us imagine that a rod of alloy of the original composition indicated on the figure is placed in a temperature gradient from T_{low} to T_{high} . Local equilibrium is established with the result that, at T_{low} , we have a two-phase system consisting of an α -phase and a γ -phase with the composition indicated by α . At T_{high} , the system is all γ -phase of the original composition. Within the γ phase, therefore, concentration gradients which drive migration are established. The concentration of B is higher and the

Fig. I-10. Schematic Phase Diagram Illustrating Component Redistribution

concentration of A is lower at T_{low} than at T_{high} . Component B migrates to the hotter end, and component A migrates to the colder end. This process continues and a sharp boundary develops at a temperature T' , which is determined by mass-balance considerations. At equilibrium, the cooler end is essentially all α -phase (nearly pure A), and the hotter end is γ -phase of uniform composition (enriched in B and depleted in A). In the U-Zr system no such gradients develop in the still lower temperature $\alpha + \delta$ field, and no migration is predicted. Thus, the formation of three zones can be accounted for. Addition of plutonium does not change the essential argument. Because of its solubility relations, no Pu concentration gradients develop, and no Pu redistribution is predicted, as observed.

This model is relatively straightforward but gives no information on the times required for segregation to take place. It is the purpose of diffusion models in combination with activity estimates to provide such information. This thermodynamic model of redistribution should be amplified and quantified; at the moment, it is the most rational explanation of the observations.

C. Li₂O Target Development

(P. E. Blackburn and D. V. Steidl)

Use of a liquid-metal breeder reactor has been proposed for breeding tritium from lithium oxide by the reaction,

where LiOT is in equilibrium with T_2O by the reaction,

and $\text{T}_2\text{O(g)}$ is in equilibrium with tritium gas by

In this process, 1% of the lithium is converted to tritium per year. For safety and efficiency, tritium loss to the sodium coolant by permeation through the cladding must be limited to less than 0.1% per year. The purpose of this project is to test methods for limiting the tritium loss and to identify materials and configurations to achieve this end. Target design options include tritium getters, permeation barriers, and retention as T_2O .

In this report period, the barrier concept was tested with a tungsten capsule and a tungsten capsule lined in nickel, and the tritium oxidation concept was tested with a silver capsule. These capsules contained Li_2O and titrated water and were heated to 300-450° C.

Tungsten has a very low permeability for tritium but may react with the $\text{Li}_2\text{O}/\text{LiOH}$ contents. Kinetic factors, which are extremely difficult to predict, would determine whether or not any such reaction would be detrimental to tritium containment. The two tungsten test capsules will allow us to assess such effects. In the previous report in this series, copper test capsules showed greater-than-predicted tritium loss; thus, it was decided to include a silver capsule in this test series. Silver should develop even lower internal hydrogen pressure than copper. It was speculated that formation of a stable mixed Li-Cu oxide was responsible for the higher-than-predicted tritium loss in the copper test. Silver could behave quite differently in that respect, and this test will examine that possibility.

The test results are summarized in the Table I-3. The unlined tungsten capsule produced loss rates of tritium which agree with calculations to within a factor of four. The nickel-lined tungsten capsule produced negligible losses of tritium at 300 to 400 °C. The five runs at 450 °C produced losses of $0.085 \pm 0.025\%$ per year. The decreased loss of about one order of magnitude for the nickel-lined tungsten compared with the loss from the unlined tungsten is attributed to lower tritium pressure. This arises from a less reducing condition inside the nickel liner than that in the unlined tungsten. Although losses from the lined tungsten are about ten-fold lower than those from the unlined tungsten, they are about nine times higher than one would predict from the pressure calculated for the lined capsule. The reason for this discrepancy is under study. The nickel-lined tungsten capsule has shown the best tritium retention performance observed to date.

Table I-3. Test Results for Tritium Loss at 300-450 °C

Temp., °C	Tritium Loss, %/yr		
	Unlined Tungsten	Nickel-Lined Tungsten	Silver
300 ^a	0.014 ± 0.004	b	2.0 ± 1.3
350	0.055	b	5.4
400	0.031	b	28
450 ^c	0.86 ± 0.48	0.085 ± 0.048	33 ± 18^d

^aAverage of two runs.

^bValues below detection limits.

^cAverage of five runs.

^dAverage of steadily decreasing values: 57, 47, 23, 19, and 18% per year.

The silver capsule produced a high tritium loss rate at all temperatures. The silver capsule results are about 1000-fold higher than expected. The data indicated that the tritium loss rate was temperature dependent, suggesting that the loss is not caused by a leak in the silver capsule. There was also a decrease in the loss rate with time at 450 °C (see footnote d in Table I-3). Silver is known to dissolve in oxygen at high temperature. Since the mechanism for controlling tritium permeation in silver depends on reaction of oxygen with tritium to lower the tritium pressure, the silver reaction may defeat this process, resulting in high loss rates. The decreased rate loss with time seems to support this mechanism.

Measurements have begun on a third test series. This series is testing yttrium as a getter material. Two Y-Ni capsules are being tested in which Li_2O and tritiated water are enclosed in nickel. These capsules are sealed in yttrium, which, in turn, is enclosed in an outer nickel capsule. The inner nickel prevents contact between Li_2O and yttrium, and the outer nickel prevents oxidation of the yttrium during testing. Measurements of tritium release have been performed at 250, 300, and 350 °C for one week and at 400 °C for two weeks. At the lower temperatures, tritium release was below detection limits. After two weeks at 400 °C, we have begun to detect tritium release from one of the two capsules. Releases from the other capsule are still below detection limits. These qualitative indications suggest that yttrium should be a very effective getter for tritium.

Efforts to prepare a sample of tritiated LiAl have been delayed because of equipment problems. These should be resolved shortly and work with that capsule will proceed. We have also prepared tungsten capsules from vapor-deposited tubes obtained from L. Neimark (Materials and Components Technology Division, Argonne National Laboratory). Because of the grain structure of vapor-deposited tungsten, this material may not perform as well as the tungsten tested earlier. We have discussed, with a vendor of vapor-deposited tungsten, methods for preparing finer grained tungsten tubes by a technique of multiple layer deposition. However, tests of the standard material will be performed before attempting to obtain such tubes.

D. Adsorption, Dissolution, and Evolution of H_2O from γ -LiAlO₂
(A. K. Fischer)

Data for the adsorption of $H_2O(g)$, dissolution of OH^- , and rates of evolution of $H_2O(g)$ were reported previously for the $LiAlO_2$ - $H_2O(g)$ system for temperatures of 573-873 K.⁴² These thermodynamic and kinetic data relate to questions about tritium inventory in ceramic tritium breeder materials. The information will enable (1) comparison of candidate breeder materials in fusion reactors, (2) calculation of operating conditions, and (3) elucidation of the principles underlying the behavior of tritium in breeder materials. The adsorption data are analyzed in this report. Our general analysis of the relationships among energy levels, activation energies, and degrees of surface coverage reveals parallels to be expected between these properties and tritium release.

1. Experimental Results and Interpretation

Equilibration times for dissolution under the experimental conditions used for obtaining isotherms for $H_2O(g)$ adsorption on $LiAlO_2$ at 573-873 K were estimated on the basis of the particle size and the range of reported diffusion coefficients for proton diffusion.⁴³ For 673 K, there was borderline agreement between experimental equilibration times (approximately 1200-1400 min) and calculated ones. Therefore, for measurements at temperatures lower than 673 K, it was regarded that dissolution was slowed sufficiently so that dissolution equilibrium was not likely to be reached. However, the curves recording $H_2O(g)$ uptake after the breakthrough point did not correspond to a step-function condition, as they would be expected to if no uptake at all was occurring after breakthrough. Earlier, it had been recognized that, though the dissolution rate is considerably lower than the adsorption rate for the higher temperatures, dissolution makes some contribution to the overall observed uptake before the breakthrough point. Consequently, the earlier quantities of "adsorption" (for the higher temperatures) had to be corrected for some degree of simultaneous dissolution. For the series at lower temperature, the remaining post-breakthrough uptake, presumably not significantly affected by dissolution, can be regarded as another adsorption that involves surfaces that are not accessible to relatively large krypton atoms in the Brunauer-Emmett-Teller (BET) surface area measurement. Such non-BET surfaces could be on grains forming a crevice that is too narrow to admit krypton but that allows the very small protons to diffuse in by surface diffusion (inter-oxide hopping) from OH^- at the mouth of the crevice. Pores with narrow openings could contribute additional surface that is inaccessible to krypton. Tanaka et al⁴⁴ have recently reported a study of H_2O adsorption on $LiAlO_2$, also using the breakthrough technique. They labeled phenomena in the post-breakthrough region as "Sorption-II" and the pre-breakthrough adsorption as "Sorption-I." They did not attempt corrections.

Figure I-11 presents the five adsorption isotherms measured to this time, where θ is the fraction of surface covered and p is the pressure. Figure I-12 shows isobars for 10^{-3} to 10^{-5} atm (100 to 1 Pa) derived from the isotherm data and from extrapolations of them. At high water vapor pressures, the isobar is essentially decreasing monotonically with rising temperature, the typical behavior. At low water

Fig. I-11.

Adsorption Isotherms for $\text{LiAlO}_2\text{-H}_2\text{O(g)}$
System at 573-873 K

Fig. I-12.

Adsorption Isobars for $\text{LiAlO}_2\text{-H}_2\text{O(g)}$
at 1-100 Pa

vapor pressures, a maximum appears in the isobar. Greater adsorption was found at 773 K than at 673 K. Such increasing adsorption at higher temperature is a fairly common phenomenon, involving two processes with different activation energies.

The slopes of the 573-773 K isotherms decrease monotonically from a value of essentially 1 (1.2 ± 0.2) at 573 K. A slope of 1 is consistent with unimolecular physisorption of H_2O ; the low temperature process is taken to be physisorption. The decline in slope is consistent with an increasing contribution from the second process. At 873 K, the slope is essentially 0.5 (0.59 ± 0.16) and is consistent with dissociative chemisorption (formation of two $\text{OH}^\cdot$) being the dominant process at this temperature. A decline in slope from 0.5 would occur as temperature declines, and the low-temperature process becomes operative. Therefore, a minimum in slope in the intervening temperature range is expected and was observed. Adsorption of $\text{H}_2\text{O}(\text{g})$ on LiAlO_2 is viewed as involving two kinds of adsorption in the temperature and pressure range of the measurements: physisorption and chemisorption. Within each regime, the fact that the adsorption is described by Freundlich isotherms is consistent with surface heterogeneity.⁴⁵

A system-wide atomic basis for heterogeneity of adsorption sites could be that one kind of adsorption site involves lithium ions and adjacent oxides, and another kind involves aluminum ions and adjacent oxides. Further evidence consistent with surface processes involving different kinds of sites was found for the reverse process relative to adsorption, the evolution of water vapor from LiAlO_2 , and was reported earlier.⁴⁶ During heatup after a run, the water evolution curve showed a double peak, which was interpreted as indicating that different kinds of sites were involved.

For designers and planners needing estimates of degrees of adsorption for various combinations of temperature and pressure, the isosteres (pressure vs. temperature curves for constant coverage) derived from the isotherms and plotted for $\theta = 0.1$ to 0.001 in Fig. I-13 are useful. Furthermore,

Fig. I-13.

Adsorption Isosteres for $\text{LiAlO}_2\text{-H}_2\text{O}(\text{g})$ at Fractional Coverages of 10^{-1} to 10^{-3}

the isosteres between 773 and 873 K provide a minimum estimated value for the heat of adsorption, which ranges from about 10 kcal/mol at $\Theta=0.1$ (high coverage) to about 90 kcal/mol at $\Theta=0.001$ (low coverage). Heats of chemisorption are typically greater than about 10 kcal/mol. Low coverage involves the most active sites and leads to large heats of adsorption. For alumina, values of 100 kcal/mol at low coverage have been reported.

Activation energies of desorption are needed in the modeling of the tritium release process. Since the activation energy for desorption is equal to the heat of adsorption plus the activation energy for adsorption, and since the activation energy for adsorption is often small, it follows that the activation energy for desorption will range from about 10 to 90 kcal/mol for desorption of $\text{H}_2\text{O}(\text{g})$ from LiAlO_2 , depending on the degree of surface coverage.

Data for adsorption of $\text{H}_2\text{O}(\text{g})$ on LiAlO_2 from Tanaka et al.⁴⁴ cover a somewhat higher temperature region (673-973 K) and a higher pressure range (1.7×10^{-4} to 1.7×10^{-3} atm, 17 to 170 Pa) than the present work. Only a few points in the present study fell in their pressure range. Therefore, the Tanaka study did not get into the lower-pressure and lower-coverage regions that reveal the physisorption process which emerged in the present work. Post-breakthrough corrections for their data also would be needed. For example, their 973 K curve is reported to have a slope of 0.36. If this curve is for a chemisorption process, which has an expected slope of 0.5, the lower slope would suggest the presence of a systematic error leading to too high values of adsorption, such as would come from data uncorrected for dissolution and/or non-BET adsorption.

The 673, 773, and 873 K isotherms in the present work were corrected for post-breakthrough uptake by a slightly different technique than the 573 and 623 K isotherms, but these curves are not expected to change substantially when they are treated by the same method. Post-breakthrough corrections were made as follows. First, raw values for the rate of uptake after the breakthrough point were corrected for the response curve of the water analyzer that measured the concentration of $\text{H}_2\text{O}(\text{g})$ in the gas stream leaving the sample. This correction, derived from separate calibration runs, takes into account the lag in response of the analyzer to a step change in the H_2O content of the gas stream. Next, the corrected rate of uptake of $\text{H}_2\text{O}(\text{g})$ was calculated and plotted as the log of the rate vs. time after injection. Over a period lasting about 1 h and starting soon after breakthrough, this curve was linear and was used to evaluate A and k in the equation, $r_u = A \exp(-kt_i)$, where r_u is the rate of uptake, A and k are constants, and t_i is the time after injection. Evaluation of $\int r_u dt$, where the limits are 0 for the time of injection and t_b for the breakthrough time, gave the amount of uptake due to the second, slower process during the period up to the breakthrough time. This was subtracted from the gross amount of uptake up to the breakthrough point to give the corrected amount of adsorption on the BET surface of the sample.

2. Relationships among Energy Levels and Activation Energies

In developing a theory or model for the relationships among the adsorption-dissolution-desorption-evolution processes as they relate to tritium inventory and release for ceramic breeders, thermodynamic and kinetic aspects of a number of processes need to be considered.

Figure I-14 shows conceptually the relationships among energy levels of various states and activation energies of processes connecting them. It pertains to a general ceramic breeder and it is assumed that the energy levels are progressively lower, as shown. For Li_2O , some significant differences with Fig. I-14 appear and they are also discussed below.

Fig. I-14. Generalized Adsorption-Dissolution Energy Levels

Considering H_2O in its passage from the gaseous state interacting with the breeder to the final state as OH^- solute, one can distinguish a number of steps. The first is adsorption of H_2O as $H_2O(g) \rightleftharpoons H_2O(ads.)$. The absorption process is often only slightly activated, even showing no discernible activation energy. For simplicity in the figure, it is presumed to be unactivated. The next step is the formation of surface OH^- groups. This step is generally accepted in the chemisorption of H_2O on oxides and leads to a lower energy level with the activation energy for surface uptake shown at the top of the figure.

Overall, the composite of these two processes can be termed H_2O "surface uptake." The reverse process starting from surface OH^- is, strictly speaking, $H_2O(g)$ evolution, involving formation of $H_2O(ads.)$ from OH^- on surface followed by desorption to $H_2O(g)$, rather than simply "desorption." From a collection of adsorption isotherms, it is possible to calculate the heat of adsorption, or the energy for surface uptake. From the figure, it is seen that the activation energy for evolution is greater than the activation energy for surface uptake by an amount equal to the energy for surface uptake.

From the adsorbed state as surface OH^- , entry of protons from the surface (dissolution) and diffusion into the bulk will occur, forming a uniform solid solution of dissolved OH^- . The activation energy for the dissolution and diffusion from the surface involves penetration of the surface space charge layer and the activation energy of diffusion itself. The reverse process to remove protons (OH^-) from the bulk to the surface and to form surface OH^- has a different activation energy, represented at the far right in the figure. Measurements of solubility by equilibration with $H_2O(g)$ yield the enthalpy of solution shown at the far left in the figure.

Having made some necessary distinctions, one may wish to simplify the diagram for modeling purposes, bearing in mind that circumstances may require a return to the more rigorous view. Two simplifications are (1) to equate the activation energy for evolution to the desorption activation energy, which in effect enfold the process of desorption in the overall process of evolution under the overall label of desorption, and (2) to equate the activation energy for diffusion to surface and OH^- formation to the diffusion activation energy. Then, one can consider a somewhat simplified diagram, given in Fig. I-15.

Fig. I-15. Energy Levels for Adsorption-Dissolution of General Breeder

Apart from this simplification, Fig. I-15 illustrates an additional feature. It is well known that the heat of adsorption varies with degree of coverage, a fact reflected in non-Langmuir (e.g., Freundlich) isotherms. At low coverages, where adsorption involves the most active sites, the heat of adsorption can be tens of kilocalories greater than at high coverages. In the figure, this range of heats of adsorption is represented by the shaded area. It follows that there will be corresponding ranges for two activation energies, that for desorption and that for dissolution and diffusion. The diffusion activation energy is regarded as constant.

A different conceptual diagram, Fig. I-16, must be used for Li_2O . It shows the final state of solute OH^- at higher level than the initial one. This results from the endothermic solution process measured by Tetenbaum⁴⁷ and by Norman and Hightower.⁴⁸ From the Tetenbaum data, the heat of

solution is +17 kcal/mol; from the Norman-Hightower report, the heat of solution is +18 to +21 kcal/mol, depending on temperature.

Quantitative placement of all energy levels cannot be made at the present time, but inspection of Fig. I-16 (or Fig. I-15 for that matter) suggests that, for high surface coverage, the diffusion activation energy is greater than the desorption activation energy, and the reverse is true for low surface coverage. Consequently, the trend would be for increasing surface coverage to increasingly favor diffusion-controlled release, and for low coverage to be associated with desorption-controlled release. From another perspective, if the diffusion activation energy is nearly constant, then the ratio of diffusion activation energy to desorption activation energy will decrease as coverage decreases. This would favor the growing importance of desorption as the rate-controlling process.

Fig. I-16. Energy Levels for Adsorption-Dissolution of Li_2O

A further observation arising from Fig. I-16 is that, for Li_2O , as far as the indicated energy levels alone are concerned and apart from activation energies, there is a driving force favoring diffusion to the surface, from a higher level (far right) to a lower level (2OH^-), followed by a relatively unfavored desorption (H_2O). However, driving force comparisons alone cannot predict rates.

It is important to emphasize that, for modeling purposes, all of these considerations of energy levels and activation energies and their dependencies on coverage must be combined with considerations of pre-exponential terms in the rate equations; otherwise an incomplete, even erroneous, model would emerge.

In light of the findings that the adsorption isobars for LiAlO_2 reflect two different adsorption processes that dominate at different temperatures because they have different activation energies, it follows that the placement of at least certain energy levels in the diagrams will be temperature dependent as well as coverage dependent.

3. Implications for Tritium Release Studies

Studying the use of H_2 in the gas to promote tritium release has been a major theme in many tritium release studies. Recent observations of release enhanced by $\text{H}_2\text{O}(\text{g})$ are of growing interest. Regarding H_2 , chemisorption of $\text{H}_2(\text{g})$ on the surface will increase the number of OH^- groups on the surface. Therefore, the levels labeled "high coverage" in the figures can be reached with H_2 in the gas phase. Of course, H_2O adsorption will have a similar effect. From the diagrams these higher coverage levels can be seen to lead to decreases in the activation energies for desorption and for dissolution-diffusion. Decreases in these desorption activation energies, if desorption is rate-controlling, will accelerate the release process so that tritium release should be enhanced by either gas. With both present, coadsorption of the two must be dealt with. In this connection, it is interesting that the adsorption of H_2 on alumina reported by Gruber⁴⁹ shows, similar to the present results for H_2O on LiAlO_2 , a minimum in adsorption at about 573 K. However, the degree of adsorption is likely to be lower for H_2 than for H_2O because, even for a relatively high H_2 partial pressure of 0.25 atm (2.5×10^4 Pa), the adsorption amounted to only about $\theta=0.001$.

E. Modeling of Tritium Transport (J. P. Kopasz and P. MacLean*)

The modeling of tritium transport and release is currently being directed toward (1) developing a model that describes the unusual behavior observed in the CRITIC tritium release experiment, (2) performing calculations based on a vacancy-assisted tritium diffusion model to investigate the possibility of enhanced tritium release via doping, and (3) setting up a diffusion/desorption/adsorption model.

The samples from the CRITIC experiment revealed some unusual tritium release behavior.⁵⁰ In some regimes, when the temperature of the samples was increased, the tritium release decreased. This decrease in release was followed by an increase to a maximum greater than the steady-state release, which was, in turn, followed by a slow decrease to the steady-state value (see Fig. I-17). The opposite behavior was observed for some temperature decreases. This behavior could not be modeled by a simple diffusion-desorption model, as used in the past, unless a negative activation energy of desorption was used. This suggested that there may be two or more desorption processes occurring, each with a different activation energy. The presence of two or more sites (or modes) for desorption is not unusual. Desorption studies of H_2O from ZnO single-crystal surfaces revealed six different desorption sites.⁵¹ Adsorption studies on alumina suggest at least two sites for hydrogen desorption,^{52,53} while current studies for H_2O on LiAlO_2 suggest multiple desorption sites.⁵⁴ Using a model with two activation energies of desorption, with the activation energy for the higher temperature being greater than that for the lower temperature, led to tritium release curves like that shown in Fig. I-18. This model used an instantaneous change in the temperature and the desorption activation energy. When the activation energy and temperature were changed more smoothly, the width of the curve for the release-rate decrease could be matched for the

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Fig. I-17. Observed Tritium Release from CRITIC Run 1
(temperature increase)

Fig. I-18.
Calculated Tritium Release for an
Instantaneous Temperature Increase

model calculations and the data from the CRITIC experiment (see Fig. I-19). The temperature and activation energy were varied according to the equation

$$Y = Y_0 + (Y_1 - Y_0)(1 - \exp(-bt)) \quad (I-29)$$

Where Y_0 = initial value (of temperature or activation energy) and Y_1 = final value. The time constant b has an effect on both the magnitude and the width of the curve for the decrease in tritium release. We are currently attempting to find a set of values for the time constant and the desorption activation energies which will provide a good fit to all the CRITIC data.

Fig. I-19.

Calculated and Observed Tritium
Release for CRITIC Run 5

The data available from CRITIC so far show a pattern which is consistent with a desorption activation energy that is dependent on surface coverage. The available tritium release data were obtained with hydrogen concentrations of 0.1% and 1.0% in the helium purge gas. The temperature range covered was from 400 to 750 °C. The temperature changes covered and the type of release curve observed are shown in Table I-4. For the experiments with 0.1% H₂, release curves suggesting a change in desorption activation energy were observed when the temperature change included the region from 475 to 525 °C. For temperature changes which occurred above this region, normal tritium release curves were observed. For the 1.0% H₂ experiments, normal release curves were observed over the temperature range from 400 to 650 °C; however, the tritium release curve for a temperature change from 750 to 650 °C suggests a change in desorption activation energy. At a hydrogen concentration of 0.1% and low temperature (400 °C), coverage is relatively high, and desorption occurs from the most favorable sites (those with the lowest activation energy for desorption). As the temperature is increased at the same hydrogen concentration, the surface coverage decreases, and desorption must now occur from less favorable sites (higher activation energy of desorption) since the favored sites are unoccupied. When the hydrogen concentration is increased, the surface coverage also increases. This results in a shift in the temperature range where the favored sites become unoccupied and the curve shows a decrease in the tritium release with increasing temperature. The CRITIC results are consistent with this model; however, more data

Table I-4. Temperature Changes for CRITIC Experiment

Temp. Range, °C	Temp. Change Direction	H ₂ Conc., %	Type of Release Curve
650-438	Decrease	1.0%	a
430-525	Increase	1.0%	a
525-640	Increase	1.0%	a
400-540	Increase	1.0%	a
740-600	Decrease	1.0%	c
670-575	Decrease	0.1%	a
525-685	Increase	0.1%	a
600-750	Increase	0.1%	a
575-500	Decrease	0.1%	a
444-505	Increase	0.1%	b
505-650	Increase	0.1%	b
740-475	Decrease	0.1%	c
400-600	Increase	0.1%	b
450-545	Increase	0.1%	b
450-545	Increase	0.1%	b
435-625	Increase	0.1%	b
425-700	Increase	0.01%	b

^aNormal release curve.

^bInitial decrease in release with an increase in temperature.

^cInitial increase in release with a decrease in temperature.

are needed. The model also suggests that the surface phenomena regarding H₂O and H₂ on ceramic breeder materials should be studied thoroughly in separate out-of-pile experiments to determine the desorption activation energies as functions of temperature, oxygen potential, and hydrogen surface coverage.

A mechanistic model for tritium diffusion in lithium ceramics was developed in which the tritium diffuses as a lithium vacancy/triton complex. This model suggests that it may be possible to increase the tritium diffusivity by increasing the number of lithium vacancies present. A simple version of the model indicated that the tritium inventory in Li₂O could be reduced by a significant amount if the number of lithium vacancies could be increased from 1 ppm to 1000 ppm. The model was improved to calculate the total lithium vacancy concentration at a given temperature due to vacancies introduced by magnesium doping and those caused by thermal motion. However, the data for lithium self-diffusion on which the model is based are ambiguous.

There are two conflicting groups of data which lead to the following sets of activation energies for vacancy formation (H_{form}) and diffusion (H_{diff}):

$$\text{case 1: } H_{\text{form}} = 23.58 \text{ kcal, } H_{\text{diff}} = 12.648 \text{ kcal}$$

$$\text{case 2: } H_{\text{form}} = 69.6 \text{ kcal, } H_{\text{diff}} = 23.4 \text{ kcal}$$

A third parameter on which the model depends heavily is the binding energy of the vacancy/tritium complex. Since the charge on the lithium vacancy (V_{Li}) is one-half that for a magnesium vacancy (V_{Mg}), we have used two approximations for this energy: the energy observed as the binding energy for a V_{Mg}/T^+ complex (23 kcal) and half the binding energy of the V_{Mg}/T^+ complex.

A calculation was performed to determine which set of activation energies of diffusion and vacancy formation better corresponds to reality. In metals, the mole fraction of vacancies near their melting point is approximately 1×10^{-4} . Using the activation energies for vacancy formation as given above and assuming that Schottky defects are the dominant defects, the mole fraction of vacancies at the melting point of Li_2O ($\sim 1438^\circ C$) is calculated to be 2.0×10^{-2} for case 1 and 3.4×10^{-5} for case 2. This suggests that the activation energies in case 2 are more accurate; however, we have decided to perform calculations using both sets of activation energies to provide some insight into how these parameters affect the tritium inventory.

Model calculations for case 1 were performed with a binding energy of 23 kcal. The results show that little decrease in tritium inventory will be achieved by doping to introduce a 1×10^{-3} vacancy concentration. This is due to two factors: (1) the number of vacancies due to thermal motion is large, and (2) practically all the tritium ($>99.999\%$) is in the more mobile form of the V_{Li}/T^+ complex. Increasing the vacancies due to impurities in this case decreases the concentration of the free T^+ by about an order of magnitude; however, the T^+ concentration is five to six orders of magnitude lower than that of the complex (compare Fig. 1-20a and b).

Calculations for case 1 with a binding energy of 11.5 kcal are not yet completed. Initial results indicate that the concentration of T^+ at short times (several minutes) is as high as one-tenth that of the complex when the concentration of vacancies is low. This suggests that the inventory can be reduced in this case by increasing the number of vacancies and decreasing the T^+ concentration. For case 2, the vacancy formation energy is large enough that at $100^\circ C$ the vacancy mole fraction is approximately 1×10^{-6} when the dopant level is at this same concentration. An increase in dopant level to 1×10^{-3} would increase the vacancy concentration by three orders of magnitude and should decrease the inventory substantially.

The calculations using the vacancy-assisted diffusion model have shown that, for doping to cause a discernible decrease in the tritium inventory, the vacancy concentration due to thermal motion should be low at the temperature of interest (a high H_{form}) or the binding energy of the tritium-vacancy complex should be low. Either of these two conditions would result in a significant concentration of free T^+ in the undoped material. The binding energy depends mainly on the coulombic attraction between the lithium vacancy and the triton and should be fairly constant for the breeder materials. The formation energy for a lithium vacancy should vary considerably. Values calculated from ionic conductivity data in the literature are: Li_2O , 23.58 kcal (case 1) and 69.6 kcal (case 2); $LiAlO_2$, 21.68 kcal; and Li_2SiO_3 , 52.4 kcal. The data for Li_2O (case 1) and $LiAlO_2$ are suspect since they lead to inordinately high concentrations of vacancies at temperatures near the breeder material melting point, when Schottky defects are assumed to be the dominant defect. This suggests that the ionic conductivity measurements did not extend into the temperature region for intrinsic conductivity or that the main type of defect formed is not a Schottky defect.

As part of the modeling effort, we have analyzed existing experimental data using our diffusion-desorption model. One of the data sets we have chosen to analyze is that reported by Tanifuji et al. for tritium release from Li_2O .⁵⁵ Their conclusion was that release is diffusion controlled over the temperature range studied. The Li_2O samples which were used ranged in grain radius from 150 to 840 μm . According to the diffusion-desorption model, the tritium release will be close to diffusion controlled when

(a)

(b)

Fig. I-20. Calculated Concentration Profiles for Vacancy-Assisted Diffusion at 400°C with Dopant Mole Fraction of (a) 10^{-3} and (b) 10^{-6}

the ratio aK/D is greater than 10 (a = grain radius, K = desorption rate constant, D = diffusivity). Using the values for the diffusion coefficients determined by Gugli et al.⁵⁶ and the desorption rate constant reported by Bertone⁵⁷ leads to diffusion-controlled release when $T > -4.49 \times 10^3 / \ln(4.09 \times 10^{-5}/a)$.

For the sample sizes used in the Tanifuji experiment, our model predicts that tritium release will be diffusion controlled for temperatures above about 410 °C for the largest samples (590-840 μm) and above about 550 °C for the smallest samples (150-297 μm). Since the Tanifuji data span the temperature range of 300-700 °C, the tritium release should show regions of diffusion-controlled release and desorption-controlled release. However, in a careful study of the Tanifuji plot of the diffusion coefficient vs. reciprocal temperature, which is used to obtain the diffusion activation energy, we observed an apparent break in the data, which suggested that two mechanisms were responsible for tritium release over the temperature range studied. A least-squares calculation was performed on the data using a single activation energy, resulting in the plot shown in Fig. I-21 with a χ square of 3.238. If the three points at the lowest temperature are discarded, as was done by Tanifuji, a least-squares fit results in a χ square of 2.2395. We plotted the graph in several ways which correlated to the observed break in the graph and least-squares calculations. The best fit obtained is shown in Fig. I-22 and resulted in a χ square of 0.1043 for the high-temperature region and 1.0535 for the low-temperature region. The slopes of the two lines correspond to activation energies of 20.2 and 27.8 kcal/mol for the high- and low-temperature regions, respectively. These activation energies correspond well with the activation energies of diffusion determined by Gugli et al. (19.5 kcal/mol)⁵⁶ and the activation energy for desorption observed by Bertone (28.4 kcal/mol)⁵⁷ and Kudo et al. (28.6 kcal/mol).⁵⁸

In a more-detailed analysis, we plotted the data for each of the three ranges of grain sizes reported by Tanifuji. When the data are plotted in this manner for the smallest-sized samples (150-297 μm), no break in the plot is observed at the high temperature end. The data for this size sample only extend to 450 °C, which is below the predicted temperature of 550 °C where diffusion-controlled release would begin to be observed. There appears to be a change in slope at low temperatures for this sample size,

Fig. I-21.

Diffusion Coefficient vs. Temperature for
Tanifuji et al.⁵⁵ Data with Least-Squares
Curve Calculated with one Activation Energy

Fig. I-22.

Diffusion Coefficient vs. Temperature for Tanifuji et al.⁵⁵ Data with Least-Squares Curve Calculated with Two Activation Energies

which may correspond to a change in the desorption mechanism; however, this is based on only two data points and is, therefore, questionable. The slope for the plot of natural log R (where R is the diffusivity obtained in the Tanifuji paper) as a function of reciprocal temperature gives an activation energy of 27.7 kcal/mol, in very good agreement with the above values for desorption activation energies.

The data for the intermediate-sized sample (297-590 μm) include only three points above the predicted temperature where diffusion will dominate the tritium release. A plot of the data (Fig. I-23) suggests there may be a break in the plot near the predicted temperature of 490° C; however, the scarcity of data leaves some doubt as to the strength of this interpretation. If the data are interpreted on the basis of one mechanism (no break in the curve), then the activation energy obtained is 25.3 kcal/mol, and the resulting plot has a χ square of 0.2301. If the data are interpreted on the basis of two mechanisms with a break in the curve at about 470° C, then the activation energies are 19.2 kcal/mol for the high-temperature region and 28.6 kcal/mol for the low-temperature region; again, these values are in good agreement with the diffusion and desorption activation energies reported above. The least-squares fit for this plot resulted in a χ square of 0.0063 for the high-temperature region and 0.03888 for the low-temperature region--an improvement over the single mechanism plot.

For the largest-sized sample (590-840 μm), there is clearly a change in the slope in the plot; however, the position of the break is not so clear (Fig. I-24). The activation energy ranges between 26.2 and 35.8 kcal/mol in the high-temperature region and between 17.9 and 21.0 kcal/mol in the low-temperature region, depending on where the break is positioned. The plot in Fig. I-25 corresponds to an activation energy of 26.7 kcal/mol in the low-temperature region (desorption) and 19.9 kcal/mol in the high-temperature region (diffusion). The χ square for this fit is good but is comparable to that for interpretations in which the break in the slope occurs at other temperatures.

Fig. I-23.

Diffusion Coefficient vs. Temperature for
Tanifuji et al.⁵⁵ Data with Grain Radius
of 297-590 μm

Fig. I-24.

Diffusion Coefficient vs. Temperature for
Tanifuji et al.⁵⁵ Data with Grain Radius
of 590-840 μm

Fig. I-25. Diffusion Coefficient vs. Temperature for Tanifuji et al.⁵⁵ Data with Least-Squares Curve Calculated for Two Activation Energies

In conclusion, the data from the Tanifuji experiment seem to support a two-mechanism tritium release model. The similarity between the activation energies reported in the literature for diffusion and desorption and those obtained when reanalyzing the Tanifuji data suggests that the two mechanisms are diffusion and desorption, with diffusion controlling the tritium release at higher temperatures.

F. FLIBE Experiments (R. G. Clemmer and E. Van Deventer)

The ASPIRE [Advanced Safe Pool Immersed REactor]⁵⁹ concept is potentially very attractive, owing to its simplicity, safety, reliability, and economics. The concept involves the use of a pool of molten LiF-BeF₂ (FLIBE) as the breeder blanket and shield. The feasibility of the concept depends upon the ability to control the FLIBE chemistry with respect to TF/T₂ ratio and corrosion. The tritium must be kept oxidized to the TF form to control tritium permeation. At the same time, the corrosion must be controlled. The proposed solution to these two problems is to add MoF₆, a material which will plate out molybdenum on metal surfaces and oxidize T₂ to TF. This concept is schematically represented in Fig. I-26. The key issues to be tested involve (1) what the ratio of HF to H₂ is in the salt system, (2) whether a high HF/H₂ ratio can be attained by adding MoF₆, and (3) whether corrosion of structural materials can be controlled by using the MoF₆ as an *in situ* plating agent.

An experimental apparatus, shown in Fig. I-27, has been constructed for testing the FLIBE chemistry. The metal surface used for T₂ oxidation is the stirrer paddle. Other than the sample, the

Fig. I-26.

Schematic of Chemical Reactions in
ASPIRE

Fig. I-27.

Experimental Apparatus for FILBE Testing

FILBE contacts only molybdenum parts. The sparge gas (He plus H_2 , HF, and/or MoF_6) is bubbled into the Li_2BeF_4 solution. After bubbling through the FLIBE, the sparge gas is passed to an analytical train where the amount of H_2 and the HT/ H_2 ratio are measured. The experimental test apparatus fits into a furnace well of a helium glove box.

The primary objective of this work is to demonstrate the critical assumptions on FLIBE chemistry which form the basis of the ASPIRE concept: namely, that MoF_6 oxidizes H_2 , and in situ passivation occurs. A series of experiments with the following objectives is planned:

1. Demonstrate that MoF_6 is effective in the oxidation of H_2 : $H_2 + MoF_6 \rightarrow HF$.
2. Test the reduction of HF by an untreated candidate alloy (HT-9): $HF + Fe \rightarrow H_2$.
3. Test a metal (HT-9) specimen after it is treated with MoF_6 in salt solution and determine if plating of Mo occurs. Compare the behavior of treated specimen with untreated.

G. Tritium Oxidation Experiment
(P. A. Finn and E. H. Van Deventer)

The objective of this work is to assess the usefulness of tritium oxidation as a means of minimizing permeation of molecular tritium in fusion reactor systems. To this end, the heterogeneous oxidation of tritium (atomic species) at the surface of 316 stainless steel is being examined in a double-wall tube made of 316 stainless steel. A tritium/helium gas mixture is circulated through the inner tube, and an oxygen/helium gas mixture is circulated through the outer tube. A metal oxide coating is produced on the external surface of the inner tube. Further experimental details can be found in a previous report in this series (ANL-88-28, Sec. I.C.4).

Recently, we examined the effect on the tritiated water yield of the temperature at which the metal oxide is formed. A series of runs was completed in which an iron oxide was formed at $400^\circ C$, and then tests were undertaken at 400, 450, 500, and $550^\circ C$ for up to 265 h. In previous runs, the metal oxide formed at $550^\circ C$ was determined to be chromium oxide. The water yields at the different temperatures for runs with the metal oxide formed at $400^\circ C$ are summarized in Table I-5. Upon completion of the series, we could account for 97.5% of the tritium (41,400 mCi versus 42,569 mCi at the start of the series). The uncertainty in the initial tritium present was ± 0.4 mCi.

The tritiated water yield for runs done at $550^\circ C$ with iron oxide dominant at the surface (Nos. 8, 9, and 13) was greater than found for previous runs when chromium oxide (see Table I-6) was dominant at the surface. Specifically, the tritiated water yield for run 8, in which the oxygen concentration was 1000 ppm, was 99.2% (versus 97.8% found previously for 2000 ppm oxygen). More significantly, run 13 (500 ppm oxygen) showed a 99% water yield, whereas in previous runs at this oxygen concentration with chromium oxide dominant at the surface, the yield was 94%. Figure 1-28 is a plot of water yield as a function of oxygen concentration for two series of runs at $550^\circ C$, each with a different metal oxide present (iron or chromium). The difference in water yields between the two sets of runs, as shown in Table I-6, indicates the importance of the metal oxide on the stainless steel.

Figure 1-29 shows the water yield as a function of oxygen concentration and temperature for the runs with iron oxide. The water yields for runs at $400^\circ C$ (e.g., No. 12) are lower than those for runs at 450- $550^\circ C$. However, the decreased tritium concentration reaching the metal surface was more important than the effect of temperature, as indicated by our earlier runs at $350^\circ C$ and $400^\circ C$.

Table I-5. Results of a Series of Oxidation Runs for Different Oxygen Concentration, Temperature, and Metal Oxide

Run No. ^a	Temp., °C	O ₂ Conc., ppm	Time, min	Tritium Conc., $\mu\text{Ci}/\text{min}$	Ratio HTO/HT	Yield, %
1	400	<0.1	8183	7.82(E-4)	1.75	63.6
2	400	1300	7208	5.60(E-4)	5.59	84.8
3	400	30	9672	4.40(E-4)	4.18	80.7
4	400	250	5571	1.97(E-2)	81.7	98.8
4 ^b	400	250	195	2.50(E-2)	10.3	91.5
5	500	20	3056	8.11(E-2)	6.5	86.7
6	500	4	8247	9.91(E-2)	3.3	77.0
7 ^c	450	1000	8297	1.99(E-2)	75.5	98.7
8	550	1000	8198	2.75(E-1)	131.9	99.2
9	550	7	9768	3.71(E-1)	4.8	82.8
10 ^d	550	<0.1	9630	2.51(E-1)	<0.9	<47.9
11 ^e	400	500	4343	2.93(E-2)	29.2	96.7
12	400	500	15703	9.59(E-3)	9.55	90.5
13	550	500	8303	2.32(E-1)	137.5	99.3
14	500	500	12683	7.07(E-2)	225	99.6

^aFirst three runs show the conditions under which the metal oxide was formed. The remaining eleven runs were done as a series.

^bThese conditions are those at the end of run 4.

^cTest section had been saturated with tritium at 500°C, in run 6, so that the total tritium flux was enhanced. This run may not have attained steady state.

^dTritium partial pressure had decreased due to tritium transport.

^eThe oxygen-18 used contained two impurities identified by mass spectrometry, carbon monoxide and water. At 500 ppm O₂, there were 7 ppm water and 7 ppm CO in the oxygen/helium mixture. The flow rate was 5 mL/min, one-half that in the other runs.

Table I-6 Tritiated Water Yield for Different Metal Oxides at 550°C

Oxygen Conc., ppm	Yield, %	
	Cr Oxide	Fe Oxide
<0.01	52	48
7	--	83
12	60	--
500	94 ^a	99.3
1000	--	99.2
2000	97.8	--

^aInterpolated.

Fig. I-28. Tritiated Water Yield at 550°C in the Presence of Different Metal Oxides

Fig. I-29. Tritiated Water Yield as Function of Temperature for Runs with Iron Oxide

This dependence of water yield on the tritium concentration was also affected by the preconditioning resulting from a previous run. For example, in run 4, the test cell was not saturated with tritium. (Saturation did not occur until midway through run 5.) Therefore, the tritium which we collected in run 4 represents products from a surface at which the tritium concentration is slowly increasing, or the oxygen concentrations is slowly decreasing. Thus, the initial water yield in run 4 is representative of a higher oxygen potential at the surface than that represented by the 250 ppm oxygen concentration in the gas phase. The time at test temperature, ~6500 min, which includes a day of preconditioning, was insufficient to obtain steady-state conditions. In an attempt to obtain a representative yield, we determined the water yield in the last 3 hours at 400 °C and 250 ppm oxygen concentration. During this time, the water yield was 91.5% (versus 98.8% for total time); this value was used in Fig. I-29.

For run 11, we used $^{18}\text{O}_2$ and a low flow rate for the oxygen/helium mixture, 5 mL/min (versus 10-20 mL/min for other runs). The low flow was dictated by the $^{18}\text{O}_2$ container. The steady-state conditions during run 11 were, therefore, representative of a longer residence time in the test zone. The HTO yield in this run was 96.7%. In earlier runs, we saw that a lower flow rate increased the water yield from 32% to 55% when the flow rate was decreased by a factor of 15. Run 12 is a representative run for a 10-20 mL/min flow rate and steady-state conditions for oxygen and tritium. Here, the water yield was 90.5%. (This value was also used in Fig. I-29.)

To determine the metal oxides present, three test cells (blank, 550 °C/low-oxygen, 400 °C/high-oxygen) were sectioned and examined optically and under a scanning electron microscope (SEM). In the blank cell, the steel grain size was 96 μm in the bulk and 16 μm at the tube edge. Scattered inclusions or healed cracks were noted between the inner and outer edges of the tube. The appearance of the 550 °C/low-oxygen test cell did not differ appreciably from the blank. Its oxide appeared as a light gray tinge. The elemental ratio in the 550 °C/low-oxygen test cell is given in Table I-7. The 400 °C/high-oxygen test cell had an oxide layer that was >5000 Å thick. The oxide was composed of large islands heavily enriched in iron uniformly scattered across a fine surface oxide enriched in chromium. Typical elemental ratios for the iron-rich islands and the chromium-rich surface oxide are listed in Table I-7.

Table I-7. Elemental Ratio for Different Test Cells with Fe = 1.0

	Fe	Cr	Mn	Ni
550 °C/Low O_2	1.0	0.4	0.1	0.1
400 °C/High O_2				
Fe Rich Island	1.0	0.09	0.07	0.06
Cr Rich Section	1.0	1.78	0.6	0.1

The islands were of various sizes but their average diameter was 16-20 μm ; each island appeared porous, whereas the surface oxide appeared as fine (~1 μm) crystallites (see Fig. I-30). During hydrogen reduction of iron oxide,⁶⁰ oxide islands were also reported to be formed. The maximum yield of tritiated water occurred when the island oxide was present, an oxide created under conditions of simultaneous oxidation and reduction.

To ascertain if the types of metal oxides formed in our experiments were representative, we reviewed studies on low-temperature (<550 °C) metal oxidation. Using X-ray photoelectron

Fig. I-30. Micrograph of Metal Surface from 400°C/High-Oxygen Run

spectroscopy (XPS), Olefjord measured the Cr/Fe ratio at a stainless steel surface as a function of oxidation temperature at 0.02 MPa oxygen.⁶¹ The Cr/Fe ratio was 0.5 at 350°C and 1.35 at 500°C. At 500°C, the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio was 2.7. Brundle⁶² found that the amount of Fe^{3+} increased at high levels of oxygen exposure, whereas the amount of Fe^{2+} increased at low levels of oxygen.

To determine the metal oxide composition as a function of oxygen content, we completed ideal solution thermodynamic calculations using the SOLGASMIX code⁶³ at temperatures of 400 and 550°C. The two general cases considered were excess metal or excess oxygen present at the oxide surface. (Tritium species were assumed to be 10^{-3} to 10^{-4} that of the diffusing metal.) To determine the effect of the type of metal present, the ratio of iron to chromium was also varied. The results from these calculations at 550°C are presented in Table I-8 as a comparison between the ratio of $\text{Fe}_3\text{O}_4/\text{FeO}_x$ and $\text{T}_2\text{O}/\text{T}_2$ produced. Similar results were obtained for calculations at 400°C.

The major conclusions from the SOLGASMIX calculations and our experimental results are as follows:

1. When excess metal is present (i.e., the diffusion rate for metal reaching the oxide surface exceeds the amount of oxygen present), the metal is preferentially oxidized, forming the species FeO_x . The presence of a large excess of chromium exaggerates this effect. Molecular tritium is formed preferentially.
2. When the oxygen present exceeds the amount of metal, Fe_3O_4 is formed and the preferred tritium product is T_2O .
3. In our experiments, the maximum yield of tritiated water (>99%) occurred at oxygen levels >550 ppm in the presence of an iron oxide formed at 400°C. From the results of the SOLGASMIX calculations and microscopic observations, Fe_3O_4 is assumed to be the iron species present. Because Fe_3O_4 contains iron in two oxidation states, it can be an intermediate in the formation of tritiated water.

4. A mixed oxide containing iron-rich islands is expected at high oxygen concentrations (K. Natesan, ANL Materials Science Division). However, as the time at temperatures $>500^{\circ}\text{C}$ increases to months, the islands may flake off, leaving the fine crystallite surface. This suggests that an oxygen level of 1000-2000 ppm may be required for extended (years) operation in a fusion environment.

Table I-8. SOLGASMIX Results for Combined Metal Oxide and Tritiated Water Formation at 550°C

	Ratio	
	$\text{Fe}_3\text{O}_4/\text{FeO}_x$	$\text{T}_2\text{O}/\text{T}_2$
Excess Metal		
Cr/Fe = 10^3	10^{-19}	10^{-8}
Fe/Cr = 10^3	10^{-2}	10^{-1}
Fe/Cr = 1	10^{-2}	10^{-1}
Excess Oxygen		
Fe/Cr = 1	1	10
Fe/Cr = 10^2	10^4	10^{13}
Cr/Fe = 10^2	10^3	10^{13}

H. Design Studies of Aqueous Salt Blanket
(P. A. Finn and D. K. Sze)

The International Thermonuclear Experimental Reactor (ITER) is a joint International Atomic Energy Agency project among the European Economic Community, Japan, the United States, and the Soviet Union. In support of the pre-conceptual design of ITER, we evaluated the tritium breeder blankets, one concept being an aqueous lithium salt solution blanket. We have recently addressed a potential problem for the design of the aqueous lithium salt solution blanket (2 M LiNO_3 or 2 M LiOH), namely, radiolysis.

The function of the blanket in a fusion reactor is to produce enough tritium to satisfy the needs of plasma operation and to replace processing losses. The energetic particles produced from neutron irradiation of lithium in the salt solution (^3T and ^4He) will induce radiolysis of the water and the dissolved salt. Radiolysis of the water results in the production of hydrogen and oxygen gas; that of the nitrate salt produces nitrogen and oxygen gas. To assess the extent of radiolysis in the salt blanket, the radiolysis yields for these gases are needed. (The macroscopic yield for species X, $G(X)$, is defined as the number of molecules decomposed or produced per 100 eV of absorbed energy.)

The two salts exhibit differing radiolysis effects. In the LiNO_3 solution, the nitrate ion acts as an energy sink so that water decomposition is reduced. This contrasts with the LiOH solution in which no radiolysis effect due to the hydroxide ion is noted. Because irradiation data on LiNO_3 and LiOH solutions

were not available, literature data⁶⁴ from other aqueous salt systems containing NO_3^- and OH^- were used to estimate the radiolysis yields. The $G(\text{H}_2)$ was estimated to be 0.99 for the nitrate solution and 1.2 for the hydroxide solution. The $G(\text{O}_2)$ for both solutions is about one-half that of the $G(\text{H}_2)$. The yield for nitrogen, $G(\text{N}_2)$, is 0.01.

The rate of hydrogen produced by radiolysis, R (mol/s), is:

$$R = \text{TBU} \times E \times \text{LBR} \times G(\text{H}_2) \quad (1-30)$$

where TBU is the tritium burned, g/s; E is the total energy, eV, of the charged particles (triton and alpha); LBR is the local tritium breeding ratio; and $G(\text{H}_2)$ is the hydrogen yield.

In the ITER blanket, the amount of tritium burned is 1.76×10^{-3} g/s, the total energy of the charged particles is 4.78×10^6 eV, the local tritium breeding ratio is 1.5, and $G(\text{H}_2)$ is 0.99 for the nitrate salt and 1.2 for the hydroxide. From Eq. 1-30, one finds that 22 mol/s of hydrogen is produced in the LiNO_3 solution, and 26 mol/s of hydrogen is produced in the LiOH solution. The total oxygen produced is 11 mol/s in the LiNO_3 solution and 13 mol/s in the LiOH solution. The nitrogen production is 0.2 mol/s in the LiNO_3 solution.

Because single phase flow is a desired design feature (it minimizes the volumetric flow rate), the blanket has to be pressurized to dissolve the gases in the circulating salt solutions. The overpressure required to keep the evolved gas in solution is derived by summing the product [(Henry's Law constant, MPa/mole fraction) times (the mole fraction of the gas)] for each gas solute. For LiNO_3 and LiOH salt solutions, the total pressure is 2.0 and 2.5 MPa, respectively.

The presence of dissolved gas in the salt solution has several major implications for the ITER design effort: (1) the blanket must be designed for high pressure operation, (2) depressurization of the salt solution is required to effect recovery of tritium, (3) a gas recombiner is required to prevent ignition of the gas mixture during depressurization, and (4) unplanned depressurizations have to be accommodated in the design, i.e., all high points in the design have to be vented to the recombiner. These operational issues are certain to increase the complexity and the capital cost of the aqueous salt solution blanket option.

I. Dosimetry and Damage Analysis (L. R. Greenwood)

Fusion materials are being irradiated in a variety of facilities, including fission reactors, 14 MeV d-t neutron sources, and higher energy accelerator-based neutron sources. We are determining the neutron energy spectrum, flux levels, and damage parameters for the materials irradiated in these facilities, along with exposure parameters for each irradiation.

1. Neutron Fluences for Helium Production Measurements (L. R. Greenwood, C. A. Seils, and A. Intasorn)

Numerous experiments have been performed at the Rotating Target Neutron Source (RTNS) II at Lawrence Livermore National Laboratory to measure helium production near 14 MeV neutron energies. Results for 25 elements, separated isotopes, and alloy steels have already been published⁶⁵ in collaboration with D. Kneff (Rockwell International). Several more experiments were performed to investigate additional materials. The present results are for a short irradiation (23.6 h) on January 8-9, 1987, at $\sim 75^\circ$ to the beam and an average neutron energy of 14.3 MeV.

Dosimetry and helium samples were irradiated in an aluminum capsule measuring 1.7-cm OD and 2.41-cm thick. Dosimetry foils were located at five different positions interspersed with helium samples of Fe, Cu, Cr, Al, Ni, C, Mn, V, Ti, Si, and Be. The circular dosimetry foils measured 1-cm OD by 0.025-0.25 mm thick. All samples were gamma counted to determine activation rates.

The activation measurements of the samples are listed in Table I-9 in the order according to their placement in the assembly. Neutron fluences were then calculated by dividing the activation rate by

Table I-9. Activities and Neutron Fluences* for RTNS II at 75° and 14.3 MeV

Distance in Assembly, in.	Sample Position	Isotope	Isotopic Production, 10^{-10} atom/atom	Fluence, 10^{15} n/cm ²
0.0075	Fe-1	⁵⁴ Mn	10.7	3.07
		⁵¹ Cr	2.89	3.19
0.0105	Ti-1	⁴⁶ Sc	9.21	3.01
0.0160	Co-1	⁵⁸ Co	23.8	3.16
0.0235	Nb-1	^{92m} Nb	14.3	3.09
0.0265	Ni-1	⁵⁸ Co	10.8	3.04
0.0275	Au-1	¹⁹⁶ Au	58.6	2.76
0.0480	Fe-He-3	⁵⁴ Mn	10.2	2.93
		⁵¹ Cr	2.72	3.00
0.0880	Cu-He-4	⁶⁰ Co	1.25	2.84
0.1480	Cr-He-2	⁵¹ Cr	10.7	-
0.2275	Ni-2	⁵⁸ Co	8.47	2.39
0.2285	Au-2	¹⁹⁶ Au	48.3	2.28
0.2300	Fe-2	⁵⁴ Mn	8.40	2.41
		⁵¹ Cr	2.17	2.39
0.2565	Ni-He-1	⁵⁸ Co	8.50	2.39
0.3570	Mn-He-4	⁵⁴ Mn	16.3	2.11
0.4325	Ni-3	⁵⁸ Co	6.82	1.92
0.4335	Au-3	¹⁹⁶ Au	39.1	1.84
0.4365	Fe-3	⁵⁴ Mn	6.55	1.88
		⁵¹ Cr	1.63	1.80
0.4415	Nb-3	^{92m} Nb	9.11	1.97
0.4895	Ti-He-2	⁴⁶ Sc	5.95	1.94
0.7520	Ni-He-4	⁵⁸ Co	5.12	1.44
0.7745	Ni-4	⁵⁸ Co	5.05	1.42
0.7755	Au-4	¹⁹⁶ Au	28.1	1.33
0.7770	Fe-4	⁵⁴ Mn	4.74	1.36
		⁵¹ Cr	1.21	1.33
0.8585	Cu-He-2	⁶⁰ Co	0.569	1.29
0.8815	Nb-5	^{92m} Nb	6.10	1.32
0.8865	Ni-5	⁵⁸ Co	4.29	1.21
0.8915	Au-5	¹⁹⁶ Au	25.5	1.20
0.8990	Co-5	⁵⁸ Co	9.51	1.26
		⁵⁹ Fe	0.630	-
0.9065	Ti-5	⁴⁶ Sc	3.79	1.24
0.9140	Zr-5	⁹⁵ Zr	19.2	1.20
0.9215	Fe-5	⁵⁴ Mn	4.18	1.20
		⁵¹ Cr	1.12	1.23

*Relative uncertainty, 2-3%.

the production cross section. Cross sections were taken from our previously published data;⁶⁶ however, it was necessary to extrapolate from our largest angle at 60° to 75° using the trend of the data as well as trends from ENDF/B-V (Evaluated Nuclear Data File, Part B, Version V, National Nuclear Data Center, Brookhaven National Laboratory, 1979.) The fluences have an uncertainty of $\pm 4\%$ due to our normalization to the $^{93}\text{Nb}(n,2n)^{92}\text{Nb}$ reaction cross section of 463 mb, as well as counting uncertainties of 2-4%. The net absolute uncertainty is thus about 6%. The derived fluences are plotted in Fig. I-31 as a function of distance into the assembly. As can be seen, fluences decline about a factor of three over a distance of 2.41 cm.

To determine the detailed fluence distribution over the surface of the 10 mm dosimetry foils, three niobium foils were segmented into nine concentric pieces with diameters of 3 mm (1 piece), as well as 6.5 and 10 mm (4 pieces each). Each segment was then gamma counted, and the results are listed in Table I-10. As can be seen, the fluence gradients vary up to 17% for the segment from the 10-mm diameter discs. Helium cross sections can be easily determined by dividing the measured helium concentration by the fluence at each sample.

Fig. I-31.

Measured Dependence of Neutron Fluence
on Distance from the Front of the Sample
Capsule

Table I-10. Neutron Fluence Gradients at RTNS II^a

Foil Position 1		Foil Position 3		Foil Position 5	
Segment	Fluence, 10^{15} n/cm^2	Segment	Fluence, 10^{15} n/cm^2	Segment	Fluence, 10^{15} n/cm^2
0	3.00	0	1.87	0	1.19
1	3.11	1	1.75	1	1.26
2	3.17	2	1.90	2	1.24
3	3.00	3	1.97	3	1.14
4	3.00	4	1.73	4	1.20
5	2.92	5	1.94	5	1.33
6	3.13	6	1.83	6	1.24
7	2.90	7	1.95	7	1.31
8	3.02	8	1.88	8	1.18

^aResults from $^{93}\text{Nb}(n,2n)^{92m}\text{Nb}$; counting uncertainty, $\pm 5\%$.

2. Neutron Yields and Energy Spectra for 113 and 256 MeV Protons (L. R. Greenwood and A. Intasom)

Neutron yield and energy spectra measurements have been completed using the foil activation technique for 113 and 256 MeV protons stopped in thick targets of aluminum and depleted uranium. The aluminum runs were conducted on December 10, 1987; the 113 MeV uranium run was on January 27, 1988; and the 256 MeV uranium run was on February 24, 1988. All of the irradiations were conducted in the beam dump area of the proton transport tunnel of the Intense Pulsed Neutron Source (IPNS) at Argonne. Beam currents varied between 1 and 4 μA for irradiation times of 60-90 min. Beam currents had to be carefully controlled to maintain target temperatures below 300°C.

Targets consisted of 10 cm OD cylinders measuring 2 and 5 cm long for U at 113 and 256 MeV, respectively, and 5 and 20 cm long for Al at 113 and 256 MeV, respectively. In all cases the targets were thick enough to completely stop the beam. The depleted uranium targets are identical to those normally used for the primary IPNS target and have a 1.5 mm Zircalloy cladding. Water cooling was required for the uranium targets due to the relatively poor heat conduction. Thermocouples were attached to all targets, and the beam currents were raised until target temperatures reached about 300°C. There was never any problem in controlling temperatures since it took 10-15 min to reach equilibrium and temperatures could be reduced almost immediately by stopping or reducing beam currents.

Foils were placed at angles of 0, 7.5, 30, 60, 90, 120, and 150° with respect to the beam on an aluminum spiderwork. The foils were on a 22 cm radius arc for all runs except 256 MeV with an Al target, where the radius was increased to 32 cm due to the large size of the target. Foil stacks consisted of 1-in. (2-cm) diameter foils of Al, Au, Fe, In, Nb, Ni, Co, Cu, Ti, and Zr with thicknesses between 25 and 890 μm . Foils were also placed at other locations, further from the target, to determine neutron scattering effects.

Following each irradiation, each foil was gamma counted to measure about 40 different radioisotopes, and the results are listed in Table I-11. In most cases, foils had to be counted several times to obtain measurements for both short-lived and long-lived isotopes. Furthermore, care had to be taken to identify cases where one radioisotope decays to another, similar to chain yields in a fission reaction. Corrections were then made for geometry, coincidence summing, decay during irradiation, and gamma self-absorption. The resulting activation rates are illustrated in Fig. I-32. As can be deduced from the figure, thermal and low-threshold reactions (the top two) have only a weak angular dependence, since the low-energy neutron flux is nearly isotropic. However, the higher threshold reactions have a very steep angular dependence, since the high energy neutron flux is preferentially emitted in the forward direction.

The activation rates were used to determine the neutron energy spectra. A generalized least-squares computer code, STAY'SL, was used to minimize χ^2 for the variance-covariance matrix of input activities, cross sections, and flux spectra. The activities generally have an uncertainty of 2-3% due to counting statistics and detector efficiency calibrations. Cross sections were taken from ENDF/B-V below 20 MeV, where uncertainties vary from 1% to 10%. At energies up to 50 MeV, cross sections were taken from the literature, and integral testing was performed in Be(d,n) fields. Above 50 MeV, spallation yields were taken from proton activation data (assuming charge independence at high energies). Uncertainties generally increased with energy, ranging from about 10 to 30%.

Input neutron spectra were taken from calculations performed by Dave Ek (Air Force Weapons Laboratory) using the High Energy Transport Code (HETC). Only statistical uncertainties are available for these calculations; however, model-dependent uncertainties are believed to be much larger (factor of two or worse).

Table I-11. Foil Materials and Activation Reactions at IPNS

Material	Reaction	T _{1/2}	Material	Reaction	T _{1/2}
¹⁹⁷ Au	(n,γ) ¹⁹⁸ Au	2.70 d	⁵⁴ Fe	(n,p) ⁵⁴ Mn	313 d
	(n,2n) ¹⁹⁶ Au	6.18 d		(n,α) ⁵¹ Cr	27.7 d
				(n,3n) ⁵² Fe	8.3 h
	(n,3n) ¹⁹⁵ Au	183 d	⁵⁶ Fe	(n,p) ⁵⁶ Mn	2.58 h
²⁷ Al	(n,4n) ¹⁹⁴ Au	39.5 h			
	(n,α) ²⁴ Na	15 h	⁵⁸ Fe	(n,γ) ⁵⁹ Fe	44.6 d
				(n,*) ⁵² Mn	5.59 d
⁵⁹ Co	(n,γ) ⁶⁰ Co	5.27 y		(n,*) ⁴⁷ Sc	3.42 d
	(n,p) ⁵⁹ Fe	44.6 d	Fe	(n,*) ⁴⁸ Sc	43.7 h
	(n,α) ⁵⁶ Mn	2.58 h		(n,*) ⁴⁸ V	16.0 d
	(n,2n) ⁵⁸ Co	70.8 d		(n,2n) ^{92m} Nb	10.15 d
	(n,3n) ⁵⁷ Co	271 d	⁹³ Nb	(n,4n) ⁹⁰ Nb	14.6 h
	(n,4n) ⁵⁶ Co	78.8 d		(n,*) ⁸⁹ Zr	78.4 h
	(n,*) ⁵² Mn	5.59 d		(n,*) ⁸⁸ Zr	83.4 d
	(n,*) ⁵⁴ Mn	313 d		(n,*) ^{90m} Y	3.19 d
	(n,3n) ⁶¹ Cu	3.41 h		(n,*) ⁸⁸ Y	107 d
	(n,p) ⁶⁵ Ni	2.52 h		(n,*) ⁸⁷ Y	80.3 h
	(n,*) ⁶⁴ Cu	12.7 h		(n,*) ⁸⁶ Y	14.7 h
	(n,*) ⁵⁸ Co	70.8 d		(n,p) ⁵⁸ Co	70.8 d
	(n,*) ⁶⁰ Co	5.27 y		(n,2n) ⁵⁷ Ni	36.1 h
	(n,*) ⁵² Mn	5.59 d		(n,x) ⁵⁷ Co	271 d
⁶³ Cu	(n,*) ⁵⁴ Mn	313 d		(n,3n) ⁵⁶ Ni	6.10 d
	(n,*) ⁵⁶ Co	78.8 d	⁶⁰ Ni	(n,p) ⁶⁰ Co	5.27 y
⁶⁵ Cu	(n,3n) ¹¹¹ In	2.83 d		(n,*) ⁵⁶ Co	78.8 d
	(n,γ) ^{116m} In	54.2 m		(n,*) ⁵⁴ Mn	313 d
¹¹³ In	(n,n') ^{115m} In	4.36 h		(n,*) ⁵² Mn	5.59 d
	(n,2n) ^{114m} In	49.5 d		(n,*) ⁵⁵ Co	17.5 h
				(n,*) ⁵² Fe	8.28 h
				(n,*) ⁵¹ Cr	27.7 d
				(n,*) ⁴⁸ V	16.0 d
⁴⁶ Ti	(n,p) ⁴⁶ Sc	83.8 d			
	(n,p) ⁴⁷ Sc	3.42 d			
⁴⁷ Ti	(n,p) ⁴⁸ Sc	43.7 h			
	(n,*) ^{44m} Sc	3.93 h			
⁴⁸ Ti	(n,*) ⁴³ K	22.6 h			
	(n,*) ⁴² K	12.4 h			
Ti					
⁹⁰ Zr	(n,2n) ⁸⁹ Zr	78.4 h			
	(n,3n) ⁸⁸ Zr	83.4 d			
⁹⁶ Zr	(n,γ) ⁹⁷ Zr	16.9 h			
	(n,*) ⁹⁵ Zr	64.0 d			
Zr	(n,*) ⁸⁸ Y	107 d			
	(n,*) ⁸⁷ Y	80.3 h			
	(n,*) ⁸⁶ Y	14.7 h			

Note: The notation (n,*) refers to a spallation reaction.

Fig. I-32.

Activation Rates as a Function of Angle for Various Reactions for 256 MeV Protons on Aluminum

The results of the STAY'SL flux spectra adjustments are plotted in Figs. I-33 to I-37. The spectral dependence as a function of angle is shown in Table I-12.

The most important conclusion is that we have been able to achieve consistent adjustments ($\chi^2 < 2$) using 20-30 different reaction rates with standard deviations of $\pm 20\%$. A typical case is illustrated by the printout in Fig. I-38. Note that Fig. I-38 lists the energy ranges covered by each reaction in the last two columns (90% energy limits). Figure I-36 shows typical group flux uncertainties (1σ) for this case. As can be seen, the uncertainties are rather good ($< 20\%$) at 1-30 MeV and increase at higher energies, where activation cross sections are not so well known. However, we should note that uncertainties are much smaller in coarser group structures due to the strong covariances. This is illustrated in Table I-12.

Several conclusions can be drawn from comparison of our foil adjustments with HETC calculations. It is clear that HETC overpredicts the flux at forward angles (especially at higher energies) and underpredicts the flux at back angles. This general behavior is found at both 113 and 256 MeV and for both Al and U targets. The discrepancies with HETC can be as large as a factor of two or three. Other groups have reported similar problems with HETC, and work is now in progress to improve the calculations.

We expect to receive time-of-flight (TOF) neutron spectral measurements performed by Los Alamos National Laboratory at both 113 and 256 MeV. The inherent accuracy of the TOF technique should provide us with a much better test of our foil activation technique and will further allow us to integrally test and adjust cross sections for poorly known reactions, which were not used in the present adjustments.

Fig. I-33.

Neutron Spectra at 0° for 256 MeV Protons on Uranium. (Here and in Figs. I-34 to I-37, calculations are compared with foil adjustments.)

Fig. I-34.

Neutron Spectra at 30° for 256 MeV Protons on Uranium

Fig. I-35.

Neutron Spectra at 120° for 256 MeV
Protons on Uranium

Fig. I-36.

Illustration of 1σ Group Flux Uncertainties
from Foil Adjustments at 30° for 256 MeV
Protons on Uranium

Fig. I-37.

Foil-Adjusted Neutron Spectra for All Angles for 256 MeV Protons on Uranium

We are also evaluating neutron scattering and proton effects. Scattering effects can be estimated by examining foils placed further away from the beam. Preliminary results indicate that neutron backscatter from the walls is not very important (<10%) except at very low neutron energies. The thermal flux is, in fact, mostly due to room-return neutrons, as can be seen by the nearly isotopic $^{197}\text{Au}(n,\gamma)^{198}\text{Au}$ activities in Fig. I-32. However, at higher energies, we see no significant spectral effects.

Protons are also certainly present at our foil positions since they can be made equally as well as neutrons in the target and in the accelerator beam exit foils. We can determine the proton flux by looking for reaction products which can only be made by protons. In the present case, we are measuring the proton flux using the $^{56}\text{Fe}(p,n)^{56}\text{Co}$, $^{56}\text{Fe}(p,2n)^{55}\text{Co}$, $^{63}\text{Cu}(p,2n)^{62}\text{Zn}$, and $^{65}\text{Cu}(p,n)^{65}\text{Zn}$ reactions. Protons generated by the target will be severely degraded in energy due to the large sizes of the targets. At angles less than 90° , all protons will be stopped in the target. At back angles, protons can be emitted; however, they will be degraded in energy due to energy loss of the beam going in and the protons coming out. Hence, the average proton energy is expected to be less than half the beam energy. Protons can also be generated by the beam exit foil (130 μm , Ti). Assuming Rutherford scattering, we can estimate yields. In this case, protons will have a very high energy (near the beam energy); however, the target still shields foils at angles less than 30° . Preliminary analysis shows that proton fluxes are less than 1% of the total neutron flux. However, at back angles the proton fluxes at high energies (>20 MeV) could be 10% or more of the high energy neutron flux. A more detailed analysis is now in progress.

Fig. I-38. STAY'SL Spectral Adjustment for 265 MeV Protons on Uranium at 30° ($\chi^2 = 0.99$, activities in units of 10^{24} atoms/atom)

DOSIMETRY ACTIVITIES									
	MEASURED	+OR- %	BEFORE	DIFF %	AFTER	DIFF %	CHI	REACTION	90 % ENERGY LIMITS
1	3.240E+09	2.20	2.660E+09	-17.89	3.133E+09	-3.29	0.621	C059(N,G)C060	1.00E-10 1.00E-04
2	2.750E+10	2.60	2.221E+10	-19.24	2.756E+10	0.22	-0.231	IN115(N,G)IN116	1.00E-10 6.30E-06
3	2.990E+10	2.10	2.206E+10	-26.24	2.981E+10	-0.32	0.419	AU197(N,G)AU198	1.00E-10 1.35E-05
4	3.840E+08	3.10	3.383E+08	-11.90	3.870E+08	0.79	-0.394	CU(N,*)64CU	1.00E-10 1.80E+01
5	9.070E+08	2.30	5.765E+08	-36.44	8.856E+08	-2.36	1.176	IN115(N,N')IN115	1.00E+00 1.00E+01
6	4.050E+08	2.30	4.095E+08	1.11	4.150E+08	2.46	0.014	AU197(N,2N)AU196	9.00E+00 6.80E+01
7	2.810E+08	3.00	2.767E+08	-1.52	3.364E+08	19.72	-0.090	AU197(N,3N)AU195	1.80E+01 1.00E+02
8	3.140E+07	2.20	3.218E+07	2.49	3.338E+07	6.30	0.206	AL27(N,*)NA24	7.00E+00 9.20E+01
9	2.210E+07	2.50	1.679E+07	-24.02	2.026E+07	-8.31	1.159	C059(N,P)FE59	3.00E+00 2.00E+01
10	1.180E+07	2.10	1.279E+07	8.42	1.267E+07	7.41	0.727	C059(N,A)MN56	7.00E+00 1.30E+02
11	1.770E+08	2.20	1.596E+08	-9.82	1.804E+08	1.92	-0.212	C059(N,2N)C058	1.20E+01 4.00E+01
12	6.270E+07	2.30	4.563E+07	-27.23	5.749E+07	-8.31	0.370	C059(N,3N)C057	2.00E+01 5.60E+01
13	8.360E+06	4.80	9.162E+06	9.60	1.030E+07	23.24	0.142	C059(N,4N)C056	3.20E+01 7.20E+01
14	2.380E+06	3.20	2.617E+06	9.97	2.222E+06	-6.66	-0.110	C059(N,*)MN52	4.40E+01 1.60E+02
15	2.210E+07	3.60	2.048E+07	-7.32	1.954E+07	-11.57	0.509	C059(N,*)MN54	3.20E+01 1.50E+02
16	2.510E+07	3.00	2.197E+07	-12.46	2.195E+07	-12.55	1.648	CU63(N,*)C060	6.00E+00 1.40E+02
17	3.810E+05	2.40	6.510E+05	70.87	4.872E+05	27.88	2.482	CU(N,*)52MN	8.00E+01 1.90E+02
18	3.120E+06	2.80	2.703E+06	-13.38	2.129E+06	-31.75	2.489	CU(N,*)54MN	5.20E+01 1.80E+02
19	2.070E+07	2.40	2.463E+07	19.00	2.436E+07	17.69	1.615	CU(N,*)58CO	2.80E+01 1.50E+02
20	8.480E+04	4.00	1.446E+05	70.49	9.795E+04	15.51	1.756	CU(N,*)48V	1.00E+02 2.00E+02
21	1.570E+09	2.50	1.190E+09	-24.18	1.412E+09	-10.04	4.825	FE54(N,*)MN54	3.00E+00 1.10E+02
22	4.060E+08	2.60	5.527E+08	36.12	5.003E+08	23.22	4.448	FE54(N,*)CR51	2.00E+01 1.50E+02
23	3.010E+07	2.20	2.769E+07	-8.01	3.027E+07	0.55	-0.226	FE56(N,P)MN56	6.00E+00 4.00E+01
24	7.210E+06	2.50	9.121E+06	26.51	8.442E+06	17.09	0.405	FE(N,*)52MN	3.20E+01 1.50E+02
25	8.620E+07	2.40	8.121E+07	-5.79	8.312E+07	-3.58	0.179	NB93(N,2N)NB92M	1.00E+01 2.00E+01
26	2.890E+08	2.30	2.434E+08	-15.78	2.849E+08	-1.41	0.137	ZR290(N,2N)ZR89	1.40E+01 7.20E+01
27	6.640E+08	2.50	5.014E+08	-24.50	5.594E+08	-15.76	2.622	TI46(N,X)SC46	5.00E+00 1.20E+02
28	8.140E+08	2.30	5.217E+08	-35.91	6.263E+08	-23.06	7.470	TI47(N,*)SC47	3.00E+00 1.00E+02
29	2.090E+07	2.50	1.799E+07	-13.93	1.967E+07	-5.89	0.605	TI48(N,*)SC48	7.00E+00 6.00E+01
30	4.830E+06	3.00	5.771E+06	19.49	5.228E+06	8.24	0.224	TI(N,*)44MSC	3.20E+01 1.50E+02
31	6.940E+08	2.20	4.879E+08	-29.69	7.077E+08	1.98	-1.658	NI58(N,*)C058	2.00E+00 2.40E+01
32	2.690E+07	2.30	2.346E+07	-12.81	2.640E+07	-1.84	0.128	NI58(N,*)NI57	1.60E+01 1.10E+02
33	2.340E+08	2.40	2.258E+08	-3.48	2.521E+08	7.75	-0.118	NI58(N,X)57CO	1.00E+01 9.20E+01
34	5.660E+06	2.40	5.180E+06	-8.48	4.510E+06	-20.32	0.226	NI(N,*)52MN	2.80E+01 1.70E+02
35	3.720E+07	2.20	3.815E+07	2.55	4.287E+07	15.25	0.128	NI(N,*)56CO	2.80E+01 1.10E+02
				STD. DEV. =					
				13.73					

Table I-12. STAY'SL Results for 256 MeV Protons on Uranium at 30°

Lower Energy, MeV	Flux, n/cm ² -s	Flux, n/sr-p ^a	SDEV, %
Total	5.839E+09	2.937E-01	± 15.83
1.000E-10	6.777E+07	3.409E-03	± 40.27
5.500E-07	2.834E+08	1.426E-02	± 25.81
1.000E-01	1.577E+09	7.930E-02	± 38.80
1.000E+00	2.725E+09	1.371E-01	± 16.36
5.000E+00	4.422E+08	2.224E-02	± 17.36
1.000E+01	1.625E+08	8.310E-03	± 7.81
2.000E+01	2.140E+08	1.076E-02	± 15.34
4.000E+01	2.388E+08	1.201E-02	± 13.98
1.000E+02	1.216E+08	6.114E-03	± 20.37
2.000E+02	3.914E+06	1.969E-04	± 67.91

Relative Covariance Matrix (10 x 10)

1000	-67	21	13	-1	15	-2	4	1	0
1000	367	66	-3	22	-5	7	0	2	
1000	486	-87	3	12	10	-3	2		
1000	-410	157	-6	2	8	0			
1000	-417	-43	-29	7	0				
1000	-361	76	-14	7					
1000	-432	96	-21						
1000	-675	183							
1000	292								
1000									

^aNeutrons/steradian-proton.

3. Production of ⁹³Mo and ^{93m}Nb (L. R. Greenwood, D. L. Bowers, and A. Intasorn)

We are engaged in an ongoing program to measure neutron activation cross sections near 14 MeV for long-lived isotopes. Such data are needed to determine the activity of fusion reactor materials, especially for waste disposal applications. We have previously reported data for the production of ²⁶Al, ⁵⁵Fe, ⁶³Ni, ⁵⁹Ni, ⁹¹Nb, and ⁹⁴Nb.⁶⁶⁻⁶⁸ The present work summarizes our measurements of ⁹³Mo (3500 y) and ^{93m}Nb (16.1 y) from natural and ⁹⁴Mo-enriched samples of molybdenum.

The Mo samples were metallic powders pressed into discs of 3 mm diameter by 1 mm thick. These discs were irradiated at the RTNS II to a neutron fluence of about 10¹⁸ n/cm². Details of the irradiation were published previously,⁶⁷ where we reported cross sections for the ⁹⁴Mo(n,p)⁹⁴Nb, ⁹⁵Mo(n,x)⁹⁴Nb, ⁹²Mo(n,x)^{91m}Nb, ⁹²Mo(n,x)^{91B}Nb, and ⁹⁸Mo(n,α)⁹⁵Zr reactions in the energy range from 14.5 to 14.8 MeV. These same samples are now being analyzed for ⁹³Mo and ^{93m}Nb, both of which decay to the ground state of ⁹³Nb and emit Nb X-rays at 16.6 and 18.6 keV. Hence, it is necessary to chemically

separate Mo and Nb before determining cross sections for each isotope. Furthermore, ^{93}Mo decays to $^{93\text{m}}\text{Nb}$, thus complicating the analysis.

All of the samples were dissolved in a mixture of concentrated HNO_3 and HCl . Ion-exchange chemical separations were then performed. Small aliquots of the dissolution and each fraction were then taken to dryness for X-ray analysis. Several checks were available to determine both the degree of separation as well as the absolute yields from the chemical procedures. Since $^{91\text{g}}\text{Nb}$ (~ 680 y) is also present in the samples, we used the Zr X-rays at 15.7 and 17.6 keV as an Nb tracer. We were also able to obtain some ^{99}Mo (kindly supplied by J. D. Kwok, ANL Chemical Technical Division), which was added to our samples as a Mo tracer. In both cases, we were able to demonstrate that the chemical separation of Mo and Nb was good to at least 99%. Finally, we were able to demonstrate that the sum of the X-ray activities in the Nb and Mo fractions was equal to that of the original dissolution and that losses were less than 5%.

The natural Mo samples have now been analyzed, and work on the ^{94}Mo -enriched samples is in progress. Preliminary results indicate a cross section of 540 mb for the $^{94}\text{Mo}(n,2n)^{93}\text{Mo}$ reaction and 0.73 mb for the $\text{Mo}(n,x)^{93\text{m}}\text{Nb}$ reaction. Cross sections for these reactions have not been measured previously. Data from the enriched targets will allow us to obtain separate cross sections for the production of $^{93\text{m}}\text{Nb}$ from both ^{94}Mo and ^{95}Mo . The results will then be used to predict the production of these isotopes in fusion reactor materials.

4. Calculations for the REAL88 Exercise (L. R. Greenwood and A. Intasom)

We are participating in a project to compare neutron spectral adjustment codes and damage predictions sponsored by the International Atomic Energy Agency (IAEA) in Vienna, Austria. Neutron activation data were collected and distributed by the IAEA for six distinctly different neutron spectra, including that from a pressure vessel surveillance capsule from the Arkansas Nuclear One power reactor, that from two pressure vessel simulator experiments in the Oak Ridge Research Reactor, a ^{235}U fission spectrum obtained from the Coupled Fast Reactivity Measurement Facility at Idaho Nuclear Engineering Laboratory, and a fusion-simulation spectrum measured at RTNS II.

The REAL88 exercise followed the previous REAL80 and REAL84 exercises. Each successive exercise has placed tighter restrictions on the quality of the input data, knowledge of covariance information, nuclear data, and types of computer codes which are allowed. The goal is to standardize procedures and to establish reference data sets.

Over fifteen different laboratories are expected to participate in eight different countries. We have submitted our results to the Energieonderzoek Centrum Nederland (ECN) Laboratory in Petten, The Netherlands, where all results will be compared. A meeting will then be held in Petten in October 1988 to assess the preliminary results of the comparison and to plan future work.

5. Neutron Fluence Measurements at RTNS II (L. R. Greenwood and C. A. Seils)

A helium production experiment was conducted at RTNS II in collaboration with Rockwell International (D. Kneff). The purpose of the experiment was to measure helium production cross sections near 14 MeV for various materials, including Be, C, Nb, Al, Cu, and Fe. Similar measurements for 25 elements, separated isotopes, and alloy steels have been published previously.⁶⁵

The helium specimens and radiometric dosimeters were enclosed in a cylindrical package measuring 1.1 cm diameter by 0.6 cm thick. Dosimetry foils of Fe, Nb, and Co, each measuring 130 μm thick, were placed at seven different depths in the capsule to measure the neutron fluence gradients. Wires and helium accumulation fluence monitors were placed at four different locations in the assembly. The entire capsule was irradiated at 110° to the incident beam so that the average neutron energy was 13.8 MeV (± 200 keV). The irradiation took place over the extended period between February 23, 1987, and May 23, 1987. A detailed irradiation history was used to correct for decay during irradiation.

All of the dosimetry foils and helium samples were gamma counted and saturated activation rates were calculated, as listed in Table I-13. The neutron fluences have an estimated absolute uncertainty of about 6-8% due to counting uncertainties (as listed) and cross section uncertainties (4-6%). The activity values and uncertainties are reported as the total number of active atoms per atom of target material. Neutron fluences were then derived by dividing by the appropriate neutron cross section. Cross section values were taken from ENDF/B-V assuming a mean neutron energy of 13.8 MeV. In the case of the ^{59}Co reactions to ^{59}Fe and ^{58}Co , the cross sections were adjusted according to previous measurements at RTNS II.⁶⁵

The neutron fluences were in the range of $1.5\text{-}2.0 \times 10^{16} \text{ n/cm}^2$ and declined with increasing distance from the neutron source. The neutron fluence values for sample positions (numbers) represent wire and helium samples (letters) which were much smaller than the 1.1 cm diameter dosimetry foils. Wire fluences thus show some scatter from the foil values, since the neutron fluences are changing across the dimensions of the foil. All of the data will be fit to a more detailed flux map to more accurately predict fluences at the location of each helium sample. Helium analyses are now in progress at Rockwell International.

Table I-13. Activities and Neutron Fluences for RTNS II at 110° and 13.8 MeV

Sample Position	Isotope	Isotopic Production, 10 ⁻⁹ at./at.	Neutron Fluence, 10 ¹⁶ n/cm ²
Fe-F	⁵⁴ Mn	7.35(0.7) ^d	1.91
	⁵¹ Cr	1.70(2.6)	1.89
Co-F	⁵⁸ Co	12.4(0.3)	1.80
	⁵⁹ Fe	1.03(1.7)	1.74
Nb-1	^{92m} Nb	9.07(0.9)	1.95
Fe-1	⁵⁴ Mn	7.31(1.1)	1.90
	⁵¹ Cr	1.60(3.2)	1.78
Fe-S1 ^a	⁵⁴ Mn	7.35(1.8)	1.91
	⁵¹ Cr	1.49(6.0)	1.66
Nb-8D ^b	^{92m} Nb	9.30(1.2)	2.04
Fe-2	⁵⁴ Mn	7.08(0.8)	1.84
	⁵¹ Cr	1.58(2.5)	1.76
Nb-S1 ^a	^{92m} Nb	8.48(0.4)	1.86
Nb-1E ^b	^{92m} Nb	8.73(1.3)	1.92
Nb-7Y ^b	^{92m} Nb	7.87(0.9)	1.73
Cu-S1 ^a	⁶⁰ Co	0.829(1.5)	1.88
Fe-3	⁵⁴ Mn	6.78(0.8)	1.77
	⁵¹ Cr	1.51(3.1)	1.68
Fe-S3 ^c	⁵⁴ Mn	7.01(1.2)	1.83
	⁵¹ Cr	1.57(3.7)	1.75
Nb-S3 ^c	^{92m} Nb	8.62(1.1)	1.89
Nb-9V ^b	^{92m} Nb	8.39(1.3)	1.84
Cu-S2 ^a	⁶⁰ Co	0.772(1.2)	1.63
Cu-S4 ^c	⁶⁰ Co	0.763(1.2)	1.73
Fe-4	⁵⁴ Mn	6.70(1.3)	1.74
	⁵¹ Cr	1.50(4.0)	1.67
Fe-S2 ^a	⁵⁴ Mn	6.52(1.0)	1.70
	⁵¹ Cr	1.41(3.9)	1.57
Nb-B2 ^b	^{92m} Nb	8.61(1.5)	1.89
Nb-S2 ^b	^{92m} Nb	7.81(1.1)	1.72
Cu-S3 ^c	⁶⁰ Co	0.755(1.9)	1.71
Fe-5	⁵⁴ Mn	6.44(0.9)	1.68
	⁵¹ Cr	1.41(4.3)	1.57
Nb-5	^{92m} Nb	7.89(0.7)	1.73
Co-B	⁵⁸ Co	10.8(0.4)	1.57
	⁵⁹ Fe	0.901(1.5)	1.52
Fe-B	⁵⁴ Mn	6.33(0.9)	1.65
	⁵¹ Cr	1.37(4.2)	1.53

^aWire samples inside main assembly.^bHelium accumulation fluence monitors.^cWire samples outside of main package.^dRelative counting uncertainties (%) are listed in parentheses; absolute uncertainties also include 2% for detector efficiency and 4-6% for cross sections.

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II. SEPARATION SCIENCE AND TECHNOLOGY (G. F. Vandegrift)

The Division's work in separation science and technology is mainly concerned with developing a technology base for the TRUEX (TRansUranic EXtraction) solvent extraction process. The TRUEX process extracts, separates, and recovers TRU elements from solutions containing a wide range of nitric acid and nitrate salt concentrations. The extractant found most satisfactory for the TRUEX process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is abbreviated CMPO. This extractant is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX process solvent. The diluent is typically a normal paraffinic hydrocarbon (NPH) or a nonflammable chlorocarbon such as carbon tetrachloride (CCl_4) or tetrachloroethylene (TCE). The TRUEX flowsheet includes a multistage extraction/scrub section that recovers and purifies the TRU elements from the waste stream and multistage strip sections that separate TRU elements from each other and the solvent. Our current work is focused on facilitating the implementation of TRUEX processing of TRU-containing waste and high-level defense waste, where such processing can be of financial and operational advantage to the DOE community.

The major effort in TRUEX technology-base development involves developing a generic data base and modeling capability for the TRUEX process, referred to as the Generic TRUEX Model (GTM). The GTM will be directly useful for site-specific flowsheet development directed to (1) establishing a TRUEX process for specific waste streams, (2) assessing the economic and facility requirements for installing the process, and (3) improving, monitoring, and controlling on-line TRUEX processes. The GTM is composed of three sections that are linked together and executed by HyperCard and Excel software. The heart of the model is the SASSE (Spreadsheet Algorithm for Staged Solvent Extraction) code, which calculates multistaged, countercurrent flowsheets based on distribution ratios calculated in the SASPE (Spreadsheet Algorithms for Speciation and Partitioning Equilibria) section. The third section of the GTM, SPACE (Size of Plant and Cost Estimation), estimates the space and cost requirements for installing a specific TRUEX process in a glove box, shielded-cell, or canyon facility. The development of centrifugal contactors for feed- and site-specific applications is also an important part of the effort.

Another project is underway to determine the feasibility of substituting low-enriched uranium for the high-enriched uranium currently used in producing fission-product ^{99}Mo . Technetium-99m, the daughter of ^{99}Mo , is widely used in medical diagnosis.

A. Spreadsheet Integration for Generic TRUEX Model (J. M. Copple)

Development of the Macintosh version of the Generic TRUEX model is almost complete. This model calculates a TRUEX solvent extraction flowsheet based on input of a specific feed and a specific set of process goals and constraints. The output of this code is (1) the compositions of all effluent streams and compositions of both phases (organic and aqueous) in each stage of the contactor at steady state and (2) estimates of the space and cost requirements for installing this flowsheet in a plant. The GTM can be run on a Macintosh computer by a person who is not a computer expert.

The GTM will be directly useful for development of site-specific flowsheets directed to (1) establishing a TRUEX process for specific waste streams, (2) assessing the economic and facility requirements for installing the process, and (3) improving, monitoring, and controlling on-line TRUEX processes.

The GTM is composed of three sections (SASPE, SASSE, and SPACE) that are linked together and executed by HyperCard and Excel software. The interactions of these sections are schematically represented in Fig. II-1.

Fig. II-1. Interactions among Computer Program Modules of the Generic TRUEX Model

The SASSE section has been developed to allow the design and detailed evaluation of proposed flowsheets in conjunction with distribution ratios generated in SASPE. In addition to (1) establishing that each feed component will be able to reach its design composition in the extraction raffinate and product streams and (2) providing the compositions of the organic and aqueous solutions in each stage of the flowsheet at steady state, SASSE can be used to identify key points for process monitoring and control. According to user specifications, an Excel Macro will produce a SASSE spreadsheet with an extraction section, up to three scrub sections, and up to four strip sections. Any number of stages can be specified in each section.

The SASPE section of the GTM will calculate distribution ratio (D) values for each aqueous phase composition from user-specified feeds (feed menu) or from stage compositions generated in SASSE. Many modules in the SASPE section are necessary for calculating D values for all conceivable aqueous phase and TRUEX solvent combinations. These models include the following: (1) charge-balance check of feed solution, (2) estimate of densities of complex aqueous solution, (3) molar-to-molal concentration conversion, (4) ionic strength of complex aqueous solutions, (5) activities of aqueous phase species, (6) oxalic-acid additions to fission-product-containing waste, (7) aqueous-phase speciation of individual-component distribution ratios.

Distribution ratios for all components are transferred from SASPE to SASSE so that SASSE can calculate aqueous- and organic-phase compositions in the flowsheet. These calculated compositions are

then transferred from SASSE to SASPE so that SASPE can calculate updated distribution ratios, which are then returned to SASSE. This interaction between SASSE and SASPE continues until steady state is achieved.

The resultant flowsheet from SASSE is combined with user-specified plant-specific information in the SPACE section to calculate equipment size, plant space, and capital costs. The options in SPACE are to include a hot (radioactive) processing area that is either a glovebox, a shielded cell, or a canyon. The SPACE worksheet correlations assume that the processing area (including glovebox, shielded cell, or canyon) (1) is available and (2) has been cleaned out (that is, it does not contain any equipment and is nonradioactive enough that persons can work in the area).

1. Flowchart of Generic TRUEX Model

The Generic TRUEX Model consists of the HyperCard stack "GTM_HC" and the 27 files listed in Fig. II-2. To use the model, one does not need to know the order in which these files are opened or executed. The user opens "GTM_HC," and the rest of the files are automatically opened when needed.

Operation	File Name	Operation	File Name
User Input:	GTM_HC HC export	SASSE Calculations:	SASSE_generate SASSE_report_generator SASSE_summary_full SASSE_profile SASSE_summary_concise SASSE_chart
Program Control:	GTM GTM_setup GTM_Driver GTM_Banner	SPACE Calculations:	SPACE_generate SPACE_template SPACE_report_generator SPACE_summary_template
Oxalate Calculations:	Oxalate_driver Oxalate_Module Oxalate_Input Oxalate_Output Oxalate_Banner	Report Folder:	Reports
SASPE Calculations:	SASPE_NPH SASPE_TCE HNO3_EXTR.TRUEX-TCE HNO3_EXTR.TRUEX-NPH CMPOf_TBPf-MACRO FitCoefs		

Fig. II-2. File Listing for the Generic TRUEX Model

The flowchart in Fig. II-3 shows the major operations performed by the model and also indicates how various conditions affect the flow of these operations. The actual files that perform these operations are not shown in the figure. The following text will guide the reader through the flowchart.

Fig. II-3. Flowchart of the Generic TRUEX Model

2. Brief Guide through the Generic TRUEX Model

The Generic TRUEX Model begins with the user entering information about the process (e.g., the number of sections, the number of stages in a section, the type of each section, the flow rates into each section, the compositions for the feed into each section). After this information has been entered, the amount of oxalic acid that would need to be added to the extraction feed to suppress noble-metal extraction is calculated. Then, thermodynamic activities of water, hydrogen ion, and nitrate ion are calculated. Next, if ruthenium is present in the extraction feed, the amount of extractable ruthenium is calculated based on nitrate ion activities and oxalate ion concentration.

With the information that was entered by the user concerning the flowsheet specifications, the SASSE worksheet can be generated. After SASSE is generated, SASPE and related files, which are needed to calculate the distribution coefficients, are opened. Now the SASSE-SASPE interaction can begin. SASSE calculates the concentration for the components in both phases (organic and aqueous) in each stage of the flowsheet based on incoming stream compositions and the distribution coefficients that SASPE generates for each stage. SASSE calculates the concentrations for all components in all stages simultaneously, while SASPE can only calculate the distribution coefficients for a single stage one stage at a time. Therefore, SASPE must loop through all stages, transferring the distribution coefficients for each stage to SASSE before SASSE can perform 50 internal iterations.* After the 50 internal iterations performed in SASSE, a new set of D values is calculated in SASPE.

The SASSE-SASPE iteration can be terminated in one of two ways:

1. The new set of calculated distribution ratios is within 1% of the previously calculated set.
2. The maximum number of iterations between SASSE and SASPE allowed by the model has been performed. The maximum number is three times the number of stages plus 25. In this case, a dialog box is displayed that tells the user that the distribution coefficients have not converged.

In either case, the material balance for the process flowsheet being calculated in SASSE is then checked.

If the material balance converges for all components to $\leq 0.01\%$, the model goes on to generate SASSE reports. If it does not converge, a dialog box is displayed, informing the user that the material-balance check did not converge. The user is then given the option to calculate SASSE further. If this option is selected, SASSE calculates through 200 more iterations, and the material-balance check is performed again. The user can loop in the material-balance check until either SASSE converges or the user decides to go on to SASSE reports.

Next the SASSE reports are generated and displayed. After the user has finished viewing and printing reports, SPACE is generated. The space and cost estimates are calculated based on the user input provided at the front end of the model.

The SPACE worksheet displayed on the screen is originally calculated based on default values. The user may modify most of the values on the SPACE worksheet while it is displayed. When a

*If values in all cells in the SASSE worksheet do not change by $<10^{-12}$, SASSE will complete iterations in less than 50.

value is changed, the entire SPACE worksheet is recalculated automatically. After the user has finished modifying values in SPACE, SPACE reports are generated. When the user has finished viewing and printing SPACE reports, all unnecessary files are closed. The user is then given the opportunity to run the model again or to quit the GTM completely.

The above describes the flowchart for the entire Generic TRUEX Model. It is also possible to enter and leave this flowsheet at several places by options selected in the front end:

- Activity calculations can be made independently.
- SASPE-SASSE flowsheet calculations can be run independently of SPACE.
- SASSE calculations can be made independently.
- SPACE calculations can be made independently.

B. SASSE Section Development

(R. A. Leonard, J. M. Copple, and D. B. Chamberlain)

An electronic worksheet called SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) has been developed to allow detailed evaluation of proposed flowsheets in conjunction with information from the generic TRUEX data base. In addition to establishing that each effluent will reach its specified composition, the SASSE worksheet (spreadsheet) can be used to identify key points for process monitoring and control. An early version of SASSE was used to assist the Westinghouse Hanford Co. in countercurrent testing of the TRUEX flowsheet using actual Plutonium Finishing Plant (PFP) wastes. An Excel macro that generates a new SASSE spreadsheet for a given number of (1) sections, (2) stages in each section, and (3) chemical components has been written and tested. This "SASSE_generate macro" is a part of the Generic TRUEX Model for calculating TRUEX process flowsheets in conjunction with the Spreadsheet Algorithms for Speciation and Partitioning Equilibria (SASPE). The output from the joint SASSE/SASPE calculations will be combined with plant-specific information in a separate worksheet to calculate equipment size, plant space, and capital costs.

The Excel macro that is written to generate SASSE worksheets, called "SASSE_generate," was systematically tested and debugged starting with one component, one stage, and one section. This testing and debugging have been completed, and the macro should now work for any number of components, stages, and sections up to the limit of the Excel worksheet, that is, up to a total of 255 stages divided into sections in any manner as needed. Typically, one will need 8 to 30 stages. In the testing of the macro, up to 16 components, 14 stages, and 4 sections were used. Special configurations tested included taking all or part of the aqueous effluent from one section and making it the feed for the next section, with and without an external aqueous feed. Although there can be only one organic feed, a side stream of organic effluent can be taken between any section as long as there is also an aqueous effluent from that section. As set up, the SASSE worksheet allows for the organic feed to be either the organic effluent from the last section with the calculated concentration for each component or fresh solvent with a concentration for each component that is specified by the user. The SASSE_generate macro was also checked against (1) a SASSE worksheet set up using an earlier version of the macro and (2) a SASSE worksheet that was set up before the macro was available. Both tests showed no problems with the macro. The work on this macro has now been halted so that it can be properly interfaced with the rest of the GTM. Changes will be made only as needed to accommodate the overall operation of the GTM.

The biggest change in the SASSE worksheet from earlier versions is that each component concentration for the organic and aqueous phases flowing to each stage is shown on separate rows of the SASSE worksheet. This change allows these values to be used in the SASPE part of the Generic TRUEX Model for certain distribution coefficients (D values) that change with time, for example, iron. This change was been incorporated into the SASSE_generate macro.

In the process of testing and debugging the SASSE_generate macro, a number of problems were addressed and resolved. These problems are discussed next.

1. Convergence of SASSE Worksheet

In using the SASSE worksheet to model the first verification runs (Sec. II.K.), we found that the worksheet did not always converge. In this modeling effort, we used a previously developed correlation for $D(\text{HNO}_3)$ as a function of HNO_3 , nitrate salt, TBP, and CMPO concentrations and for $D(\text{Am})$ as a function of HNO_3 , Am, nitrate salt, TBP, and CMPO concentrations¹ because the SASPE portion of the GTM that does this convergence was not ready. This convergence problem was partially solved by noting the double-diamond nature of the SASSE calculation, that is, that two independent sets of calculations are underway at the same time.² By delaying the use of the previous nitric acid and americium concentrations for each stage by one iteration cycle, these concentrations are returned to be used on the same diamond, not on the other diamond. This change solved most of the convergence problem.

To solve the rest of the problem, we used a second technique, which involved setting a lower limit for the amount by which americium loading of the solvent could affect the americium distribution coefficient. If, after steady state was reached, one or more stages had solvent loaded to this limit, the limit was reduced; further iterations then allowed convergence to a new steady state. This reduction of the lower limit for the amount by which americium loading of the solvent can affect the americium distribution coefficient was repeated until the limit was not a factor in the steady-state solution for the americium profile through the contactor stages.

When the SASPE portion of the GTM is available, the first part of the convergence problem will be resolved automatically because the SASSE worksheet will be iterated many times before new D values are transferred to the SASSE worksheet. The second part of the convergence problem may need to be solved by building an algorithm into GTM that only allows the distribution coefficient for a component to change by no more than a certain amount, for example, a factor of two, for successive iterations between SASSE and SASPE.

2. Application to Molten Salt Extraction

In the course of this development work, the SASSE_generate macro was applied to the problem of multistage metal extraction between a molten salt (A) and a liquid metal (O). Because of the generic nature of the SASSE worksheet, it was easy to adapt this problem in pyrochemical processing to the SASSE worksheet. The biggest challenge was to incorporate the equations for the equilibrium coefficients in such a way that the iterative solution converges. As this work was applied to molten salt extraction, ways to clarify the layout of the SASSE_generate macro and the SASSE worksheet were noted. Based on these notes, changes were made to both the SASSE_generate macro and the SASSE worksheet.

3. Worksheet Initialization

Because of the double-diamond nature of the SASSE calculation, two independent sets of calculations are underway at the same time, as noted above. To be sure that both diamonds are cleared out on initialization, that is, when setting $N = 0$ in the worksheet, the initialization procedure should be carried out twice, that is, for two iterations of the worksheet.

With certain flowsheets, one or more components will reach concentrations in one or more contactor stages at steady state which are much higher than the concentration in the incoming feed. For those components, which are said to be "pinched" by the process, it is helpful to make the initial concentration in these pinched stages near to the expected final concentration. By doing this, the convergence to a steady-state solution will be much faster. If this high concentration profile is not used to initialize the SASSE worksheet, all the component concentrations in each stage will have to be increased by the amount entering with the feed. This will take time, both in reaching the computer solution and in reaching steady-state plant operation.

C. SPACE Section Development (R. A. Leonard and L. S. Chow)

The results from the SASSE/SASPE calculations will be combined with plant-specific information in a separate Excel worksheet to calculate equipment size, plant space, and capital costs. This worksheet for calculating the Size of Plant And Cost Estimate is called SPACE. The options in the worksheet include a hot (radioactive) processing area that is either a glovebox, a shielded cell, or a canyon. The SPACE worksheet correlations assume that the processing area including glovebox, shielded cell, or canyon (1) is available, (2) has been cleaned out, that is, it does not contain any equipment, and (3) is nonradioactive enough so that people can work in the area.

In its final form, the GTM will pass the results of the SASSE/SASPE calculations to the SPACE worksheet and then return the results of the calculations to a HyperCard front end. It will also be possible to use SPACE worksheet by itself.

Figure II-4 shows the flowsheet of a basic TRUEX processing plant. The objective here is to develop a worksheet that calculates the size and cost of the equipment needed for such a plant. A typical TRUEX processing plant consists of an extraction section, one or two scrub sections, one to three aqueous strip sections, one or two solvent wash sections, and an acid rinse section. Each section requires equipment to store and feed the chemicals into the sections and equipment to store and dispose of the raffinate out of the section. A schematic showing the minimum equipment required for a TRUEX processing plant is given in Fig. II-5. Each section of the plant is equipped with source tanks to store the chemicals needed for the operation of that section. Chemicals with known concentrations and in known quantities will be transferred from the source tanks to the feed makeup tank. Within each section, the TRUEX process takes place within a specified number of stages in the centrifugal contactor. At the exit of each section (except the scrub section), a tank is included for the temporary storage of the aqueous effluent. The effluent will be transported for component recovery, sent to waste storage, or recycled back to the process. The appropriate action will depend on the type and/or quality of the effluent. (Note: the water source and the related piping systems are not shown in Fig. II-5).

Components and equipment outside the boundary of the hot area can be located in an open area. Components and equipment within the hot boundary have to be in a glovebox, shielded-cell area, or remote canyon. The solution wash raffinate and acid rinse raffinate are also located in the hot area.

Fig. II-4. Schematic of Basic TRUEX Flowsheet

A layout for the SPACE worksheet is shown in Fig. II-6. The first part of the worksheet is reserved for inputting data, such as the type of solvent, number of contactor stages, absolute (feed) and relative flow rates, and feed tank requirements. Following the input data are the output results from calculations that include the overall cost and space requirements and the space breakdown inside and outside the hot area (glovebox, shielded cell, or canyon). The third part of the worksheet includes the calculations that (1) convert to SI units and determine the maximum contactor throughput, rotor diameter, and tank volumes, (2) estimate equipment space and costs for centrifugal contactors, tanks, and pumps, and (3) estimate fixed capital investment costs. Listed at the end of the worksheet are the tables and constants for cost indices, conversion factors, and correlation constants.

A preliminary version of the SPACE worksheet is complete. The input data needed include the number of contactor stages; number of sections or columns of the same type; the year for cost estimate or current cost index; location of each feed and raffinate systems; the diluent used in the TRUEX solvent; feed rates (absolute or relative); cost calculation method; tank size calculation method; and tank and pump information. The output data include the diameter and spacing of the contactor stages; volumes, dimensions, and flow rates of the storage tanks; the purchased cost of the contactor and the tanks and pumps for each section or column; the total purchased cost of the conventional equipment (tanks and pumps) of the processing plant; the fixed capital cost to equipment cost ratios (these ratios are functions of the location of the equipment); the fixed capital costs for the contactor stages, conventional equipment, and CMPO; and the total fixed capital cost of the entire processing plant.

Correlations are used in calculating the size and cost of the various pieces of processing equipment when they are installed in an open plant area. These correlations for calculating (1) the space for the equipment, (2) the appropriate installation costs, and (3) the cost factors will be applied to the capital equipment costs when the equipment is installed in a glovebox, shielded cell, or canyon. To get some assistance on these last two items, especially on the cost factor for equipment installed in a canyon, we used Fluor Daniel in Irvine, California, as consultants.

Fig. II-5. Schematic of Basic TRUEX Processing Plant

Fig. II-6. Layout of SPACE Worksheet

Future work involves (1) checking and revising the SPACE algorithm, especially the space calculations, installation costs, and radioactive area cost factors; (2) testing the link from the SPACE worksheet to the Generic TRUEX Model; and (3) writing a report on the use of the SPACE worksheet and the sources for the correlations used there.

D. Data Base Development (W. B. Seefeldt)

The success of the TRUEX process and the development of models useful to designing flowsheets is strongly dependent on the quality and the retrievability of underlying measurements of distribution coefficients of the many chemical species likely to be present.

A program was initiated to collect all such information and enter it, if judged to be reliable, into a data base using the software package 4th Dimension™ (ACI, Acius Inc.) on a Macintosh computer. The data were obtained from the literature and our own laboratory measurements. The design of the data base will place strong emphasis on including various modes of retrievability and anticipated report formats useful to the project.

The data base is intended to be used by at least four customer types: program managers responsible for developing and implementing TRUEX processes, individual experimenters who measure distribution coefficients, modelers who develop the algorithms useful to the design of TRUEX flowsheets, and quality assurance auditors. The ability to rapidly identify categories of information in need of development is especially important to program managers and modelers.

The design of the structure of the data base has been completed and the data base is, in great part, now functional. Debugging continues, and further improvements to facilitate use are in progress. A feature yet to be added is the creation of text files for export to a graphics application.

Most of the distribution coefficient data generated by the Separation Science and Technology Group through September 1988 have been entered into the data base. Additions will be made as further data are generated.

E. Modeling of Extraction Data

Models of extraction data for use in the Generic TRUEX Model (GTM) are based on electrolyte activities so that extraction constants that are independent of aqueous phase composition can be derived. In large part, the necessary thermodynamic data are available in the literature. Reliable data for aluminum nitrate and ferric nitrate, however, are not available. For these electrolytes, it has been necessary to estimate their thermodynamic behavior. The methods for doing this are discussed below.

In other areas, models of nitric acid and metal extraction have been improved and expanded, and terms for aqueous-phase metal complexation and electrolyte association have been incorporated.

1. Activity Coefficients for $\text{Al}(\text{NO}_3)_3$ (D. J. Chaiko)

The literature has a limited amount of activity coefficient data³ for $\text{Al}(\text{NO}_3)_3$, which were obtained from water vapor pressure measurements through the Gibbs-Duhem equation. Aluminum hydrolysis, however, was not accounted for in the original data analysis. Therefore, it was necessary to estimate $\text{Al}(\text{NO}_3)_3$ activity coefficients from nitric acid extraction data. This was possible because of the poor extraction of Al^{3+} ($D_{\text{Al}} \approx 10^{-3}$). The procedure involved fitting the distribution ratio data for HNO_3 between $\text{HNO}_3/\text{Al}(\text{NO}_3)_3$ and $\text{HNO}_3/\text{NaNO}_3/\text{Al}(\text{NO}_3)_3$ mixtures and 0.25M CMPO-TCE and TRUEX-TCE at 25°C (see Figs. II-19 and II-20 for these data). For each measurement of the HNO_3 distribution coefficient, the nitric acid extraction model was used to calculate the nitric acid activities that would have been expected if the aqueous phase contained only HNO_3 . From these nitric acid activities, it was then possible to calculate the mean activity coefficients of $\text{Al}(\text{NO}_3)_3$ (in mixed $\text{HNO}_3/\text{Al}(\text{NO}_3)_3$ solutions). For each activity coefficient value, the Bromley ionic interaction parameter (B) was calculated.⁴ The B values tended to increase with ionic strength. However, they were quite close to the B value (0.0594) that is calculated from Bromley's correlation⁵ using the published individual ion interaction parameters B_{H^+} and δ_{H^+} :

$$B = B_{\text{H}^+} + B_{\text{Al}^{3+}} + (\delta_{\text{H}^+} + \delta_{\text{Al}^{3+}}) \quad (\text{II-1})$$

Over a broad range of ionic strengths, however, a single B value could not be used to represent the activity behavior of $\text{Al}(\text{NO}_3)_3$. For an ionic strength range of 0.5 to 3.6 molal, the experimental B value was 0.056 and increased to 0.1 at ionic strengths between 4 and 8 molal.

The range of ionic strengths over which $\text{Al}(\text{NO}_3)_3$ activity coefficient values have been obtained is 0.3-8.35 molal. These data are plotted in Fig. II-7. In this same figure, the data were fitted to the following equation:

$$\log \gamma_{\pm} = - \frac{|Z_+ Z_-| 0.5108 \sqrt{I}}{1 + B \sqrt{I}} + \beta I + CI^2 + DI^3 + EI^4 \quad (\text{II-2})$$

where Z_i is the ionic charge, I is the ionic strength, and B^* , β , C , D , and E are constants. These values are $B^* = 1.833$, $\beta = -0.07$, $C = 0.02$, $D = 0.00108$, and $E = -1.51 \times 10^{-4}$.

Fig. II-7. Activity Coefficients of $\text{Al}(\text{NO}_3)_3$ Determined from HNO_3 Extraction Measurements at 25°C

2. Activity Coefficients for $\text{Fe}(\text{NO}_3)_3$ (D. J. Chaiko)

In addition to aluminum nitrate data, there is also a lack of published activity data for ferric nitrate. Unfortunately, the activity coefficients of this electrolyte could not be measured from nitric acid extraction data using either CMPO or TBP, as in the case of $\text{Al}(\text{NO}_3)_3$, because of significant coextraction of iron.

To estimate a $B(\text{Fe}^{3+})$ value, we used the correlation suggested by Bromley,⁵ in which B_+ values are plotted as a function of the product between the ionic entropies of individual ions (S°) and the ionic charge (Z), as shown in Fig. II-8. The entropies were obtained from Latimer⁶ and are based on the convention $S^\circ(\text{H}^+, \text{aq}) = 0$.

This approach gives a B_+ value for Fe^{3+} of 0.062. The δ values used in Eq. II-1 for cations are typically around 0.2 with very little variation except for the heavy alkali metals, which have δ values near zero. For Fe^{3+} , δ_+ was therefore taken to be 0.2. The estimated B value for $\text{Fe}(\text{NO}_3)_3$ was calculated as:

$$B = (0.062) + (-0.025) + (0.2)(0.27) = 0.091 \quad (\text{II-3})$$

Fig. II-8. Plot of B^+ vs. Ionic Entropy Times Ionic Charge

The activity behavior of $\text{Fe}(\text{NO}_3)_3$ should be very similar to that of $\text{Cr}(\text{NO}_3)_3$, given that the cations are both in a III valance state and their ionic radii are very similar (i.e., 0.64 Å for Fe^{3+} and 0.63 Å for Cr^{3+}). Bromley⁴ reports a B value of 0.0919 for $\text{Cr}(\text{NO}_3)_3$, which is very close to the B value estimated here for $\text{Fe}(\text{NO}_3)_3$.

In the absence of any thermodynamic data for $\text{Al}(\text{NO}_3)_3$ and $\text{Fe}(\text{NO}_3)_3$, it was necessary to use the approximations as described above. These electrolytes are major components in a number of TRU and high-level waste streams and, as such, demand further attention. Current plans call for the measurement of activity data by vapor pressure osmometry techniques.

3. Nitric Acid Extraction (D. J. Chaiko)

a. Extraction by TBP-Dodecane

Estimates of the extraction constants for the HNO_3/TBP system were originally developed using literature data for various TBP concentrations in AMSCO 125-85 as the diluent.⁷ Since this diluent is a branched hydrocarbon, we believed that the differences in the physicochemical properties of AMSCO and the Conoco-NPH diluent might be large enough to warrant a reevaluation of the extraction constants. This reevaluation was done using TBP-dodecane solutions at 1.4 and 0.7M TBP. Organic-phase nitric acid concentrations were measured directly with a nonaqueous titration method and tetrabutylammonium hydroxide as titrant.* Direct titration of the organic phase greatly extends the usable range of the extraction data in the region of low acid concentration. This is very important for increasing the reliability of the extraction constants. This enables one to curve fit for KT_2 [the equilibrium constant for the formation of $(\text{TBP})_2 \cdot \text{HNO}_3$] in a region where acid extraction is dominated by this species. An extraction model⁷ based on the formation of the species $(\text{TBP})_2 \cdot \text{HNO}_3$ and $\text{TBP} \cdot \text{HNO}_3$ was fitted to the extraction data. This fitting was done using a least squares criteria (i.e., $\sum ([\text{H}^+]_{\text{meas}} - [\text{H}^+]_{\text{calc}})^2$) which gave a weighting that was proportional to $[\text{H}^+]$ and was judged appropriate

*Data were collected by Sheila Lorton, a Summer Research Participant from Olivet Nazarene University, Kankakee, Illinois.

since the uncertainty in $[\overline{\text{H}^+}]$ was greatest at the lowest organic acid concentrations. However, giving equal weighting to all the data points by minimizing the function $\Sigma(1 - [\overline{\text{H}^+}]_{\text{meas}}/[\overline{\text{H}^+}]_{\text{calc}})^2$ gave somewhat similar constants (see Table II-1). Plots of the experimental data and the model calculations are shown in Fig. II-9. The model fits quite well with a single set of extraction constants for both 0.7 and 1.4M TBP. The fit is good enough, in fact, to suggest that the model can be considered to be independent of the organic-phase TBP concentration.

Table II-1. Equilibrium Constants for HNO_3 Extraction by TBP-Dodecane at 25 °C

Species	Value
$\text{TBP} \cdot \text{HNO}_3$	$\text{KT1} = 0.181 \pm 0.002^{\text{a}}; 0.169 \pm 0.02^{\text{b}}$
$(\text{TBP})_2 \cdot \text{HNO}_3$	$\text{KT2} = 0.356 \pm 0.009^{\text{a}}; 0.46 \pm 0.03^{\text{b}}$

^aObtained by $\Sigma([\overline{\text{H}^+}]_{\text{meas}} - [\overline{\text{H}^+}]_{\text{calc}})^2$ criteria

^bObtained by $\Sigma(1 - [\overline{\text{H}^+}]_{\text{meas}}/[\overline{\text{H}^+}]_{\text{calc}})^2$ criteria.

The extraction constants obtained for the AMSCO 125-85 system were $\text{KT1} = 0.185$, $\text{KT2} = 0.444$.⁷

Fig. II-9. Nitric Acid Extraction by TBP-Dodecane at 25 °C. The extraction constants were $\text{KT1} = 0.181$ and $\text{KT2} = 0.356$.

b. Extraction by CMPO-Dodecane

Data for the acid extraction by CMPO-dodecane solutions* were modeled using the same model developed previously for the TCE-based solvent system.⁸ Because of third-phase formation, however, the highest aqueous acid concentration was limited to 3M. In addition, the extractions were done at 50° C to inhibit third-phase formation to as high an acid concentration as possible. It should be noted that the presence of TBP in the TRUEX solvent inhibits third-phase formation to an acid concentration of ~8M at 25° C. Earlier work indicated that HNO₃ extraction by the TRUEX-NPH solvent was independent of temperature in the range of 20-65° C.⁹ This was assumed to also be the case for the CMPO-dodecane solutions. For the modeling calculations, acid activities were calculated at 25° C, even though the extractions were done at 50° C.

Because of the limit on the highest aqueous acid concentration permitted, we could not determine a value for KC2, the constant for the formation of the organic-phase species CMPO·2HNO₃. The values for KC1 (CMPO·HNO₃) and KC3 [(CMPO)₂·HNO₃] were 1.89 and 4.63, respectively. An estimate for KC2 was obtained by fitting TRUEX-NPH data. The use of KC2 obtained in this way had little effect on the model's fit to the CMPO-dodecane data. Figure II-10 shows the excellent fit of the model to the extraction data.

The increasing importance of dimer formation for the NPH diluent is evidenced by the changes in KC3 between the TCE and NPH systems. For CMPO dissolved in TCE, KC3 had a value of 1.66 and increased almost three-fold, to 4.63, for CMPO dissolved in dodecane. It is not known for sure what effect, if any, temperature has on the extraction constants, although there is no particular reason to believe that a change in temperature from 25 to 50° C would have a significant effect. Experimental data have shown that nitric acid extraction by TRUEX-TCE and TRUEX-NPH solvents is independent of temperature; more importantly, however, it is not known if the extraction constants are dependent upon CMPO concentration. For experiments at higher CMPO concentrations, third-phase formation occurs at lower HNO₃ concentrations, and lowering CMPO concentration (i.e., lowering the likelihood of third-phase formation) results in too little acid being extracted into the organic phase for accurate measurement. The dependence on CMPO concentration will be examined in the TCE system, where third-phase formation is not a problem.

c. Extraction by TRUEX-NPH

The TRUEX-NPH system was modeled by combining the separate models for TBP and CMPO. The TRUEX extraction data were then used to obtain KM (CMPO·HNO₃·TBP) and KC2 (CMPO·2HNO₃). The values of these constants were KC2 = 4.4×10^{-2} and KM = 1.74 (25° C). Changing the diluent from TCE to NPH had almost no effect on KM (its value for TRUEX-TCE was 1.75) but resulted in a four-fold increase in KC2.

The curve fitting showed, as demonstrated earlier for the TRUEX-TCE solvent, that independent extraction models for CMPO and TBP can be combined to predict HNO₃ extraction by a TRUEX solvent. Figure II-11 shows the fit of the model to the acid extraction data. Extraction of nitric acid between TRUEX-NPH and HNO₃/NaNO₃, as well as TRUEX-NPH and HNO₃/NaNO₃/Al(NO₃)₃, was also calculated. Again, a good fit between the model and the data was obtained. The results are given in Tables II-2 and II-3.

*Data were collected by Sheila Lorton, a Summer Research Participant from Olivet Nazarene University, Kankakee, Illinois.

Fig. II-10. Nitric Acid Extraction by 0.25M CMPO-Dodecane at 50° C
($KC1 = 1.89$, $KC2 = 4.4 \times 10^{-2}$, $KC3 = 4.63$)

Fig. II-11. Nitric Acid Extraction by TRUEX-NPH at 25° C

Table II-2. Nitric Acid Extraction by TRUEX-NPH from $\text{HNO}_3/\text{NaNO}_3$ Mixtures at 25 °C

$[\text{HNO}_3], \underline{\text{M}}$	$[\text{NaNO}_3], \underline{\text{M}}$	$[\text{HNO}_3], \underline{\text{M}}$	
		Data	Model
1	2	0.62	0.65
2	1	0.83	0.86
1	4	0.82	0.83
2	3	1.04	1.05
3	2	1.19	1.22
4	1	1.27	1.35

Table II-3. Nitric Acid Extraction by TRUEX-NPH from $\text{HNO}_3/\text{NaNO}_3/\text{Al}(\text{NO}_3)_3$ Mixtures at 25 °C

$[\text{HNO}_3], \underline{\text{M}}$	$[\text{NaNO}_3], \underline{\text{M}}$	$[\text{Al}(\text{NO}_3)_3], \underline{\text{M}}$	$[\text{HNO}_3], \underline{\text{M}}$	
			Data	Model
1	1.6	0.8	0.97	1.04
2	1.2	0.6	1.14	1.21
3	0.8	0.4	1.22	1.31
4	0.4	0.2	1.30	1.39

4. Extraction of Yttrium, Lanthanum, and the Lanthanides (L. Reichley-Yinger)

The first phase of the development of the TRUEX-NPH and TRUEX-TCE extraction models for Y, La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd has been completed. Since these metals behave very similarly to americium, the chemical equilibria used in the models were assumed to be the same as those used to model the extraction of americium. As a result of this assumption, the distribution ratio equations for the TRUEX-NPH and TRUEX-TCE models are identical to those for americium. Therefore, development of the extraction models consisted of obtaining the values of the equilibrium constants from the experimental distribution data.

The TRUEX-NPH and the TRUEX-TCE extraction models include four equilibria for metal ion extraction:

where the overbar indicates an organic species. A fifth equilibrium was required in the TRUEX-NPH model:

Five equilibria for the complexation of the metal ions in the aqueous phase were also incorporated into both models:

The M in these equilibria represents the trivalent metal cation involved.

From these ten equilibria, the following expression has been derived for the metal distribution ratios between TRUEX-NPH and aqueous phases containing nitric, hydrofluoric, phosphoric, oxalic, and sulfuric acids:

$$D_{M(III)} = \frac{\{NO_3^-\}^3 [CMPD]_f^3}{\{H_2O\}^9} \left[K_0 + K_1 \{H^+\} \{NO_3^-\} + K_2 \{H^+\}^2 \{NO_3^-\}^2 + K_3 \{H^+\}^3 \{NO_3^-\}^3 \right. \\ \left. + K_4 \{H^+\}^2 \{NO_3^-\}^2 / [CMPD]_f \right] / \left[1 + \beta_1 \{NO_3^-\} / \{H_2O\} \right. \\ \left. + \beta(HF) [HF] / (\{H^+\} \{H_2O\}) + \beta(H_2PO_4) [H_2PO_4^{2-}] / (\{H^+\} \{H_2O\}) \right. \\ \left. + \beta(Ox) [HC_2O_4^-] / (\{H^+\} \{H_2O\}^6) + \beta(HSO_4) [HSO_4^-] / \{H_2O\}^4 \right] \quad (II-14)$$

where the brackets and braces stand for concentration and activity of a species, respectively. The distribution ratio expression for TRUEX-TCE is the same as that for TRUEX-NPH, but without the K_4 term.

The equilibrium constants (K_0 , K_1 , K_2 , K_3 , and K_4) for the TRUEX-NPH model were obtained from distribution data determined between TRUEX-NPH and HNO_3 -only solutions. For Y, Ce, and Pm, these five constants were obtained by varying the value of the constants until the calculated curve fit the experimental distribution data for aqueous phases containing 0.1 to 8M HNO_3 . The constants for La, Pr, Nd, Sm, and Eu were obtained from experimental data for aqueous phases containing 0.1 to 1.0M HNO_3 . The values of the constants were initially assumed to be the same as those for either cerium or promethium. The K values were then varied slightly until the calculated curve fit the experimental data. Because no distribution data were available for gadolinium, the constants were assumed to be the same as those for europium. Since all the equilibrium constants were obtained from a limited amount of data, each constant could vary by as much as 100%. Even with this amount of uncertainty in individual constants, the models that used all the constants were able to predict the measured distribution ratios for the HNO_3 -only system rather well. The calculated distribution ratios differed from the experimental data by <15% for Y, Ce, and Pm and by <30% for La, Pr, Nd, Sm, and Eu. Table II-4 summarizes the K values determined for the TRUEX-NPH model.

The four constants (K_0 , K_1 , K_2 , and K_3) for the TRUEX-TCE models were obtained from the TRUEX-TCE distribution data in a way similar to that used for the TRUEX-NPH models. The constants for cerium and promethium were obtained by varying the values of the constants until the calculated curve fit the experimental distribution data for aqueous phases containing 0.1 to 8M HNO_3 . The constants for Y, La, Pr, Nd, Sm, and Eu were obtained from literature data for aqueous phases containing 1.0, 3.1, and 6.0M HNO_3 .¹⁰ The values of the constants were initially assumed to be the same as those for either cerium or promethium. The K values were then varied slightly until the calculated curve fit the experimental data. As was the case for the TRUEX-NPH model, the gadolinium constants were assumed to be the same as those for europium since no distribution data were available. Since all the equilibrium constants were obtained from a limited amount of data, they could vary by as much as 100%. Even with this amount of uncertainty in the constants, the models were able to predict the measured distribution ratios to better than 15%. Table II-5 summarizes the K values determined for the TRUEX-TCE model.

The aqueous-phase equilibrium constant, β_1 , which should be independent of the solvent used, was determined from the TRUEX-NPH and TRUEX-TCE distribution data for cerium in 0.1 and

0.2M HNO₃. The TRUEX-NPH results gave a β_1 value of 40.5, while the TRUEX-TCE results gave a β_1 value of 39.7. A value of 40 was assumed for yttrium and promethium, which had much greater uncertainties in their β_1 values, and for the remaining metals, which had insufficient data to determine β_1 values. No data were available from which $\beta(\text{HF})$, $\beta(\text{HSO}_4)$, $\beta(\text{H}_2\text{PO}_4)$, and $\beta(\text{Ox})$ could be obtained; until distribution data become available, these constants are assumed to be equal to the β values for americium.

Table II-4. Equilibrium Constants for Metal Extraction by TRUEX-NPH from HNO₃

Metal Ion	β_1^a	K_0^b	K_1^c	K_2^d	K_3^e	K_4^f
Y(III)	40	8.5×10^4	6.8×10^5	8.5×10^4	0	140
La(III)	40	7×10^5	3×10^6	2×10^5	7×10^3	80
Ce(III)	40	1.0×10^6	6.5×10^6	2.4×10^5	7.3×10^3	32
Pr(III)	40	9×10^5	6×10^6	2×10^5	7×10^3	80
Nd(III)	40	9×10^5	6×10^6	2×10^5	7×10^3	80
Pm(III)	40	8.2×10^5	6.5×10^6	2.4×10^5	7.6×10^3	100
Sm(III)	40	9×10^5	6×10^6	2×10^5	7×10^3	80
Eu(III)	40	8×10^5	4×10^6	2×10^5	7×10^3	80
Gd(III)	40	9×10^5	6×10^6	2×10^5	7×10^3	80

^aFor the formation of $\text{M}(\text{NO}_3)(\text{H}_2\text{O})_8^{2+}$.

^bFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3$.

^cFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3(\text{HNO}_3)$.

^dFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3(\text{HNO}_3)_2$.

^eFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3(\text{HNO}_3)_3$.

^fFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3(\text{HNO}_3)_2$.

Table II-5. Equilibrium Constants for Metal Extraction by TRUEX-TCE from HNO₃

Metal Ion	β_1^a	K_0^b	K_1^c	K_2^d	K_3^e
Y(III)	40	9.2×10^4	9.9×10^4	6.6×10^3	0
La(III)	40	2×10^5	3×10^5	4×10^2	10
Ce(III)	40	3.9×10^5	4.6×10^5	2.3×10^3	30
Pr(III)	40	4×10^5	6×10^5	2×10^3	30
Nd(III)	40	4×10^5	6×10^5	4×10^3	35
Pm(III)	40	7.0×10^5	6.9×10^5	8.7×10^3	69
Sm(III)	40	3×10^5	7×10^5	6×10^3	50
Eu(III)	40	4×10^5	6×10^5	7×10^3	50
Gd(III)	40	4×10^5	6×10^5	7×10^3	50

^aFor the formation of $\text{M}(\text{NO}_3)(\text{H}_2\text{O})_8^{2+}$.

^bFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3$.

^cFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3(\text{HNO}_3)$.

^dFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3(\text{HNO}_3)_2$.

^eFor the formation of $\text{M}(\text{NO}_3)_3(\text{CMPO})_3(\text{HNO}_3)_3$.

5. Stability Constants for Am³⁺, Pu⁴⁺, and Np⁴⁺
(I. R. Tasker)

Data necessary for the calculation of stability constants (β values) of complex species of transuranic elements were collected from the literature. The focus of the search was upon solvent extraction data for an acid extractant. The data sources and extractants used are summarized in Table II-6.

Table II-6. Data Sources for Calculation of Stability Constants

	Am ³⁺	Pu ⁴⁺	Np ⁴⁺
NO ₃ ⁻	Peppard ¹¹ (HDO ϕ P) ^a	Danesi ¹² (HTTA) ^b	Shilin ¹³ (HTTA) ^b
F ⁻	Aziz ¹⁴ (HDEHP) ^c	--	--
SO ₄ ²⁻	Sekine ¹⁵ (HTTA) ^{b,d}	--	Sullivan ¹⁶ (HTTA) ^b
C ₂ O ₄ ²⁻	Sekine ¹⁷ (HTTA) ^{b,d}	--	Bansal ¹⁸ (HTTA) ^b

^adi[para (1,1,3,3-tetramethylbutyl)phenyl]phosphoric acid.

^bThenoyltrifluoroacetone.

^cbis(2-ethylhexyl)phosphoric acid.

^dUsing TBP as synergist.

For the vacant spaces in Table II-6, no solvent extraction data were available. It was planned to take data from other sources (e.g., ion exchange data) to obtain the missing information. The references listed in Table II-6 give experimental data and calculated β values (stoichiometric stability constants) in terms of concentrations. The GTM attempts a more rigorous representation of the underlying physicochemical basis of the extraction procedure by using, when available, thermodynamic activities rather than concentrations in the equilibrium constant equations. This, in theory, permits a wider range of conditions to be more accurately modeled. Thus, the β values in the listed references could not be used directly; rather, their underlying experimental data needed to be reworked into terms appropriate for GTM.

In this report period, only the quasi-thermodynamic overall stability constants for the systems Am(III)/NO₃⁻, Pu(IV)/NO₃⁻, and Am(III)/SO₄²⁻ were determined. Calculations for the remaining systems, i.e., Np(IV)/NO₃⁻, Np(IV)/SO₄²⁻, Np(IV)/C₂O₄²⁻, Am(III)/F⁻, and Am(III)/C₂O₄²⁻, were not pursued since, in the light of calculations already performed, we decided that the approach being taken did not yield the quantity and quality of data available for the subsequent modeling of the extraction processes. Details of the calculations used in the three systems that were reworked are given below.

a. Am(III)/NO₃⁻

The stability constants (β_1) for americium nitrate were calculated from the data in Table II-7. The first two columns are taken from Peppard et al.¹¹ Peppard uses thenoyltrifluoro-acetone (HTTA) as extractant. The extraction is represented by the reaction:

with an "equilibrium constant," K' , of

$$K' = \frac{[\overline{\text{Am}(\text{TTA})}_3] \{\text{H}^+\}^3 \{\text{H}_2\text{O}\}^n}{[\text{Am}_{(\text{aq})}^{3+}] [\overline{\text{HTTA}}]^3} \quad (\text{II-16})$$

In the presence of NO₃⁻ in the aqueous phase, complexation equilibria occur:

Table II-7. Data Used in Determining Stability Constants for Am(NO₃)₃²⁺

C(NO ₃) ^a	1/K ^b	M(NO ₃) ^c	D ^d	ρ ^e	{H ⁺ } ^f	{H ₂ O} ^f	{NO ₃ ⁻ } ^f	LHS ^g
0.000	2.968	0.00	0.337	1.0752	0.8642	0.9619	0.000	-0.027
0.052	3.393	0.05	0.295	1.0729	0.8611	0.9620	0.036	0.124
0.102	3.634	0.10	0.275	1.0707	0.8518	0.9621	0.072	0.242
0.201	4.043	0.21	0.247	1.0663	0.8257	0.9623	0.152	0.514
0.304	4.439	0.31	0.225	1.0617	0.8079	0.9626	0.224	0.769
0.404	5.374	0.42	0.186	1.0572	0.7889	0.9628	0.304	1.297
0.505	5.735	0.52	0.174	1.0528	0.7719	0.9631	0.376	1.609
0.602	6.308	0.62	0.159	1.0484	0.7554	0.9633	0.449	2.057
0.701	6.713	0.72	0.149	1.0440	0.7391	0.9636	0.521	2.463
0.803	7.138	0.83	0.140	1.0395	0.7217	0.9638	0.601	2.948
0.899	7.924	0.93	0.126	1.0352	0.7062	0.9641	0.673	3.664
1.000	8.176	1.03	0.122	1.0307	0.6910	0.9643	0.746	4.127

^aConcentration of nitrate in mol/L.

^bThe reciprocal of the D value adjusted to 1M H⁺ and extractant concentration.

^cMolality of nitrate ion.

^dDistribution ratio calculated from Peppard data.¹¹

^eDensity in g/mL.

^fActivity.

^gLeft-hand side of Eq. II-31.

$$\beta_1 = \frac{[\text{AmNO}_3^{2+}] \{ \text{H}_2\text{O} \}^x}{[\text{Am}^{3+}] \{ \text{NO}_3^- \}} \quad (\text{II-18})$$

$$\beta_2 = \frac{[\text{Am}(\text{NO}_3)_2^+] \{ \text{H}_2\text{O} \}^x}{[\text{Am}^{3+}] \{ \text{NO}_3^- \}^2} \quad (\text{II-20})$$

In the presence of TBP in the organic phase, adduct formation equilibria occur:

$$\beta_{A1} = \frac{[\overline{\text{Am}(\text{TTA})_3(\text{TBP})}]}{[\overline{\text{Am}(\text{TTA})_3}] [\overline{\text{TBP}}]} \quad (\text{II-22})$$

$$\beta_{A2} = \frac{[\overline{\text{Am}(\text{TTA})_3(\text{TBP})_2}]}{[\overline{\text{Am}(\text{TTA})_3}] [\overline{\text{TBP}}]^2} \quad (\text{II-24})$$

For Am(III), the distribution ratio D is

$$D = \frac{\Sigma [\overline{\text{Am}}]}{\Sigma [\text{Am}]} \quad (\text{II-25})$$

For the organic phase, from mass balance considerations,

$$\Sigma [\overline{\text{Am}}] = [\overline{\text{Am}(\text{TTA})_3}] (1 + \beta_{A1} [\overline{\text{TBP}}] + \beta_{A2} [\overline{\text{TBP}}]^2 \dots) \quad (\text{II-26})$$

Similarly, for the aqueous phase

$$\Sigma [\text{Am}] = [\text{Am}^{3+}] \left(1 + \beta_1 \frac{\{ \text{NO}_3^- \}}{\{ \text{H}_2\text{O} \}^x} + \beta_2 \frac{\{ \text{NO}_3^- \}^2}{\{ \text{H}_2\text{O} \}^x} \dots \right) \quad (\text{II-27})$$

Summing all the organic species (Eqs. II-16, -22, and -24) in the numerator of Eq. II-25 and summing all the aqueous species (Eqs. II-18 and II-20) in the denominator give the following equation:

$$D = \frac{K' [Am^{3+}] [\overline{HTTA}]^3 (1 + \beta_{A1} [\overline{TBP}] + \beta_{A2} [\overline{TBP}]^2 \dots)}{\{H^+\}^3 \{H_2O\}^n [Am^{3+}] (1 + \beta_1 \frac{\{NO_3^-\}}{\{H_2O\}^x} + \beta_2 \frac{\{NO_3^-\}^2}{\{H_2O\}^x} \dots)} \quad (II-28)$$

In the absence of NO_3^- , the β terms in the denominator drop out, giving

$$D_o = \frac{K' [\overline{HTTA}]^3 (1 + \beta_{A1} [\overline{TBP}] + \beta_{A2} [\overline{TBP}]^2 \dots)}{\{H^+\}_o^3 \{H_2O\}_o^n} \quad (II-29)$$

Dividing Eq. II-29 by II-28 gives the form:

$$\frac{D_o}{D} = \left[\frac{\{H^+\}}{\{H^+\}_o} \right]^3 \cdot \left[\frac{\{H_2O\}}{\{H_2O\}_o} \right]^n \cdot \left[1 + \frac{\beta_1 \{NO_3^-\}}{\{H_2O\}^x} + \frac{\beta_2 \{NO_3^-\}^2}{\{H_2O\}^x} \dots \right] \quad (II-30)$$

Upon rearrangement this gives:

$$\left[\frac{D_o}{D} \cdot \left[\frac{\{H_{aq}^+\}_o}{\{H_{aq}^+\}} \right]^3 \cdot \left[\frac{\{H_2O\}_o^n}{\{H_2O\}} - 1 \right] \right] = \beta_1 \left[\frac{\{NO_{3(aq)}^-\}}{\{H_2O\}^x} \right] + \beta_2 \left[\frac{\{NO_{3(aq)}^-\}^2}{\{H_2O\}^x} \right] \quad (II-31)$$

As mentioned previously, Peppard's experimental data are listed in columns 1 and 2 of Table II-7. The fourth column, D, is the reciprocal of 1/K. The columns headed $M(NO_3^-)$, ρ , $\{H^+\}$, $\{H_2O\}$, and $\{NO_3^-\}$ were all calculated using algorithms developed by the Separation Science and Technology Group. Activities were calculated by the method of others.^{19,20} The final column, LHS, is the left-hand side of Eq. II-31 where $D_o = 0.3279$ from a fit of $C(NO_3^-)$ vs. $1/K$; the terms $n = 9$ and $x = 1$ come from the following stoichiometries:

For n,

where $HDO\phi P$ is di[para(1,1,3,3-tetramethyl butyl) phenyl] phosphoric acid.

For x,

The value of $x = 1$ was used to maintain consistency with other work on modeling americium extraction. A value of $x = 6$ was tested after consideration of the work of Marcus^{21,22} but did not significantly affect the results. The data fit the equation

$$\left(\frac{D_o}{D} \cdot \left(\frac{\{\text{H}^+_{(\text{aq})}\}_o}{\{\text{H}^+_{(\text{aq})}\}} \right)^3 \cdot \left(\frac{\{\text{H}_2\text{O}\}_o}{\{\text{H}_2\text{O}\}} \right)^9 - 1 \right) =$$

$$0.085 + 2.87 \cdot \left(\frac{\{\text{NO}_3^-_{(\text{aq})}\}}{\{\text{H}_2\text{O}\}} \right) + 3.24 \cdot \left(\frac{\{\text{NO}_3^-_{(\text{aq})}\}}{\{\text{H}_2\text{O}\}} \right)^2 \quad (\text{II-34})$$

with $R^2 = 0.999$.

In conclusion, the stability constant for the $\text{Am}(\text{NO}_3)_2^{2+}$ species (β_1) is 2.87, and that for the $\text{Am}(\text{NO}_3)_3^+$ species (β_2) is 3.24.

b. Pu(IV)/NO₃

The data treatment for determination of pseudo-thermodynamic overall stability constants for Pu(IV)/NO₃ is similar to that given for Am(III)/NO₃ above. Hence,

$$K = \frac{[\overline{\text{Pu}(\text{TТА})}_4] \{\text{H}^+\}^4 \{\text{H}_2\text{O}\}^9}{\{\text{Pu}^{4+}\} [\overline{\text{HTTA}}]^4} \quad (\text{II-36})$$

$$D = \frac{[\overline{\text{Pu}}]}{[\text{Pu}]} \quad (\text{II-37})$$

$$[\overline{\text{Pu}}] = [\overline{\text{Pu}(\text{TТА})}_4] = \frac{K \{\text{Pu}^{4+}\} [\overline{\text{HTTA}}]^4}{\{\text{H}^+\}^4 \{\text{H}_2\text{O}\}^9} \quad (\text{II-38})$$

In the absence of NO_3^- in the aqueous phase (indicated by subscript o), no complexation of Pu^{4+} occurs; thus,

$$[\text{Pu}] = [\text{Pu}^{4+}] \quad (\text{II-39})$$

$$D_o = \frac{K [\text{HTTA}]^4}{\{\text{H}^+\}_o^4 \{\text{H}_2\text{O}\}_o^9} \quad (\text{II-40})$$

where it is assumed that $[\text{HTTA}]$ will remain constant throughout the experiments, while $\{\text{H}^+\}$ and $\{\text{H}_2\text{O}\}$ will vary. With aqueous-phase NO_3^- present, complexation equilibria occur:

$$\beta_1 = \frac{[\text{Pu}(\text{NO}_3)^{3+}] \{\text{H}_2\text{O}\}}{[\text{Pu}^{4+}] \{\text{NO}_3^-\}} \quad (\text{II-42})$$

$$\beta_2 = \frac{[\text{Pu}(\text{NO}_3)_2^{2+}] \{\text{H}_2\text{O}\}^2}{[\text{Pu}^{4+}] \{\text{NO}_3^-\}^2} \quad (\text{II-44})$$

Similarly,

$$\beta_3 = \frac{[\text{Pu}(\text{NO}_3)_3^+] \{\text{H}_2\text{O}\}^3}{[\text{Pu}^{4+}] \{\text{NO}_3^-\}^3} \quad (\text{II-45})$$

Since $[\text{Pu}] = \Sigma \text{Pu aqueous species}$,

$$\text{Pu} = [\text{Pu}^{4+}] + [\text{Pu}(\text{NO}_3)^{3+}] + [\text{Pu}(\text{NO}_3)_2^{2+}] + [\text{Pu}(\text{NO}_3)_3^+] \quad (\text{II-46})$$

then

$$[\text{Pu}] = [\text{Pu}^{4+}] \left[1 + \beta_1 \frac{\{\text{NO}_3^-\}}{\{\text{H}_2\text{O}\}} + \beta_2 \left[\frac{\{\text{NO}_3^-\}}{\{\text{H}_2\text{O}\}} \right]^2 + \beta_3 \left[\frac{\{\text{NO}_3^-\}}{\{\text{H}_2\text{O}\}} \right]^3 \right] = [\text{Pu}^{4+}] (\Sigma \beta) \quad (\text{II-47})$$

Using Eqs. II-47 and II-38 in Eq. II-37 yields

$$D = \frac{K [\overline{\text{HTTA}}]}{\{\text{H}^+\}^4 \{\text{H}_2\text{O}\}^9 (\Sigma\beta)} \quad (\text{II-48})$$

$$\frac{D_o}{D} = \frac{\{\text{H}^+\}_o^4 \{\text{H}_2\text{O}\}_o^9 (\Sigma\beta)}{\{\text{H}^+\}^4 \{\text{H}_2\text{O}\}^9} \quad (\text{II-49})$$

$$\left(\frac{D_o}{D} \frac{\{\text{H}^+\}_o^4}{\{\text{H}^+\}^4} \frac{\{\text{H}_2\text{O}\}_o^9}{\{\text{H}_2\text{O}\}^9} \right) - 1 =$$

$$\beta_1 \frac{\{\text{NO}_3^-\}}{\{\text{H}_2\text{O}\}} + \beta_2 \frac{\{\text{NO}_3^-\}^2}{\{\text{H}_2\text{O}\}} + \beta_3 \frac{\{\text{NO}_3^-\}^3}{\{\text{H}_2\text{O}\}} \quad (\text{II-50})$$

Table II-8. Data Used in Determination of Stability Constants for Pu(IV)NO₃

[HNO ₃], <u>M</u>	D	{NO ₃ }	{H ⁺ }	{H ₂ O}	LHS ^a	$\frac{[\text{NO}]}{[\text{H}_2\text{O}]}$
0.001	0.398445	0.0012	10.7630	0.7606	0.0033	0.0016
0.005	0.382523	0.0062	10.7552	0.7607	0.0469	0.0082
0.045	0.293474	0.0558	10.6800	0.7611	0.3968	0.0733
0.089	0.194659	0.1104	10.5997	0.7616	1.158	0.1450
0.175	0.124689	0.2172	10.4424	0.7626	2.534	0.2848
0.253	0.065308	0.3142	10.3003	0.7634	6.060	0.4116
0.410	0.036183	0.5102	10.0213	0.7652	12.92	0.6668
0.576	0.022069	0.7188	9.7313	0.7671	24.1	0.9370
0.850	0.011064	1.0631	9.2712	0.7702	57.62	1.3803
1.271	0.006894	1.5972	8.6016	0.7751	118.9	2.0606
1.611	0.003419	2.0382	8.0908	0.7793	293.3	2.6154
3.253	0.000807	4.1844	5.9805	0.8001	3293.0	5.2298

^aLeft-hand side of Eq. II-50.

Data in the first two columns of Table II-8 were obtained from Danesi et al.¹² A plot of [HNO₃] vs. 1/D was extrapolated to [HNO₃] = 0 to give D_o = 0.3994. The data for {H⁺} and {NO₃} were obtained from Bromley's model, while {H₂O} was obtained from Meissner's model. The LHS data for Eq. II-50 are plotted in Fig. II-12. Two data points were eliminated: the final solution in Table II-8 was rejected since its D was sufficiently small to carry with it considerable experimental error; the tenth solution was rejected on statistical grounds. The data in Table II-8 yield $\beta_1 = 9.54$, $\beta_2 = 5.80$, and $\beta_3 = 12.79$.

Fig. II-12. Plot of Left-Hand Side of Eq. II-50 vs. $\{\text{NO}_3\}\{\text{H}_2\text{O}\}$ for Plutonium Distribution Data from Danesi¹²

c. Am(III)/SO_4^{2-}

First and second overall stability constants (β_1 , β_2) for aqueous americium sulfate were calculated from literature data^{15,17} and the data treatment given previously for Am(III)/NO_3^- . Since the procedures and solution compositions given by Sekine^{15,17} are somewhat lacking in clarity, certain assumptions have been made:

- All solutions were prepared from 0.5M Na_2SO_4 stock.
- All solutions were diluted using 1.0M NaClO_4 stock.
- The effect of sulfanilic acid-sulfanilate buffer upon the activities of species other than H^+ was ignored; the effect of the buffer was to maintain pH constant at 3.5.

For the extraction, it was assumed that the hydration number of americium is 9; thus

Further, it was assumed that sulfate was a bidentate ligand; hence

In view of these assumptions, the equation for calculating β 's becomes

$$\frac{D_o}{D} \cdot \left[\frac{\{H_2O\}_o}{\{H_2O\}} \right]^9 - 1 = \beta_1 \frac{\{SO_4^{2-}\}}{\{H_2O\}^2} + \beta_2 \left[\frac{\{SO_4^{2-}\}}{\{H_2O\}} \right]^2 \quad (II-54)$$

Data used in the calculations are given in Table II-9, and results are plotted in Fig. II-13.

Table II-9. Data Used in Determining Stability Constants for $Am(III)SO_4^{2-}$

$\frac{D_o}{D}$	I ^a	$\{SO_4^{2-}\}$	$\{H_2O\}$	$\frac{\{H_2O\}_o}{\{H_2O\}}$ Ratio ^b	LHS ^c	$\frac{\{SO_4^{2-}\}}{\{H_2O\}^2}$
26.30	1.222	0.0175	0.9630	1.0367	26.27	0.0188
22.91	1.203	0.0159	0.9634	1.0331	22.67	0.0172
17.78	1.183	0.0144	0.9638	1.0296	17.31	0.0155
19.50	1.173	0.0135	0.9639	1.0281	19.05	0.0146
15.85	1.163	0.0127	0.9642	1.0256	15.25	0.0137
16.22	1.154	0.0119	0.9643	1.0241	15.61	0.0128
11.22	1.149	0.0115	0.9644	1.0232	10.48	0.0123
12.30	1.144	0.0111	0.9646	1.0221	11.57	0.0119
10.23	1.139	0.0107	0.9646	1.0216	9.45	0.0114
11.48	1.134	0.0102	0.9648	1.0202	10.71	0.0110
8.32	1.124	0.0094	0.9649	1.0191	7.48	0.0101
8.71	1.119	0.0089	0.9650	1.0180	7.87	0.0096
7.41	1.114	0.0085	0.9651	1.0166	6.54	0.0091
8.51	1.114	0.0085	0.9651	1.0166	7.65	0.0091
7.59	1.109	0.0081	0.9652	1.0162	6.71	0.0087
6.31	1.104	0.0076	0.9653	1.0151	5.40	0.0082
7.41	1.104	0.0076	0.9653	1.0151	6.52	0.0082
6.46	1.099	0.0072	0.9654	1.0144	5.55	0.0077
5.50	1.094	0.0067	0.9655	1.0133	4.57	0.0072
5.89	1.094	0.0067	0.9655	1.0133	4.97	0.0072
5.25	1.085	0.0058	0.9656	1.0117	4.31	0.0062
4.57	1.085	0.0058	0.9656	1.0117	3.62	0.0062
3.89	1.075	0.0049	0.9658	1.0100	2.93	0.0053
3.31	1.065	0.0040	0.9660	1.0082	2.34	0.0043
2.51	1.055	0.0030	0.9663	1.0059	1.53	0.0032
2.19	1.050	0.0025	0.9663	1.0054	1.20	0.0027
2.04	1.045	0.0021	0.9665	1.0042	1.05	0.0022
1.62	1.040	0.0016	0.9666	1.0029	0.63	0.0017
1.58	1.035	0.0011	0.9666	1.0025	0.59	0.0012
1.26	1.032	0.0008	0.9667	1.0020	0.26	0.0008
1.17	1.030	0.0006	0.9668	1.0013	0.18	0.0006
1.12	1.029	0.0004	0.9668	1.0008	0.12	0.0004

^aIonic strength on molal composition scale.

^bUsing $\{H_2O\}_o = 0.9669$.

^cLeft-hand side of Eq. II-59.

Fig. II-13. Plot of Data for Americium Extraction by HTTA

The data may be represented by:

$$\frac{D_o}{D} \cdot \left(\frac{\{H_2O\}_0}{\{H_2O\}} \right)^9 - 1 = 0.15861 + 179.69 \left(\frac{\{SO_4^{2-}\}}{\{H_2O\}} \right) + 65,487 \left(\frac{\{SO_4^{2-}\}}{\{H_2O\}} \right)^2 \quad (II-55)$$

with $R^2 = 0.985$, yielding $\beta_1 = 180$ and $\beta_2 = 6.55 \times 10_4$.

6. Extraction of Pu(IV) from TRUEX-TCE (I. R. Tasker)

A large amount of time was expended in an unsuccessful attempt to develop a theoretical model, with a sound underlying physicochemical basis, for the extraction of Pu(IV) by the TRUEX-TCE solvent. Because of the complexities in the plutonium chemistry, the available literature data were not sufficient to permit such a model to be developed. Eventually, an interim empirical model was developed.

In this effort, a plot of $\log (D_{Pu}/[CMPO]_{free}^2)$ vs. $\log \{NO_3^-\}$ was examined and found to have a slope of about two. For nitric acid solution alone, the data could be fit with a straight line in the form:

$$\log_{10} (D_{Pu} / [\overline{CMPO}]_{free}^2) = 5.4980 + 2.1269 (\log_{10} \{NO_3^-\}) \quad R^2 = 1.000 \quad (II-56)$$

The remaining constants for complexation of Pu(IV) in the aqueous phase by fluoride, sulfate, phosphate, and oxalate were calculated from the best fit of the model to the existing literature data. Therefore, the model adopted as an interim measure while more experimental data are collected is an empirical equation, shaped by the form of equations developed in prior attempts and adjusted in the light of results from lengthy slope analysis of individual data subsets. The equation is

$$D_{Pu} = \frac{K_o \{NO_3^-\}^2}{1 + B_1^N \{NO_3^-\} + B_2^N \{NO_3^-\}^2 + B_1^F [HF] + B_2^F [HF]^2 + B_1^{SN} \{HSO_4^-\} \{NO_3^-\} + B_1^S \{HSO_4^-\} + B_1^P \frac{[H_3PO_4]}{\{H^+\}} + B_2^P \left(\frac{[H_3PO_4]}{\{H^+\}} \right)^2 + B_1^{Ox} \frac{[HO_x]}{\{H^+\}} + B_2^{Ox} \left(\frac{[HO_x]}{\{H^+\}} \right)^2} \quad (II-57)$$

Values assigned to the constants are:

$$K_o = 14746.796$$

$$B_1^N = 0.408$$

$$B_2^N = 3.782$$

$$B_1^F = 85,360$$

$$B_2^F = 0.1032$$

$$B_1^{SN} = 544.7$$

$$B_1^S = 130.4$$

$$B_1^P = 2,366$$

$$B_2^P = 7.756 \times 10^{-7}$$

$$B_1^{Ox} = 8,603$$

$$B_2^{Ox} = 1,603$$

The following points should be noted:

1. The constants K_o , B_1^N , and B_2^N were first generated from a data subset consisting of experimental data on nitric acid alone and experimental data on nitric acid with 0.001M H_3PO_4 (at this low concentration, H_3PO_4 appears to have no effect). Much of these data were at D values in excess of 10^3 , a magnitude of D where data have a large uncertainty because of possible other-phase carryover. When data points were paired at a given nitric acid activity, the higher value of D was used since this is the more likely "correct" value with respect to errors produced by other-phase carryover.
2. Using the constants K_o , B_1^N , and B_2^N , a second data subset was used to determine B_1^F , B_2^F , B_1^{SN} , B_1^S , B_1^P , and B_2^P . Finally, a third data subset (incorporating K_o , B_1^N , and B_2^N) was used to determine B_1^{Ox} and B_2^{Ox} .
3. In calculating H^+ and NO_3^- activities, the effect of neutral species such as HF, H_3PO_4 , and $H_2C_2O_4$ was ignored.
4. The failure of the data to obey a fourth-power relationship with respect to nitrate concentration may be due to (1) dilution of tracer stock solutions, resulting in Pu(VI) or "plutonium polymer" being formed, and (2) a very strong dinitrate complex of plutonium present in even dilute nitric acid solutions.

7. Methods for Experimental Determination of Solute Thermodynamic Activities (I. R. Tasker)

Since the Generic TRUEX Model is based on solution chemistry, rather than mathematical or statistical correlations, and thermodynamic expressions are used to calculate the organic and aqueous

phase speciation, there is an obvious need to have available the appropriate thermodynamic quantities (i.e., the species activities) for the necessary chemical reactions. Much of the data needed are in the literature; some of what is missing can be estimated, but there is still the need to determine some important data experimentally. [Of particular importance are measurements on aluminum nitrate, iron(III) nitrate, and oxalic acid, and verification checks on typical solutions.] However, facilities available to us for activity measurements are limited. Specific ion electrodes can be used for some measurements; the solvent extraction technique can be used for others. It would be beneficial to possess a method for measuring activities that addresses the following experimental requirements:

1. Rapidity. Most methods of activity measurement require the establishment of true equilibrium conditions; in some cases (e.g., isopiestic measurements at low solute concentration) this attainment can be very slow.
2. Appropriate Accuracy. Some activity measurements methods are capable of exceedingly high accuracy but have certain drawbacks. Since the GTM models being used will only give activities to about 10%, the level of accuracy demanded from a technique need not be of the very highest degree.
3. Wide Concentration Range. Some methods used for activity measurement work only within a narrowly defined range of solute concentration. The GTM will operate over a wide range of concentrations and demands data over this range.
4. Variable Temperature. Temperature will be a variable in GTM. Some experimental methods have only been developed at one temperature; others (e.g., freezing point depression) are necessarily limited to one temperature. Activity data from such methods requires auxiliary thermodynamic data (enthalpies, heat capacity) to correct the data to the temperature of interest. Such data may not be available.
5. Flexibility. Some techniques work well but only for certain types of solute (e.g., emf techniques require ionic solutes). Also many techniques have been studied primarily using aqueous systems. For future work, where investigations may focus upon the organic phase, a flexible method is desirable. The available methods are listed below and are now being investigated for their suitability. (A further criterion involved in selection of the method is quality of commercially available equipment.)

Isopiestic Method

Freezing Point Depression

Osmotic Pressure Measurement

emf Cells with Transference

emf Cells without Transference

Bi-thermal Equilibration

Boiling Point Elevation

Solubility

Solute Vapor Pressure

Solvent/Solvent Distribution

Sedimentation Rate

Diffusion Rate

Capillarity Measurements

Vapor Pressure Osmometry

8. Speciation Considerations in Literature Data
(I. R. Tasker)

Care must be exercised in the use of some literature data for modeling purposes. An example is that of the activities of sulfuric acid solutions (necessary for the calculations involved in determining overall stability constants of systems involving sulfate). Activity coefficient (γ) and osmotic coefficient (ϕ) data for sulfuric acid²³ have been fitted to a general equation.²⁴ However, the literature

data were calculated based on the assumption that H_2SO_4 behaves as a 1:2 electrolyte, while under TRUEX conditions (and, in fact, the simple binary H_2O - H_2SO_4 system) H_2SO_4 behaves as a 1:1 electrolyte, yielding H^+ and HSO_4^- upon dissociation. Transformation of activity coefficients and osmotic coefficients from a 1:2 to a 1:1 basis is straightforward and is demonstrated below for the general case.

a. Activity Coefficients

Substance X ionizes completely in water to give v_1 moles of ion 1 and v_2 moles of ion 2:

For substance X,

$$\mu_x = \mu_x^\circ + RT \ln a_x \quad (\text{II-59})$$

where μ_x = chemical potential of X in water
 μ_x° = standard state chemical potential of X in water
 a_x = activity of X in water

For ion 1,

$$\mu_1 = \mu_1^\circ + RT \ln a_1 \quad (\text{II-60a})$$

For ion 2,

$$\mu_2 = \mu_2^\circ + RT \ln a_2 \quad (\text{II-60b})$$

Now

$$\begin{aligned} \mu_x &= v_1 \mu_1 + v_2 \mu_2 \quad (\text{II-61}) \\ &= v_1 (\mu_1^\circ + RT \ln a_1) + v_2 (\mu_2^\circ + RT \ln a_2) \\ &= (v_1 \mu_1^\circ + v_2 \mu_2^\circ) + RT(v_1 \ln a_1 + v_2 \ln a_2) \\ &= \mu_x^\circ + RT \ln [(a_1)^{v_1} (a_2)^{v_2}] \end{aligned}$$

where

$$\mu_x^\circ = v_1 \mu_1^\circ + v_2 \mu_2^\circ \quad (\text{II-62})$$

From Eqs. II-59 and II-61

$$a_x = (a_1)^{v_1} (a_2)^{v_2} \quad (\text{II-63})$$

Since $a_1 = m_1 \gamma_1$, $a_2 = m_2 \gamma_2$, $m_1 = \nu_1 m$, and $m_2 = \nu_2 m$, then $a_1 = \nu_1 \gamma_1 m$ and $a_2 = \nu_2 \gamma_2 m$. Thus,

$$a_x = (\nu_1 m \gamma_1)^{\nu_1} (\nu_2 m \gamma_2)^{\nu_2} \quad (\text{II-64})$$

or

$$a_x = m(\nu_1 + \nu_2)^{(\gamma_1^{\nu_1} \gamma_2^{\nu_2})} \nu_1^{\nu_1} \nu_2^{\nu_2} \quad (\text{II-65})$$

For substance X, μ_x° is self-defined and independent of the assumed stoichiometry of ionization. (In Eq. II-63, variations in ν_1 and ν_2 are compensated by variations in μ_1° and μ_2° , keeping μ_x° constant.)

For Case 1 (1:1 electrolyte),

$$\nu_1 = \nu_2 = 1 \quad (\text{II-66})$$

The mean ionic activity coefficient, $\gamma_{\pm}(1:1)$, is

$$\gamma_{\pm}(1:1)^2 = \gamma_1 \gamma_2 \quad (\text{II-67})$$

Equation II-65 thus becomes

$$a_x = m^2 \gamma_{\pm}(1:1)^2 \quad (\text{II-68})$$

For Case 2 (1:2 electrolyte),

$$\nu_1 = 2 \quad (\text{II-69})$$

$$\nu_2 = 1$$

Equation II-65 now becomes

$$a_x = 4m^3 \gamma_{\pm}(1:2)^3 \quad (\text{II-70})$$

where $\gamma_{\pm}(1:2)^3 = \gamma_1^2 \gamma_2$. Combining Eq. II-68 and II-70 gives

$$m^2 \gamma_{\pm}(1:1)^2 = 4m^3 \gamma_{\pm}(1:2)^3 \quad (\text{II-71})$$

$$\gamma_{\pm}(1:1) = 2m^{1/2} \gamma_{\pm}^{3/2}$$

b. Osmotic Coefficients

For a solvent with molar mass W

$$\ln a_s = \frac{-(v_1 + v_2) m W \phi}{1,000} \quad (\text{II-72})$$

where ϕ = osmotic coefficient
 m = molal composition
 a_s = activity of solvent

For 1:1 electrolyte,

$$\ln a_s = \frac{-2 m W \phi_{1:1}}{1,000} \quad (\text{II-73})$$

For 1:2 electrolyte,

$$\ln a_s = \frac{-3 m W \phi_{1:2}}{1,000} \quad (\text{II-74})$$

Hence,

$$\phi_{1:1} = 3/2 \phi_{1:2} \quad (\text{II-75})$$

c. Calculated Results

After the literature data were converted to a 1:1 electrolyte basis, we attempted to fit the following general equation²⁴ to the data:

$$\log_{10} \gamma = \frac{-|z_+ z_-| 0.5108 \sqrt{I}}{1 + B \sqrt{I}} + \beta I + C I^2 + D I^3 + E I^4 \quad (\text{II-76})$$

where B^* , β , C , D , and E are fitted coefficients.

The results are shown in Fig. II-14. The fit is very poor, and due to the nature of the data and Eq. II-56, no good fit can ever be obtained. Equation II-76 obliges $\log \gamma$ to tend toward zero as I tends toward zero. The data, at the lower end, are not approaching Debye-Huckel limiting behavior, probably due to dissociation of bisulfate ions into sulfate and hydrogen ions.

Next, we attempted to fit the following alternative equation,²⁴ used by Hamer and Wu for HF, to the data:

$$\log_{10} \gamma = 0.4342945 [a - 1 + 1/3 b m^{-3/2} + 3 c m^{1/2} + 2 d m] + (a - 1) \log_{10} m + I \quad (\text{II-77})$$

$$\phi = a + b m^{-3/2} + c m^{1/2} + d m \quad (\text{II-78})$$

where a , b , c , d , and I are fitted coefficients.

Fig. II-14. Calculated and Experimental Activity Coefficient vs. Ionic Strength for H_2SO_4 as a 1:1 Electrolyte

As shown in Fig. II-15, the fit for $\log_{10} \gamma$ was excellent. However, when the coefficients of fitting Eq. II-77 to the data were placed in Eq. II-78, the calculated low-end ϕ behavior was errant, as shown in Fig. II-16. It was decided to use the coefficients of this "whole range" fit to represent data above 4 molal and to perform a separate fit, again to Eq. II-77, for the low-end data. The coefficients from this fit were then employed in Eq. II-78 to predict ϕ . The agreement between the calculated and measured results was good, as shown in Figs. II-17 and II-18. Table II-10 lists the coefficients of Eq. II-77 with their applicable composition range. Table II-11 gives experimental and estimated osmotic and activity coefficients.

Fig. II-15. Calculated and Measured Activity Coefficient vs. Ionic Strength for H_2SO_4 as a 1:1 Electrolyte

Fig. II-16. Calculated and Measured Osmotic Coefficient vs. Ionic Strength for H_2SO_4 as a 1:1 Electrolyte

Fig. II-17. Calculated and Measured Activity Coefficient vs. Ionic Strength for H_2SO_4 as a 1:1 Electrolyte at Low Concentration

Fig. II-18. Calculated and Measured Osmotic Coefficient vs. Ionic Strength for H_2SO_4 as a 1:1 Electrolyte at Low Concentration

Table II-10. Coefficients Used in Eqs. II-77 and II-78 for Two Different Composition Ranges

	Coefficient Values	
	0-4 ^a	4-15 ^a
a	1.096	-0.25467
b	0.001708	-0.08557
c	-0.3367	1.02904
d	0.3256	-0.02587
I	-0.9061	-1.81576

^aComposition range in mol/kg H_2O .

Table II-11. Experimental and Estimated Activity and Osmotic Coefficients

mol/kg H ₂ O	ϕ		{H ₂ O}		log γ		γ	
	Expt. ^a	Est. ^b	Expt. ^a	Est. ^b	Expt. ^a	Est. ^b	Expt. ^a	Est. ^b
0.1	1.020	1.076	0.9963	0.9961	-1.063	-1.063	0.0865	0.0865
0.2	1.002	1.030	0.9928	0.9926	-1.068	-1.068	0.0855	0.0855
0.3	1.002	1.020	0.9892	0.9890	-1.068	-1.068	0.0855	0.0855
0.5	1.014	1.026	0.9819	0.9817	-1.061	-1.061	0.0869	0.0869
0.7	1.034	1.045	0.9743	0.9740	-1.049	-1.048	0.0893	0.0895
1.0	1.082	1.087	0.9618	0.9616	-1.020	-1.020	0.0955	0.0955
1.5	1.170	1.173	0.9387	0.9386	-0.959	-0.960	0.1099	0.1096
2.0	1.269	1.272	0.9126	0.9124	-0.890	-0.890	0.1288	0.1288
2.5	1.374	1.378	0.8836	0.8833	-0.814	-0.813	0.1535	0.1538
3.0	1.487	1.490	0.8515	0.8513	-0.731	-0.730	0.1858	0.1862
3.5	1.607	1.606	0.8166	0.8167	-0.643	-0.643	0.2275	0.2275
4.0	1.725	1.725	0.7799	0.7799	-0.552	-0.553	0.2805	0.2799
4.5	1.839	1.803	0.7422	0.7465	-0.463	-0.439	0.3445	0.3639
5.0	1.955	1.909	0.7031	0.7090	-0.372	-0.353	0.4245	0.4436
5.5	2.064	2.010	0.6643	0.6715	-0.283	-0.270	0.5214	0.5370
6.0	2.168	2.105	0.6258	0.6344	-0.196	-0.189	0.6372	0.6471
6.5	2.268	2.196	0.5879	0.5980	-0.110	-0.109	0.7766	0.7780
7.0	2.364	2.282	0.5509	0.5624	-0.026	-0.032	0.9426	0.9290
7.5	2.454	2.365	0.5152	0.5277	0.055	0.044	1.1341	1.1066
8.0	2.537	2.445	0.4813	0.4942	0.132	0.118	1.3566	1.3122
8.5	2.616	2.522	0.4488	0.4619	0.210	0.191	1.6213	1.5524
9.0	2.690	2.596	0.4180	0.4309	0.282	0.262	1.9148	1.8281
9.5	2.762	2.668	0.3885	0.4012	0.354	0.331	2.2584	2.1429
10.0	2.826	2.738	0.3612	0.3729	0.422	0.399	2.6433	2.5061
11.0	2.946	2.871	0.3111	0.3205	0.552	0.532	3.5647	3.4041
12.0	3.045	2.998	0.2681	0.2736	0.670	0.660	4.6812	4.5709
13.0	3.132	3.117	0.2306	0.2322	0.781	0.783	6.0342	6.0674
14.0	3.210	3.232	0.1981	0.1959	0.885	0.903	7.6749	7.9983

^aExperimental data from Ref. 23.^bEstimated values using Eqs. II-77 and II-78.

F. Distribution Ratio Measurement

1. Americium and Nitric Acid Extraction (D. R. Fredrickson)

Six series of experiments were performed to provide extraction data for americium and nitric acid, which will be used in modeling the TRUEX solvent extraction process. Three series of extraction experiments with 0.25M CMPO-TCE were run to study the effect of concentrations of neodymium (a stand-in for americium) on the extraction of ^{241}Am from 0.01M and 0.05M nitric acid. All three series contained 0.001M neodymium. Table II-12 summarizes the data giving D_{Am} values [forward (F) and reverse (R)] at 0.01M and 0.05M HNO_3 with and without neodymium. Pre-equilibration of the CMPO-TCE varied as noted in Table II-12. The conclusion of this study is that the higher-than-expected D_{Am} value at low acidities is not unequivocally due to low concentrations of acidic extractants in the TRUEX solvent. It may be explainable by hydrolysis of americium in the aqueous phase.

Table II-12. Effects of Macro Concentrations of Neodymium on the Distribution Ratios for Am(III) between 0.25M CMPO-TCE and HNO_3 Solution at 25°C

Aqueous Comp., M		No Nd		With Nd ^{a,b}	
HNO_3	$\text{Al}(\text{NO}_3)_3$	$D_{\text{Am}}(\text{F})$	$D_{\text{Am}}(\text{R})$	$D_{\text{Am}}(\text{F})$	$D_{\text{Am}}(\text{R})$
0.012	0	0.025	0.028	0.026	0.015
0.052	0	0.374	0.342	0.416	0.355
0.012	0.001	0.029	0.025	0.029	0.026
0.052	0.001	0.477	0.439	0.470	0.439
0.012	0.01	0.196	0.188	0.202	0.183
0.052	0.01	0.909	0.810	0.852	0.791

^aAqueous phase for forward extraction contained 0.001M $\text{Nd}(\text{NO}_3)_3$.

^bTotal nitrate concentration was held constant by substituting Al^{3+} for Nd^{3+} for solution with $\text{Al}(\text{NO}_3)_3$ added.

Two series of experiments were run to study the effect of nitric acid (0.05M and 0.5M)/aluminum nitrate concentrations on the extraction of ^{241}Am by 0.25M CMPO-TCE. The five $\text{Al}(\text{NO}_3)_3$ concentrations were 0.1, 0.2, 0.3, 0.4, and 0.5M. These data will be used in modeling D_{Am} in terms of total nitrate activity of the aqueous phase. Twelve solutions (five for each acid concentration at the appropriate $[\text{Al}(\text{NO}_3)_3]$, plus two with nitric acid alone) were prepared, and a few solutions were titrated with standardized base to check acid concentrations. Results of this study are presented in Fig. II-19.

Finally, a series of experiments was performed to measure HNO_3 distribution ratio values as a function of $\text{Al}(\text{NO}_3)_3$ concentrations. Results are plotted in Fig. II-20.

Fig. II-19.

Effect of $[\text{Al}(\text{NO}_3)_3]$ on D_{Am} Values between 0.25M CMPO in TCE and either 0.05 or 0.5M HNO_3 Solutions of $\text{Al}(\text{NO}_3)_3$ at 25 °C

Fig. II-20.

Nitric Acid Distribution Ratio vs. $[\text{Al}(\text{NO}_3)_3]$ in 0.25M CMPO-TCE

2. Zirconium and Yttrium Extraction (D. R. Fredrickson)

A series of experiments was run to study the extraction of ^{88}Zr and ^{88}Y by the TRUEX-NPH solvent. Both Zr and Y distribution coefficients are determined simultaneously in the same solution.

An isotopic mixture of 0.5 mCi ^{88}Zr and 0.5 mCi ^{88}Y in HCl (0.24 mL) was obtained from Los Alamos National Laboratory. The chloride solution was converted to nitrate by successive evaporations (three) with 0.5M nitric acid (final volume 1 mL). A sample of this solution was diluted and counted in an automatic NaI detector gamma counter. Because the gamma ray energy is 392.9 keV for ^{88}Zr (97.3% abundance) and 1836 keV for ^{88}Y (99% abundance), the γ -ray peaks are widely separated.

In these experiments, we measured both D_{Zr} and D_Y (forward and reverse) between the TRUEX-NPH solvent and HNO_3 solutions for 25 °C at two different contact times: 15 and 60 s. This allowed evaluation of equilibrium conditions. The experimental results tabulated in Table II-13 for zirconium show that at least two species are present in the ^{88}Zr tracer. The forward D values for zirconium for 15- and 60-s contact times are nearly equivalent to each other, as are the reverse D values, thereby showing that an equilibrium condition had been reached in all contacts. However, the significant difference between forward and reverse D_{Zr} values suggests that more than one species is being measured, one extracting significantly better than the other. On the other hand, D_Y values for forward and reverse extraction are nearly equivalent (Table II-14).

Table II-13. Zirconium-88 Extraction by 0.20M CMPO, 1.4M TBP (TRUEX-NPH), and Various Acid Concentrations at 25 °C

[HNO ₃], M	15-s Contact Time		60-s Contact Time	
	$D_{Zr}(F)$	$D_{Zr}(R)$	$D_{Zr}(F)$	$D_{Zr}(R)$
0.1	1.61	5.13	1.60	4.32
0.5	6.00	15.6	6.66	15.1
1	10.4	24.3	13.1	24.3
2	16.5	35.9	21.8	35.6
3	29.4	49.7	28.6	51.0
4	37.2	62.3	38.8	64.1
5	43.6	72.0	46.1	73.5
6	50.7	85.4	53.6	91.8

Table II-14. Yttrium-88 Extraction by 0.20M CMPO, 1.4M TBP (TRUEX-NPH), and Various Acid Concentrations at 25 °C

[HNO ₃], M	15-s Contact Time		60-s Contact Time	
	$D_Y(F)$	$D_Y(R)$	$D_Y(F)$	$D_Y(R)$
0.1	0.09	0.09	0.08	0.07
0.5	0.97	1.07	1.00	0.95
1	1.86	2.00	1.89	1.81
2	2.80	3.03	2.90	2.81
3	3.82	3.93	3.76	3.69
4	4.59	4.78	4.67	4.58
5	5.34	5.59	5.29	5.24
6	6.60	6.77	6.52	6.77

In another series of experiments, the effect of oxalic acid on the extraction behavior of Zr and Y was determined. Experimental results are shown in Table II-15 and Table II-16.

Table II-15. Zirconium-88 Extraction between TRUEX-NPH and Various Nitric Acid Concentrations with 0.1M Oxalic Acid (60-s Contact at 25 ° C)

[HNO ₃], M	D _{Zr} (F)	D _{Zr} (R)
0.1	<10 ⁻³	--
0.5	0.02	0.18
1	0.05	0.85
2	0.08	2.08
3	0.09	2.47
4	0.14	1.28
5	0.34	0.67
6	2.41	2.70

Table II-16. Yttrium-88 Extraction between TRUEX-NPH and Various Nitric Acid Concentration with 0.1M Oxalic Acid (60-s contact at 25 ° C)

[HNO ₃], M	D _Y (Forward)	D _Y (Reverse)
0.1	0.001	--
0.5	0.18	0.18
1	0.87	0.85
2	2.22	2.08
3	3.47	3.40
4	4.44	4.23
5	5.21	5.16
6	6.44	6.48

A series of experiments was also run to study the effect of oxalic acid, hydrofluoric acid, nitrate salts, and nitric acid on the extraction of ⁸⁸Zr and ⁸⁸Y by TRUEX-NPH at 50 ° C and 60-s contact time. The results of these experiments are reported in Tables II-17 and II-18.

3. Neptunium Extraction (J. Sedlet)

The behavior of neptunium in the TRUEX actinide separation process is important since the isotope of mass number 237 is a long-lived alpha emitter that is produced in nuclear reactors along with other transuranic elements. In acid solution, neptunium can exist in the III, IV, V, and VI oxidation states. Because of this multiplicity of possible oxidation states, neptunium distribution in the TRUEX process is difficult to predict and control.

The most stable oxidation state in aqueous solution is Np(V). However, it disproportionates into Np(IV) and Np(VI), and the degree of disproportionation increases with increasing Np(V) concentration and increasing acid concentration. Two NpO₂⁺ ions must react, and hydrogen ions are required to take up the oxygen released in the reaction:

Table II-17. Zirconium-88 and Yttrium-88 Extraction between TRUEX-NPH and Various Aqueous Solutions at 50° C and 60-s Contact Time

Conc., M					D _{Zr}		D _Y	
[H ₂ C ₂ O ₄]	[HNO ₃]	[NaNO ₃]	[Fe(NO ₃) ₃]	[Al(NO ₃) ₃]	For.	Rev.	For.	Rev.
0	0.5	2.7	-	-	29.2	91.9	11.9	12.4
0.1	0.5	2.7	-	-	0.122	6.28	5.77	6.04
0.2	0.5	2.7	-	-	0.117	4.44	4.04	4.37
0.3	0.5	2.7	-	-	0.114	3.96	3.67	3.90
0	0.5	2.4	-	0.1	27.8	106.6	12.8	13.9
0.1	0.5	2.4	-	0.1	0.128	8.39	7.62	8.29
0.2	0.5	2.4	-	0.1	0.121	6.07	5.77	5.94
0.3	0.5	2.4	-	0.1	0.110	4.25	3.90	4.24
0	0.5	1.8	-	0.3	38.7	121.2	13.6	15.7
0.1	0.5	1.8	-	0.3	0.138	5.63	8.55	8.21
0.2	0.5	1.8	-	0.3	0.126	6.66	6.69	6.91
0.3	0.5	1.8	-	0.3	0.124	5.51	5.05	5.53
0	0.5	0.6	-	0.7	41.9	141.8	17.6	18.9
0.1	0.5	0.6	-	0.7	0.177	2.10	10.8	11.1
0.2	0.5	0.6	-	0.7	0.136	5.56	8.13	9.07
0.3	0.5	0.6	-	0.7	0.125	5.63	5.89	6.63
0	0.5	2.4	0.1	-	30.1	78.9	6.07	5.93
0.1	0.5	2.4	0.1	-				
0.2	0.5	2.4	0.1	-				
0.3	0.5	2.4	0.1	-				
0	0.5	2.1	0.2	-	26.6	68.4	4.35	4.32
0.1	0.5	2.1	0.2					
0.2	0.5	2.1	0.2					
0.3	0.5	2.1	0.2					
0	0.5	1.2	0.2	0.3	29.0	63.2	4.40	4.10
0.1	0.5	1.2	0.2	0.3				
0.2	0.5	1.2	0.2	0.3				
0.3	0.5	1.2	0.2	0.3				
0	1.0	2.2	-	-	29.2	55.1	5.22	5.16
0	1.0	2.2	-	-	22.8	39.0	6.15	6.24
0.1	1.0	2.2	-	-	0.132	4.71	4.48	4.63
0.2	1.0	2.2	-	-	0.125	3.80	3.39	3.67
0.3	1.0	2.2	-	-	0.118	3.14	2.71	3.08

Table II-18. Effects of HF on Zirconium-88 and Yttrium-88 Extraction by 0.20M CMPO, 1.4M TBP (TRUEX-NPH) at 50°C and 60-s Contact Time

Conc., M				D_{Zr}		D_Y	
[HNO ₃]	[HF]	[NaNO ₃]	[Al ⁺³]	Forward	Reverse	Forward	Reverse
0.5	0.1	2.7	0	0.159	7.21	8.98	9.22
0.5	0.3	2.7	0	0.133	5.09	4.68	5.14
0.5	0.5	2.7	0	0.117	3.17	2.91	3.14
0.5	0.1	2.4	0.1	8.32	9.16	11.98	13.5

Because Np(III) is difficult to maintain in aqueous solution, its distribution was not studied. However, its extraction behavior is expected to be similar to that of Am(III). As the hydrated $Np(H_2O)_9^{4+}$ ion, Np(IV) is expected to behave similarly to Pu(IV), with high distribution coefficients at high nitric acid concentrations in the absence of complexing agents. The Np(VI) species exists in a doubly charged oxygenated ion, NpO_2^{2+} , and is expected to extract well at high nitric acid concentrations, as does the uranyl ion UO_2^{2+} . The Np(V) species exists as a singly charged ion, NpO_2^+ , and is expected to be poorly extracted in TRUEX solvents, as do other singly charged ions.

In addition to multiple oxidation states with large differences in extractability, other considerations include the rate of conversion between oxidation states, the difficulty of converting all the neptunium in a solution to a single oxidation state, and the possibility of radiocolloid formation of Np(IV) at low acid concentrations.

a. Experimental

(1) Reagents

The neptunium isotope used in this study was ^{239}Np , a beta-gamma emitter with a half-life of 56.64 h. It was obtained before each use by (1) extraction from its parent, ^{243}Am , in concentrated hydrochloric acid with tri-isooctylamine dissolved in xylene or benzene and (2) back extraction into water. The back extract, which becomes about 1.3M HCl, was evaporated to dryness and dissolved in nitric acid, and the oxidation state was adjusted as desired.

Most results obtained in this reporting period were made with the TRUEX-NPH solvent, which has the composition 0.2M CMPO and 1.4M TBP dissolved in Conoco C₁₂-C₁₄, a normal paraffinic hydrocarbon with an average carbon chain length of 13.4. However, one series of extractions of Np(V) and Np(VI) was made with the TRUEX-TCE solvent having the composition 0.25M CMPO and 0.75M TBP in TCE.

Neptunium distribution ratios were measured at 25°C with an organic/aqueous (o/a) volume ratio of unity. All organic phases were pre-equilibrated three times with an acid solution of the same composition as used in the distribution ratio measurements. Phases were mixed for one minute in a vortex mixer and centrifuged, the phases were separated, and the ^{239}Np gamma rays counted.

The reducing and oxidizing agents used were hydroxylamine nitrate ($NH_2OH \cdot HNO_3$), hydrazine hydrate ($N_2H_4 \cdot H_2O$), sodium nitrite, ferrous ammonium sulfate, potassium permanganate and potassium dichromate; all were commercially obtained reagent-grade chemicals. Ferrous nitrate was prepared by two procedures: reduction of ferric nitrate with hydroxylamine nitrate and

hydrazine hydrate, and mixing of stoichiometric amounts of ferrous sulfate and barium nitrate in the presence of hydroxylamine nitrate. The first procedure gave solutions of uncertain concentration, and its use was soon discontinued in favor of the second procedure.

(2) Preparation and Extraction of Neptunium (IV), (V), and (VI)

Although tri-isooctylamine extracts the tetravalent oxidation state, some of the neptunium became oxidized to Np(V) during the evaporation and conversion of the back-extracted neptunium to the nitrate form. (Hexavalent neptunium is also extracted by tri-isooctylamine, but should not be present in the concentrated hydrochloric acid solution of ^{243}Am .) Consequently, the ^{239}Np tracer nitric acid solution was increased from 0.1 to 1M HNO_3 and treated with ferrous nitrate or ferrous ammonium sulfate, each containing hydroxylamine nitrate, at concentrations ranging from 0.01 to 0.33M Fe(II) and for periods ranging from a few minutes to overnight. Aliquots of this solution were added to nitric acid solution of various concentrations and extracted with TRUEX solvent, or the entire tracer solution after reduction with Fe(II) was extracted into the TRUEX solvent from 3M HNO_3 , and small aliquots of this "solvent-loaded" ^{239}Np tracer were added to pre-equilibrated TRUEX-NPH, which was then contacted with nitric acid solutions of various concentrations to obtain the distribution ratios.

Since the oxidation of Np(IV) to Np(V) by nitric acid is slow, the pentavalent state was prepared by oxidation of the ^{239}Np tracer to Np(VI) with KMnO_4 , followed by reduction to the (V) state with NaNO_2 in 1M HNO_3 . These reactions are rapid. Aliquots of this solution were added to solutions with nitric acid concentrations between 0.05 and 5.0M and extracted with TRUEX-NPH and TRUEX-TCE to measure distribution ratios.

The Np(VI) species was prepared by oxidation of the separated ^{239}Np with 5M HNO_3 in the presence of 0.05M NaNO_2 . The Np(VI) was extracted into a small volume of TRUEX-NPH solvent, and small aliquots of this solution were added to pre-equilibrated TRUEX-NPH and contacted with nitric acid at concentrations ranging from 0.05 to 5.0M HNO_3 . Each aqueous phase was made 0.01M in $\text{Kr}_2\text{Cr}_2\text{O}_7$ as a means of maintaining the hexavalent state.

b. Results and Discussion

(1) Np(V)

The results for Np(V) extraction behavior are discussed first, since (1) it is the most stable oxidation state in acidic nitrate media, and (2) the variations observed in the distribution ratios for Np(IV) can be explained if one assumes that the Np(IV) solutions often contain some Np(V). Aliquots of the solution obtained as described above were added to various concentrations of nitric acid and extracted with TRUEX solvents to obtain the distribution ratios shown in Table II-19 and plotted in Fig. II-21. Since the conversion of the ^{239}Np tracer to the (V) state was probably not quantitative and the distribution ratios of the (IV) and (VI) states are substantially greater than those for the (V) state, successive extraction of the original aqueous phases were performed to remove the other oxidation states and leave only the (V) state in the aqueous phase. The results indicate that the distribution ratios become low and remain low and constant after the first extraction. Earlier experiments, performed with different phase ratios and with metabisulfite as a holding reductant, had yielded similar results (see previous report in this series). The differences in Np(V) distribution ratios for the NPH and TCE diluents were reproducible.

Table II-19. Distribution Ratios for $^{239}\text{Np(V)}$ between Nitric Acid and TRUEX Solvents^a

[HNO ₃], M	TRUEX-NPH				TRUEX-TCE			
	#1	#2	#3	#4	#1	#2	#3	#4
0.05	0.035	0.019	0.026	0.024	0.023	0.016	0.015	0.016
0.1	0.130	0.037	0.029	0.032	0.038	0.027	0.027	0.027
0.2	0.35	0.076	0.066	0.061	0.173	0.048	0.044	0.048
0.5	1.03	0.161	0.135	0.146	0.232	0.083	0.088	0.089
1.0	1.24	0.270	0.227	0.239	0.312	0.135	0.110	0.110
2.0	2.14	0.644	0.637	0.711	0.455	0.285	0.173	0.176
3.0	1.44	1.07	1.00	1.00	0.519	0.310	0.271	0.284
5.0	4.99	2.97	1.58	3.05	0.875	0.647	0.603	1.51

^aFour successive extractions of the aqueous phases were performed at phase ratios of 1:1.

Fig. II-21.

Plot of Distribution Ratios for Np(V) between Nitric Acid and TRUEX Solvents. The data plotted are the ratios for Extraction No. 4 in Table II-19; NPH is TRUEX-NPH and TCE is TRUEX-TCE.

At high nitric acid concentrations, nitrite ion catalyzes the oxidation of neptunium to the (VI) state, and the results in Table II-19 at 3 and 5M HNO₃ indicate the presence of some hexavalent neptunium.

An experiment was performed to judge the oxidation state of the neptunium extracted by the solvent during the first forward extraction. The results are shown in Table II-20. We performed two successive forward extractions, followed by a back extraction with the solvent from the first forward extraction. The first forward extraction gave results greater than those determined in Table II-19 for Extraction No. 1, indicating that some (IV) and/or (VI) neptunium was present in the original aqueous phase. The ratios for the back extraction, however, were very close to those obtained for the second forward extraction. This finding suggests that the neptunium extracted during the first forward extraction was converted to the (V) state prior to or during the back extraction--an indication of the tendency for neptunium to remain in the pentavalent state.

Table II-20. Distribution Ratios for Forward and Back Extraction of Np(V) between Nitric Acid and TRUEX-NPH

[HNO ₃], M	Forward Extractions		Back Extraction
	#1	#2	
0.05	0.29	0.019	0.024
0.5	2.6	0.127	0.238
2.0	3.5	0.566	0.619
5.0	6.20	2.81	2.92

In summary, Np(V) appeared to be well behaved and gave fairly reproducible distribution ratios. This is to be expected since the pentavalent state is the most stable oxidation state in aqueous solution.

(2) Np(IV)

Extractions with ²³⁹Np tracer, first treated with Fe(II) preparations to obtain the (IV) state, were always performed with a holding reductant in the aqueous phase, usually Fe(NO₃)₂ plus NH₂OH·HNO₃. A few extractions were performed with NH₂OH·HNO₃ alone, but this reducing agent was judged unsatisfactory since lower distribution ratios were obtained than when Fe(II) was also present. The reduction of neptunium to Np(IV) by Fe(II) is rapid, while reduction with NH₂OH·HNO₃ is slow. We thus expected that, in the presence of both reducing agents, ferrous ion would maintain Np(IV), while NH₂OH·HNO₃ would prevent the oxidation of ferrous ion.

Results were inconsistent whether the ²³⁹Np tracer, after treatment with Fe(II), was added to the aqueous phase or extracted first into solvent and added to the solvent phase. The forward extraction, aqueous to solvent, gave lower distribution ratios than the back extractions (solvent to aqueous). A second forward extraction always gave much lower distribution ratios than the first, and successive back extractions gave variable results. In some experiments the ratios decreased with each successive back extraction, and in others the changes were reversed.

An example of the results obtained from two separate experiments is given in Table II-21. In these two experiments, the distribution ratios increased in each successive back extraction, and, at low acidities, the neptunium that was unextracted in the first forward extraction remained largely unextractable. If we assume that two species are present, Np⁴⁺ and NpO₂⁺, the fractions of each can be calculated with the further assumption that the highest distribution ratio obtained at each acidity is close to the true ratio for Np(IV). The equation that describes the distribution of the species (for equal volumes of both phases) is

$$C_4/C_5 = (D_4 + 1)(D_m - D_5) / (D_5 + 1)(D_4 - D_m) \quad (\text{II-80})$$

where C₄ and C₅ are the initial concentrations of Np(IV) and Np(V), respectively, in one of the phases before it is contacted with the phase that contains no neptunium; D₄ and D₅ are the true distribution ratios of species Np(IV) and Np(V), respectively; and D_m is the measured ratio for the mixture of Np(IV) and Np(V).

The parameters used to calculate percentages of the two oxidation states for some of the data in Table II-21 are given in Table II-22. The distribution ratios given in Table II-22 for Np(IV) are the highest values observed in Table II-21; the values for Np(V) are taken from Table II-19. The percentages of the two oxidation states obtained in this way are given in Table II-23.

Table II-21. Distribution Ratios for $^{239}\text{Np(IV)}$ between TRUEX-NPH and Nitric Acid

Expt. No. ^a	[HNO ₃], <u>M</u>	Forward Extractions		Back Extractions			
		#1	#2	#1	#2	#3	#4
1	0.05	5.5	0.10	37	66	--	
2		2.2	2.7	22	43	43	47
1	0.10	10.7	0.39	108	275	--	--
2		94	14	47	89	95	112
1	0.50	190	3.4	604	3.0×10^3	--	--
2		395	>100	3.7×10^3	1.3×10^3	4.2×10^3	1.9×10^3
1	5.0	969	3.5	1.1×10^4	2.0×10^4	--	--
2		1.1×10^4	>100	5.1×10^4	3.7×10^4	3.2×10^4	6.0×10^4

^a For all experiments, ^{239}Np tracer solution was reduced with Fe(II) before use, and aliquots of the reduced solution were added to the aqueous phase for the first forward extraction.

Reducing Conditions:

Expt. 1 - 0.04M Fe(NO₃)₂, 0.09M NH₂OH·HNO₃ in 0.5M HNO₃, 40 min.

Expt. 2 - 0.05M ferrous ammonium sulfate, 0.11M NH₂OH·HNO₃, 30 min.

Extraction Conditions:

Expt. 1 - All aqueous phases made with 0.02M in Fe(NO₃)₂ and 0.02M in NH₂OH·HNO₃ before extraction.

Expt. 2 - All aqueous phases made with 0.015M Fe(NO₃)₂ and 0.015M NH₂OH before extraction.

Table II-22. Measured and True Distribution Ratios Used to Calculate Np(IV) and Np(V) Percentages

[HNO ₃], <u>M</u>	$D_{\text{Np(IV)}}$	$D_{\text{Np(V)}}$	D_m Forward Extr.		D_m Back Extr.	
			#1	#2	#1	#2
0.05	66	0.019	5.5	0.10	22	43
0.10	275	0.029	10.7	0.39	47	89
0.50	4.2×10^3	0.135	190	3.4	3.7×10^3	1.3×10^3
5.0	6.0×10^4	1.6	969	3.5	5.1×10^4	3.7×10^4

Table II-23. Np(IV) and Np(V) Composition (%) of Aqueous and Organic Phases before Extraction

(HNO ₃), <u>M</u>	Forward Extractions				Back Extractions			
	#1		#2		#1		#2	
	Np(IV)	Np(V)	Np(IV)	Np(V)	Np(IV)	Np(V)	Np(IV)	Np(V)
0.05	85.6	14.4	7.3	92.7	97.0	3.0	99.2	0.8
0.1	91.6	8.4	26.7	73.3	98.1	1.9	99.2	0.8
0.5	99.5	0.5	76.3	23.7	99.99+	<0.01	99.95	0.05
5.0	99.7	0.3	42.2	57.7	99.99+	<0.01	99.99+	<0.01

The data indicated that small amounts of Np(V) affect the distribution ratios markedly. It is evident that the treatment with Fe(II) and hydroxylamine nitrate did not reduce the neptunium completely to the (IV) state, but that the Np(IV) once extracted into the organic phase remained predominately in that oxidation state. At high acidities, where the distribution ratios are greater than 10^3 , very small amounts of pentavalent neptunium will produce large percentage differences in the distribution ratios, and thus, a high degree of reproducibility cannot be obtained between experiments because of the very low distribution ratios of Np(V). At lower acidities the reproducibility problem is even greater, since it is evidently more difficult to obtain or maintain greater than 99% Np(IV). This difference is probably due to the strong Np(IV)/nitrate complex formed in high nitric acid concentrations.

In the separation of ^{239}Np from ^{243}Am , only Np(IV) extracts into tri-isooctylamine, and subsequent treatment evidently oxidizes some of the neptunium to the pentavalent state. The reduction methods used thus far have been inadequate to effect complete reduction.

For this reason, we assumed that distribution ratios obtained from back extractions or from experiments with solvent-tagged $^{239}\text{Np(V)}$ represent the best values for Np(IV). Representative distribution ratios obtained from a series of solvent-tagged extractions are given in Table II-24. This series was chosen because it gave, on the average, the largest ratios, and the ^{239}Np is thus believed to have been predominately Np(IV). A graph of these results (Fig. II-22) shows a slight inflection point between 1 and 2M HNO_3 , but the ratio did not increase to 10^5 , as had been earlier observed on occasion. At 0.2M HNO_3 and below, the ratios are substantially greater than obtained earlier, for reasons that are not yet clear.

To determine if reproducible results could be obtained with the same tracer preparation, we performed quadruplicate extractions at two nitric acid concentrations, 0.1 and 0.5M . The results are given in Table II-25. The values were quite consistent for each extraction, although the distribution ratios increased substantially between the first and second back extractions. Interestingly, the distribution ratio of the second back extraction divided by that of the first back extractions at 0.1M HNO_3 is 2.0 ± 0.3 (1σ), and the corresponding value for 0.5M HNO_3 is 3.2 ± 0.1 . The good agreement between the forward and first back extractions implies that only one neptunium species was present, or that the Np(IV)/Np(V) ratio remained constant. The neptunium obviously undergoes some change in the organic phase after the first back extraction. If the increase in the ratio for the second back extraction is due to some conversion of Np(V) to Np(IV), and if the distribution ratios for Np(IV) and Np(V) in Table II-22 are used to calculate the percentages of each oxidation state, then the percentage of Np(IV) at 0.1M HNO_3 is 95.6% for the forward and first back extraction and 99.6% for the second back extraction. At 0.5M , the corresponding values are 99.83% and 99.97% Np(IV). Thus, very small amounts of Np(V) markedly affect the apparent distribution ratio for Np(IV).

Table II-24. Distribution Ratios for $^{239}\text{Np(IV)}$ ^a

$[\text{HNO}_3], \text{ M}$	D_{Np}
0.05	40
0.1	65
0.2	199
0.5	2.0×10^3
1.0	1.0×10^4
2.0	2.5×10^4
3.0	5.1×10^4
5.0	5.1×10^4

^a $^{239}\text{Np(IV)}$ stock solution was prepared by treating ^{239}Np (separated from ^{243}Am) with 0.08M ferrous ammonium sulfate in 2M HNO_3 for 30 min, and extracted into 1 mL TRUEX-NPH. Aliquots of this solution (20 μL) were added to 3 mL of acid pre-equilibrated TRUEX-NPH and contacted with fresh nitric acid for 1 min at 25 °C. The nitric acid phase contained 0.015M $\text{Fe(NO}_3)_2$ and 0.014M $\text{NH}_2\text{OH}\cdot\text{HNO}_3$ as holding reductants.

Fig. II-22.

Distribution Ratios for $^{239}\text{Np(IV)}$ vs. HNO_3 Concentration. The data and experimental details are given in the note for Table II-24.

Table II-26 shows the effect of sulfuric acid on the distribution coefficients of Np(IV) . At the lower acidities, 0.1 and 0.2M HNO_3 , the distribution coefficients are fairly reproducible between the first and second forward extractions and between the forward and back extractions, probably because the sulfate ion stabilizes the Np(IV) as a complex ion and because the total acidity is high. At 0.5 and 6M HNO_3 the poor reproducibility observed with nitric acid alone (at all acidities) is again apparent, and additional studies are needed.

The effect of oxalic acid on the distribution ratios for Np(IV) is shown in Table II-27. Up to at least 0.5M HNO_3 , the complexing action of oxalate lowers the distribution ratio markedly. The increase in the distribution ratio for the second forward extraction over that of the first back extraction is probably due to the extraction of oxalic acid by the TRUEX-NPH solvent during the first extraction, since in this case the solvent was not pre-equilibrated with the nitric/oxalic acid mixture before use, but with nitric acid alone. The experiment should be repeated.

Table II-25. Distribution Ratios of $^{239}\text{Np(IV)}$ between Nitric Acid Solution and TRUEX-NPH^a

Run No.	[HNO ₃], <u>M</u>	Forward Extraction	Back Extractions		
			#1	#2	Ratio 2/1
0.1-1	0.10	24	28	52	1.82
0.1-2	0.10	23	25	58	2.32
0.1-3	0.10	23	26	47	1.85
0.1-4	0.10	22	--	--	--
		24 ± 1.7	26 ± 1.5	52 ± 5	2.0 ± 0.3
0.5-1	0.50	525	--	--	--
0.5-2	0.50	583	589	1945	3.31
0.5-3	0.50	518	624	2051	3.27
0.5-4	0.50	558	672	2069	3.07
		545 ± 30	627 ± 43	2013 ± 67	3.2 ± 0.1

^aThe ^{239}Np tracer solution was reduced with 0.33M ferrous ammonium sulfate in 0.67M HNO₃ for 30 min, and aliquots of this solution were added to each aqueous phase for the forward extraction. All aqueous phases were made 0.015M in Fe(NO₃)₂ and 0.014M in NH₂OH•HNO₃ before each extraction.

Table II-26. Distribution of Np(IV) between Nitric/Sulfuric Acid Mixtures and TRUEX-NPH

Expt. No. ^a	Conc., <u>M</u>		Forward Extractions		Back Extractions			
	[H ₂ SO ₄]	[HNO ₃]	#1	#2	#1	#2	#3	#4
1	1.0	0.1	4.1	--	5.5	6.1	--	--
2			3.7	3.4	4.1	5.2	4.5	5.1
1	1.0	0.2	7.8	--	11	12	--	--
2			9.7	9.2	10	11	11	12
1	1.0	0.5	15		27	33	--	--
2			103	233	56	44	45	44
1	1.0	6.0	190	--	253	206	--	--
2			5.8×10^3	>100	6.2×10^3	1.7×10^4	1.6×10^4	8.0×10^3

^aIn both experiments, ^{239}Np tracer solution was reduced with 0.08M ferrous ammonium sulfate in 1M HNO₃ for 30 min, and aliquots of this solution were added to the aqueous phase for each first forward extraction. Extraction conditions:

Expt. 1 - Each aqueous phase was made 0.015M Fe(NO₃)₂ and 0.014M NH₂OH•HNO₃ before extraction.

Expt. 2 - Each aqueous phase was made 0.014M NH₂OH•HNO₃ before extraction. No Fe(II) was used.

Table 27. Distribution of $^{239}\text{Np(IV)}$ between Oxalic/Nitric Acid Solution and TRUEX-NPH^a

Conc., <u>M</u>		Forward Extractions		Back Extraction			
[H ₂ C ₂ O ₄]	[HNO ₃]	#1	#2	#1	#2	#3	#4
0.01	0.10	0.030	0.18	0.05	--	--	--
0.01	0.20	0.123	1.24	0.159	0.140	0.343	--
0.01	0.50	5.05	58	4.94	3.21	2.80	2.44
0.01	6.0	7.4x10 ³	--	9.7x10 ³	1.57x10 ⁴	1.33x10 ⁴	2.8x10 ³

^aThe ^{239}Np tracer was reduced with 0.05M ferrous ammonium sulfate in 1M HNO₃ for 30 minutes, and aliquots of this solution were added to each aqueous phase before extraction. Each aqueous phase was made 0.015M in Fe(NO₃)₂ and 0.014M in NH₂OH•HNO₃ before extraction.

Table II-28 shows the ratio effect of hydrofluoric acid on the distribution ratios. As expected, the fluoride ion lowers the distribution ratio greatly at all acid concentrations. The reason for the increase in the back extractions at 6M HNO₃ is not obvious; perhaps, the fluoride complex is weaker since most of the fluoride is present as undissociated HF.

Table II-28. Distribution Ratios of $^{239}\text{Np(IV)}$ between Hydrofluoric Acid/Nitric Acid Solutions and TRUEX-NPH^a

Conc., <u>M</u>		Forward Extractions	Back Extractions	
[HF]	[HNO ₃]		#1	#2
0.25	0.1	0.0036	0.0048	--
0.25	0.2	0.017	0.019	--
0.25	0.5	0.18	0.18	0.18
0.25	6.0	9.0	50	73

^aThe ^{239}Np tracer solution was reduced with 0.05M ferrous ammonium sulfate in 1M HNO₃ for 30 min, and aliquots of this solution were added to each aqueous phase before extraction. Each aqueous phase was made 0.015M in Fe(NO₃)₂ and 0.014M in NH₂OH•HNO₃ before extraction.

(3) Neptunium(VI)

The Np(VI) distribution ratio results are given in Table II-29 for TRUEX-TCE and TRUEX-NPH. In the first back extraction with TRUEX-TCE, some reduction to Np(V) occurred at the lower acid concentrations, but at 0.5M HNO₃ and above, the first and second extractions were similar. In the case of TRUEX-NPH, reduction to Np(V) apparently occurred during the first extraction, and a holding oxidant was needed. The Np(VI) distribution ratios are approximately similar for the second back extraction with two solvents. Values greater than 10³ are difficult to obtain because the hexavalent neptunium is difficult to maintain in the presence of the TRUEX solvent, and dichromate reacts rapidly with CMPO at high acidities.

Table II-29. Distribution Ratios for $^{239}\text{Np(VI)}$ between Nitric Acid and TRUEX-NPH or TRUEX-TCE

[HNO ₃], M	TRUEX-TCE ^a		TRUEX-NPH ^b	
	Back Extraction		Back Extraction	
	#1	#2	#1	#2
0.05	15	28	0.06	38
0.10	8.8	50	0.31	52
0.20	50	92	0.27	77
0.50	189	175	0.70	210
1.0	309	382	0.66	325
2.0	420	498	1.2	418
3.0	505	450	1.4	565
5.0	781	852	3.8	1.13x10 ³

^aEach aqueous phase was made 0.01M K₂Cr₂O₇ before extraction.

^bK₂Cr₂O₇ was not added to the aqueous phase for the first back extraction but was used in the second back extraction at a concentration of 0.01M.

c. Conclusions

The distribution of neptunium between TRUEX solvents and acidic aqueous solutions was studied with the use of the ^{239}Np isotope. Distribution ratios for the (IV), (V), and (VI) oxidation states were measured. For each oxidation state, the distribution ratios increased as the nitric acid concentration was increased from 0.05 to 5M, except that with Np(IV) the ratio appeared to level off, or decrease slightly, from 3 to 5M. The Np(V) species extracted poorly, as expected for the singly charged ion, NpO_2^+ . The distribution ratio varied from about 0.02 at 0.05M HNO₃ to about 2 at 5M. The results were reproducible, as expected, since the pentavalent state is the most stable oxidation state in acid solution.

The hexavalent state, NpO_2^{2+} , was well extracted, with distribution ratios ranging from about 30 at 0.05M to about 10³ at 5M HNO₃ in the presence of potassium dichromate as a holding oxidant. The hexavalent state, however, is not of much importance in the TRUEX process since it is readily reduced.

Most of the effort in this study was devoted to the highly extractable Np(IV) species. Several methods were used to obtain and stabilize Np(IV), but results varied widely between experiments. Since the presence of a small amount of Np(V) in a Np(IV) tracer preparation will lower the distribution ratio significantly, we believe that the highest ratio at any acid concentration is the most reliable one for Np(IV). On this basis, the distribution ratio ranged from about 50 at 0.05M HNO₃ to about 10⁵ at 5M HNO₃. At 0.5M HNO₃ and above, a distribution ratio of the order of 10³ could usually be obtained. Small amounts of Np(V) affected the observed distribution ratio for Np(IV). However, the presence of other species of the Np(IV) state (e.g., complexes or radiocolloids) cannot be discounted. Distribution ratios in nitric acid solutions containing sulfuric acid, oxalic acid, or hydrofluoric acid were also measured. The presence of these acids, which form complexes with Np(IV), lowered the distribution ratios substantially and gave more reproducible results than was the case with nitric acid alone.

G. Testing of New Strip and Scrub Reagents
(L. Reichley-Yinger)

Although the TRUEX solvent effectively extracts low concentrations of americium and other TRU elements from acidic nitrate solutions, the selective stripping and scrubbing of the loaded solvent are the most problematic steps of the entire process when it is applied to waste streams with a wide range of compositions. This work is directed toward improving the TRUEX process for generic applications by testing new stripping and scrubbing reagents.

Americium distribution ratios between two CMPO-containing solvents and dilute HNO_3 solutions were measured. Figure II-23 is a plot of $\log(D_{\text{Am}})$ vs. $\log\{\text{NO}_3^-\}$ for 0.25M CMPO in TCE. Figure II-24 is a similar plot for TRUEX-NPH. In both plots the distribution ratios at $\{\text{NO}_3^-\} < 10^{-2}$ level off at about 0.03, which is above the measurable limit of 10^{-3} . At these low concentrations of HNO_3 , the slope of the best-fit lines is between one and two, not three as predicted if one assumes that a neutral americium species is extracted and neglect competition for CMPO by nitric acid extraction and any aqueous-phase complexation of americium by NO_3^- , i.e.,

Fig. II-23. Extraction of Americium from HNO_3 Solutions by 0.25M CMPO in Tetrachloroethylene at 25 °C

The leveling off of the distribution ratios at low $\{\text{NO}_3^-\}$ and $\{\text{H}^+\}$ suggests either (1) the presence of an acidic impurity or impurities that can extract americium or (2) complications on the extraction of $\text{Am}(\text{II})$ due to its hydrolysis:

Since the solvent was prepared with recrystallized CMPO having a purity of >99%, apparently only a small amount of this impurity increases the americium distribution ratio. The magnitude of the effect can

be estimated from Fig. II-23 by assuming that the D_{Am} value for 0.353M HNO_3 results entirely from extraction by CMPO, as described in Eq. II-81. If D_{Am} for 0.353M HNO_3 is extrapolated to 0.04M HNO_3 (the $[HNO_3]$ of the americium strip in the TRUEX flowsheet), then D_{Am} for 0.04M HNO_3 would be 0.03, significantly lower than the measured value of 0.3. More information is needed to model this effect.

Fig. II-24. Extraction of Americium from Dilute HNO_3 Solutions by TRUEX-NPH at 25°C

To determine the effects of sulfate, oxalate, fluoride, and phosphate on the partitioning of americium between TRUEX-NPH and acidic nitrate solutions, americium distribution ratios were measured for aqueous phases containing either sulfuric, oxalic, hydrofluoric, or phosphoric acids. Figures II-25 to II-28 plot the distribution results for aqueous phases containing sulfuric, oxalic, hydrofluoric, and phosphoric acids, respectively. The nitrate activities used were calculated by assuming that oxalic, hydrofluoric, and phosphoric acids had no effect on the nitrate activities. This assumption is approximately true because these weak acids, which have acid association constants of 1.27, 3.18, and 2.15 for oxalic, hydrofluoric, and phosphoric acids, respectively,²⁵ are not highly dissociated in HNO_3 solutions. For example, at 0.1M HNO_3 , where the acids will be the most dissociated, the concentration of ionic species in solution due to the acids will be <0.03M.

The results show that all four acids depress the americium distribution ratios but to different extents. Sulfuric acid, a strong acid, uniformly depressed the distribution ratios for all HNO_3 concentrations, while the three weak acids (oxalic, hydrofluoric, and phosphoric) generally depressed the distribution ratios more at the lower HNO_3 concentrations. These results show the effect of a good stripping agent; that is, it depresses the distribution ratios at low HNO_3 concentrations but has little effect at high concentrations. This behavior permits stripping of americium at low HNO_3 concentrations but will not affect the extraction of americium if the stripping agent enters the extraction stages. The depression of the distribution ratios of americium occurs due to the formation of americium-anion complexes in the aqueous phase. Complexes most likely to be present in the aqueous phase under the conditions of these experiments include $Am(NO_3)_m(X)_n^{(3-m-n)}$, where X represents HSO_4^- , $HC_2O_4^-$, F^- , and $H_2PO_4^-$.

Fig. II-25. Effect of 1M H_2SO_4 on Americium Extraction by TRUEX-NPH at 25°C

Fig. II-26. Effect of 0.01M $\text{H}_2\text{C}_2\text{O}_4$ on Americium Extraction by TRUEX-NPH at 25°C

Fig. II-27. Effect of 0.25M HF on Americium Extraction by TRUEX-NPH at 25°C

Fig. II-28. Effect of 0.25M H₃PO₄ on Americium Extraction by TRUEX-NPH at 25°C

H. Radiolysis and Hydrolysis of TRUEX-NPH Solvent (N. Simonzadeh, A. Crabtree, and L. Trevorrow)

1. Introduction

During contact with PUREX raffinates from the reprocessing of irradiated fuel, a fraction of the TRUEX-NPH solvent will be converted, through radiolysis and hydrolysis, to other chemical species. The purpose of this study is to (1) derive parameters expressing the effects of these reactions that can be used in the Generic TRUEX Model and (2) determine the effectiveness of removing the products of these reactions from the solvent by aqueous washes. Studies of the hydrolysis and radiolysis of various solvents used in extraction of transuranics were carried out earlier.²⁶⁻²⁸ The present study is concerned specifically with the TRUEX-NPH solvent (0.2M CMPO and 1.4M TBP in Conoco C₁₂-C₁₄).

The effects of radiolysis and hydrolysis of the solvent were evaluated by observing the distribution of americium between aqueous HNO₃ solutions and solvent that had been exposed to radiation or to above-ambient temperatures while in contact with aqueous HNO₃ solutions. The previous semiannual report (Sec. I.I.3) described the distribution of americium between aqueous nitric acid solutions and TRUEX-NPH solvent that had been exposed to gamma radiation while in contact with aqueous solutions of 0.25 and 6M HNO₃. The distribution was shown to be dependent on received dose. Furthermore, for these systems, the effect of radiolysis on distribution ratio was shown to be partially reversed by washing the irradiated solvent with aqueous sodium carbonate.

This report describes (1) additional distributions of americium between aqueous nitric acid solutions and TRUEX-NPH solvent that has been degraded by gamma radiolysis, (2) the distribution of americium between aqueous nitric acid solutions and TRUEX-NPH solvent that has been degraded by hydrolysis, (3) the effects on the distribution ratios described in items 1 and 2 of washing degraded solvent with water or aqueous sodium carbonate, and (4) changes in the acidity of aqueous HNO₃ and of TRUEX-NPH solvent in contact with it, accompanying radiolysis and hydrolysis.

2. Distribution Measurements

Coefficients were measured for the distribution of americium, at 25 °C, between samples of solvent that had been previously subjected to hydrolysis or radiolysis and nitric acid solutions with concentrations of 0.01, 0.05, and 2.0M HNO₃. In the TRUEX process, aqueous ≤0.05M HNO₃ is used to strip americium away from the solvent, but the solvent-degradation products foster the extraction of americium into the organic phase, thus decreasing the stripping effectiveness. Hence, testing the distribution of americium between 0.05M HNO₃ and solvent is especially relevant to application of the TRUEX process. (The coefficients for distribution of americium, D_{Am} , are the ratios of americium concentration in the organic phase to that in the aqueous phase.)

a. Effects of Radiolysis

Radiolysis of TRUEX-NPH solvent in contact with aqueous nitric acid was carried out by exposure to a ⁶⁰Co source at 50 °C at a received dose rate of 2.2-2.5 x 10⁵ rad/h, for doses up to about 200 Wh/L. The aqueous solutions included nitric acid at concentrations of 0.25, 2.5, and 6M. Additional aqueous solutions used in this work included a simulated high-level waste stream that is a candidate for application of the TRUEX process: the CAW (current acid waste) stream generated at the Hanford site. This waste stream contains nitric acid at concentrations of 1.4M and 2.4M HNO₃ plus a variety of dissolved salts. For the work reported here, stock solutions simulating the acid and salt

concentrations of the CAW stream were prepared. For radiolysis of TRUEX-NPH in contact with CAW, formation of a solid phase in the sample was observed after about 100 Wh/L of received dose. For irradiation of TRUEX-NPH in contact with nitric acid solutions, however, there was no formation of solid phase over the entire range of received dose.

Figure II-29 presents, as a function of dose received, coefficients for distribution of americium between aqueous nitric acid of three different initial concentrations and samples of TRUEX-NPH solvent that had received varying doses of gamma radiation at 50° C while in contact with 0.25M HNO₃. Figures II-30 and II-31 present the results of analogous experiments in which the solvent had been exposed to gamma radiation while in contact with 2.5 and 6M HNO₃, respectively. These three figures suggest two general observations: (1) for the range 0.25-6M, the concentration of HNO₃ in contact with solvent during radiolysis seems to produce no definite, regular trend in subsequent tests of the distribution of americium between solvent and nitric acid for a given concentration, and (2) increases in dose received by the solvent cause the coefficient in subsequent distribution tests to increase greatly for distributions involving 0.01 and 0.05M HNO₃. In contrast, for distributions involving 2.0M HNO₃, the same dose causes the coefficient to decrease slightly.

Fig. II-29.

Dependence of Coefficient on Dose Received by Solvent for Distribution of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Previously Exposed to Gamma Radiation While in Contact with 0.25M HNO₃

Figure II-32 presents, as a function of dose received, coefficients for distribution of americium between aqueous nitric acid of three different initial concentrations (0.01, 0.05, and 2.0M) and TRUEX-NPH solvent that had received varying doses of gamma radiation at 50° C while in contact with simulated CAW containing 1.4M HNO₃. Comparison of Fig. II-32 with Figs. II-29 to II-31 suggests that, for distributions involving 0.01 and 0.05M HNO₃, the initial rate of change of the distribution coefficient with dose received by solvent is much greater for the CAW system than for any of the others, regardless of acid concentration present during radiolysis. This observation suggests that the metal ions in CAW had accelerated the radiolysis.

Fig. II-30.

Dependence of Coefficient on Dose Received by Solvent for Distribution of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Previously Exposed to Gamma Radiation While in Contact with 2.5M HNO₃

Fig. II-31.

Dependence of Coefficient on Dose Received by Solvent for Distribution of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Previously Exposed to Gamma Radiation While in Contact with 6M HNO₃

b. Effects of Radiolysis after Solvent Wash

Figure II-33 presents, as a function of dose received, coefficients for distribution of americium between aqueous 0.01M HNO₃ and TRUEX-NPH solvent that had been exposed previously to gamma radiation at 50°C while in contact with 0.25M HNO₃ and then washed with water or with aqueous sodium carbonate. Figure II-34 presents the results for an analogous set of experiments in which

the solvent had been subjected to radiolysis at 50° C while in contact with 6M HNO₃. These two figures suggest that coefficients for distribution of americium between 0.01M HNO₃ and TRUEX-NPH solvent that had been subjected to radiolysis followed by washing were lower for aqueous carbonate wash than for water wash.

Fig. II-32.

Dependence of Coefficient on Dose Received by Solvent for Distribution of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Previously Exposed to Gamma Radiation While in Contact with Simulated CAW containing 1.4M HNO₃

Fig. II-33.

Dependence of Coefficient on Dose Received by Solvent for Distribution of Americium between Aqueous 0.01M HNO₃ and TRUEX-NPH Solvent Previously Exposed to Gamma Radiation While in Contact with 0.25M HNO₃, Then Washed with Water or Aqueous Sodium Carbonate

Fig. II-34.

Dependence of Coefficient on Dose Received by Solvent for Distribution of Americium between Aqueous 0.01M HNO₃ and TRUEX-NPH Solvent Previously Exposed to Gamma Radiation While in Contact with 6M HNO₃, Then Washed with Water or Aqueous Sodium Carbonate

c. Effects of Hydrolysis

To measure the effects of solvent hydrolysis on the distribution coefficient of americium, samples of TRUEX-NPH solvent were partially hydrolyzed by stirring them in contact with aqueous nitric acid at several values of concentration, temperature, and time. The nitric acid concentrations included 0.25, 2.5, and 6M, as well as 1.4 and 2.4M for the simulated CAW solutions. The hydrolysis times ranged from about 24 to 600 h. The temperatures included 50, 70, and 95 °C.

Figure II-35 presents, as a function of hydrolysis time, coefficients for distribution of americium between aqueous nitric acid of three different initial concentrations and TRUEX-NPH solvent that had been hydrolyzed by 2.5M HNO₃ at 50 °C. (Analysis of other data is not yet complete and will be reported for the next semiannual.) Figures II-36 and II-37 present the results of analogous experiments in which the solvent had been hydrolyzed by 2.5M HNO₃ at 70 and 95 °C, respectively. These figures show that (1) hydrolysis increases with temperature, and (2) the coefficients for distribution of americium between 0.01M HNO₃ and partially hydrolyzed TRUEX-NPH solvent generally increased by 3-4 orders of magnitude as the hydrolysis time increased over a range of about 400 h. The coefficients for distribution of americium between 0.05M HNO₃ and partially hydrolyzed TRUEX-NPH solvent behaved similarly. In contrast, the coefficients for distribution of americium between 2.0M HNO₃ and partially hydrolyzed TRUEX-NPH solvent generally decreased with hydrolysis time.

d. Effects of Hydrolysis and Solvent Washing

Washing as a means of nullifying the effects of hydrolysis on the extraction properties of the solvent was tested by contacting samples of partially hydrolyzed solvent with water or with 0.25M aqueous sodium carbonate. Triplicate samples of washed solvent were then taken, and coefficients for distribution of americium between these and three different concentrations of nitric acid--0.01, 0.05, and 2.0M -- were measured.

Fig. II-35. Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Hydrolyzed by 2.5M HNO₃ at 50°C

Fig. II-36.

Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Hydrolyzed by 2.5M HNO₃ at 70°C

Table II-30 presents, for a range of hydrolysis times, coefficients for distribution of americium between aqueous nitric acid solutions and TRUEX-NPH solvent that had been previously hydrolyzed at 50°C by 2.5M HNO₃ and then washed with water or with aqueous sodium carbonate. For these conditions, the distribution coefficients remain essentially constant over the range of hydrolysis times, suggesting that little hydrolysis has taken place.

Figure II-38 presents, as a function of hydrolysis time, coefficients for distribution of americium between aqueous 0.01M HNO₃ and TRUEX-NPH solvent that had been previously hydrolyzed at 70°C by 2.5M HNO₃ and then washed with water or with aqueous sodium carbonate. Figures II-39 and II-40 present the results of analogous experiments in which the aqueous phase in the distribution was

0.05M and 2.0M HNO₃, respectively. Figure II-38 shows that the coefficients for distribution of americium between 0.01M HNO₃ and partially hydrolyzed solvent are lower for carbonate wash than for water wash. Similar behavior was found for samples involving americium distribution between 0.05M HNO₃ and solvent (Fig. II-39). On the other hand, for analogous systems involving distribution between 2.0M HNO₃ and solvent, the coefficients for water-washed solvent are lower than those for carbonate-washed solvent (Fig. II-40).

Fig. II-37. Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Hydrolyzed by 2.5M HNO₃ at 95 °C

Table II-30. Distribution Coefficient of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Hydrolyzed at 50 °C by 2.5M HNO₃, Then Washed with Water or Aqueous Sodium Carbonate

Hydrolysis Time, h	D _{Am} ^a (Water Washed)			D _{Am} ^a (Carbonate Washed)		
	0.01M	0.05M	2.0M	0.01M	0.05M	2.0M
0.0	0.012	0.215	29.7	0.010	0.244	29.5
28	0.014	0.235	32.1	0.015	0.266	36.2
126.3	0.015	0.253	31.5	0.014	0.255	34.8
220.6	0.021	0.260	30.7	0.017	0.260	35.2

^aD_{Am} values were obtained for 0.01, 0.05, and 2.0M HNO₃ solutions and the degraded TRUEX-NPH at 25 °C.

Table II-31 presents, for a range of hydrolysis times, coefficients for distribution of americium between aqueous nitric acid solutions and TRUEX-NPH solvent that had been previously hydrolyzed at 70° C while in contact with simulated CAW containing 1.4M HNO₃, then washed with water or with aqueous sodium carbonate. This system exhibits higher americium distribution coefficients than the analogous system for which the solvent had been exposed to hydrolysis at a higher acid concentration, 2.5M HNO₃, as described above (Table II-30). Also, D_{Am} values after carbonate washing were higher at all HNO₃ concentrations. This result suggests an effect of metal ions, present in simulated CAW, on hydrolysis.

Fig. II-38.

Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between 0.01M HNO₃ and TRUEX-NPH Solvent Hydrolyzed by 2.5M HNO₃ at 70° C, Then Washed with Water or Aqueous Sodium Carbonate

Fig. II-39.

Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between 0.05M HNO₃ and TRUEX-NPH Solvent Hydrolyzed by 2.5M HNO₃ at 70° C, Then Washed with Water or Aqueous Sodium Carbonate

Fig. II-40.

Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between 2.0M HNO_3 and TRUEX-NPH Solvent Hydrolyzed by 2.5M HNO_3 at 70° C, Then Washed with Water or Aqueous Sodium Carbonate

Table II-31. Distribution Coefficient of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Hydrolyzed at 70° C by Simulated CAW Containing 1.4M HNO_3 , Then Washed with Water or Aqueous Sodium Carbonate

Hydrolysis Time, h	D_{Am} Water Washed ^a			D_{Am} Carbonate Washed ^{a,b}		
	0.01M	0.05M	2.0M	0.01M	0.05M	2.0M
0.0	0.123	0.215	29.7	0.047	0.226	29.7
24	8.08	5.09	27.5	11.05	1.78	26.5
98	12.6	9.20	19.3	18.5	10.1	19.6
193.5	33.1	17.3	14.5	43.5	19.7	15.4
268.4	44.2	18.0	13.7	69.0	24.3	13.7
436.7	51.4	19.6	9.36	125.9	28.4	9.39

^a D_{Am} values were obtained for 0.01, 0.05 and 2.0M HNO_3 solutions and the degraded TRUEX-NPH at 25° C.

^bBecause forward-extraction D_{Am} values were lost, back-extraction data were used.

Figure II-41 presents, as a function of hydrolysis time, coefficients for distribution of americium between aqueous 0.01M HNO_3 and TRUEX-NPH solvent that had been previously hydrolyzed at 70° C by 6M HNO_3 and then washed with water or with aqueous sodium carbonate. Figures II-42 and II-43 present results of analogous experiments in which the aqueous phase in the distribution was 0.05M HNO_3 and 2.0M HNO_3 , respectively. Examination of Fig. II-41 shows that the coefficients for distribution of americium between 0.01M HNO_3 and solvent that had been partially hydrolyzed at 70° C in contact with 6M HNO_3 and then washed by aqueous carbonate are lower than those for samples where the solvent had been washed by water. Similar behavior is shown for samples involving distribution between 0.05M HNO_3 and solvent (Fig. II-42). On the other hand, for analogous systems involving distribution between 2.0M HNO_3 and solvent, the coefficients for water-washed solvent are lower than those for carbonate-washed solvent (Fig. II-43).

Fig. II-41. Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between 0.01M HNO_3 and TRUEX-NPH Solvent Hydrolyzed by 6M HNO_3 at 70°C, Then Washed with Water or Aqueous Sodium Carbonate

Fig. II-42. Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between 0.05M HNO_3 and TRUEX-NPH Solvent Hydrolyzed by 6M HNO_3 at 70°C, Then Washed with Water or Aqueous Sodium Carbonate

Fig. II-43. Dependence of Coefficient on Hydrolysis Time for Distribution of Americium between 2.0M HNO_3 and TRUEX-NPH Solvent Hydrolyzed by 6M HNO_3 at 70°C, Then Washed with Water or Aqueous Sodium Carbonate

Table II-32 presents, for a range of hydrolysis times, coefficients for distribution of americium between aqueous nitric acid solutions and TRUEX-NPH solvent that had been previously hydrolyzed at 95°C by 2.5M HNO_3 and then washed with water or with aqueous sodium carbonate. These data show that, because of the significant damage done to the solvent by hydrolysis at 95°C, there is no significant difference in the extraction behavior of non-washed, water-washed, and carbonate-washed solvents.

Table II-32. Distribution Coefficient of Americium between Aqueous Nitric Acid Solutions and TRUEX-NPH Solvent Hydrolyzed at 95°C by 2.5M HNO_3 , Then Washed with Water or Aqueous Sodium Carbonate

Hydrolysis Time, h	D_{Am} Water Washed ^a			D_{Am} Carbonate Washed ^b		
	0.01M	0.05M	2.0M	0.01M	0.05M	2.0M
0	0.012	0.215	29.7	0.047	0.226	29.7
24	4.93	1.92	13.2	4.97	1.79	12.7
48	37.9	5.20	4.11	34.1	4.60	3.99
72	61.2	7.67	2.31	69.1	6.91	2.22
147.5	105	13.0	0.999	110	11.8	0.974
388.5	148	21.6	0.372	138	19.2	0.360

^a D_{Am} values were obtained for 0.01, 0.05, and 2.0M HNO_3 solutions and the degraded TRUEX-NPH at 25°C.

^bBecause D_{Am} values for the forward extraction were lost, back-extraction data are presented.

3. Changes in Acidity Accompanying Radiolysis and Hydrolysis

Radiolysis or hydrolysis of TRUEX-NPH solvent in contact with aqueous nitric acid is accompanied by changes in the acidities of both the organic and the aqueous phases. This phenomenon has been investigated by measuring the acidities of the solvent and the contacted aqueous phase.

The concentration of acidic species in a sample of solvent was determined by washing with three portions of water, diluting the collected washings to a measured volume, and titrating an aliquot of it with standard base. The acidity of aqueous nitric acid that had been in contact with solvent during radiolysis or hydrolysis was determined by similar titration.

Figures II-44 through II-55 show the concentration of acid in aqueous and organic phases that had been subjected to hydrolysis and radiolysis. Figures II-44 to II-46 represent the acidity of aqueous phases, whereas Figs. II-47 to II-55 represent the acidity of organic phases determined from washings.

Figure II-44 indicates that when 0.25M HNO_3 in contact with TRUEX-NPH is exposed to gamma radiation, the acidity of the aqueous phase increases with received dose. Figure II-45 indicates, conversely, that when 6M HNO_3 in contact with TRUEX-NPH is exposed to gamma radiation, the acidity of the aqueous phase decreases with received dose.

Figure II-46 shows that, for 6M HNO_3 in contact with TRUEX-NPH at 95°C , the acidity of the aqueous phase decreases with time and thus, presumably, with the extent of hydrolysis.

Fig. II-44. Effect of Gamma Dose on Acid Concentration of Aqueous Phase, Initially 0.25M HNO_3 , in Contact with TRUEX-NPH at 50°C

Fig. II-45. Effect of Gamma Dose on Acid Concentration of Aqueous Phase, Initially 6M HNO_3 , in Contact with TRUEX-NPH at 50°C

Fig. II-46. Effect of Hydrolysis Time on Acid Concentration of Aqueous Phase, Initially 6M HNO_3 , in Contact with TRUEX-NPH at 95°C

Fig. II-47. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 0.25M HNO_3 at 50°C

Fig. II-48. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 0.25M HNO_3 at 70°C

Fig. II-49. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 0.25M HNO_3 at 95°C

Fig. II-50. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 2.5M HNO_3 at 50°C

Fig. II-51. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 2.5M HNO_3 at 70°C

Fig. II-52. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 2.5M HNO_3 at 95°C

Fig. II-53. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 6M HNO_3 at 50°C

Fig. II-54. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 6M HNO_3 at 70°C

Fig. II-55. Acid Concentration in Organic Phase as a Function of Contact Time between TRUEX-NPH Solvent and 6M HNO_3 at 95 °C

Figures II-47 to II-49 represent, as a function of time in contact with 0.25M HNO_3 at 50, 70, and 95 °C, the acidity of the organic phase. At 50 °C, the acidity of the organic phase changed very little with hydrolysis time; at 70 and 95 °C, however, the acidity of the organic phase increased as hydrolysis time increased.

Figures II-50 to II-52 represent, as a function of time in contact with 2.5M HNO_3 , the acidity of the organic phase at 50, 70, and 95 °C. At 50 °C, the acidity of the organic phase, except for a couple of apparently high values, changed very little with hydrolysis time. At 70 and 95 °C, however, the acidity of the organic phase decreased as hydrolysis time increased. Figures II-53 to II-55 indicate similar behavior for analogous systems involving 6M HNO_3 .

I. Supercritical Fluid Chromatography (P.-K. Tse)

1. Introduction

The analytical technique which we have chosen to develop for CMPO and TRUEX solvent analyses is supercritical fluid chromatography (SFC). The reasons for this decision are:

- It is a low temperature technique that can accurately measure CMPO without decomposing it and thus giving spurious results. Since CMPO begins to decompose at ~180 °C, SFC analyses are performed at <120 °C.
- It has the ability to be used with all the detectors that are presently available for gas chromatography (GC) and high performance liquid chromatography (HPLC), including the highly sensitive and efficient flame ionization detector (FID) and mass spectrometer (MS).

- SFC analyses are run much like GC and HPLC and can be easily automated for increased productivity and quality control.

2. Experimental

a. Equipment

A Lee Scientific Model 622 supercritical-fluid chromatograph/ gas chromatograph with FID detector was used for most of the work in this study. A schematic diagram of the SFC is shown in Fig. II-56. Split injection was done using a 50 μm ID fused silica capillary as a split restrictor (20:1 split ratio). A 50 μm ID frit restrictor was used to control the column flow rate. Optimized experimental parameters were:

1. Carrier fluid, SFC grade CO_2 (Scott Specialty Gas). Linear flow rate was controlled by the length of the frit restrictor (usually ten times above the minimum linear velocity).
2. Injection temperature at room temperature.
3. Density (pressure) program: initial 0.25 g/mL, hold for 5 to 10 min (depending on the length of frit restrictor); ramp 0.01 g/mL/min to 0.55 g/mL; hold for 2 min.
4. Oven temperature, 110° C.
5. Detector temperature, 325° C.

Lee Scientific superbond capillary columns were used. Table II-33 lists the columns that were tested in this study.

Fig. II-56. Schematic Diagram of SFC Instrumentation

Table II-33. List of SFC Columns Tested

Stationary Phase	Film Thickness, μm	Length, m	Internal Diameter (ID), μm
SB-Octyl-50	0.25	10	50
SB-Methyl-100	0.25	10	50
SB-Methyl-100	0.25	20	100
SB-Phenyl-5	0.25	20	100
SB-Phenyl-50	0.25	10	50
SB-Biphenyl-30	0.25	20	50

b. Reagents

The bulk of the CMPO used in this study was purchased from M&T Chemical Company; its purity was defined as "crude" CMPO for the purposes of this report.* A second sample of CMPO was prepared by Occident Chemical Company, Glad Island, NY, and was supplied to us by E. P. Horwitz, ANL Chemistry Division. Gold label TBP (99+% purity) and reagent grade TBP (99%) were obtained from Aldrich Chemical Company. Dichloromethane (HPLC or GC grade from Aldrich) is a common solvent for GC and SFC because it is only slightly retained in the column, and most organic compounds can be easily dissolved in dichloromethane.

c. Purification of CMPO

Purification of CMPO was performed by the method reported by Horwitz et al.²⁹ but with slight modification. One hundred-twenty grams of ~92% pure CMPO was dissolved into 250 mL of n-heptane. Twenty-six grams of Dowex AG-MP50, which had been dehydrated and equilibrated with heptane, was added to the heptane solution. The mixture was stirred for one hour at room temperature. After an hour, 50 g of dehydrated Amberlyst A-26 resin in the hydroxide form, which had also been equilibrated with heptane, was added to the mixture. Stirring was continued for 1-1/2 h at room temperature. The resin was removed by filtration. The heptane solution was washed with 0.25M Na_2CO_3 (2:1 O/A), 0.1M HNO_3 (O/A = 2), and H_2O (O/A = 1) and dried overnight with anhydrous Na_2SO_4 . After filtration, a fraction of the heptane was removed by rotatory evaporation. The solution was stored in a freezer. Crystals found at the bottom of the beaker after three days were removed from the mother liquor by filtration and dried under vacuum. The final weight of the purified CMPO was 81 g. Multiple recrystallizations were performed by repeating the above procedure.

d. Decomposition of CMPO

The white crystalline CMPO (crude or purified) was sealed under vacuum in a glass tube and heated in an oven with the temperature maintained at 190°C for 15 h. During treatment, the CMPO changed to a brown liquid. It solidified on standing at room temperature to a pale brown solid.

*Later defined as solvent extraction grade.

3. Conclusions

The goal of this study was to test the applicability of SFC to quantitating (1) the purity of commercially available CMPO and (2) the compositions of the TRUEX-TCE and TRUEX-NPH solvents under plant conditions. Although actual in-plant use has not been established, results obtained in this laboratory show that the SFC technique should be useful in this situation. The results of this study are published in an ANL topical report³⁰ and will only be summarized below.

Supercritical fluid chromatography has been demonstrated to be a very useful technique to analyze thermally unstable compounds such as CMPO. Under the operating conditions chosen for analysis of CMPO and the TRUEX-NPH and TRUEX-TCE solvents, no decomposition products of CMPO will be detected in the injection valve or in the column. The CMPO and TBP are well separated from each other and from their impurities and the TCE and NPH diluents. The separation factor between CMPO and TBP is greater than 10. The reproducibility between duplicate samples is <0.1% for retention times and 2% for peak areas. Running replicate samples for each analysis and using an internal standard can decrease the errors in peak-area measurements even further.

The SFC technique allows wide flexibility in optimization of chromatographic conditions for the analysis. In an SFC system, analysis temperature, mobile-phase composition, mobile-phase density, stationary-phase composition, column dimensions, and specific detectors are parameters that can be varied to meet the desired analysis requirements. This study demonstrated that the efficiency of chromatographic separation of TRUEX solvent components and their impurities and degradation products is affected by several of these factors. The optimum conditions for analysis of CMPO and the TRUEX-NPH and TRUEX-TCE solvents are described in Appendixes A-D of Ref. 30. A method for quantitatively standardizing the system using an internal standard is described in Appendix E of Ref. 30.

Several SFC chromatograms are presented below. Figure II-57 is an SFC chromatogram of purified CMPO. As a comparison, Figs. II-58 and II-59 are chromatograms of crude and thermally decomposed CMPO. Figures II-60 and II-61 give SFC chromatograms of the TRUEX-TCE and the TRUEX-NPH solvent, respectively.

Fig. II-57.

Supercritical Fluid Chromatogram of CMPO at 110 °C. Experimental conditions:
50 μ m ID x 10 m SB-methyl-100 Column.
Pressure program from 100 to 250 atm,
ramped at 2 atm/min.

Fig. II-58.

Supercritical Fluid Chromatogram of Crude CMPO at 120 °C. Experimental conditions: 100 μm ID x 20 m SB-methyl-100 column. Density program from 0.25 g/mL to 0.55 g/mL, ramped at 0.01 g/mL/min. Oven temperature at 110 °C.

Fig. II-59.

Supercritical Fluid Chromatogram of Thermally Decomposed Crude CMPO. Experimental conditions: 10 μm ID x 20 m SB-methyl-100 column. Density program from 0.25 to 0.55 g/mL, ramped 0.01 g/mL/min. Oven temperature at 110 °C.

Fig. II-60.

Supercritical Fluid Chromatogram of the TRUEX-TCE Solvent. Experimental conditions: 50 μm ID x 10 m SB-methyl-100 column. Density program from 0.25 to 0.60 g/mL, ramped at 0.02 g/mL/min. Oven temperature at 100°C.

Fig. II-61.

Supercritical Fluid Chromatogram of the TRUEX-NPH Solvent:

1) CH_2Cl_2	5) $\text{n-C}_{15}\text{H}_{32}$
2) $\text{n-C}_{12}\text{H}_{26}$	6) TBP
3) $\text{n-C}_{13}\text{H}_{28}$	7) C-24 Standard
4) $\text{n-C}_{14}\text{H}_{30}$	8) CMPO

Experimental conditions: 50 μm ID x 10 m SB-methyl-100 column. Density program from 0.25 to 0.60 g/mL, ramped at 0.02 g/mL/min. Oven temperature at 100°C.

J. Centrifugal Contactor Development

(R. A. Leonard, D. B. Chamberlain, J. C. Hoh, R. A. Benson, J. E. Stangel,* and K. A. Barnhouse**)

1. Introduction

The Argonne centrifugal contactor is modified as needed to work with specific solvent extraction processes. To evaluate processes involving high alpha/beta activity levels (in a glove box) and/or high gamma radiation (in a shielded cell facility), a 4-cm contactor was designed and built that can be used where remote handling is required. It has been evaluated under typical operating conditions in both a glove box and a shielded-cell mockup area with good success. The basic design for remote handling is now being used in the new 2-cm contactor ("minicontactor"). This minicontactor is being designed and built to minimize the feed needed for testing solvent extraction flowsheets. To allow the use of the contactors with the TRUEX-NPH solvent at all densities and O/A flow ratios, the 4-cm rotor is being modified. To operate the 4-cm contactor at slightly elevated temperatures (30 to 50 °C), a heating system is being designed.

In support of these various contactor development efforts, vibrational frequencies and amplitudes are being measured with proximity probes and real-time analyzers. The results are related to the rotor design with the BEAM IV program, which models vibrations in rotating systems.

2. Contactors for Remote Handling

During the previous report period, the 4-cm centrifugal contactor design was modified so that the contactors could be used in a remote facility with manipulators and a window to provide visual access, and an eight-stage unit was fabricated. This unit has been successfully operated in (1) a shielded-cell mockup area with manipulators and a viewing window and (2) a glove box. In both cases, the design was shown to work as specified. Video tapes were made of these operations for future reference. Finally, the hydraulic performance of the unit was tested and found to be satisfactory. The work here reports on the operation of the high-level liquid detector in the remote-handled 4-cm contactor.

An off-the-shelf optical-electronic liquid-level control system, available from Cole-Parmer (Chicago, Illinois), was used to test the operation of the standpipe that holds the high-level liquid detector in the remote-handled 4-cm contactor. This chemically resistant probe (held in place by a 1/2-in. NPT male fitting and using a pulsed infrared signal to detect when the probe has contacted a liquid phase) was tested in an open beaker of water and found to be quite responsive. However, when the probe was used in the standpipe, it was not as responsive. The problem seemed to be that the rise of liquid in the standpipe was restricted by the close fit of the detector in the detector holder. This close fit impeded the rising liquid from displacing the air. This problem was corrected by drilling an air hole in the detector holder, just below the point where the detector threads end. Detector operation is now satisfactory, although the liquid level is still a little high before it is detected. As a result, a small quantity of liquid is displaced to the next stage before the detector senses the high level of the liquid in the annular mixing zone. Some further work is needed on the operation of the standpipe for the high-level liquid detector before we rely on it fully.

At one point during these tests, the annular mixing zone was filled up to the upper collector ring. This happened while the rotor was spinning, and liquid was pumped out the upper exit port

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with a considerable head, possibly a foot or more above the upper collector ring. This liquid head gives some idea of the momentum that can be transferred from the slinger ring of the rotor to the liquid in (or going into) the upper collector ring of the contactor housing.

3. Rotors for TRUEX-NPH Solvent

In the first verification run, some TRUEX-NPH solvent exited with the aqueous effluent from the second strip section. The contactor operation at this stage was modeled with the ROTOR worksheet running under Microsoft Excel. (This ROTOR worksheet is a spreadsheet version of the contactor model given as a FORTRAN program called CCD in an earlier report.³¹) We found that the organic phase in the aqueous effluent was a result of the density of the TRUEX-NPH solvent being fairly close (only 14% lower) to that of water. (The 4-cm rotors were initially designed for 30% TBP dissolved in NPH. Later, it was found that this same design would also work for TRUEX-CCl₄ and TRUEX-TCE solvents, but not for the TRUEX-NPH solvent.) Using the ROTOR worksheet, we designed a new 4-cm rotor for use with the TRUEX-NPH solvent. This rotor, designated Rotor II, will work even though the density of the organic phase is only 10% lower than that of the aqueous phase. In addition, Rotor II can still be used with the other solvents. The trade-off for good operation over a wider range of solvent densities is that the nominal maximum throughput for Rotor II is reduced from 620 to 340 mL/min.

Based on the design calculations, new rotors are being fabricated for the "open," "closed," and "remote" 4-cm contactors. These new rotors, which are almost complete, will be used in future flowsheet tests with TRUEX-NPH as the solvent.

4. Minicontactors

Fabrication of a 16-stage 2-cm contactor was completed in September 1988. This minicontactor was designed and built for testing solvent extraction flowsheets. The 4-cm contactor is also used for this purpose and has done quite well; however, it requires about 10 L of feed to run one test. The new minicontactor will be smaller and will require only 10 mL liquid per stage, which is about 1/10th the liquid in a 4-cm contactor stage; thus, only 1 L of feed will be required for testing a typical flowsheet with the minicontactor. While the rotor diameter of the new minicontactor is 2 cm, the same as that for earlier minicontactors which did not work well at low O/A flow ratios,³² the rotors in the new minicontactor are longer. At the same time, the rotor internals and the annular mixing zone have been redesigned so that the total liquid in each stage is less. This longer rotor was tested in a single-stage unit and found to give good operation at all O/A flow ratios, as the 4-cm and larger contactors do. Based on these successful tests, the new rotor design was used in the multistage 2-cm contactor.

a. Single-Stage Tests

A single-stage 2-cm contactor was built to test the hydraulic and mechanical performance of the new 2-cm rotor before using it in the 16-stage 2-cm contactor. Two single-stage housings were built for these tests. The one housing was made of acrylic plastic so that it would be transparent. This transparent housing allowed us to evaluate mixing zone operation when the diluent is NPH or nDD (normal dodecane). From the results, we could determine if the increased length of the new 2-cm rotor was sufficient to obtain good contactor operation at all O/A flow ratios. The other housing was made of stainless steel so that we could operate the contactor with TCE diluent. (The TCE could not be used with the transparent housing because it dissolves acrylic plastics.) The steel contactor housing was used with pure TCE, which is the worst possible case because the liquid in the rotor has the highest density that it will ever have for the TRUEX process. If the vibrations of the new motor/rotor system are at an acceptably low level for this case, then they will be acceptable for all other cases since their liquid density will be lower.

The motor/rotor assembly for the single-stage tests is pictured in Fig. II-62. The experimental setup, showing both the motor and the rotor in the acrylic housing, can be viewed in Fig. II-63. A closeup of the annular mixing zone while the contactor is operating can be seen in Fig. II-64. The operating conditions for this photograph were that the organic (O) phase was 30% TBP in nDD, the aqueous (A) phase was 0.01M HNO_3 , the total throughput was 60 mL/min, and the O/A flow ratio was 1.0.

Fig. II-62. Motor/Rotor Assembly for Single-Stage 2-cm Contactor

(1) Mixing-Zone Tests

Using the transparent contactor housing, four series of tests were carried out to evaluate mixing zone operation. The first test series was done with 30% TBP in nDD and 0.01M HNO_3 . By operating at 50 mL/min total throughput with an O/A of 1.0, the flow rate of one phase was cut off entirely. Then we determined whether the liquid height in the mixing zone increased during phase transition from O to A or from A to O. No such change was observed. Thus, the new 2-cm rotor does not seem to have a problem with phase inversion.

In a second test series, which also tested for phase inversion, only one phase was in the mixing zone at the start of the test. To do this, the mixing zone was drained of all liquid while the rotor was kept running. Then one phase was introduced into the mixing zone. When it began to flow out the contactor, the flow to the unit was shut off. Finally, the other phase was introduced into the mixing zone at a fixed flow rate. When this was done, the liquid height in the mixing zone rose as the turbulent mixture of the two immiscible liquids approached phase inversion. However, the maximum liquid level, which occurred just before phase inversion, was only 3.9 cm (1.54 in.) above the bottom of the rotor. At this height, the liquid level in the mixing zone is just about even with the centerline of the

inlet ports. The top of the mixing zone, at the lip of the lower collector ring, is 5.7 cm (2.23-in.) above the bottom of the rotor. As long as the liquid level in the mixing zone is below the lower collector ring, it will not hinder contactor operation. Upon achieving phase inversion, the liquid level in the mixing zone drops quickly. The momentarily higher flow rate that this drop at phase inversion creates causes some liquid to flow from the lower collector ring down into the mixing zone. After a few seconds, the contactor returns to normal operation with good hydraulic performance. This phase-inversion flow spurt, if it occurs at all, will occur only once on startup. Thus, phase inversion will not be a problem.

Fig. II-63. Single-Stage 2-cm Contactor with Transparent Housing

In the third test series, the minimum throughput at which the liquid maintains contact with the rotor was determined. Past experience has shown that mixing zone operation is good as long as the liquid there maintains contact with the rotor. If the mixing-zone liquid drops to the bottom of the mixing zone and no longer contacts the rotor, extraction efficiency drops substantially. For the new 2-cm rotor, we found that, even at no-flow conditions, the liquid in the mixing zone never lost contact with the rotor. Thus, there appears to be no lower limit for the flow rate at which the 2-cm contactor can be operated.

The fourth series of mixing-zone tests was completed at an O/A ratio of 1.0. For these tests, the liquid height in the mixing zone was constant, being 2.4 ± 0.2 cm (0.93 ± 0.05 in.) above the bottom of the rotor as the total flow rate was varied from 26 to 128 mL/min. At the highest flow rate, 128 mL/min, which is well beyond the satisfactory operating region for this 2-cm contactor, the other-phase carryover for both effluents was 10%.

Fig. II-64. Operating Single-Stage 2-cm Contactor

(2) Separating-Zone Tests

As a first test of the separating zone, that is, the centrifugal settling region inside the rotor, the single-stage 2-cm contactor was operated with 33.7% TBP in NPH (essentially PUREX-NPH solvent, which has 30% TBP in NPH) and 0.01M HNO_3 . The maximum flow rates obtained from these tests are listed in Table II-34 along with the mode of failure when the maximum flow rate was reached. Using a value for the dispersion number (N_{Di}) of 8×10^{-4} , a reasonable value based on the results of the batch dispersion test listed in Table II-35 and the ROTOR worksheet, we derived design curves at the three O/A flow ratios tested (0.33, 1.0, and 3.0). These curves, shown in Fig. II-65, were used with results listed in Table II-34 to calculate an apparent radius for the upper (more-dense-phase) weir. These apparent radii, also listed in Table II-34, are less than the actual radius of 6.01 mm by 0.09 to 0.18 mm. Since the contactor has a nominal total throughput of 40 mL/min, it would meet the design criteria for PUREX-NPH solvents. The design curves indicate that a somewhat larger radius for the upper weir should allow the rotor to work even better with the PUREX-NPH solvent.

In a second test of the separating zone, the single-stage 2-cm contactor was operated with the TRUEX-NPH solvent and 0.01M HNO_3 at O/A ratios of 0.33, 1.0, and 3.0. The maximum flow rates obtained from these tests are listed in Table II-36 along with the mode of failure when the maximum flow rate was reached. Using N_{Di} of 8×10^{-4} , again a reasonable value based on the batch dispersion tests listed in Table II-35, and the ROTOR worksheet, we derived the design curves for the three O/A flow ratios tested. These curves, shown in Fig. II 66, were used with results listed in Table II-36 to calculate an apparent radius for the upper (more-dense-phase) weir. These apparent radii, also listed in Table II-36, are less than the actual radius of 6.01 mm by 0.11 to 0.19 mm. Note that, since the

nominal total throughput for the contactor is 40 mL/min, the design criteria for TRUEX-NPH solvents are not quite met. The design curves indicate that a somewhat larger radius for the upper weir should allow the rotor to operate at throughputs greater than 40 mL/min with TRUEX-NPH solvent for all O/A flow ratios.

Table II-34. Apparent Radius for Upper Weir Based on Two-Phase Tests with PUREX-NPH Solvent

Organic Phase		PUREX-NPH ^a	
Aqueous Phase		0.01M HNO ₃ ^b	
Measured Radius for Upper (More-Dense-Phase) Weir, mm		6.01	
Measured Radius for Lower (Less-Dense-Phase) Weir, mm		5.70	

O/A Flow Ratio	Maximum Flow Rate, mL/min	Mode of Failure	Apparent Radius for Upper Weir, ^c mm
0.33	40.0 ± 2.5 ^d	>1% A in C	5.92
1.0	53.5 ± 1.5	>1% A in O	5.89
3.0	53 ± 2 ^d	>1% A in O	5.83

^aHas 33.7% (by volume) TBP in NPH with a density of 828 g/L at 25 °C. The solvent density would have been 819 g/L if we had had 30% TBP in NPH.

^bHas a density of 997 g/L at 25 °C.

^cBased on a dispersion number of 8×10^{-4} . See Fig. II-65 and Table II-35.

^dIn some cases, one would get a spurt of aqueous phase in organic effluent that exceeded 1% of the total effluent volume at flow rates less than the maximum shown here.

Based on these tests, the radius of the upper weir was increased from 6.01 mm (0.4735-in. dia) to 6.09 mm (0.4795-in. dia). As shown by the curves in Fig. II-67, this new design radius is on the upper side for the region of satisfactory operation with the TRUEX-NPH solvent. Contactor operation will now meet or exceed the design throughput if the apparent radius of the upper weir is lower than the actual radius by 0.08 to 0.19 mm, or if the apparent radius is the same as the actual radius. With this change, the contactor should meet the design criterion of a nominal throughput of 40 mL/min for both PUREX-NPH and TRUEX-NPH solvents.

Since the apparent radius of the upper weir was typically lower than the actual radius, the data were evaluated to determine the reason behind this result. One possible explanation comes from the flow spurts out the organic (less-dense-phase) exit, as noted in Tables II-34 and II-36. These flow spurts occurred every few seconds in the less-dense (organic) phase effluent. The largest spurts, which occurred at intervals from 10 to 120 s, contained some of the more-dense (aqueous) phase. Because the aqueous phase in the organic effluent was essentially separated from the organic phase, the spurts were not due to dispersion in the mixing zone. From observations through the clear acrylic housing, it did

Table II-35. Dispersion Number for Two Solvents with Dilute Acid

Liquid height, m	0.186 ± 0.003	
Gravitational acceleration, m/s ²	9.81	
Total liquid volume, mL	100	
Liquid flow	None ^a	
Aqueous phase (A)	0.01M HNO ₃	
Organic Phase (O)	O/A Ratio	Dispersion Number (N _{DI}) ^b
33.7% TBP in NPH	0.33	(10.5 ± 0.1) × 10 ⁻⁴
	1.00	(9.2 ± 0.5) × 10 ⁻⁴
	3.0	(13.8 ± 0.5) × 10 ⁻⁴
TRUEX-NPH	0.33	(13.5 ± 0.3) × 10 ⁻⁴
	1.00	(8.5 ± 0.2) × 10 ⁻⁴
	3.0	(7.0 ± 0.2) × 10 ⁻⁴

^aBatch test done in 100 mL graduated cylinder with O/A volume ratio as shown.

^bThese dispersion numbers were measured as described in Appendix A of Ref. 33.

Fig. II-65. PUREX-NPH Design Curves with an Upper Weir Radius of 6.01 mm

Table II-36. Apparent Radius for Upper Weir Based on Two-Phase Tests with TRUEX-NPH Solvent

Organic Phase	TRUEX-NPH ^a		
Aqueous Phase	0.01M HNO ₃ ^b		
Measured Radius for Upper (More-Dense-Phase) Weir, mm	6.01		
Measured Radius for Lower (Less-Dense-Phase) Weir, mm	5.70		

O/A Flow Ratio	Maximum Flow Rate, mL/min	Mode of Failure	Apparent Radius for Upper Weir, ^c mm
0.33	34 ± 2	>1% A in O	5.90
1.0	35.2 ± 0.8 ^d	>1% A in O	5.86
3.0	>40.5	--	>5.82

^aHas 0.20M CMPO and 1.4M TBP in NHP with a density of 858 g/L at 25 °C.

^bHas a density of 997 g/L at 25 °C.

^cBased on a dispersion number of 8×10^{-4} . See Fig. II-66 and Table II-35.

^dOccasional spurt of organic effluent with some aqueous phase in it.

Fig. II-66. TRUEX-NPH Design Curves with an Upper Weir Radius of 6.01 mm

not appear that any of the more-dense-phase liquid was flowing past the slinger ring at the more-dense-phase collector ring and draining down into the less-dense-phase collector ring. We speculate that flow surging was caused by momentary changes in the liquid level in the mixing zone of the contactor. Such changes would momentarily cause high flow rates, and would thus allow some of the dispersion band to flow over the lower (less-dense-phase) weir. If the radius of the upper weir is increased, the dispersion band is moved further away (out) from the lower weir, and so, is less likely to cause a problem. However, the upper radius must not be increased so much that some of the dispersion (now closer to the underflow) escapes to the upper weir and out the aqueous (more-dense-phase) exit. For this reason, the radius of the upper weir was not increased as much as the low values for the apparent radius would suggest that it should be. Further work is needed to understand this effect more fully.

Fig. II-67. TRUEX-NPH Design Curves with an Upper Weir Radius of 6.09 mm

The liquid spurts of the less-dense phase from the rotor will give rise to some variation of the flow rate with time in the interstage lines of a multistage unit. At the low flow rates in the 2-cm contactor, the incoming liquids from the two smoothly operating pumps entered the mixing zone drop by drop. These two sources of flow rate variation will be somewhat lessened by the liquid volume in the mixing zone. However, there will be some variation of the actual O/A flow ratio about its average value. Although we do not expect this variation to be important, it suggests that we are near a lower limit for the size of the centrifugal contactors.

(3) Mechanical and Stage-Volume Tests

Using the stainless steel housing, the contactor was run with pure TCE, which is the most dense component of the various TRUEX solvents. Because this case results in the greatest liquid mass in the rotor, it is an appropriate test for the contactor mechanical performance. For this case, vibrations are most likely to be a problem. The motor/rotor vibrations were found to be at an acceptably low level so that the contactor passed its basic mechanical performance test.

After the mechanical tests with TCE, the flow of TCE to the contactor was stopped, and the liquid in the annular mixing zone was drained with the rotor still running. A total of 3.0 mL was found there. Then, the rotor was stopped, and the volume of liquid that was still in the rotor was collected. A total of 5.5 mL was found there. Thus, the total liquid in the contactor is below the 10-mL design limit for no-flow conditions. As flow is increased, the total liquid in a contactor stage will increase toward, and possibly exceed at times, the 10-mL design value. This increase is expected and will not be a problem.

b. Final Contactor Design

The final design for the sixteen-stage 2-cm contactor includes a support frame with a linear design so that four stages in a row make up the basic module. The modules are connected to each other so that a sixteen-stage contactor uses four modules and has 16 stages in a row. Remote-handling features that were developed and tested earlier on the 4-cm contactor are included in this 2-cm design. In this new 2-cm design, the rotor was made longer than earlier 2-cm rotors to prevent the dispersion in the mixing zone from backing up and overflowing into the lower collector ring when undergoing a phase inversion. The annular gap is made smaller, 1.6 mm (1/16 in.), to keep the extraction efficiency in the mixing zone above 98%. This small annular gap also limits the range of O/A flow ratios where either phase can be the continuous phase, and thus contributes to solving the phase inversion problem. The small annular gap also reduces the liquid volume in the mixing zone and thus helps to keep the total liquid volume in the stage to less than 10 mL. To further reduce the liquid volume in the stage, the two weir diameters were increased so that the volume in the separating zone inside the rotor was decreased. Then, because the rotor weirs were larger, the rotor inlet diameter was also increased. To further reduce the liquid volume in the rotor, the region where the radius is greater than the inner radius of the underflow was eliminated from the separating zone of the rotor. Only enough of this region was left to allow liquid flow to the underflow holes. For ease of fabrication, the underflow holes were replaced by four underflow slots, and the divertor disk in the separating zone was eliminated. In one final design change, the contactor housings were tack-welded into the box beam support frame (rather than continuously welded) so that potential warping of the box beam would not occur.

One of the key criterion for rotor design was to get the contactor stage volume for the 2-cm contactor to be only 1/10th that of the 4-cm contactor. In the final design for the new 2-cm rotor, the liquid volume in a 2-cm (minicontactor) stage is 8.5 mL (no flow), compared with about 85 mL (no flow) for a typical 4-cm stage. The other key design criterion, good operation over the entire range of O/A flow ratios, was established in actual single-stage tests.

c. Sixteen-Stage Fabrication

Based on the successful single-stage tests of this new 2-cm contactor, a sixteen-stage unit was designed and fabricated. An overall view of the completed contactors is shown in Fig. II-68. A close-up of the end of the multistage unit, Fig. II-69, shows the box beam used for the support frame and the attachment of the legs to this box beam. The multistage minicontactor is now ready for laboratory testing.

5. Centrifugal Contactor Costs

An Excel worksheet, called "Fabrication Costs," was designed for estimating the cost of designing, testing, and Argonne-design fabricating centrifugal contactors. This worksheet incorporates our past best estimates of these costs and some actual cost data. As needed, the worksheet will be extended to include new design considerations. In addition, the correlations used will be checked and updated as actual design and fabrication cost data become available.

Fig. II-68. Overall View of 16-Stage 2-cm Contactor

Fig. II-69. End View of Multistage 2-cm Contactor

K. Verification Studies

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1. Introduction

Laboratory verification tests of the TRUEX process are being completed to (1) develop a better understanding of the TRUEX process chemistry, (2) test and verify process modifications, and (3) verify the results of the GTM, which is being developed for predicting species extraction behavior and calculating flowsheets for the TRUEX process. These tests will be completed in 4-cm centrifugal contactors during FY 1988 and FY 1989.

Three 4-cm centrifugal contactor units are available for completing these tests. A sixteen-stage 4-cm centrifugal contactor will be used for nonradioactive tests. A second 16-stage unit located in a glovebox will be used when radioactive solutions are required. A new eight-stage 4-cm unit, designed for remote operation, can be used for either radioactive or nonradioactive experiments.

Although specific waste solution compositions will be used in these tests, the purpose is not to demonstrate flowsheets for specific waste streams, but to collect data that will verify whether the TRUEX model predicts actual extraction behavior. Because these tests are not demonstration tests, the flowsheets used have not been optimized.

A large number of samples will be collected in each of these experiments. Typical analysis of the nonradioactive samples will include metals analysis (by inductively coupled plasma atomic emission spectrometry, ICP-AES), anion analysis (by ion chromatography, IC), acid analysis (by pH), measurement of solution density, and ion specific electrode analysis for NO_3^- and F^- concentrations. For tests with radioactive components, the radioactive elements will be measured by appropriate analytical techniques. With these samples, other analysis will be limited since much of the equipment needed for detailed analysis is available only for non-radioactive samples. Therefore, data collected in the nonradioactive tests will be used to help analyze the data from the radioactive-tracer experiments. To accomplish this, conditions set for the nonradioactive tests will be duplicated in the radioactive experiments.

Two verification tests (Nos. 2 and 3) were completed this period, both with the TRUEX-TCE solvent. These tests are discussed in detail below.

2. Verification Run 2

Verification Run 2 was the first nonradioactive test completed in the sixteen-stage 4-cm centrifugal contactor using the TRUEX-TCE solvent (0.25M CMPO, 0.75M TBP in TCE). The purpose of this test was to evaluate the extraction of nitric acid, iron, oxalic acid, and fluoride from a simplified acidic waste solution.

a. Flowsheet

The flowsheet used for this test is shown in Fig. 1E-70. The aqueous feed to the extraction section is a simulated acidic waste solution containing HNO_3 , Al, Fe, Na, Ca, $\text{H}_2\text{C}_2\text{O}_4$, HF, and H_2SO_4 . Two scrub sections were included in this flowsheet; the first scrub (DS) was added to scrub nitric acid and oxalic acid from the organic phase. A small stream was collected from stage number 4 (DW1) to

analyze the composition of the aqueous phase in the scrub section. The second scrub (EF) contained 0.005M Fe^{3+} , which was used to strip any residual oxalic acid from the organic phase. All of the second strip solution was removed at stage 7 (EW) so that its composition could be monitored throughout the run. The feed to the first strip section (FF) was 0.04M HNO_3 , while the feed to the second strip section (GF) was 0.1M HF.

Fig. II-70. Flowsheet for Verification Run 2

The extraction feed solution identified in Fig. II-70 was prepared by dissolving each nitrate, sulfate, and carbonate salt in water before combining them in a 20 L carboy. Table II-37 gives further details of sample preparation. The NaF was added to the aluminum nitrate salt solution to enhance its solubility. The nitric, sulfuric, and hydrofluoric acids were added last. The solution was then diluted to 20 L with distilled water. The feed solution was analyzed by acid titration and by ICP, and results of these analyses are shown in Table II-38.

The TRUEX-TCE solvent for this test was the same solvent used for the cold demonstration of the PFP flowsheet in FY 1986.³³ This solvent was treated by contacting it with a 0.1M HEDP (1-hydroxyethane-1,1-diphosphonic acid) solution followed by 0.25M sodium carbonate. The solvent was then filtered to remove any entrained aqueous phase and was stored in clear glass reagent bottles in the laboratory.

Table II-37. Preparation of Simplified CAW Solution

Species Added	Form of Addition	Amount Added, 20 L	Concentration, M
H ⁺	HNO ₃ , H ₂ C ₂ O ₄ •2H ₂ O, HF, H ₂ SO ₄		1.205
NO ₃ ⁻	Fe(NO ₃) ₃ , Ca(NO ₃) ₂ , Al(NO ₃) ₃ , HNO ₃	840.19 mL of 15.9M	3.24 ^a
C ₂ O ₄ ²⁻	H ₂ C ₂ O ₄ •2H ₂ O	438.32 g	0.17
F ⁻	HF NaF	6.92 mL of 28.9M 117.57 g	0.01 <u>0.14</u> 0.15
HSO ₄ ⁻	H ₂ SO ₄ NaHSO ₄	255.56 mL of 18M	0.23 <u>0.04</u> 0.27
Fe ³⁺	Fe(NO ₃) ₃ •9H ₂ O	1050.45 g	0.13
Al ³⁺	Al(NO ₃) ₃ •9H ₂ O	5401.87 g	0.72
Na ⁺	NaF NaHSO ₄	117.57 g 110.48 g	0.14 <u>0.04</u> 0.18
Ca ²⁺	Ca(NO ₃) ₂ •4H ₂ O	94.46 g	0.02

^aThis value is the total of all nitrate additions.

Table II-38. Composition of the DF Feed Solution in Verification Run 2

Component	Conc., M	
	As prepared	As measured
H ⁺	1.475	1.402
Al	0.72	0.71
Fe	0.13	0.128
Na	0.18	0.179
Ca	0.02	0.019
NO ₃ ⁻	3.25	n/m ^a
C ₂ O ₄ ²⁻	0.17	n/m
F ⁻	0.15	n/m
HSO ₄ ⁻	0.27	n/m

^aNot measured.

Before using the solvent in this test, we adjusted its composition to correct for evaporative losses of the TCE over the two years of storage. To determine how much TCE had evaporated, we measured the density of a solvent sample after being equilibrated with water. Using the density correlation given in the previous semiannual (Sec. II.B), we calculated the amount of TCE required to adjust the solvent composition (1.99 g) and added this amount to a 25 mL TRUEX-TCE sample. Then, to verify that the solvent was acceptable for our use, distribution coefficients for americium were measured at two acid concentrations, 0.01 and 2M HNO_3 , and compared with previously collected data. Since the americium distribution coefficients compared favorably with previous measurements, we added TCE to the rest of the solvent, thereby adjusting the CMPO and TBP concentrations to 0.25 and 0.75M, respectively.

b. Overview of Verification Run 2 Operations

Verification Run 2 was completed on April 22, 1988. The checklist used for this run is shown in Table II-39, which includes both the planned schedule and the actual times of the various events.

This run proceeded fairly close to the planned schedule (Table II-39) with no major problems. Flow rates for the various streams were checked between 10 and 15 min into the run; all the streams measured were found to be close to the expected flow rates. A second check of the process flow rates was completed at the end of the run by measuring the depletion rate of the feed tanks. These data, which are reported in Table II-40, indicate that the scrub feed (DS) was approximately one-half of the expected flow rate, and the aqueous feed to the extraction section (DF) was approximately 28 mL/min lower than expected.

The sampling procedure, which started 15 min into the run, was completed without incident. At shutdown, solutions contained in the annular region of the contactor stages were drained, their volume measured, then discarded. The solutions in the rotors were then collected and their volumes estimated. These stage samples were then used to determine the acid and metal concentration profiles in the system.

To study the acid profile, HNO_3 concentrations in the feed samples, raffinate samples, and both the organic and the aqueous phases from the stage samples were measured by pH titration. Sample preparation for acid titration was not required for the aqueous samples; aliquots from 100 to 500 μL were collected from each sample and then titrated. Organic portions of the stage samples, however, needed considerably more preparation. Because an acceptable technique for nonaqueous acid/base titration had not been developed at this time, the loaded organic was stripped of its acidic contents by repeated washes with water.

c. Results

The acid titration results for the stage samples are listed in Table II-41 and plotted in Fig. II-71. The results from the SASSE model (see Sec. II.B) are also shown in this figure. In general, there is good agreement between the experimental data and the SASSE model calculations. Also included in Fig. II-71 are the averaged raffinate concentrations for DW, DW1, EW, and FW. These concentrations correspond to stage samples 1, 4, 7, and 9, respectively. These data are described in more detail below.

Raffinate samples were collected and analyzed to evaluate the metal and acid concentrations as they approach and reach steady-state operation. Concentrations from the titration of the extraction section raffinate samples (DW) are plotted in Fig. II-72 versus the time that the samples were collected. For these samples, several endpoints (4 to 6) were detected during titration, and we assumed

Table II-39. Checklist for Verification Run 2

Expected Time Line ^a (min:sec)	Actual Time Line ^a (min:sec)	Action Required/Noted
-10:00		Sample Feed Solutions.
-10:00	-10:00	Turn DX Mixer on.
-10:00		Check Air Purge.
-5:00	-5:00	Verify Open DX Feed Valve.
-5:00		Verify CLOSED BOTH Organic Sample Valves. Vent Organic Feed Tank.
-0:30	-0:30	Contactor Motors on.
0:00		DX Pump on (TRUEX Solvent).
-	1:03	Organic Solvent (DX) Overflows Stage #3
-	1:29	Organic Solvent (DX) Overflows Stage #4.
-	1:55	Organic Solvent (DX) Overflows Stage #5.
2:55	2:23	Organic Solvent (DX) Overflows Stage #6.
3:00	2:53	DS Pump on (1st Scrub).
3:55	3:17	Organic Solvent (DX) Overflows Stage #8.
-	3:45	Organic Solvent (DX) Overflows Stage #9.
4:00	3:45	EF Pump on (2nd Scrub).
4:30	4:25	Collect DX Sample.
-	4:50	EF Entering Stage #8 (EF Feed Stage).
-	5:20	DS Entering Stage #6 (DS Feed Stage).
5:40	5:47	EW Overflow Detected (2nd Scrub).
6:15	8:10	DW1 Raffinate Detected (1st Scrub).
6:30	8:10	Check DW1 Flow Rate.
6:55	7:25	Organic Solvent Overflows Stage #14.
7:00	7:25	FF Pump on (1st Strip).
7:15	7:35 (est.)	GP Raffinate Detected (Organic Solvent).
7:30	7:50	GF Pump on (2nd Strip).
7:50	8:10	DW Effluent Detected (Stage 1 Overflow).
8:15	8:45	FW Raffinate Detected (1st Strip).
8:50	9:22	GW Raffinate Detected (2nd Strip).
9:00	9:40	DF Pump on (CAW Feed).
9:30	10:20	Collect GP Sample.
10:00-15:00	10:00-15:00	Check Flow Rates. (DW, DW1, EW, FW, GW, GP).
15:00	15:00	Begin Sampling Effluent Streams.
35:00	36:00	End Sampling.
37:00	37:00	Shut off Pumps, Open Drain Valves. Leave Motors Running.
-		Close Drain Valves, Record Volumes.
-	51:10	Shut off Motors, Replace Sample Beakers.
-		Sample Stages.

Table II-40. Process Stream Flow Rates (mL/min) for Verification Run 2 Stream

	DF	DW	DS	DW1	EW	FW	GW	GP
Setting ^a	300	340	50	10	50	200	100	200
Flow Check ^b	n/a ^d	300	n/a	8	51	210	98	205
Tank Depletion ^c	272.2	n/a	26.1	n/a	49.0	190.3	100.6	n/a

^aExpected Flow Rate based upon pump calibration curves.

^bFlow Rates calculated by collecting a timed sample.

^cFlow Rates calculated by measuring how much feed solution was used.

^dn/a = data not available.

Fig. II-71. Comparison of Experimental Data for $[H^+]$ with the Generic TRUEX Model Predictions for Verification Run 2

that the first endpoint was the HNO_3 concentration. This figure shows that the GTM prediction (the horizontal line) is higher than the measured concentrations. However, because of the many cations in these aqueous samples, these results may not be as accurate as those for other sections. For example, the raffinate concentrations from the first strip section (FW) are shown in Fig. II-73. For this section, the model agrees very well with the experimental data. Similar plots were generated for the other raffinate streams, but are not included here.

In addition to measurements of the hydrogen ion concentration, metal ion concentrations in the various samples were measured by ICP-AES analysis (Edmund Huff, ANL's Analytical Chemistry Laboratory). Aqueous samples were easily prepared for this analysis, since they required only dilution of a 4-mL aliquot to a known volume with 1.0M HNO_3 . Aliquots from the DF and EF feeds (stage numbers 1, 2, 15, and 16) and the DW and DW1 raffinates were diluted to 50 mL in nalgene volumetric flasks to prevent contamination of the sample (from the reaction of the fluoride ions with glass).

Table II-41. Acid Titration Data for Verification Run 2.

Sample Name			[H ⁺], M				Ave. [H ⁺], M
DF	1.40	1.41					1.402
DS	0.0400	0.0400					0.04
EF	0.0474	0.0543					0.0542
FF	0.0394	0.0393					0.0394
GF ^a							
DW #1	0.827	0.946					0.887
DW #2	0.908	0.955					0.932
DW #3	0.960	0.877					0.918
DW #4	0.979	0.962					0.971
DW #5	0.936	0.936					0.936
DW1 #0	0.647	0.758	0.761	0.758			0.731
DW1 #1	1.77	1.76					1.77
DW1 #2	1.91	1.92					1.91
DW1 #3	1.92	1.94					1.93
DW1 #4	1.96	1.91					1.94
EW #1	0.737	0.738					0.737
EW #2	0.794	0.794					0.794
EW #3	0.773	0.800					0.786
EW #4	0.824	0.817					0.821
FW #1	0.117	0.117					0.117
FW #2	0.135	0.138					0.137
FW #3	0.137	0.138					0.138
FW #4	0.142	0.142					0.142
FW #5	0.145	0.143					0.144
GW #1 ^b	0.0373	0.0405	0.0445	0.0424	0.0445	0.0424	0.042
GW #2 ^b	0.039	0.0399	0.0490	0.0424	0.0441	0.0424	0.043
GW #3 ^b	0.0398	0.0415	0.0439	0.0426	0.0439	0.0426	0.042
GW #4 ^b	0.0413	0.0414	0.0439	0.0424	0.0439	0.0424	0.043
GP #0 ^b	0.00387	0.00394					0.004
GP #1 ^b	0.00517	0.00515					0.005
GP #2 ^b	0.00510	0.00507					0.005
GP #3 ^b	0.00505	0.00501					0.005
GP #4 ^b	0.00522	0.00527					0.005
GP #5 ^b	0.00531	0.00527					0.005

Table II-41. (contd)

Sample Name	[H ⁺], <u>M</u>				Ave. [H ⁺], <u>M</u>
<u>Organic</u>					
Stage #1	0.417	0.409			0.413
Stage #2	0.489	0.487			0.488
Stage #3	0.498	0.519			0.508
Stage #4	0.457	0.464			0.461
Stage #4	0.697	0.711			0.704
Stage #5	0.398	0.397			0.397
Stage #6	0.289	0.288			0.288
Stage #7	0.185	0.192			0.189
Stage #8	0.0986	0.0985			0.0985
Stage #9	0.0134	0.0133	0.0146	0.0147	0.0140
Stage #10	0.00333	0.00337			0.00335
Stage #11	0.00241	0.00234			0.00238
Stage #12	0.00218	0.00215			0.00217
Stage #13	0.00198	0.00199			0.00199
Stage #14	0.00196	0.00198	0.00212	0.0021	0.0020
Stage #15 ^b	0.0211	0.0176			0.0193
Stage #16 ^b	0.0231	0.0227			0.0229
<u>Aqueous</u>					
Stage #1	0.749	0.733	1.1918	1.2726	0.987
Stage #2	1.03	0.994			1.01
Stage #3	2.13	2.18			2.15
Stage #4	1.97	1.95			1.96
Stage #5	1.65	1.67			1.66
Stage #6	1.16	1.12			1.14
Stage #7	0.814	0.820			0.817
Stage #8	0.490	0.486			0.488
Stage #9	0.152	0.153			0.152
Stage #10	0.0622	0.0623			0.0622
Stage #11	0.0477	0.047			0.0474
Stage #12	0.0455	0.0456			0.0455
Stage #13	0.0457	0.0456			0.0456
Stage #14	0.045	0.0449			0.0449
Stage #15 ^b	0.0661	0.0647			0.0654
Stage #16 ^b	0.0645	0.0642			0.0644

^aFrom HF only.^bMay include from both nitrate and fluoride anions.

Fig. II-72. Approach to Steady State for Extraction Section Raffinate Samples (DW) in Verification Run 2 (data based upon first endpoint in pH titration)

Fig. II-73. Approach to Steady State for First Strip Section Raffinate Samples (FW) in Verification Run 2

Organic samples were not so straightforward, because the metal cations had to be stripped from the organic phase. In the case of the organic stage samples, stripping was accomplished through contacting a 4-mL aliquot of the organic twice with 12 mL 0.05M oxalic acid/0.5M HNO₃, twice with 2 mL 5M HNO₃, and three times with 4 mL of water. Strippings/washings from each stage sample were collected and diluted to 50 mL in nalgene volumetric flasks. Organic product samples (GP) were treated similarly to the organic stage samples; an 8-mL aliquot of each sample was contacted twice with

12 mL of 0.05M oxalic acid, twice with 2 mL of 5.0M HNO₃, and four times with 4 mL water. These were also diluted to 50 mL in a volumetric flask.

Metals analyzed by ICP-AES included Fe, Al, Na, and Ca. These data are listed in Table II-42. As examples of the data, the stage sample ICP-AES results for Fe and Na are shown in Figs. II-74 and II-75, respectively. In Fig. II-74, where iron concentration is shown plotted versus stage number, it is evident that the experimental data for iron do not agree with the GTM predictions. To check out the possibility of inaccurate measurements of the iron, material balances were completed for all of the components measured. These calculations are summarized in Table II-43. Based upon these data, the overall material balance for iron was reasonably good (103.8%), but the material balance around the scrub and strip sections was not (4.2% to 4400%). This indicates that the measurements for iron in the scrub and strip sections are suspect. The discrepancy could also have arisen from the model for iron being in error. Since iron extraction has a kinetics effect, it was more difficult to model. Additional data on the extraction of iron are needed to clarify these findings.

The measured sodium concentrations in each stage are shown in Fig. II-75. Again, the GTM predictions do not agree with the experimental data. After the extraction section (stages 1 and 2), both the organic and aqueous concentrations reached a constant value. This finding is inconsistent with the model, which indicated that sodium does not extract and should not be seen after the first several stages. This same trend was observed for Ca and Al. Possible explanations include (1) contamination of the samples during the sample preparation for ICP-AES analysis or (2) contamination from the centrifugal contactor equipment. Unfortunately, the solutions used to prepare the samples for ICP-AES analysis were not sent for analysis, although the scrub solution (EF) was. Although low calcium levels were detected in the scrub feed (5.0×10^{-6} M), neither Al nor Na was detected. Again, further data are needed to resolve this problem.

3. Verification Run 3

Verification Run 3 was the second nonradioactive test completed with the sixteen-stage centrifugal contactor and the TRUEX-TCE solvent (0.25M CMPO, 0.75M TBP in TCE). The purpose of this test was to (1) evaluate the extraction of neodymium, nitric acid, iron, oxalic acid, and fluoride from a simplified acidic waste solution and (2) study the variability of the steady-state concentrations of various species. Neodymium was added to the feed solution to measure its own extraction and to simulate the extraction behavior of other rare earths and americium.

In general, the same flowsheet and procedures used in Verification Run 2 were followed for this test. However, three significant changes were made. First, 15 min was added to the test to verify that steady-state operation was reached and to determine the variations in raffinate concentrations during steady-state operation. Second, during sampling, the length of time needed to collect a sample was recorded. The sample volumes were then used to check the system flow rates. Third, the test was run with two operators on each side of the contactor. This was one extra person for the organic side of the contactor and one less for the aqueous side, which made the sample collection simpler than in Run 2.

a. Flowsheet

The flowsheet for this test is shown in Fig. II-76, which is similar to that for Verification Run 2. The simulated aqueous feed solution to the extraction section (DF) used in this test was a combination of the feed solutions remaining from the first two verification runs. The composition of this feed was determined by acid titration and by ICP-AES, and these results are given in Table II-44.

Table II-42. Results from ICP-AES Analysis Results (molar units) for Verification Run 2

Sample	[Al]	[Fe]	[Ca]	[Na]	[Mo]	[Ni]
DF A	7.00E-01	1.27E-01	1.91E-02	1.79E-01		
DF B	7.09E-01	1.28E-01	1.94E-02	1.78E-01		
EF A		5.03E-03	4.99E-06			
EF B		5.00E-03	4.99E-06			
DW #1	6.02E-01	1.08E-01	1.67E-02	1.50E-01		
DW #2	6.02E-01	1.08E-01	1.67E-02	1.50E-01		
DW #3	6.07E-01	1.10E-01	1.70E-02	1.52E-01		
DW #4	6.02E-01	1.09E-01	1.66E-02	1.51E-01		
DW #5	5.98E-01	1.08E-01	1.66E-02	1.50E-01		
DW1 #0	3.50E-03	2.46E-03	1.96E-04	3.43E-04		
DW1 #1	1.67E-04	6.00E-03	1.06E-04	6.52E-05		
DW1 #2	7.88E-05	5.48E-03	1.25E-04	8.16E-05		
DW1 #3	6.49E-05	5.60E-03	1.37E-04			
DW1 #4	1.20E-04	6.31E-03	1.53E-0			
EW #1		4.61E-02				
EW #2		4.73E-02				
EW #3		4.71E-02				
EW #4		4.70E-02				
FW #1	8.57E-05	5.48E-03				
FW #2	6.25E-05	6.39E-03				
FW #3	5.56E-05	6.23E-03				
FW #4	5.79E-05	6.36E-03				
FW #5	5.56E-05	6.39E-03				
GW #1	5.56E-05	6.61E-03				1.60E-05
GW #2	1.32E-04	5.99E-03	3.12E-06	5.98E-05		1.49E-05
GW #3	2.59E-04	5.60E-03	6.24E-06	8.70E-05		1.49E-05
GW #4	1.39E-04	5.22E-03	3.12E-06	5.71E-05		1.38E-05
GP #0	<2.32E-5	2.01E-04	7.33E-05	1.55E-04		
GP #1	<2.32E-5	1.68E-05	2.81E-05	1.33E-04		
GP #2	<2.32E-5	2.35E-05	3.27E-05	1.41E-04		
GP #3	<2.32E-5	1.79E-05	2.96E-05	1.55E-04		
GP #4	<2.32E-5	1.68E-05	2.50E-05	1.39E-04		
GP #5	<2.32E-5	1.79E-05	3.43E-05	1.36E-04		

Table II-42. (contd)

Sample	[Al]	[Fe]	[Ca]	[Na]	[Mo]	[Ni]
1 Org	1.86E-03	1.03E-02	2.53E-04	6.91E-04	<6.5E-6	<1.1E-5
2 Org	1.69E-03	1.03E-02	1.93E-04	6.63E-04	<6.5E-6	<1.1E-5
3 Org	<4.6E-5	9.42E-04	6.55E-05	2.61E-04	<6.5E-6	<1.1E-5
4 Org	<4.6E-5	7.77E-04	6.55E-05	2.61E-04	<6.5E-6	<1.1E-5
5 Org	<4.6E-5	5.30E-04	4.99E-05	2.50E-04	<6.5E-6	<1.1E-5
6 Org	<4.6E-5	3.74E-04	5.30E-05	2.56E-04	<6.5E-6	<1.1E-5
7 Org	<4.6E-5	3.60E-04	3.74E-05	2.45E-04	<6.5E-6	<1.1E-5
8 Org	<4.6E-5	2.71E-04	5.61E-05	2.45E-04	<6.5E-6	<1.1E-5
9 Org	<4.6E-5	1.34E-04	4.68E-05	2.28E-04	<6.5E-6	<1.1E-5
10 Org	<4.6E-5	1.92E-04	4.37E-05	2.17E-04	<6.5E-6	<1.1E-5
11 Org	<4.6E-5	2.39E-04	6.86E-05	2.34E-04	<6.5E-6	<1.1E-5
12 Org	<4.6E-5	2.08E-04	4.37E-05	2.34E-04	<6.5E-6	<1.1E-5
13 Org	<4.6E-5	2.08E-04	7.17E-05	2.07E-04	<6.5E-6	<1.1E-5
14 Org	<4.6E-5	2.62E-04	1.22E-04	2.07E-04	<6.5E-6	<1.1E-5
15 Org	<4.6E-5	3.36E-05	6.86E-05	2.07E-04	<6.5E-6	<1.1E-5
16 Org	<4.6E-5	1.12E-05	5.61E-05	2.17E-04	<6.5E-6	<1.1E-5
1 Aq	6.07E-01	9.60E-02	1.66E-02	1.51E-01		
2 Aq	5.74E-01	9.45E-02	1.60E-02	1.43E-01		
3 Aq	3.87E-03	2.73E-02	2.00E-03	1.20E-03		
4 Aq	2.92E-04	2.53E-02	7.45E-04	1.69E-04		
5 Aq	1.53E-04	2.24E-02	5.30E-05	7.61E-05		
6 Aq	8.34E-05	2.11E-02	3.74E-05	5.44E-05		
7 Aq	1.20E-04	2.48E-02	4.68E-05	1.63E-04		
8 Aq	--	2.13E-02	1.56E-05	1.36E-04		
9 Aq	7.88E-05	7.21E-03	1.87E-05	8.70E-05		
10 Aq	6.95E-05	3.96E-03	2.50E-05	2.61E-04		
11 Aq	1.67E-04	2.80E-03	3.74E-05	8.16E-05		
12 Aq	--	2.04E-03	1.56E-05	2.39E-04		
13 Aq	6.49E-05	1.90E-03	1.56E-05	1.30E-04		
14 Aq	1.53E-04	1.48E-03	2.18E-05	1.41E-04		
15 Aq	1.20E-04	2.37E-03	1.56E-05	7.07E-05		5.96E-05
16 Aq	8.34E-05	1.19E-03	1.87E-05	9.79E-05		3.41E-05

Fig. II-74. Comparison of Experimental Data for Iron with the Generic TRUEX Model Calculations for Verification Run 2

Fig. II-75. Comparison of Experimental Data for Sodium with the Generic TRUEX Model Calculations for Verification Run 2

Table II-43. Material Balance Calculations (percentages) for Acid Titration and ICP-AES Data, Verification Run 2

Section for Material Balance	H ⁺	Na	Ca	Fe	Al
Overall ^a	93.1	91.5	93.3	103.8	91.7
Extraction/Scrub 1	83.6	98.8	100.8	99.8	98.9
Scrub 2	187.5	88.6	78.0	4423	-- ^b
Strip 1	339	95.4	279	3472	--
Strip 2	--	104.8	46.0	4.2	--

^aMaterial balance includes the following sections: Extraction, Scrub 1, Scrub 2, Strip 1, and Strip 2.

^bData not available.

Fig. II-76. Flowsheet for Verification Run 3

Table II-44. Composition of the DF Feed Solution from Verification Run 3

Component	Conc., M	
	As-Prepared	As-Measured
H ⁺	1.475	1.304
Al	0.72	0.804
Fe	0.13	0.149
Nd	0.008	0.0065
Na	0.18	0.194
Ca	0.02	0.213
Zr	0.006	0.004
NO ₃ ⁻	3.25	n/m ^a
C ₂ O ₄ ²⁻	0.17	n/m
F ⁻	0.15	n/m
HSO ₄ ⁻	0.27	n/m

^aNot Measured.

The same TRUEX-TCE solvent used in Verification Run 2 was used in this test. To prepare the solvent, it was washed twice with water, twice with 0.25M Na_2CO_3 , three times with HEDP, and once with 0.05M HNO_3 . All of these washes were completed in a 2 L separatory funnel at an O/A ratio of 1:2. Following these washes, the solvent was filtered to remove any entrained aqueous from the organic phase, then the solvent density was measured and the appropriate volume of TCE added to adjust the CMPO and TBP concentrations to 0.25M and 0.75M, respectively. The density correlation was used to calculate the TCE addition.

b. Overview of Verification Run 3 Operations

Verification Run 3 was completed on May 20, 1988. The checklist for this run, including both the planned schedule and the actual times of the various events, is shown in Table II-45. This run proceeded fairly close to the planned schedule, with no major problems. The new sample procedure worked very well and will be used in future tests. At shutdown, solutions contained in the annular region of the contactor stages were drained, their volume was measured, then they were discarded. After the annular region had been drained, the solution in the rotors was collected and the solution volume was estimated. The rotor samples were used to determine the acid and metal concentration profiles in the contactor.

c. Results

The same procedures described above for Verification Run 2 were used to prepare and analyze samples for this run. The acid titration results for the stage-to-stage samples are listed in Table II-46, and the averaged values are plotted in Fig. II-77. The calculated results from the GTM are also shown in Fig. II-77. (Version 1.1c of the GTM was used to generate the predictions.) Many of the stage aqueous and organic samples were titrated several times, and the averages of these data are plotted in Fig. II-77. As shown in the figure, the agreement between the experimental data and the GTM results was not as good as in Run 2 (Fig. II-71). Although the results for the raffinate samples agree with those for the stage samples, they do not agree with the GTM predictions.

In Figs. II-78 and II-79, all of the titration measurements for the aqueous and the organic phases are plotted with the GTM predictions for these phases (solid lines). The dotted lines in these two figures are the average concentrations for each phase. The measured data show considerable scatter, especially for the aqueous phase samples, and the GTM predictions differ from the measured values. To compare the calculated distribution coefficients for H^+ with the GTM predictions, we plotted both sets of data in Fig. II-80. These data again show that the measured data do not agree with the GTM predictions.

To measure the Fe, Al, Na, Ca, Nd, Mo, Ni and Zr concentrations, samples were submitted to the ANL Analytical Chemistry Laboratory for ICP-AES analysis. The procedures followed to prepare these samples for analysis were the same as described for Verification Run 2. Results of this analysis are listed in Table II-47. The stage sample ICP-AES results for Nd and Zr are shown in Figs. II-81 and II-82, respectively. Again, the experimental data and the GTM predictions for these two components do not agree with each other. The other elements in the solution show this same trend.

Table II-45. Checklist for Verification Run 3

Planned Schedule (min:sec)	Actual Times (min:sec)	Action Required
--		Sample Feed Solutions.
-10:00	-10:00	Turn DX Mixer on.
-10:00	-10:00	Measure Solution, Hood Temperatures.
-9:00	-5:00	Check Air Purge.
-5:00		Verify Open DX Feed Valve.
		Verify CLOSED BOTH Organic Sample Valves. Vent Organic Feed Tank.
-0:30	-0:30	Contactor Motors on.
0:00	0:00	DX Pump on (TRUEX Solvent).
--	1:37	Organic Solvent (DX) Overflows Stage #2.
1:00	1:54	Organic Solvent (DX) Overflows Stage #3.
1:00	2:22	Organic Solvent (DX) Overflows Stage #4.
--	2:49	Organic Solvent (DX) Overflows Stage #5.
2:30	2:57	DS Pump on (1st Scrub).
--	3:15	DS Enters Stage #6 (feed stage).
3:20	4:06	Organic Solvent (DX) Overflows Stage #8.
3:30	4:20	EF Pump on (2nd Scrub).
4:30	4:40	Collect DX Sample #2.
5:45		EW Overflow Detected (2nd Scrub).
6:15	<5:00	DW1 Sample Detected (1st Scrub).
--	5:55	Organic Solvent Overflows Stage #12.
6:30	6:55	Check DW1 Flow Rate.
7:00	7:27	GP Pump on (Organic Product).
7:25	6:55	Organic Solvent Overflows Stage #14.
7:30	7:15	FF Pump on (1st Strip).
7:35	7:55	GP Raffinate Detected (Organic Solvent).
7:45	8:08	GF Pump on (2nd Strip).
8:10	<8:20	DW Raffinate Detected (from Stage 1).
8:45	<8:40	FW Raffinate Detected (1st Strip).
9:20	<9:05	GW Raffinate Detected (2nd Strip).
9:30	10:10	DF Pump on (CAW Feed).
9:30		Collect GP Sample #1.
9:45	10:28	Color Change in DW Effluent Detected.
10:00	11:05	Begin Sampling, Check Flow Rates DW, DW1, EW, FW, GW, GP).
52:00	~52:00	End Sampling.
53:00		Shut off Pumps, Open Drain Valves Leave Motors Running.
--		Close Drain Valves, Record Volumes.
--		Shut off Motors.
--		Replace Sample Beakers, Sample Stages.

Table II-46. Acid Titration Results for Verification Run 3

Sample Name	$[H^+], M$						Avg. $[H^+], M$
DF	1.303	1.306					1.304
EF	0.0541	0.0541					0.0541
FF	0.0389	0.0384					0.0387
DS	0.0415	0.0412					0.0414
GF ^a	0.1015	0.1015					0.102
DW #2	1.206	1.227					1.217
DW #3	1.206	1.172					1.189
DW #4	1.142	1.125					1.134
DW #5	1.189	1.093					1.141
DW #6	1.091	1.131					1.111
DW #7	1.122	1.135					1.129
DW #8	1.422	1.384	1.167	1.197			1.292
DW1 #0	0.0465	0.0556					0.0511
DW1 #1	0.950	0.961					0.955
DW1 #2	0.904	0.814					0.859
DW1 #3	1.234	1.121					1.178
DW1 #4	1.422	1.370					1.396
DW1 #5	1.144	1.117					1.131
DW1 #6	1.417	1.258					1.337
EW #1	0.092	0.112	0.104	0.106			0.103
EW #2	0.372	0.370					0.371
EW #3	0.276	0.296					0.286
EW #4	0.386	0.407					0.396
EW #5	0.200	0.394	0.358	0.345			0.324
EW #6	0.356	0.363					0.359
EW #7	0.383	0.380					0.38
FW #1	0.071	0.0661	0.0392	0.0390			0.0538
FW #2	0.0911	0.0871	0.0493	0.0485			0.0690
FW #3	0.105	0.100	0.0600	0.0600			0.0812
FW #4	0.108	0.110	0.0604	0.0606			0.0846
FW #5	0.111	0.112	0.0600	0.0604			0.0860
FW #6	0.115	0.114	0.0620	0.0616			0.0881
FW #7	0.111	0.097	0.0636	0.0625			0.0836
FW #8	0.0742	0.0797	0.0518	0.0524	0.0496	0.048	0.0593
GW #1 ^b	0.0636	0.0586					0.0611
GW #2 ^b	0.0545	0.0475					0.0510
GW #3 ^b	0.0667	0.0616					0.0642
GW #4 ^b	0.0455	0.0455					0.0455
GW #5 ^b	0.0576	0.0677					0.0627
GW #6 ^b	0.0737	0.0727					0.0732
GW #7 ^b	0.0606	0.0586					0.0596

Table II-46. (contd)

Sample Name	[H ⁺], M							Avg. [H ⁺], M
GP #1 ^b	0.0134	0.0149	0.0183	0.0187				0.0163
GP #2 ^b	0.0204	0.0206	0.0236	0.0228				0.0219
GP #3 ^b	0.0213	0.0215	0.0241	0.0239				0.0227
GP #4 ^b	0.0253	0.0252	0.0289	0.0281				0.0269
GP #5 ^b	0.0270	0.0269	0.0305	0.0306				0.0288
GP #6 ^b	0.0331	0.0321	0.0326					
GP #7 ^b	0.0348	0.0347	0.0348					
<u>Aqueous</u>								
Stage 1	1.587	1.065	1.220	1.216				1.272
Stage 2	1.901	1.710						1.805
Stage 3	1.861	2.163						.012
Stage 4	1.208	1.148	1.366	1.362				1.271
Stage 5	0.990	1.139						1.065
Stage 6	0.613	0.554						0.583
Stage 7	0.427	0.421						0.424
Stage 8	0.236	0.246	0.220	0.219				0.230
Stage 9	0.151	0.136	0.103	0.080				0.117
Stage 10	0.0975	0.0988	0.0712	0.0687				0.0841
Stage 11	0.107	0.100	0.0702	0.0677				0.0863
Stage 12	0.0945	0.0847	0.0626	0.0566				0.0746
Stage 13	0.0995	0.0874	0.0687	0.0687				0.0811
Stage 14	0.0997	0.1122	0.0646	0.0646				0.0853
Stage 15 ^b	0.108	0.109	0.0661	0.0647	0.120	0.121		0.0981
Stage 16 ^b	0.102	0.103	0.0645	0.0642	0.113	0.116		0.0939
<u>Organic</u>								
Stage 1	0.721	0.829						0.0755
Stage 2	0.866	0.830						0.848
Stage 3	0.669	0.649						0.659
Stage 4	0.519	0.538	0.697	0.711				0.616
Stage 5	0.361	0.355						0.358
Stage 6	0.165	0.152						0.159
Stage 7	0.0675	0.0672						0.0674
Stage 8	0.0316	0.0294						0.0305
Stage 9	0.0009	0.001	0.0079	0.0077	0.0079	0.0085	0.0079	0.0060
Stage 10	0.0103	0.0095	0.0117	0.0117				0.0108
Stage 11	0.0004	0.0009	0.012	0.0096	0.011	0.011		0.0075
Stage 12	0.002	0.0028	0.0039	0.0038				0.0031
Stage 13	0.0033	0.0032	0.0036	0.0036	0.0036	0.0031		0.0034
Stage 14	0.0029	0.0027	0.0034	0.0032				0.0031
Stage 15 ^b	0.0335	0.031	0.0228	0.0215	0.0211	0.0176	0.0236	0.0247
Stage 16 ^b	0.0257	0.0256	0.0231	0.0227	0.0298	0.0298		0.0261

^a[H⁺] from HF only.^b[H⁺] may include H⁺ from both nitrate and fluoride anions.

Fig. II-77. Comparison of Experimental Stage Data for $[H^+]$ with Generic TRUEX Model Calculations for Verification Run 3

Fig. II-78. Comparison of the Aqueous Phase Titration Results with the GTM Calculations for Verification Run 3

Fig. II-79. Comparison of the Organic Phase Titration Results with the GTM Calculations for Verification Run 3

Fig. II-80. Distribution Coefficients Based upon Aqueous and Organic Titration Results for Verification Run 3

Table II-47. ICP-AES Analysis Results (molar units) for Verification Run 3

Sample	[Al]	[Fe]	[Ca]	[Na]	[Zr]	[Nd]	[Mo]	[Ni]
DF	8.04E-01	1.49E-01	2.13E-02	1.94E-01	4.11E-03	6.47E-03	<2.61E-05	<2.13E-05
DS	<7.41E-06	<8.95E-07	<1.25E-06	5.22E-06	<5.48E-07	<6.93E-07	<1.04E-06	<8.52E-07
EF	<1.85E-04	1.24E-02	5.61E-05	<1.09E-04	<1.37E-05	<1.73E-06	<2.61E-05	<2.13E-05
FF	<7.41E-06	<8.95E-07	<1.25E-06	<4.35E-06	<5.48E-07	<6.93E-07	<1.04E-06	<8.52E-07
GF	<7.41E-06	<8.95E-07	<1.25E-06	<4.35E-06	<5.48E-07	<6.93E-07	<1.04E-06	<8.52E-07
DW #2	6.35E-01	1.14E-01	1.68E-02	1.52E-01	2.71E-03	1.19E-04	<1.30E-04	<2.13E-05
DW #3	6.49E-01	1.17E-01	1.72E-02	1.57E-01	2.75E-03	1.27E-04	<1.30E-04	<2.13E-05
DW #4	6.58E-01	1.20E-01	1.74E-02	1.56E-01	2.80E-03	1.31E-04	<1.30E-04	<2.13E-05
DW #4	6.58E-01	1.20E-01	1.73E-02	1.55E-01	2.71E-03	1.28E-04	<1.30E-04	<2.13E-05
DW #5	6.53E-01	1.19E-01	1.73E-02	1.58E-01	2.77E-03	1.33E-04	<1.30E-04	<2.13E-05
DW #6	6.53E-01	1.20E-01	1.74E-02	1.56E-01	2.80E-03	1.17E-04	<1.30E-04	<2.13E-05
DW #7	6.49E-01	1.18E-01	1.73E-02	1.56E-01	2.73E-03	1.18E-04	<1.30E-04	<2.13E-05
DW #8	6.44E-01	1.17E-01	1.71E-02	1.51E-01	2.71E-03	1.24E-04	<1.30E-04	<2.13E-05
DW1 #0	1.53E-04	2.08E-04	5.61E-05	2.66E-04	8.22E-06	<8.67E-06	<1.30E-05	<1.07E-05
DW1 #1	<9.26E-05	5.08E-03	1.87E-05	<5.44E-04	6.95E-04	1.14E-03	<1.30E-05	<1.07E-05
DW1 #2	<9.26E-05	6.20E-03	2.18E-05	<5.44E-04	7.80E-04	1.20E-03	<1.30E-05	<1.07E-05
DW1 #2	<9.26E-05	6.45E-03	1.87E-05	<5.44E-04	8.39E-04	1.45E-03	<1.30E-05	<1.07E-05
DW1 #3	<9.26E-05	6.20E-03	2.81E-05	<5.44E-04	7.84E-04	1.23E-03	<1.30E-05	<1.07E-05
DW1 #4	<9.26E-05	6.31E-03	3.12E-05	8.70E-05	7.87E-04	1.26E-03	<1.30E-05	<1.07E-05
DW1 #5	<9.26E-05	6.27E-03	3.43E-05	<5.44E-04	7.82E-04	1.22E-03	<1.30E-05	<1.07E-05
DW1 #6	<9.26E-05	6.33E-03	2.18E-05	<5.44E-04	7.84E-04	1.27E-03	<1.30E-05	<1.07E-05
DW1 END	<9.26E-05	6.33E-03	3.12E-05	<5.44E-04	7.95E-04	1.30E-03	<1.30E-05	<1.07E-05
FW #1	2.37E-05	1.36E-05	3.49E-06	1.13E-05	5.48E-07	<6.93E-07	<1.30E-05	<8.52E-06
FW #2	<7.41E-05	2.94E-04	<1.25E-05	1.74E-05	2.30E-04	7.10E-03	<1.30E-04	<8.52E-06
FW #3	<7.41E-05	5.23E-04	<1.25E-05	1.96E-05	4.96E-04	8.17E-03	<1.30E-04	<8.52E-06
FW #4	<7.41E-05	5.19E-04	<1.25E-05	<4.35E-06	5.46E-04	8.24E-03	<1.30E-04	<8.52E-06
FW #4	<7.41E-05	4.98E-04	<1.25E-05	1.91E-05	5.22E-04	7.84E-03	<1.30E-04	<8.52E-06
FW #5	<7.41E-05	5.00E-04	<1.25E-05	1.87E-05	5.77E-04	8.21E-03	<1.30E-04	<8.52E-06

Table II-47. (contd)

Sample	[Al]	[Fe]	[Ca]	[Na]	[Zr]	[Nd]	[Mo]	[Ni]
FW #6	<7.41E-05	5.01E-04	<1.25E-05	1.87E-05	5.96E-04	8.32E-03	<1.30E-04	<8.52E-06
FW #7	<7.41E-05	4.83E-04	<1.25E-05	1.91E-05	6.05E-04	8.36E-03	<1.30E-04	<8.52E-06
FW #8	<7.41E-06	1.25E-04	<1.25E-06	<4.35E-06	2.58E-04	<6.93E-07	<1.30E-05	<8.52E-07
GW #1	<7.41E-06	4.48E-05	1.75E-06	1.09E-05	2.67E-05	<6.93E-07	<1.30E-05	<8.52E-07
GW #2	<7.41E-06	1.64E-04	<1.25E-06	8.26E-06	1.90E-04	<6.93E-07	<1.30E-05	<8.52E-07
GW #3	<7.41E-06	1.40E-04	<1.25E-06	1.26E-05	2.27E-04	<6.93E-07	<1.30E-05	<8.52E-07
GW #4	<7.41E-06	1.40E-04	<1.25E-06	<4.35E-06	2.40E-04	<6.93E-07	<1.30E-05	8.52E-07
GW #5	<7.41E-06	1.31E-04	<1.25E-06	<4.35E-06	2.46E-04	<6.93E-07	<1.30E-05	0.00000102
GW #6	<7.41E-06	1.30E-04	<1.25E-06	<4.35E-06	2.50E-04	<6.93E-07	<1.30E-05	0.00000136
GW #7	<7.41E-06	1.29E-04	<1.25E-06	<4.35E-06	2.51E-04	<6.93E-07	<1.30E-05	0.00000187
GP #1	<4.63E-05	6.71E-06	1.72E-05	5.98E-05	3.43E-06	2.17E-06	<1.30E-05	<8.52E-07
GP #2	<4.63E-05	6.71E-06	1.87E-05	8.43E-05	<3.43E-06	<2.17E-06	<1.30E-05	<8.52E-07
GP #3	<4.63E-05	5.60E-06	2.03E-05	8.97E-05	<3.43E-06	<2.17E-06	<1.30E-05	<8.52E-07
GP #4	<4.63E-05	1.12E-05	3.74E-05	5.98E-05	<3.43E-06	<2.17E-06	<1.30E-05	<8.52E-07
GP #5	<4.63E-05	6.71E-06	2.03E-05	5.71E-05	<3.43E-06	<2.17E-06	<1.30E-05	<8.52E-07
GP #6	<4.63E-05	6.71E-06	1.87E-05	3.81E-05	<3.43E-06	<2.17E-06	<1.30E-05	<8.52E-07
GP #7	<4.63E-05	6.71E-06	1.87E-05	<2.72E-04	<3.43E-06	<2.17E-06	<1.30E-05	<8.52E-07
EW #1	<7.41E-05	5.96E-03	<1.25E-05	2.09E-05	1.89E-04	5.26E-03	<1.30E-04	<8.52E-06
EW #2	<7.41E-05	7.88E-03	<1.25E-05	1.35E-05	4.69E-04	3.11E-03	<1.30E-04	<8.52E-06
EW #3	<7.41E-05	7.88E-03	<1.25E-05	1.17E-05	4.74E-04	3.08E-03	<1.30E-04	<8.52E-06
EW #3	<7.41E-05	7.81E-03	<1.25E-05	1.17E-05	4.76E-04	3.08E-03	<1.30E-04	<8.52E-06
EW #4	<7.41E-05	7.77E-03	<1.25E-05	1.30E-05	4.80E-04	3.09E-03	<1.30E-04	<8.52E-06
EW #5	<7.41E-05	7.88E-03	<1.25E-05	8.70E-06	4.91E-04	3.19E-03	<1.30E-04	<8.52E-06
EW #6	<7.41E-05	7.86E-03	<1.25E-05	7.39E-06	4.93E-04	3.22E-03	<1.30E-04	<8.52E-06
EW #7	<7.41E-05	7.84E-03	<1.25E-05	8.70E-06	4.93E-04	3.22E-03	<1.30E-04	<8.52E-06
ORG 1	<9.27E-05	5.80E-03	1.25E-04	9.79E-05	1.38E-03	1.07E-03	<1.30E-05	<1.06E-05
ORG 2	<9.27E-05	6.04E-03	1.19E-04	9.79E-05	1.49E-03	5.46E-03	<1.30E-05	<1.06E-05
ORG 3	<9.27E-05	6.85E-04	4.05E-05	8.16E-05	1.43E-03	3.67E-03	<1.30E-05	<1.06E-05

Table II-47. (conid)

Sample	[Al]	[Fe]	[Ca]	[Na]	[Zr]	[Nd]	[Mo]	[Ni]
ORG 4	<9.27E-05	3.76E-04	4.99E-05	6.52E-05	1.16E-03	3.20E-03	<1.30E-05	<1.06E-05
ORG 5	<9.27E-05	1.84E-04	2.18E-05	<5.44E-05	1.07E-03	2.93E-03	<1.30E-05	<1.06E-05
ORG 6	<9.27E-05	9.18E-05	4.05E-05	5.44E-05	8.98E-04	2.81E-03	<1.30E-05	<1.06E-05
ORG 7	<9.27E-05	1.03E-04	4.05E-05	1.58E-04	9.32E-04	2.87E-03	<1.30E-05	<1.06E-05
ORG 8	<9.27E-05	5.82E-05	4.68E-05	1.63E-04	8.26E-04	2.76E-03	<1.30E-05	<1.06E-05
ORG 9	<9.27E-05	1.34E-05	4.37E-05	1.63E-04	4.84E-04	2.76E-03	<1.30E-05	<1.06E-05
ORG 10	<9.27E-05	2.69E-05	4.05E-05	1.41E-04	2.43E-04	6.45E-04	<1.30E-05	<1.06E-05
ORG 11	<9.27E-05	1.34E-05	4.99E-05	1.74E-04	1.77E-04	8.06E-05	<1.30E-05	<1.06E-05
ORG 12	<9.27E-05	1.34E-05	5.93E-05	1.63E-04	1.38E-04	1.13E-04	<1.30E-05	<1.06E-05
ORG 13	<9.27E-05	<1.12E-05	3.43E-05	2.99E-04	1.21E-04	<8.67E-06	<1.30E-05	<1.06E-05
ORG 14	<9.27E-05	2.01E-05	3.74E-05	2.28E-04	1.11E-04	<8.67E-06	<1.30E-05	<1.06E-05
ORG 15	<9.27E-05	<1.12E-05	3.74E-05	2.66E-04	<6.85E-06	<8.67E-06	<1.30E-05	<1.06E-05
ORG 16	<9.27E-05	<1.12E-05	4.05E-05	2.77E-04	<6.85E-06	<8.67E-06	<1.30E-05	<1.06E-05
AQ 1	6.49E-01	1.13E-01	1.72E-02	1.55E-01	3.45E-03	7.80E-05	<1.30E-04	<2.13E-05
AQ 2	6.12E-01	1.10E-01	1.63E-02	1.47E-01	3.95E-03	5.94E-04	<1.30E-04	<2.13E-05
AQ 3	1.02E-03	1.59E-02	3.01E-04	3.10E-04	6.65E-04	8.88E-04	<6.51E-06	<5.32E-05
AQ 4	<2.32E-04	1.32E-02	2.96E-05	4.62E-05	5.16E-04	8.41E-04	<6.51E-06	<5.32E-05
AQ 5	<2.32E-04	8.80E-03	2.34E-05	1.03E-04	4.46E-04	8.97E-04	<6.51E-06	<5.32E-05
AQ 6	<2.32E-04	6.31E-03	2.96E-05	9.52E-05	4.12E-04	1.21E-03	<6.51E-06	<5.32E-05
AQ 7	<2.32E-04	1.05E-02	3.43E-05	5.63E-04	3.28E-04	1.80E-03	<6.51E-06	<5.32E-05
AQ 8	<2.32E-04	8.30E-03	1.25E-05	5.44E-05	2.86E-04	3.02E-03	<6.51E-06	<5.32E-05
AQ 9	<2.32E-04	9.83E-04	2.03E-05	7.07E-05	5.77E-04	4.64E-03	<6.51E-06	<5.32E-05
AQ 10	<2.32E-04	4.26E-04	1.72E-05	5.71E-05	2.56E-04	1.77E-03	<6.51E-06	<5.32E-05
AQ 11	<2.32E-04	3.11E-04	2.18E-05	8.97E-05	7.74E-05	2.15E-04	<6.51E-06	<5.32E-05
AQ 12	<2.32E-04	2.46E-04	1.87E-05	2.99E-05	3.77E-05	2.08E-05	<6.51E-06	<5.32E-05
AQ 13	<2.32E-04	2.19E-04	3.27E-05	5.44E-05	3.29E-05	<4.33E-06	<6.51E-06	<5.32E-05
AQ 14	<2.32E-04	2.14E-04	1.40E-05	4.62E-05	3.22E-05	<4.33E-06	<6.51E-06	<5.32E-05
AQ 15	<2.32E-04	7.05E-04	<1.56E-05	5.44E-05	2.52E-04	<8.66E-06	<1.30E-05	0.0000532
AQ 16	<2.32E-04	3.29E-04	<1.56E-05	<5.44E-05	2.60E-05	<8.66E-06	<1.30E-05	0.0000319

Fig. II-81. Comparison of Experimental Data for Neodymium with the Generic TRUEX Model Predictions for Verification Run 3

Fig. II-82. Comparison of Experimental Data for Zirconium with the Generic TRUEX Model Predictions for Verification Run 3

Since none of the data agrees with the GTM predictions, it appears that something in our system is affecting the extraction of these components. This may be a substance added to one (or more) of the feed solutions or present in the contactor stages as a contaminant. To help clarify whether an error had been made, material balances were completed for all of the components that we measured. Results of this analysis are listed in Table II-48. Like Verification Run 2, the overall material balances are fairly good, although those for most of the metals are low (~90%), which means that more material entered the system than was detected in the raffinate streams. Material balances for the sections are better than those for Run 2, but they still are not very good. Although this does not prove that the measured data are acceptable, it does indicate that the data are at least reasonable. Further work is needed to explain these data.

Table II-48. Material Balance Calculations (percentages) for Acid Titration and ICP-AES Data for Verification Run 3

Section for Material Balance	H ⁺	Nd	Na	Ca	Fe	Al	Zr
Overall ^a	108.4	96.4	90.6	92.1	90.2	91.5	88.9
Extraction/Scrub 1	108.94	31.8	90.6	92.2	90.3	91.5	91.03
Scrub 2	72.9	126.8	303.4	85.8	63.2	-- ^b	105.7
Strip 1	163	300	151.4	79.9	884.5	--	76.0
Strip 2	0	--	121.5	108.3	323.4	--	112.2

^aMaterial balance includes the following sections:

Extraction, Scrub 1, Scrub 2, Strip 1, and Strip 2.

^bData not available.

I. Production and Separation of ⁹⁹Mo from Low-Enriched Uranium (LEU) (J. D. Kwok and G. F. Vandegrift)

1. Introduction

Generators produce ^{99m}Tc ($t_{1/2} = 6.02$ h) for medical purposes from ⁹⁹Mo ($t_{1/2} = 66.0$ h) that is produced in nuclear reactors as a fission product of ²³⁵U and also by the (n, γ) reaction of ⁹⁸Mo (23.7% of natural molybdenum). Our effort is concerned only with fission-product ⁹⁹Mo. At present, most of the world's supply of fission-product ⁹⁹Mo is produced in targets of high-enriched uranium (HEU, ~93% ²³⁵U). The United States is considering prohibiting the export and internal commercial use of HEU because of its potential as material for use in an atomic bomb. For the past eight years the Reduced Enrichment Research Test Reactor (RERTR) program office has been developing reactor and reactor-fuel designs to accommodate the use of low-enriched fuel. The next goal is to reduce the ²³⁵U content of targets used to produce ⁹⁹Mo from HEU to LEU. During this six-month period, two more samples of U₃Si₂ (LEU) and one uranium metal sample have been irradiated in the ANL Janus reactor. Alternative dissolution methods have been investigated.

2. Second Irradiation of U₃Si₂

a. Janus Irradiation

One quarter of a uranium silicide miniplate was irradiated in the Janus reactor on April 18, 1988, for 80 min at 48.0 kW. Two days later the sample activity was 600 mR(γ) and 6 R ($\gamma + \beta$).

b. Dissolution

A variation of the acidic dissolution method developed by the Atomic Energy of Canada Limited (AECL) was used to dissolve this sample.³⁴ The dissolution was started with 50 mL of 3M HNO₃ plus 0.5 mL of 0.2M Hg(NO₃)₂. This resulted in a fairly violent reaction which soon subsided. A fine black precipitate was observed at this point. After the reaction stopped, the sample was placed on a hot plate. Over the course of about two hours, 9 mL of concentrated HNO₃ and 70 mL of 4M HNO₃ were added to sustain the reaction. On the following day, the solution had gelled. After adding 10 mL of H₂O and heating slowly, the sample solution began liquefying. An additional 17 mL of concentrated HNO₃ and 90 mL of 4M HNO₃ were added gradually until the sample had dissolved. A small skeleton of aluminum cladding remained, which was physically removed from the solution. The solution was yellow with some black precipitate, so it appeared greenish.

This solution was gravity filtered to remove the black precipitate and the white silicates. This filtrate was diluted to 250 mL (2.1M HNO₃), and aliquots were prepared for gamma analysis.

c. Separation

An alumina column was prepared by washing 4 g of alumina several times with water to remove the finer particles. The alumina was then transferred to the column and washed with 50 mL of 0.5M HNO₃.

The filtrate was adjusted to a pH of 0.34 with NaOH pellets and diluted to 250 mL. This dissolution solution was then loaded onto the column, and 4 mL fractions of the eluant were collected with a fraction collector. The column was then washed with 25 mL of 0.5M HNO₃ followed by 25 mL of H₂O. The final wash was 50 mL of 0.01M NH₄OH. Next, molybdenum was eluted with 50 mL of 1M NH₄OH. Gamma analyses were then performed on the eluant fractions.

It should be noted that an unknown portion of the silicates remained with the filter paper and could not be separated for further analysis. Fifty milliliters of 3M NaOH was added to dissolve the silicates but some precipitate remained, presumably hydroxides. This precipitate was separated by centrifuging and then dissolved in 1:1 HNO₃ to a total of 11 mL. This solution was separated from what looked like small pieces of filter paper. These solutions were also taken for gamma analysis.

d. Results

The gamma-analysis results are presented in Table II-49. The isotope ¹³⁷Cs was not observed, but its activity was likely so small that it could not be observed in the presence of the relatively high activity of the other isotopes. In the first irradiation (discussed in previous semiannual report, Sec. II.K), after several days the activity of the short-lived isotopes decayed away enough that ¹³⁷Cs could be detected. However, in that case, much of the activity had also been separated via precipitation, whereas no initial separations were performed in the present case. Some of the short-lived isotopes (namely, ¹⁴³Ce, ¹³¹Te, and ¹⁰⁵Rh) were not observed in the silicate analysis, probably because their activities were low and the samples were counted about 14 days after irradiation.

No xenon isotopes were observed; apparently they escaped during the lengthy dissolving process. Only one iodine isotope was found (¹³¹I), and its activity was about 21% of that found for the first irradiation. Presumably, this is due to loss of iodine from the acidic solution to the atmosphere, although the 0.002M Hg²⁺ used during dissolution is expected to complex at least some of the iodide. For the first irradiation, the same fraction of iodine was lost from the dissolved sample solution after acidification.

The moles of U-235 fissioned (3.1×10^{-10}) are about the same as in the first irradiation. Here again, this number for ¹⁰⁶Ru is inexplicably two orders of magnitude too high. Moreover, this calculation for ⁹⁹Mo is low at 2.69×10^{-10} mol, indicating that 14% of the ⁹⁹Mo is unaccounted for and was lost during the chemical processing. About 6% of the ⁹⁹Mo observed remained with the silicates and went into solution upon treatment with NaOH. This is close to the 10% loss which, according to Kenneth Burrill (private communication), AECL observed for non-active U-Si-Al samples. He also mentioned that for irradiated USiAl with realistic burnups (probably around 1% compared to our Janus reactor burnup of 10⁻⁷%), approximately 90% of the ⁹⁹Mo was lost, apparently adsorbed on the silicate precipitate. Irradiated U-Si-Al forms extremely fine silicate particles, which are very efficient molybdenum adsorbers. It was suggested that a process be devised to dissolve the silicates in NaOH and add this solution to the dissolver solution for better molybdenum recovery. Care must be taken so that the silicates do not reprecipitate out upon addition to the acidic solution.

Table II-49. Gamma Analysis Results for U_3Si_2 Acidic Dissolution after Second Irradiation (4-18-88)

	Half-Life	dpm			Total	Moles U-235 Fissioned
		Filtered Supernate ^a	Sol. 2 ^b	Sol. 3 ^c		
Zr-95	64.0 d	1.71E+7	33.3E+6	3.15E+7	5.19E+7	1.82E-10
Zr-97	16.9 h	1.25E+9			1.25E+9	
Mo-99	66.02 h	1.62E+9	1.04E+8	4.69E+6	1.73E+9	2.69E-10
Ru-103	39.4 d	7.48E+7	1.36E+6		7.62E+7	3.61E-10
Rh-105	35.4 h	8.05E+8			8.05E+8	
Ru-106	367 d	1.07E+8			1.07E+8	3.56E-08
Tc-131	30 h	3.16E+8			3.16E+8	
Tc-132	70 h	1.19E+9	1.87E+7	7.96E+6	1.22E+9	
I-131	8.040 d	6.42E+7	2.51E+6		6.67E+7	6.38E-11
Ba-140	12.79 d	4.53E+8		2.79E+6	4.56E+8	3.14E-10
Ce-141	32.5 d	1.59E+8		9.95E+6	1.60E+8	3.19E-10
Ce-143	33.0 h	3.98E+9			3.98E+9	
Nd-147	11.0 d	1.87E+8		1.29E+6	1.88E+8	2.75E-10
Eu-156	15 d	2.67E+8			2.67E+8	
Np-239	2.35 d	1.15E+9			1.15E+9	

^aFiltered supernate is solution in which target has been dissolved.

^bSolution 2 is supernate of silicate precipitate dissolved in NaOH.

^cSolution 3 is supernate after solution 2 precipitate was dissolved in HNO_3 .

Of the ^{99}Mo in the filtered supernate that was loaded on the column, 94% was recovered. The molybdenum peak in the chromatogram has a tail, so some ^{99}Mo possibly remained on the column after the last sample was eluted (Fig. II-83). The reason AECL elutes with $1M NH_4OH$ rather than concentrated NH_4OH (used by Institut National des Radio Elements, Fleurus, Belgium) is not known, but according to our results, concentrated NH_4OH is a better eluant. However, depending on the temperature of the process, it is possible that concentrated NH_4OH is not used because of its low boiling point. Since about 1% of the ^{99}Mo eluted during the water wash, this amount would not be included in the final summation.

The behavior of various isotopes on the alumina column is shown in Figs. II-84 to II-86. As was the case for Fig. II-83, the loading conditions were: sample loading, 0-250 mL; $0.5M HNO_3$ wash, 250-275 mL; water wash, 275-300 mL; $0.01M NH_4OH$, 300-350 mL; and $1M NH_4OH$ elution, 250-400 mL. Some isotopes (e.g., Ce, Nd, Np) show no adsorption on the alumina column under these loading conditions. Presumably, U and Pu follow the Np chemistry and are not adsorbed; therefore, these isotopes should not interfere with ^{99}Mo purification. Europium seems to adsorb very weakly, eluting with the water wash; I, Te, Ru (to a small extent), and La (a daughter, and therefore representative of Ba) adsorb weakly and elute with water and then more strongly with the $1M NH_4OH$. This is similar to the behavior of molybdenum and suggests a weakly and a strongly adsorbed species. Technetium, similar to its behavior observed for the first irradiation, is weakly adsorbed during solution loading and eluting during the $0.01M NH_4OH$ wash. After the alumina column separation, the main radionuclidic interferences are ^{131}I , ^{132}Tc , ^{140}La , and ^{140}Ba . This should also be true for HEU.

Fig. II-83. Molybdenum and Technetium Behavior on Alumina

Sample loading: 0-250 mL
 0.5M HNO_3 wash: 250-275 mL
 Water wash: 275-300 mL
 0.01 M NH_4OH : 300-350 mL
 1M NH_4OH elution: 350-400 mL

Fig. II-84. Rhodium, Tellurium, and Cerium Behavior on Alumina Column

Fig. II-85. Lanthanum, Ruthenium, Neodymium, and Neptunium Behavior on Alumina Column

Fig. II-86. Molybdenum, Technetium, Iodine, and Europium Behavior on Alumina Column

3. Third Irradiation of U_3Si_2

a. Irradiation

On June 6, 1988, an 80 min irradiation of 4.2 g of U_3Si_2 was performed in the Janus reactor at one-quarter power (48 kW). After the aluminum capsule was opened, the sample activity measured 500 mK (γ) and 4 R ($\beta + \gamma$).

b. Dissolution

For this irradiation, a variation of the basic dissolution process used for the first irradiation will be tried. For that irradiation, a two-step dissolving process was used where the 6061Al cladding was dissolved first in NaOH. This solution was decanted, leaving the silicide fuel behind for subsequent dissolution in a peroxide/hydroxide solution. However, about 20% of the ^{99}Mo dissolved out of the fuel into the cladding solution. The processing procedure for this irradiation was changed to recover the ^{99}Mo by combining the cladding supernatant and the fuel supernatant before further processing.

The 6061Al cladding was dissolved in 80 mL of 3M NaOH. This solution was centrifuged, and the precipitate was washed with 20 mL of 1.5M NaOH and centrifuged again. The combined supernatants totaled 48.6 mL; a 1-mL aliquot was taken for gamma analysis. The cladding precipitate was added to 6M HNO_3 . Not all the aluminum redissolved, but the sample was shaken to homogenize the sample as much as possible before a 1-mL aliquot was taken for gamma analysis.

To the U_3Si_2 fuel, 190 mL of 1:1 3M NaOH/30% H_2O_2 was added in 10 mL aliquots. During the dissolution, 1.2 mg of molybdenum carrier was added to approximate the U/Mo ratio found in irradiated HEU targets. After complete dissolution, the sample was heated to remove peroxide. The red color of the uranium peroxide complex faded and a pale yellow color remained. The solution was centrifuged. The precipitate was washed with NaOH solution and centrifuged, and the supernatants were combined. The resulting solution (60 mL) was cloudy yellow; a 0.5 mL aliquot was taken for counting.

The solution was acidified with 6M HNO_3 . As it approached neutrality, a copious amount of white precipitate formed. At this point, the supernatant from the cladding was added and acidified. The white precipitate formed and then diminished once the solution was acidic but would not dissolve and was probably aluminum. Final total volume was 500 mL with a pH of 0.3. The slow addition of 5 mL of concentrated HF to about 80 mL of this solution appeared to break up the particles to a smaller size but did not dissolve the white precipitate.

c. Results

Data for this experiment are presented in Table II-50. These results are, in general, suspect due to difficulties during the processing and gamma analysis; thus, further work (separations, etc.) will not be done.

The number of moles of ^{235}U that fissioned as calculated for each isotope is very similar to that calculated for the first and second irradiations, with ^{95}Nb exceptionally low and ^{106}Ru exceptionally high. The moles ^{235}U fissioned based on Mo-99 are lower than the mean yield and certainly lower than the previous irradiations. However, given that this sample was smaller (4.2 vs. 4.7 g), this difference is not striking. The 0.745 mCi of ^{99}Mo corresponds to a flux of 4.7×10^{10} or 80%

Table II-50. Gamma Analysis Results for U₃Si₂ Initial Separations after Third Janus Irradiation²

Half-life	Dissolved Cladding, dpm			Uranium Silicide Fuel, dpm			Total	Moles U-235 Fissioned	% Lost to Cladding
	Supernate	Precipitate		Supernate	Uranyl Ppt.				
Nb-95		7.60E+6			7.80E+6		1.54E+7	5.40E-11	49
Zr-95	1.53E+6	2.31E+7			1.91E+7		4.37E+7	1.53E-10	56
Zr-971		6.66E+8					6.66E+8		100
Mo-99	3.62E+8	2.23E+8		1.07E+9			1.66E+9	2.57E-10	35
Ru-103	4.72E+5	2.02E+7		4.46E+7	6.16E+6		7.14E+7	3.39E-10	29
Rh-105		2.62E+8					2.62E+8		100
Ru-106		1.21E+7					1.21E+7	4.03E-09	100
Te-132	6.38E+6	3.17E+8		7.68E+7	8.72E+8		1.27E+9		25
I-131	6.25E+7	4.91E+7		1.98E+8	2.10E+7		3.31E+8	3.16E-10	34
I-133		6.59E+9					6.59E+9		100
Ba-140		1.09E+8			3.46E+8		4.55E+8	3.13E-10	24
La-140		2.15E+9					2.15E+9		100
Ce-141		3.88E+7			1.16E+8		1.55E+8	3.09E-10	25
Ce-143		1.04E+9					1.04E+9		100
Ce-144		5.82E+6			1.38E+7		1.96E+7	3.21E-10	30
Nd-147		4.76E+7			1.41E+8		1.89E+8	2.75E-10	25
Eu-156					3.65E+7		3.65E+7		0
Np-239 ^b		2.41E+8					2.41E+8		100

^aAt t=0, end of irradiation.^bActivation product.

of the unperturbed flux. It is possible that ^{99}Mo was somehow "lost" during these separations, but taking a representative value of 3.14×10^{-10} mol of ^{235}U for the other isotopes would correspond to 0.91 mCi of ^{99}Mo and 97% of the unperturbed flux, which is highly unlikely. The flux depression for this sample should be identical to that of the first irradiation (86% of unperturbed flux) so that 0.81 mCi of ^{99}Mo should have formed during this irradiation, or 2.78×10^{-10} mol of ^{235}U fissioned. This is not very different from the 2.57×10^{-10} mol of ^{235}U fissioned for ^{99}Mo found experimentally.

Both the cladding and the fuel precipitates were washed once to obtain a cleaner separation of the supernatants. This appears to have been successful for the fuel precipitate since no ^{99}Mo was detected there. A significant amount was found with the cladding precipitate. Only Zr, Mo, Ru, Tc, and I were detected in the supernatants, as expected from the chemistries of the fission products.

In an effort to determine if the 20% loss of ^{99}Mo to the cladding during dissolution observed for the first irradiation is reasonable, we estimated the theoretical loss. There are basically two mechanisms for the escape of fission products from the fuel: (1) recoil of the fission products at the instant of fission and (2) dissolution of a shell that forms around particles in the fuel during irradiation. This shell is a gradient of U, Si, and Al and could dissolve during dissolution of the aluminum cladding, leading to the release of fission products. However, according to G. Hofman (EBR-II, ANL), at our very low burnups ($10^{-7}\%$), the formation of a shell around a particle is not likely, and escape of fission products should only be through recoil.

Calculations of fission product loss from the fuel due to recoil were made using fission fragment ranges from the literature. An equation for this calculation is³⁵

$$f = 0.5 (3r/d - r^3/d^3) \quad (\text{II-83})$$

where f is the fraction of fission products which recoil from a sphere of diameter d , and r is the fission fragment range. This equation gives the same results as our earlier method. The r value for U_3Si_2 is assumed to be $9.4 \mu\text{m}$ (the r for UO_2), while that for uranium metal is $6.8 \mu\text{m}$.³⁶ Wood estimates that about 12% of fission products would escape from silicide particles having sizes in the range 88-149 μm and about 60% from particles in the size range 0-44 μm . For our silicide fuel, this means a 19% theoretical loss (experimental loss was 20%). Taking this one more step, in order to have <5% loss, the particle size would need to be greater than 280 μm .

4. Irradiation of Uranium Metal

a. Irradiation

A sample of uranium metal was irradiated in the Janus reactor on August 1, 1988, at 12:50 pm for 80 min at one-quarter power (48 kW). The sample was 4.48 g of 0.20-cm thick uranium metal foil that had been wrapped in aluminum foil. Two days later, the sample activity measured 15 R ($\beta + \gamma$) and 800 mR (γ).

b. Dissolution and Separation

This sample was divided for processing, approximately half for acid dissolution and half for basic peroxide dissolution. Because the uranium was wedged tightly in the irradiation capsule, the aluminum foil was ripped off when the sample was extracted. The sample was cut in two. One piece, weighing 2.52 g, was placed in a beaker with a total of 30 mL of 3M HNO_3 , 6 mL of concentrated HNO_3 , and 0.2 mL of 0.2M $\text{Hg}(\text{NO}_3)_2$ as a catalyst. This dissolution was fast, less than 3 h. The resulting

solution was diluted to 25 mL, and an aliquot taken for gamma analysis. The remaining solution was diluted to a pH of 0.313. Problems with the alumina column's drying out caused spurious results; therefore, the chromatographic results are not shown for the basic and the acid dissolution.

c. Results

Results of the gamma analyses for the acid and basic procedures are presented in Table II-51. The total amount of ^{99}Mo produced for both samples indicates a flux that is 85% of the unperturbed flux. This is much higher than the 47% calculated based on the thickness of the uranium metal foil.

Calculation of the theoretical loss due to recoil from the uranium metal was modified for target shape (foil vs. sphere). With a metal thickness of 0.020 cm, 2.7% of the fission products should be lost to the fuel due to recoil. Since all the aluminum foil was dissolved but only half of the uranium metal was treated with NaOH, the observed loss should be between 50 and 100% of the total loss expected for the whole sample, or a range of 2.7 to 6.2%. The observed range (Table II-51) is 2 to 3%. It is interesting to note that ^{239}Np was not observed in the aluminum fraction; this finding is not surprising since ^{239}Np is an activation product rather than a fission product and would not have any recoil energy.

The basic dissolution was finished long enough after the irradiation that the activity of some short-lived nuclides may have decayed too much to observe, especially in the fuel supernate. In general, the chemistry looks straightforward, with most isotopes precipitating with uranium, leaving Mo, Ru, I, and some Ba in the supernate. No ^{99}Mo was observed with the uranium precipitate, and from its detection limit there was never more than 0.1%.

Table II-51. Gamma Analysis Results after Initial Separations of Uranium Metal for Fourth Janus Irradiation

	Half-life	disintegrations/minute				Moles U-235 Fissioned	% Lost Recoil ^a
		Fuel	Uranium	Al	Total		
		Supernate	Precipitate	Supernate			
<u>Basic Dissolution</u> (1.96 g U)							
Nb-95	35.0 d		1.9E+7	2.4E+5	1.9E+7	6.7E-11	
Zr-95	64.0 d		5.4E+7	1.4E+6	5.5E+7	1.9E-10	2.5
Mo-99	66.02 h	9.7E+8	<1E+6	3.3E+7	1.0E+9	1.6E-10	3.3
Ru-103	39.4 d	1.6E+7	2.6E+7	1.3E+6	4.3E+7	2.0E-10	2.9
Rh-105	35.4 h		1.8E+10	2.1E+7	1.8E+10		
Te-132	78 h		6.8E+8	1.8E+7	7.0E+8		2.6
I-131	8.04 d	1.1E+8	6.7E+7	5.6E+6	1.8E+8	1.7E-10	3.1
Ba-140	12.79 d	4.1E+6	2.5E+8	5.7E+6	2.6E+8	1.8E-10	2.2
Ce-141	32.5 d		8.6E+7	2.0E+6	8.8E+7	1.8E-10	2.3
Ce-143	33 h			5.7E+7	5.7E+7		
Nd-147	11 d		1.0E+8	2.6E+6	1.1E+8	1.6E-10	2.4
Eu-156	15 d		2.8E+7	2.8E+6	3.1E+7		9.1
Np-239	2.35 d		1.1E+9	<2E+6	1.1E+9		0.0

	Half-life	Fuel Supernate, ^b dpm	Moles U-235 Fissioned
<u>Acid Dissolution</u> (2.52 g U)			
Nb-95	35.0 d	9.4E+6	3.3E-11
Zr-95	64.0 d	6.4E+7	2.2E-10
Mo-99	66.02 h	1.0E+9	1.6E-10
Ru-103	39.4 d	4.5E+7	2.1E-10
Rh-105	35.4 h	4.2E+8	
Te-132	78 h	7.3E+8	
I-131	8.04 d	2.1E+8	2.0E-10
Ba-140	12.79 d	2.7E+8	1.8E-10
Ce-141	32.5 d	9.1E+7	1.8E-10
Ce-143	33 h	2.4E+9	
Nd-147	11 d	1.5E+8	2.2E-10
Eu-156	15 d	8.8E+7	
Np-239	2.35 d	7.5E+8	

^aPercent of isotope found with Al foil/total dpm.^bAt t=0, end of irradiation.

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III. HIGH-LEVEL WASTE/REPOSITORY INTERACTIONS

(J. K. Bates)

A. Glass Studies

(J. K. Bates, B. M. Biwer, W. L. Ebert, T. J. Gerding, J. J. Mazer, and A. B. Woodland)

The Yucca Mountain Project (YMP) is investigating the tuff beds of Yucca Mountain, Nevada, as a potential location for a high-level radioactive waste repository. As part of the waste package development portion of this project, which is directed by Lawrence Livermore National Laboratory (LLNL), work is being performed by the CMT Division to study the behavior of the waste form under anticipated repository conditions. Work includes (1) development and performance of a test to measure waste form behavior in unsaturated conditions, (2) performance of experiments to study the behavior of waste package components in an irradiated environment, (3) development of test methods to study the reaction of glass in water vapor and subsequently in liquid water, (4) development of static leaching tests to provide long-term release data to the glass modeling effort, and (5) detailed characterization of reacted glass surfaces. The nature and degree of glass reaction are assessed from solution analysis and examination of the reacted glass surface with various analytical techniques, including scanning electron microscopy (SEM) with energy dispersive X-ray fluorescence spectrometry (EDS), secondary ion mass spectrometry (SIMS), and X-ray diffraction (XRD).

1. Unsaturated Test Results

(J. K. Bates and T. J. Gerding)

The tuff beds of Yucca Mountain, Nevada, are being investigated as a site for the disposal of high-level nuclear waste in an underground repository. If this site is found suitable, the repository would be located in the unsaturated zone above the water table. The Site Characterization Plan (SCP) describes the repository site and the methodology of assessing its performance.¹ While many factors are accounted for during performance assessment, an important input parameter is the degradation behavior of the waste form, which may be either spent fuel or reprocessed waste contained in a borosilicate glass matrix.

To develop the necessary waste-form-degradation input, the waste package environment needs to be identified. This environment will change as the waste decays and also is a function of the repository design, which has not yet been finalized. At the present time, an exact description of the waste package environment is not available. However, the SCP does provide a conservative estimate of conditions that can be used to guide waste form evaluation. These guidelines indicate that the waste package will not be contacted by large volumes of water, but that reaction with humid air and transient amounts of liquid water may occur. Because of the unsaturated environment, it is not anticipated that the water will collect in the repository bore hole and completely submerge the waste; however, small volumes of water may collect in a bore hole at any given time. Additionally, it is anticipated that free air exchange will exist between the repository horizon and the biosphere. These conditions are deemed conservative because of the small amount of water available for radionuclide transport from the repository. The effect of varying amounts of water on the waste form reaction needs to be established.

Such a repository environment poses a challenge to developing a testing program because of the diverse conditions that may exist at a given time during the life of the repository. A starting point is to identify whether any potential wastewater contact modes are particularly deleterious to the waste form performance, and whether any interactions between materials present in the waste package environment need to be accounted for during modeling the waste form reaction. The Unsaturated Test Method is one

approach that has been developed by the YMP to investigate the above issues, and results obtained during the testing of simulated waste glass are presented here.

a. N2 Unsaturated Test

The apparatus used in the Unsaturated Test as applied to glass testing has been described previously.² The components of the apparatus are the test vessel, which provides for collection and containment of liquid and support of the waste form; the waste package assemblage (WPA), which consists of the waste form and perforated, presensitized, metallic components representing the pour canister; and a solution feed system to inject test water. The test is performed at 90° C.

The WPA is contacted intermittently by small, measured amounts (drops) of repository water (EJ-13) that has been preequilibrated with tuff at 90° C. The nature and degree of radionuclide release from the WPA are determined by collection and analysis of the solution and the WPA components. Materials interactions are noted, and secondary alteration products, which influence the nuclide release from the WPA, are identified.

The test procedure incorporates batch and continuous testing. In the batch mode, tests are terminated at periodic time intervals. The test apparatus is disassembled, and analyses of both the solution and components are performed. In the continuous mode, the WPA (including liquid associated with the assemblage) is transferred to a new test vessel at 6.5- to 26-week intervals, and the test is continued. Analyses are done on the solution in the old vessel. With the continuous-testing mode, replication of solution analysis can be achieved. In addition, investigation of the test components is possible at the termination points, and yet the test can continue for an unspecified number of test periods or until information most useful to reaction evaluation is obtained.

The N2 tests (with SRL 165 glass*) have been completed through the 130-week sampling period. All the batch tests have been completed, and three continuous tests and one blank are ongoing with samplings at 12-week intervals.

Results to date indicate that the greatest effects on glass reaction are due to spallation of the reacted glass layer and interaction between the solution, glass, and sensitized metal components of the WPA. The larger elemental release is accompanied by a striking change in the appearance of the reacted glass surface. There was evidence that layers of reacted glass had spalled from the WPA during the test period and had been included with the analyzed test solution. (The Unsaturated Test Method treats all material released from the WPA, either in solution or as a solid phase, as available for transport from the waste package.) In Fig. III-1, surface regions of bare glass not in contact with metal are shown partially covered with a precipitated clay-like phase. Small regions of such exfoliation followed by reprecipitation have been observed on the long-term samples for most of the unsaturated tests. Surrounding the exfoliated regions are usually copious quantities of Cl- and S-bearing precipitates.

While a definitive explanation of the exfoliation/ reprecipitation process is not available, it is likely that conditions were favorable for wet/damp cycling, with enough water being available to allow water plus exfoliated sample to drip from the WPA. These conditions, plus the anionic components of the glass, appear to combine to result in the increased reaction.

*Simulation of glass to be produced by the Defense Waste Processing Facility at the Savannah River Plant.

Fig. III-1. Scanning Electron Photomicrograph of a Bare Section of Glass after Exfoliation of the Reacted Layer Followed by Reprecipitation. Magnification 1000X.

b. N3 Unsaturated Test

The N3 Unsaturated Test is in progress using ATM-10 glass (simulated West Valley glass containing actinides plus ^{99}Tc) that was received from the Materials Characterization Center and remelted to obtain the required form of the glass. The test was started on July 6, 1987, according to the Unsaturated Test Matrix³ and has been completed through the 91-week sampling period.

The Li, B, and U normalized releases from ATM-10 glass through 80 weeks are shown in Fig. III-2. The releases from ATM-10 glass are about three times larger than those for SRL 165 glass under similar conditions. The striking feature in the N3 tests was that, despite a pretreatment of the metal retainer as was done in tests for SRL 165 glass, there was no evidence of strong reaction between the metal and glass. This result may be due to the composition of ATM-10 glass, which was manufactured from starting components that contained no S or Cl (no anionic composition was reported for this glass). Further analysis of the reacted components from the N3 tests may be required to better address the apparent lack of glass/metal reaction.

2. Basalt Analog
(J. J. Mazer)

a. Basalt Glass Hydration

Hawaiian basalt glass has been hydrated at 100% relative humidity (RH) and 175 and 200° C for up to 150 days. Figure III-3 presents the measured alteration layer thicknesses for these samples as a function of time. The data have typical error ranges of $\pm 20\%$ of the measured value, as

Fig. III-2. Normalized Mass Release (NL) of Li, B, and U in Glass Unsaturated Tests (ATM-10). The tests were run in triplicate and are identified as a, b, and c.

Fig. III-3. Layer Thickness as Function of Time for Hawaiian Basalt Glass at 100% RH

illustrated by the point for the 140 day, 200° C experiment. Hydration rates can be estimated from these data, and an activation energy for the hydration mechanism can be approximated from the Arrhenius relationship. The activation energy of this process is ~9 kcal/mol (~38 kJ/mol), based on these preliminary data. If clay formation is the rate-limiting step in basalt glass alteration, then similar activation energy values should be observed. The temperature dependence of crystal growth has been described for clay minerals^{4,5} and zeolites.^{6,7} Energies of activation ranging from 7 to 12 kcal/mol (29 to 50 kJ/mol) have been reported for the precipitation of smectites of various compositions. A similar compositional dependence has been described for a synthetic zeolite,⁸ where the energy of activation increased from 11.8 to 15.6 kcal/mol (49.4 to 65.4 kJ/mol) as the Si/Al ratio in the crystals increased. The energies of activation for zeolite precipitation range from 7 to 19 kcal/mol (29 to 80 kJ/mol). These values are thought to be characteristic of a surface reaction growth mechanism, rather than diffusion of dissolved species in solution, typically 3-4 kcal/mol (13-17 kJ/mol). The energies of activation of layer growth in glass/water reactions that have been reported include those of Bates et al.⁹ for waste glasses hydrated in steam. Their value of 18 kcal/mol (75 kJ/mol) is in good agreement with the values others have found for clay or zeolite crystallization.

Preliminary analyses of the alteration layer have also been performed. Table III-1 presents the compositional analysis results from three 200° C samples (JT-28, JT-38, and JT-31), along with earlier results (see previous semiannual, Sec. III.E) from tests with Hawaiian basalt at 187 and 240° C (100% RH). Differences in the values for Al and Fe, and possibly the Ca, may be significant, but overall the compositions also show similarities. When the analytical error is accounted for, the similarities become more striking. Analyses of more samples will be performed to better resolve the layer compositions. Transmission electron microscopy (TEM) will be used to examine samples generated in previous experiments. The greater spatial resolution of the TEM may enable discrimination of various phases present that cannot be resolved using the SEM.

b. Infrared Water Measurements

A qualitative relationship between intrinsic water contents and hydration rates has been described for obsidians.^{10,11} An investigation was initiated to measure the intrinsic water contents

Table III-1. Representative Layer Composition Determined from Analysis of Hawaiian Basalt after Vapor Hydration Tests at 100% Relative Humidity. Results are presented as stoichiometries normalized to eight silicon atoms. Oxygen calculated by stoichiometry. All alteration layers were formed on Hawaiian basalt glass in a 100% RH environment.

	Unreacted Hawaiian Basalt Glass	Reacted Glass ^a			Earlier Results ^b	
		JT-28 (46 days)	JT-38 (84 days)	JT-31 (136 days)	187 °C 100% RH	240 °C 100% RH
Na	1.40	0.85	0.52	0.54	0.56	0.51
Mg	1.43	2.08	2.63	2.41	2.24	2.58
Al	2.52	2.10	2.46	1.82	3.63	2.38
Si	8.00	8.00	8.00	8.00	8.00	8.00
K	0.13	0.13	0.53	0.34	0.17	0.14
Ca	1.77	2.24	1.44	1.62	1.54	2.05
Ti	0.22	0.38	0.23	0.28	0.61	0.48
Mn	0.02	0.03	0.13	0.28	0.42	0.08
Fe	1.51	2.17	3.27	2.39	4.23	2.21
O	26.48	28.38	29.76	27.93	33.78	28.96
Cation:Si	1.12	1.25	1.40	1.21	1.68	1.30

^aAt 200 °C and 100% RH.

^bAverage values for at least six measurements on glass tested for various test durations.

of obsidian and nuclear waste glasses. Water measurements were made on several obsidians with known hydration rates but unknown intrinsic water contents. The method of Newman et al.¹² was employed to determine the intrinsic water contents of seven obsidians. Results are given in Table III-2. One glass, Coso 4-1, had been previously analyzed for water by the Penfield method.¹³ The variability in intrinsic water content of obsidians from the Coso field, 0.28 to 0.53 wt % H₂O, is well known.¹⁴ (Our obsidian samples were obtained from the identical outcrop as the previous water determination.) Six Penfield determinations for Coso 4-1 resulted in a value of 0.36 ± 0.10 wt % H₂O.¹³ We measured the water content of Coso 4-1 to be 0.30 ± 0.03 wt % H₂O by Newman's method. The results presented by Newman et al.¹² suggest that IR measurements are accurate to ± 0.05 wt % H₂O. The good agreement between the values measured by separate techniques lends confidence to measurements of samples where the water content is unknown.

Infrared spectra were also obtained for three borosilicate glasses being used in hydrothermal leaching and steam hydration testing. The Newman et al. paper warns that the molar absorptivity constants have been determined only for obsidian and should be independently determined for other glass compositions. A source has been located for Penfield determinations of water contents in glasses (Diffusion Labs, Spring Mills, PA). However, until funding becomes available for these analytical verifications, Newman's obsidian constants are being used to make rough estimates of the water contents in SRL-type glasses. The measured water contents (bottom, Table III-2) indicate that these glasses are nearly anhydrous, and the concentrations of water species are near the detection limit of the technique. With respect to obsidian hydration, anhydrous conditions are favorable in terms of molecular water diffusion being inhibited. Such differences in obsidians result in huge differences in hydration

Table III-2. Summary of IR Intrinsic Water Determinations of Obsidians^a and SRL Borosilicate Glasses

Glass	Thickness, cm	Sample Density, g/cm ³	Weight Percent		
			H ₂ O	Intrinsic OH	Water
OBSIDIAN					
Coso 4-1, CA	0.100	2.35	0.09	0.21	0.30
El Choyal, Guatemala	0.130	2.23	0.05	0.20	0.25
Bodie Hills, CA	0.141	2.36	0.03	0.12	0.15
Ixtepeque, Mexico	0.130	2.39	0.03	0.03	0.06
Grasshopper, CA	0.112	2.26	0.06	0.09	0.14
Pachuca, Mexico	0.121	2.20	0.11	0.02	0.13
C. Jantzen's Snake River	0.090	2.33	0.01	0.09	0.10
BOROSILICATE					
SRL 131	0.091	2.70	0.03	0.01	0.04
SRL 202	0.085	2.60	0.04	0.01	0.05
SRL 165U	0.109	2.55	0.03	0.01	0.04

^aAverage of at least two measurements.

rates. Thus, the range of glass compositions that may be produced by the West Valley Demonstration Project may have widely varying hydration rates.

Since nuclear waste glasses and obsidian probably do not hydrate by identical mechanisms, it would be prudent to demonstrate that: (1) water content affects the reaction processes in the nuclear waste glasses of interest, and (2) water content can be measured in nuclear waste glasses. Once the importance of water content is established, we can then determine the correlation between intrinsic water content in waste glasses and their measured durabilities.

3. Gamma Irradiation Experiments (W. L. Ebert)

We performed an extensive series of experiments to determine the influence of penetrating gamma radiation on the chemistry of tuff groundwater and the reaction of simulated nuclear waste glass with tuff groundwater. At the YMP site, air that is present after repository closure will be subjected to high doses of gamma radiation. The high temperature of the repository will prevent liquid water from accumulating and contacting the waste form for several hundred years. As radionuclides decay and the waste cools, it is possible that small volumes of liquid water will collect and contact the waste form, although this condition is not anticipated to occur. This groundwater would itself be irradiated by low doses of gamma radiation and would equilibrate with irradiated air. Because liquid transport is the primary means of radionuclide release from the repository, the behavior of the glassified waste in such an environment must be characterized to assure that performance objectives of the waste glass are met.

The experiments performed were not designed to simulate a particular repository scenario; rather they were designed to determine the influence of gamma radiation on material interactions that may occur under several scenarios. Experiments were performed in gamma radiation fields with measured dose rates near 2×10^5 , 1×10^4 , and 1×10^3 R/h and in the absence of radiation. Four different glass compositions were reacted: SRL 165 black frit doped with U to generate a glass referred to as SRL U; SRL 165 black frit doped with U, Np, Pu, and Am to generate a glass referred to as SRL A; ATM-1c, which contains uranium; and ATM-8, which contains U, Np, and Pu. Samples were prepared as disks approximately 1 cm in diameter and 2 mm thick. Repository reference groundwater from well J-13 was reacted with pulverized tuff (<100 mesh) at 90°C to generate the leachant referred to as EJ-13. Wafers of tuff rock from core samples were produced at LLNL and included in some experiments. Reactions were performed in 304L stainless steel reaction vessels at 90°C. Experiments were run with air and EJ-13; air, EJ-13, and tuff; air, EJ-13, and glass; and air, EJ-13, tuff, and glass under each radiation field and without radiation. The volume of leachant added was varied to achieve a glass surface area/leachant volume ratio of 30 m^{-1} and air-to-leachant volume ratio near 0.3.

Both the leachates and the reacted solids were analyzed to characterize the glass reaction and material interactions which occur. This report describes the behavior of the radionuclides U, Np, Pu, and Am during the reaction of SRL A glass without complications due to radiation. Subsequent reports will compare the reactions in the different gamma fields.

Analysis of the leachates showed the radionuclides to be distributed among dissolved and filterable (colloidal) fractions and to be sorbed to the stainless steel vessels. That amount which passed through a 50 Å filter was assumed to be dissolved. Analysis of the reacted glass showed some nuclides to be retained on the glass surface. The amount of nuclide in the dissolved, filterable, and sorbed fractions was considered to be the total amount released from the glass. In experiments including a tuff wafer, a small amount of nuclides was sorbed onto the tuff; this, too, was included in the released total. The total amount of a nuclide released was used to compute the normalized elemental mass loss (NL) as grams of element per square meter of glass surface.

The normalized mass loss of neptunium is plotted vs. the reaction time in Fig. III-4a. The normalized lithium losses for the same experiments are shown in Fig. III-4a for comparison. Notice that both lithium and neptunium are released at a rate which decreases with the reaction time. Lithium was found to be released to the greatest degree of all glass components in all experiments, and Fig. III-4a shows neptunium to be released to a similar degree, although the error in analysis of the neptunium concentrations is much greater than that of lithium (approximately 20% for neptunium and 5% for lithium).

The normalized uranium and boron releases are shown as a function of reaction time in Fig. III-4b. These elements have similar release trends but are released to a lesser extent than lithium and neptunium. However, boron was found to be released to a large extent in parallel experiments with nonactinide-containing glasses, often to an extent similar to lithium. The different behavior may indicate a pH effect on the boron release.

As shown in Fig. III-4c, silicon is released to a large extent for the first 181 days of reaction, but the solution concentration decreases at 278 days. Analysis of the reacted glass surfaces shows a small silicon-rich phase to nucleate between 181 and 278 days; in turn, this phase lowers the silicon concentration in solution. Note that after 181 days, $\text{NL}(\text{Si})$ is about 6, $\text{NL}(\text{Li})$ is about 6, and $\text{NL}(\text{B})$ is about 4 g/m^2 (averages of two experiments given). Other experiments have shown $\text{NL}(\text{B})$ to be greater than $\text{NL}(\text{Si})$ after equivalent reaction times. The release of glass components and doped radionuclides is nonstoichiometric. The release of plutonium, also shown in Fig. III-4c, is much less than the release of

Fig. III-4. Normalized Elemental Mass Loss (in g/m^2) of (a) Neptunium and Lithium, (b) Uranium and Boron, (c) Plutonium and Silicon, and (d) Americium from SRL 165A Glass at 90°C

silicon at all reaction times. The solubility limit of plutonium at the experimental pH values (near 10) is very low, and the released plutonium was predominantly sorbed onto the stainless steel reaction vessel.

The solubility of americium in these leachates was also very low, and only small amounts were found sorbed to the stainless steel. Thus, the normalized americium mass loss was very small, as shown in Fig. III-4d. One of the duplicate experiments performed at both 181 and 278 days reached low pH values (7 and 5, respectively) due to an anomalous vessel reaction. The higher solubility limits at more acidic pH values resulted in a significant increase in the amount of dissolved americium. Except for these anomalous experiments, americium is primarily retained by the glass.

The reacted glass surfaces were analyzed to better understand the reaction processes. The analytical results can be compared to the leachate results to provide an approximate mass balance for the elements analyzed. Figure III-5 shows Li, Na, B, and Mg depth profiles obtained using SIMS. The

Fig. III-5.

SIMS Profiles of (a) Lithium and Sodium and (b) Boron and Magnesium in SRL 165 Glass Reacted for 278 Days at 90°C

intensity on the ordinate represents the elemental concentration. The far right end of the profiles (at 1.5 μm) corresponds to the unreacted glass beneath the reacted region. The concentrations of all elements are nearly constant at greater depths. As the surface ($\rightarrow 0 \mu\text{m}$) is approached, the concentrations of Li, Na, and B decrease and the concentration of Mg increases. Thus, the glass reaction depletes the near-surface region of Li, Na, and B, while it becomes enriched with Mg. The outermost 0.3-0.4 μm of the reacted layer is depleted to a nearly constant level. Moreover, the outermost surface appears to have a lower magnesium content than the rest of the reacted region.

The theoretical depletion depth was computed from the lithium content of the glass and the measured leachate concentration of lithium and determined to be about 2.5-3.0 μm . (The calculation requires an accurate value of the surface area of the glass samples, including cracks and surface roughness. The geometric surface area used in the calculation may be a factor of 2 or 3 too low; thus, theoretical depth could be a few tenths of a micron too great.) The measured depletion depth of lithium is about 0.7 μm , much less than the theoretical depth. This result implies that the outer $\sim 2 \mu\text{m}$ of the sample dissolved. The magnesium enrichment seen in Fig. III-5b supports this supposition. The low solubility of magnesium restricted the magnesium freed during the dissolution of the outer $\sim 2 \mu\text{m}$ to remain on the glass surface as insoluble residue. The redistribution of magnesium throughout the outermost region of the reacted glass suggests that the magnesium was free to migrate and possibly undergo ion exchange within the reacted layer. The high silicon concentrations shown in Fig. III-4c are consistent with the dissolution of the outermost glass surface before or during the formation of the reacted layer.

Similar analyses were made on the outermost surfaces to profile the radionuclides. Figure III-6 shows the SIMS profiles of U, Np, Pu, and Am. In this figure, the intensities of the AnO^+ fragments are plotted vs. the depth, where An = U, Np, Pu, or Am. As shown in Fig. III-6a, the Np and U concentrations continually increase with depth. This is consistent with leachate data presented in Figs. III-4a and -4b, which show Np and U to be released to extents similar to Li and B, respectively.

Fig. III-6.

SIMS Profiles of (a) UO^+ and NpO^+ and
(b) PuO^+ and AmO^+ in SRL 165 Glass Reacted
56 Days at 90°C

The plutonium concentration is nearly constant throughout the region of the reacted surface analyzed. (The first two data points of all four profiles represent sputtering through a nickel coating on the sample.) The americium is highly concentrated on the outermost surface and does not redistribute throughout the reacted layer. The profiles of Pu and Am in Fig. III-6b are consistent with the leachate results. Plutonium released as a small amount of the outer surface dissolves becomes sorbed onto the stainless steel vessel surfaces, but plutonium is not released from within the layer. Americium does not sorb onto the reaction vessel as the outer volume of glass dissolves; rather it remains as insoluble residue on the reacting surface, and in contrast to magnesium, does not redistribute within the layer. The difference in behavior can probably be attributed to magnesium's role as an ion exchange cation and as a component in devitrification products such as clays, while americium is a poorer ion exchanger or has limited mobility.

These analyses show that uranium and neptunium have sufficiently high solubilities or exist in colloidal form so that liquid phase transport is possible. The low solubilities of plutonium and

americium and the small degree of leaching maintain low concentrations of these nuclides in the leachate so that liquid transport is negligible. The release mechanisms appear to be unique for each nuclide, and further work is needed to better understand the reactions responsible for nuclide release from the glass.

B. Spent Fuel Studies

(D. J. Wronkiewicz and E. Veleckis)

The progress made during this reporting period can be subdivided into three related activities: (1) Series 5 spent fuel leach (SFL) tests, (2) tests of matrix dissolution for UO_2 under J-13 water saturated conditions, and (3) unsaturated drip tests with EJ-13 water and UO_2 pellets.

1. Series 5 Spent Fuel Leach Tests

A study is underway to determine the radionuclide release rates from spent reactor fuels immersed in site-specific groundwater at ambient hot cell temperatures. This current test is a continuation of previous SFL tests conducted at Hanford Engineering and Development Laboratory in a four-series project. The study is part of the YMP and is designed to evaluate the performance of Zircaloy-clad spent fuel as a potential high-level waste form. The SFL tests simulate conditions in which groundwater may collect in a breached waste form canister during the post-containment period.

The current tests will constitute Series 5 of the project. This test employs a "semi-static" leaching process, whereby the bare fuel specimen is immersed in 250 mL of J-13 water within matched stainless steel vessels for periods of up to six months. Both filtered and unfiltered solution analyses are planned, with the rate of radionuclide release being determined from analytical data collected during periodic sampling and cycle termination intervals.

Although most preparations for the Series 5 experiments have been completed, the tests have been delayed due to the inability of the sponsor to supply J-13 water for the leaching process. The water is expected to be obtained as soon as a revised technical procedure for its collection and storage has been approved.

2. Saturated Tests with Unirradiated UO_2

Reactant dissolution rate experiments have been initiated to examine the dissolution of enriched UO_2 powder in J-13 water under steady-state conditions. These experiments are based on a procedure utilizing the isotope dilution technique. Results should be important in modeling of spent fuel degradation rates in the repository. According to the Series 5 Test Plan, similar measurements will be incorporated in one of the SFL tests; thus, the current experiment also should establish the feasibility of such a test. Experimental arrangements and sampling procedures will parallel those of SFL tests, except that the experiments will be performed outside the hot cell and UO_2 granules will serve as a substitute for the spent fuel.

The experiment is being carried out in two cycles. In the first cycle, the UO_2 is leached in pure J-13 water until a steady-state concentration of uranium is established. In the second cycle, the leachant is replaced with fresh J-13 water that has been spiked with depleted uranium at steady-state concentrations determined from the first cycle. The spiked solution will be assayed for total uranium, ^{235}U , and ^{238}U contents.

The UO_2 reactant chosen for the experiment consists of a fine sinterable powder with an O/M ratio of 2.14. The isotopic composition of this UO_2 was <0.0005 wt% ^{233}U , 0.1559 wt% ^{234}U , 14.312 wt% ^{235}U , 0.0651 wt% ^{236}U , and 85.457 wt% ^{238}U . Impurities were determined to be 23 ppm Zn, 20 ppm Ca, 12 ppm Ni, 11 ppm Mg, and 0 ppm Na. Approximately 80 g of UO_2 powder was placed in a bailed basket and submerged in 250 mL of J-13 water within a sealed 304L stainless steel vessel. The leachate was sampled weekly for pH and uranium content.

Dissolution results are divided into two categories, those that are unfiltered and those that are filtered through Amicon CF25 and CF50 membrane cones (Fig. III-7). Unfiltered samples show considerably higher uranium contents than filtered ones, probably due to the presence of particulate or colloidal matter that has been released upon sample acidification. Particles could sometimes be observed in unacidified portions of the leachate samples. As can be seen from Fig. III-7, air sparging of the leachate and its filtration through $0.4\ \mu\text{m}$ filter do not appear to have any effect on unfiltered acidified samples. The CF25 and CF50 cone filters are expected to remove both particles and colloids; it is thus assumed that filtrates contain dissolved species only.

Uranium concentrations in CF25 and CF50 filter fractions from unirradiated UO_2 dissolution tests are much higher than those obtained with spent fuel.¹⁵ This variation may result from higher dissolution rates expected from the relatively larger surface area of finely powdered UO_2 used in

Fig. III-7. Time Dependence of Uranium Concentration in Filtered and Unfiltered Samples of a Leachate Resulting from Dissolution of UO_2 Powder in J-13 Water (Experiment RDR-1-1)

these experiments. Because of this accelerated dissolution, the reaction may have reached a state where uranium concentrations are being controlled by schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$), thereby yielding values similar to those predicted in simulation studies.¹⁶ Additional uranium content vs. time data from filtered samples will be needed to verify this interpretation.

A preliminary inspection of Cycle 1 data indicates that (1) uranium concentrations reach a maximum after approximately 75-100 days; (2) pH values undergo an initial drop and level off at ~ 5.7 ; (3) there is no perceptible difference in the uranium concentration in unfiltered and $0.4 \mu\text{m}$ -filtered samples and no differences between CF25- and CF50-filtered samples; (4) both filter sizes appear to be effective in trapping particulate matter; (5) inorganic carbon shows a steady concentration decrease with time; (6) concentrations of anions, other than NO_3^- , retain their initial values; (7) concentrations of major cations (Na, Si, Ca, and K) show initial decreases, presumably because these ions are incorporated in secondary phases; and (8) reduced silicon concentrations may promote the precipitation of schoepite, the presence of which may be responsible for the relatively high uranium concentrations observed in the experiment.

Cycle 1 will be continued until a steady uranium concentration is established. For Cycle 2, the leachant will be replaced with fresh J-13 water that is doped with depleted uranium salt at a concentration established during Cycle 1.

3. Unsaturated Tests with Unirradiated UO_2

A set of experiments, whereby Zircaloy clad- UO_2 pellets have been contacted by dripping EJ-13 water, has been in progress for over 3.5 years. The experiments are designed to develop procedures for the study of SFL reactions, to identify secondary phases formed during UO_2 alteration, and to identify parameters controlling U release from the waste package assemblage. The Unsaturated Test protocol is being employed for these tests, with temperatures maintained at 90°C and samples supported by TeflonTM plates. Two water injection rates (0.075 mL every 3.5 days and 0.0375 mL every 7 days) and variable UO_2 surface areas are being used to examine the effect of SA/V ratio on uranium release and surface alteration. Four of the original eight experiments have been terminated, and the remaining four are ongoing.

A pulse of uranium release from the UO_2 solid, combined with the formation of schoepite and dehydrated schoepite ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{UO}_3 \cdot 0.8\text{H}_2\text{O}$, respectively) on the sample surface, characterizes reactions between ~ 25 and 100 weeks (Fig. III-8). Thereafter, the U pulse subsided, and another set of secondary phases was observed to form on the top UO_2 surfaces. These later phases have incorporated cations from the EJ-13 water and include boltwoodite [$\text{K}(\text{H}_3\text{O})\text{UO}_2(\text{SiO}_4) \cdot n\text{H}_2\text{O}$], uranophane [$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$], sklodowskite [$\text{Mg}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2 \cdot 5\text{H}_2\text{O}$], compregnacite [$\text{K}_2\text{U}_6\text{O}_{19} \cdot 11\text{H}_2\text{O}$], and becquerelite [$\text{CaU}_6\text{O}_{19} \cdot 10\text{H}_2\text{O}$], as well as TeflonTM strands and the previously identified schoepite phases. Analytical results indicate that $>95\%$ of the uranium leached from the samples is recovered during the acid strip of the test vessel, suggesting that most of the uranium occurs principally as secondary precipitates and/or is sorbed onto the walls of the test vessel.

These results can be described by a sequence of events starting with the oxidative dissolution of the UO_2 matrix and the formation of the schoepite phases. A large uranium release from the sample is recorded during this period because schoepite is more soluble than later-formed uranyl phases. The alkali/alkaline earth uranyl and uranyl silicate phases that form after ~ 100 weeks are less soluble, thus resulting in a decreased rate of uranium release to solution. Although the formation of secondary phases appears to be controlled by flow patterns of water across the sample surface, there does

Fig. III-8. Cumulative Release of Uranium from (a) Tests 1 and 2 (11 UO_2 discs; 0.075 mL/3.5 day); (b) Tests 3 and 4 (crushed UO_2 pellet; 0.075 mL/3.5 days); (c) Tests 5 and 6 (three UO_3 pellets; 0.075 mL/3.5 days); and (d) Tests 7 and 8 (three UO_2 pellets; 0.0375 mL/7 days). The blocked points are for tests that were terminated.

not appear to be any direct correlation between uranium release and water injection rate or UO_2 surface area. Restricted water flow on the top UO_2 surface (as indicated by clustering of the secondary phases on the top surface) may, however, facilitate the development of alkali/alkaline earth uranyl and uranyl silicate phases by allowing evaporative concentration of cations in the EJ-13 water solvent and/or sufficient reaction time for the precipitant phases to form. We will continue to observe whether any additional phases form as the reaction process continues.

C. Radiation Studies
(D. T. Reed)

The Yucca Mountain Project is investigating the feasibility of locating a nuclear high-level waste repository in the tuff formations in southwestern Nevada. The placement of high-level waste containers in the underground facility will perturb the pre-emplacement environment by raising the ambient temperature and exposing the environment to gamma radiation levels that initially may be in excess of 0.1 MR/h. The extent of radiolytic alteration of the gas phase present and the nature of the radiolytic products generated are important considerations in evaluating waste package material performance during the early stages of repository history.

The Yucca Mountain Project, through LLNL, has initiated a program at ANL to investigate the effect of radiation on the performance of candidate materials in an irradiated environment. The emphasis of this program is (1) establishing the extent and nature of radiolytic products generated under repository-relevant conditions, (2) experimentally addressing questionable or unusual results relevant to this task reported in the literature, and (3) performing atmospheric corrosion studies in an irradiated environment. Experiments addressing all these concerns have been initiated and will be the subject of future reports.

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