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Reports (Nuclear) (UC-500)

ANL-90/16

ANL--90/16

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ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, IL 60439

NUCLEAR TECHNOLOGY PROGRAMS
SEMIANNUAL PROGRESS REPORT

October 1988 - March 1989

Chemical Technology Division

M. J. Steindler, Director
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December 1990

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NUCLEAR TECHNOLOGY PROGRAMS
SEMIANNUAL PROGRESS REPORT
October 1988-March 1989

ABSTRACT

This document reports on the work done by the Nuclear Technology Program of the Chemical Technology Division, Argonne National Laboratory, in the period October 1988-March 1989. 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 urania (doped with La_2O_3 , SrO , BaO , and ZrO_2), concrete, and either stainless steel or zirconia are vaporized at 2150-2400 K into a flowing stream of 0.6 mol gas (either He -6% H_2 or H_2). The measured release fractions for Mg, Ca, Sr, Ba, La, and U were in good agreement with results calculated by the SOLGASMIX computer code. 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. As part of our investigation on fuel-cladding compatibility, we performed differential thermal analysis (DTA) experiments with mixtures of U-Pu-Zr fuel and steel claddings (HT9, D9, and 316SS). The DTA curves on initial heating indicated solid-state transitions in the fuel at 600-700°C and an exothermal reaction forming more stable products (probably an Fe_2Zr -like phase) at 1200°C. On subsequent cooling, the DTA curve indicated primary precipitation at 1220°C and a freezing transition at 700°C. The DTA curves were used to estimate the "onset-of-melting" temperature with an accuracy of ± 10 -20°C. Scanning electron microscopy of the residues from these experiments indicated the following reaction sequence on heating: primary precipitation of a Fe_2Zr -like phase, followed by secondary precipitation of Fe_2U , followed by formation of Fe_2U - FeU_6 eutectic. Experiments

with DTA also indicated that chromium additions to the steel cladding will probably not raise the melting temperature significantly.

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 ($>573\text{ K}$) 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. Analysis of data for adsorption of H_2O on LiAlO_2 at a partial pressure of 15 Pa indicated heats of adsorption of 3 kJ/mol at 573-623 K and 15 kJ/mol at 673-773 K. The high-temperature adsorption process is probably dissociative chemisorption, and the low-temperature process is perhaps low-activation-energy chemisorption or unimolecular physisorption.

Another study is in progress to develop a computer model that will predict tritium release from neutron-irradiated lithium ceramics into a gas purge stream. In most previous studies, tritium desorption has been treated as occurring from one site with a single desorption activation energy. However, recent experiments have shown tritium release behavior that could not be explained by a diffusion-desorption model with one desorption activation energy. We modeled this behavior by using a desorption activation energy that varies with surface coverage by adsorbed hydrogen. Calculated data for tritium release were then used to estimate desorption activation energies for two breeder materials, Li_2O and Li_4SiO_4 . The calculated data showed good agreement with results reported in the literature.

A calculational effort was undertaken to study the use of a solid breeder plus neutron multiplier in a sphere-pac configuration. In previous fission-related studies, the data on sphere-pac systems immersed in a gas (e.g., He or Ar) indicated that the thermal conductivities are dependent on the gas pressure in such a way that might be exploited in breeder blanket technology. However, our calculations for the sphere-pac configuration in a fusion blanket environment indicate that the high thermal conductivity of a beryllium neutron multiplier will give rise to serious heat flux constriction and indirectly increase the importance of surface roughness in the solid contact area of the sphere-pac bed. Both factors, in conjunction, would significantly reduce the sensitivity of the thermal conductivity for a sphere-pac bed to variations in the gas pressure.

Two breeder blanket designs are being considered for the International Thermonuclear Experimental Reactor (ITER): an aqueous lithium salt blanket and a solid oxide breeder blanket. We conducted design studies to determine (1) the corrosion products formed and extent of electrolytic decomposition for the aqueous blanket and (2) the effect of radiolysis and electrolytic decomposition on the water coolant for the solid blanket. In addition, we are participating in a multilaboratory project to incorporate a Breeding Blanket Interface (BBI) into the Tritium Systems Test Assembly at Los Alamos National Laboratory. In this report period, we defined the BBI components for the two ITER candidate blankets.

In neutron dosimetry and damage analysis, fusion materials are being irradiated in a variety of facilities, including fission reactors, 14 MeV 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. Data obtained in this report period include neutron fluences, activation rates, and damage parameters for experiments in the Oak Ridge Research Reactor, cross sections for three long-lived isotopes (^{49}V , $^{93\text{m}}\text{Nb}$, and ^{93}Mo) near 14 MeV in the Rotating Target Neutron Source II, and cross sections for proton-induced activation of copper at 50-250 MeV in the Intense Pulsed Neutron Source.

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). A second 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 . A third project was initiated to develop a process for converting the hazardous red-water waste stream from TNT manufacturers to forms that are readily disposable or acceptable for recycling.

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 multistage, 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 March 1989 have been entered into a data base. Additions will be made as further data are generated.

A mathematical correlation is being developed for the GTM to treat changes in density resulting from changes in temperature. Data are given for determining densities of complex aqueous solution as a function of temperature. The species considered include Ag^+ , Am^{3+} , Ba^{2+} , Ca^{2+} , Ce^{3+} , Cm^{3+} , Cs^+ , Cu^{2+} , Eu^{3+} , Fe^{3+} , Gd^{3+} , Cd^{2+} , Mg^{2+} , La^{3+} , Na^+ , Nd^{3+} , Ni^{2+} , Pm^{3+} , Pr^{3+} , Rb^+ , Sm^{3+} , Sr^{2+} , UO_2^{2+} , Y^{3+} , Cl^- , F^- , HSO_4^- , NO_3^- , TcO_4^- , and SO_4^{2-} .

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 better estimate distribution coefficients for TRUEX-TCE extraction of plutonium, to determine the effect of varying TBP and CMPO concentrations on acid extraction for TRUEX-TCE and TRUEX-NPH solvents, and to account for the effects of solvent loading by metal salts on extraction of various species. In other work, the accuracy of the GTM was estimated for extracting miscellaneous metals, including Sr, Rh, Pd, Ag, Cd, Sn, Cs, Ba, Na, Mg, Ca, Rb, Cr, Ni, and Cu. It was concluded that additional distribution data are needed for Rh, Pd, Ag, Cd, Cr, Ni, and Cu.

In laboratory studies to obtain data for the GTM, we determined the effects of (1) nitric, oxalic, and hydrofluoric acid concentrations on the extraction of ^{88}Zr and ^{88}Y by TRUEX-NPH and TRUEX-TCE, (2) nitric, oxalic, and hydrofluoric acid concentrations on ^{59}Fe extraction by TRUEX-NPH, (3) iron, aluminum, oxalate, and fluoride ions on the extraction of noble metals, and (4) nitric acid and nitric acid/sulfuric acid solutions on Np(IV) extraction by TRUEX-NPH.

The extraction of ^{239}Np tracer from its parent ^{243}Am by extraction into triisooctylamine from nitric acid solution was studied as a method to obtain Np(IV) nitrate directly, without conversion from chloride to nitrate medium. The extraction was satisfactory, but the back extraction was incomplete. The use of

^{237}Np alone for distribution ratio measurements was also examined. Gamma ray counting with a germanium detector and separation of the ^{233}Pa together with liquid scintillation alpha counting were found to be feasible.

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. Three verification runs with TRUEX-TCE solvent were completed in this period. The measured data were obtained by analysis of samples (titration of aqueous and organic phases along with inductively coupled plasma/atomic emission spectroscopy of metals) collected during the run. Data from one of these runs have been analyzed to evaluate extraction of neodymium, nitric acid, and iron from a simplified acidic waste solution and to study the variability in the steady-state concentrations of various species. In general, the measured data showed good agreement with calculated results from the GTM. Data obtained from the other two verification runs will be given in future reports. A 16-stage 4-cm centrifugal contactor has been installed in a glove box and will be used for verification runs requiring use of radioactive solutions.

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 glove box 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. The 2-cm contactor was evaluated in stage-volume tests, one-phase (water) flow tests, and two-phase (TRUEX-NPH and 0.01M HNO_3) tests. The results of the volume and flow tests were compared with calculations using computer models (WEIR and ROTOR). After some changes, the unit was found to be fully operational for flow rates of 40 mL/min at all organic-to-aqueous flow ratios. In support of 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 computer program, which models vibrations in rotating designs.

A project was initiated to develop a conceptual design for a high-temperature centrifugal contactor (pyrocontactor) that operates with cadmium metal and chloride salts at temperatures around 500°C . In this report period, we determined the configuration of the rotor shaft such that the interface temperature between the shaft and the motor would be below 50°C . In addition, experiments are underway to investigate the mixing (dispersion) characteristics of the more dense phase (molten cadmium metal) with the less dense phase (chloride salts).

Because the TRUEX-NPH solvent will be used to treat PUREX raffinates from the reprocessing of irradiated fuel, the solvent will undergo radiolytic and hydrolytic degradation. Americium distribution ratios were measured for solvent samples that had been subjected to controlled hydrolytic conditions and then washed with aqueous sodium carbonate. It was concluded that a carbonate wash is only partially effective in removing the powerful extractants that are present in degraded solvent.

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- $^{99\text{m}}$, the daughter of ^{99}Mo , is used widely in medical applications. This report period, targets of U_3Si_2 particles mixed with aluminum powder were irradiated at low burnup and processed by basic dissolution, and the resulting solutions were counted for gamma activities. Test results indicated that ^{99}Mo loss for the fuel particles into the aluminum matrix due to fission recoil is substantial. Because of the molybdenum loss during dissolution, we investigated adding 30% hydrogen peroxide directly to the basic solution to dissolve the fuel. This addition was made after all the aluminum in the

target had been dissolved. It was concluded that a one-step process for dissolving the complete target with hydrogen peroxide is not feasible; the precipitate must be removed before uranium silicide can be dissolved.

A project was initiated to develop a new and cost-effective process for converting the hazardous red-water waste stream from TNT manufacture to forms that are readily disposable or acceptable for recycling. Our work is focused on developing the two steps in the process: separation of the inorganic and organic components of red water by foam fractionation or solvent extraction and recovery of sodium sulfite from the inorganic stream by solvent extraction.

High Level Waste/Repository Interactions

The volcanic tuff beds of Yucca Mountain, Nevada, are being studied as a potential repository site for isolating 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. These tests have been in progress for 156 weeks with SRL 165 glass and 91 weeks with ATM-10 glass. The releases of actinides and selected cations are given.

Parametric unsaturated tests with SRL 165 and ATM-10 glasses are in progress to determine the effect of varying the volume of water contacting the waste, the interval between water injection periods, the ratio of glass surface area in contact with water to water volume (SA/V), and the condition of the stainless steel in contact with the glass. Tests to date indicate that exfoliation of the surface layer occurred to varying degrees and had an important role in the observed extent of glass reaction and elemental release. The Li, B, and U releases from ATM-10 glass were about three times larger than those for SRL 165 glass under similar conditions.

To characterize the behavior of waste glass in a humid environment, experiments were performed wherein simulated waste glasses were reacted in steam at temperatures up to 200 °C for reaction times up to several months. The results for experiments at 150-200 °C showed that the depletion layer thickness increases with the reaction time, and the growth rate increases with the temperature. The formation of secondary phases was found to increase the reaction rate and so must be accounted for when projecting glass durabilities to long times. Experiments are also in progress to investigate the effect of the SA/V ratio (10, 50, 100 m⁻¹), as well as the initial leachant silicon concentrations, on the final steady-state conditions of a static leach test. Varying the SA/V ratio will allow solution concentrations to saturate at various stages in the development of the reacted surface layer.

Experiments are in progress to study the vapor-phase aging of glass by comparing the reaction progress for natural and nuclear waste glasses under different relative humidity (RH) conditions (60-100%). In tests for 365 days at 75 °C, the higher the humidity for a given glass sample, the greater the observed extent of reaction. The majority of the reaction products on all samples have a composition similar to that of the unreacted glass. The glass samples exposed to a 95% RH environment had the largest number of reaction products on their surfaces.

An analysis was performed of previous results from hydrothermal leaching and vapor-phase-hydration experiments performed using two synthetic basalts and one SRL glass. It was concluded that vapor tests appear to be the most appropriate method for accelerating glass reactions. The similarities between the interactions of vapor-reacted basalt glass and nuclear waste glass strongly suggested that the naturally reacted basalt glass can be used as an analog to aid in the interpretation of processes that may occur to waste stored in a repository.

Experiments are underway to determine the influence of penetrating gamma radiation on the reaction of simulated nuclear waste glass in tuff groundwater. Static leach tests were performed with simulated waste glasses at 90°C under gamma radiation doses of 2×10^5 , 1×10^4 , and 1×10^3 R/h; nonirradiated tests were performed for comparison. Repository reference groundwater J-13 was used as the leachant. The primary effect of radiation was found to be acidification of the leachant. The extent of acidification was limited to a pH of 6.4 because of the high bicarbonate level in the leachant by the glass reaction itself, which generates hydroxide ions during alkali release. The pH reached after long reaction times appeared to be independent of the radiation dose.

In spent fuel studies, scoping experiments were performed to determine the release rates from a nonirradiated UO_2 powder specimen in J-13 well water under saturated conditions. For this experiment, a method was developed for utilizing the mass spectrometric isotope dissolution (MSID) technique to determine the dissolution rate of the UO_2 matrix. The test specimen was an intimate mixture of two UO_2 powders, one depleted and the other enriched in ^{235}U . The test results showed that the enriched powder portion of the specimen had a significantly higher dissolution rate than the depleted powder portion, owing to some unknown morphological differences between the powders.

A set of parametric experiments, wherein nonirradiated UO_2 encased in Zircaloy cladding is contacted by dripping tuff-equilibrated J-13 water at 90°C, has been in progress for 3.5 years. Results to date indicate that water flow patterns across the test sample surface may be more important in controlling the uranium release than the water drip rate or available UO_2 surface area.

The effect of the ionizing radiation present in the vicinity of the high-level nuclear waste package is an important consideration in evaluating the waste package performance. The effect is being investigated as part of a study in which the radiolytic yield of nitrogen oxides is being determined at elevated temperature (up to 200°C) in both dry and moist air. Gamma dose rates were in the range of 0.1 to 0.4 Mrad/h. The yield of nitrous oxide as a function of absorbed dose was linear in the dry-air experiments but not the moist-air experiments. At low temperatures (28°C), initial yields in the moist air experiments were significantly lower than those in the dry air experiments and increased with absorbed dose. Experiments were also initiated to determine the nature and extent of corrosion formation on candidate container materials in irradiated dry-air and air-steam environments.

The technique of laser photoacoustic spectroscopy is being applied to the study of radionuclide speciation in groundwater-like systems. Initial studies are being conducted with Pu(IV)/carbonate and Np(V) systems.

Plutonium Residue Recovery (PuRR)

The objective of this effort is to develop an effective pyrochemical method for recovering plutonium from intractable residues. Several solvent/reductant systems have been considered for reducing the oxide residues and making the plutonium available for further pyro or aqueous processing. In this report period, experimental results for plutonium reduction and recovery from incinerator ash heels and LECO analytical crucibles were obtained with Cu-Mg-Ca and Zn-Ca reductant systems and CaCl_2 - CaF_2

salt. The results for chemical extraction of plutonium from the reduction ingots indicated that better than 94% recovery of plutonium in the extraction salt was achievable from the Zn-Mg and some Cu-Mg-Ca ingots.

Electrorefining is being considered for two applications in the PuRR process: recovery of plutonium from reduction ingots and recycle of calcium from the reduction salt. Two areas associated with electrorefining are being investigated to supply needed information for PuRR process application: (1) development of a reference electrode that can be used as a tool to measure and control variables during electrorefining and chemical extraction and (2) verification and measurement of performance parameters in electrowinning calcium from CaO into a zinc alloy.

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 Vaporization from Core-Concrete Mixtures (M. F. Roche)

The vaporization of core-concrete mixtures is being measured using a transpiration method. Mixtures of urania (doped with La_2O_3 , SrO , BaO , and ZrO_2), concrete, and stainless steel or zirconia are being heated at 2150-2400 K in a flowing stream of about 0.6 mol of gas (either He-6% H_2 or H_2) at a controlled oxygen potential. The partial molar free energy of oxygen in the inlet gas is being controlled at -420 or -550 kJ by fixing the water-to-hydrogen ratio in the gas at the appropriate value (e.g., 300 ppm H_2O in H_2 for -550 kJ). The fraction of the sample that is vaporized is determined by weight change and by chemical analyses on the condensates that are collected in a molybdenum condenser tube. The data are being compared with SOLGASMIX¹ calculations to test the thermodynamic data base and the underlying assumptions of computer codes used for prediction of fission-product release during a severe light water reactor accident.

A 1.1 kg sample of the siliceous concrete to be used in an experiment (ACE experiment No. L2) conducted in the ANL Reactor Analysis and Safety Division was pulverized. A portion was ignited for use in our experiments (the loss on ignition was 7.91%), and a portion was submitted to the ANL Analytical Chemistry Laboratory (ACL) for chemical analysis. The assay indicated the following composition (in wt%): 1.41 K_2O , 0.69 Na_2O , 0.70 MgO , 13.47 CaO , 0.02 SrO , 0.02 BaO , 4.04 Al_2O_3 , 1.00 Fe_2O_3 , 0.01 Cr_2O_3 , 0.81 TiO_2 , 68.99 SiO_2 , and 7.91 CO_2 plus H_2O (loss on ignition).

Two runs employing the ACE No. L2 concrete were completed. The molybdenum condenser tubes were blocked by high-silica deposits weighing about 0.9 and 1 g; in similar experiments with the limestone concrete and limestone-sand concrete, the deposits weighed about 0.4 g. We developed a procedure for dissolving the high-silica deposits and submitted the solutions for analyses. The procedure consisted of cutting the tube in sections, dissolving the deposit from the appropriate section or sections with a series of acid washes (HCl , HF , and HNO_3), fuming the HF and HNO_3 washes with HClO_4 (to eliminate fluoride ion, which tends to precipitate lanthanum), evaporating to dryness, and dissolving each residue in 100 mL of 1 M HCl or HNO_3 .

Analytical data for the elements Mg, Ca, Sr, Ba, La, and U from experiments using mixtures of the three types of concrete, doped urania, and either stainless steel or zirconia are summarized in Table I-1. The data were collected by the ACL using inductively coupled plasma/atomic emission spectroscopy and fluorescence spectroscopy. The values given in the table are the summed analyses for the successive etches of the Mo condenser tube. Generally, the first etch collected the major fraction of the listed elements, and the combined first and second etches usually yielded over 90% of the total shown. Up to four etches were conducted, especially if there was an indication of a significant concentration of any of the above elements in the third etch.

Table I-1. Vaporization of Mg, Ca, Sr, Ba, La, and U: Experimental Results vs. SOLGASMIX Calculations

Experiment vs. SOLGASMIX	Mg, mg	Ca, mg	Sr, μg	Ba, μg	La, μg	U, μg	Crucible, flow rate, gas, temperature, time, Calc. $\Delta G(\text{O}_2)$
55-LL ^a SOLGASMIX	40 21	0.2 0.4	6 4	18 6	<2 0.4	44 55	ZrO ₂ , 200 cm ³ /min, He-H ₂ , 2150 K, 73 min, -431 kJ/mol
62-LL SOLGASMIX	39 21	0.2 0.4	12 4	28 6	<5 0.4	28 55	ZrO ₂ , 100 cm ³ /min, He-H ₂ , 2150 K, 146 min, -431 kJ/mol
75-LL SOLGASMIX	58 8	5 0.4	40 43	65 121	5 8	170 116	Mo, 200 cm ³ /min, He-H ₂ , 2150 K, 73 min, -381 kJ/mol
79-LL SOLGASMIX	57 8	2 0.4	31 43	33 121	3 8	248 116	Mo, 100 cm ³ /min, He-H ₂ , 2150 K, 146 min, -381 kJ/mol
98-LL SOLGASMIX	114 43	11 4	84 68	103 311	15 70	1721 2468	Mo, 200 cm ³ /min, He-H ₂ , 2400 K, 73 min, -326 kJ/mol
106-LL SOLGASMIX	182 141	11 25	157 425	132 597	5 190	1879 1165	Mo, 200 cm ³ /min, H ₂ , 2400 K, 73 min, -400 kJ/mol
111-LL SOLGASMIX	72 47	2.2 2.7	25 51	13 66	<2 6	92 33	Mo, 100 cm ³ /min, H ₂ , 2150 K, 146 min, -445 kJ/mol
89-LS SOLGASMIX	5.6 3.5	0.7 0.0	1.6 0.5	55 ^b 1	<2 0.1	34 185	Mo, 100 cm ³ /min, He-H ₂ , 2150 K, 146 min, -361 kJ/mol
93-LS ^c SOLGASMIX	8.5 27	0.9 0.2	1.2 5	9 19	2.4 8	812 8719	Mo, 200 cm ³ /min, He-H ₂ , 2400 K, 73 min, -306 kJ/mol
101-LS SOLGASMIX	27 118	1.6 1.8	9 46	16 62	3.2 28	1770 2836	Mo, 200 cm ³ /min, H ₂ , 2400 K, 73 min, -377 kJ/mol
109-LS SOLGASMIX	11 32	0.32 0.12	1 3	2 2	<2 0.5	85 69	Mo, 100 cm ³ /min, H ₂ , 2150 K, 180 min, -427 kJ/mol
119-SI SOLGASMIX	0.9 1	0.4 0.05	2 2	12 3	1 2	1588 3933	Mo, 200 cm ³ /min, H ₂ , 2400 K, 49 min (plugged), -336 kJ/mol
124-SI SOLGASMIX	0.9 0.6	0.17 0.03	0.5 1	5 2	<1 1	1005 3224	Mo, 20 cm ³ /min, H ₂ , 2400 K, 39 min (plugged), -331 kJ/mol

^aThe experiment number indicates the concrete type: LL is limestone aggregate, LS is limestone-sand, and SI is siliceous concrete.

^bPossible contamination indicated by high value.

^cErratic pressure buildup and decrease during run.

In experiments 55-LL and 62-LL, the mixtures consisted of limestone-aggregate concrete, doped urania, and stainless steel in zirconia crucibles. Because the concrete etched the crucibles, we included a portion of the crucible weight (about 2.5 g ZrO_2 , estimated from optical microscopy on the cross-sectioned crucible and sample) in the SOLGASMIX calculations for these two experiments. Experiments 75-LL and 79-LL employed limestone-aggregate concrete and urania in a molybdenum crucible. Experiments 55-LL through 79-LL address, in part, the problem of equilibration in the mixture experiments. The amounts of magnesium found in 55-LL and 62-LL are nearly identical. Except for flow rate, these runs were identical. The same is true for experiments 75-LL and 79-LL (namely, nearly identical amounts of magnesium and identical experiments, except for flow rate). Magnesium is the major element being transported in these four experiments (note that the Sr, Ba, La, and U values are in micrograms, while the Mg and Ca values are in milligrams). These results demonstrate that the chosen flow rates are yielding a saturated gas phase over the mixtures.

The remaining experiments listed in Table I-1 employed mixtures of concrete (limestone-aggregate, limestone-sand, or siliceous), doped urania, and zirconia in molybdenum crucibles. We suspect barium contamination in one of these experiments (89-LS), simply because the barium result is much too high (compare, for instance, this result with that of 109-LS). We also suspect that a portion of the deposit was dislodged and lost in experiment 93-LS; we observed erratic behavior of the pressure during this experiment (pressure buildup followed by a sudden decrease in pressure).

Also summarized in Table I-1 are the results of the SOLGASMIX calculations for each experiment. In view of the complex nature of the mixtures and of the uncertainties in the thermodynamic data base, we feel the agreement between the experimental data and calculations is reasonable. The thermodynamic data base now contains free energies of formation for 220 species (19 elements). Recently included in the data base were estimated free energies of formation of liquid and solid silicates and zirconates of strontium, barium, and lanthanum. These were essential for achieving a reasonable degree of agreement between the experimental data and SOLGASMIX calculations.

B. Thermophysical Property Studies (L. Leibowitz and R. A. Blomquist)

Development of the Integral Fast Reactor (IFR) requires understanding of fuel behavior for wide temperature and composition ranges. Much of the needed information is not available, and our ongoing program is designed to provide the essential thermophysical property data. These efforts are coordinated with R&D efforts on fuel performance, design, and safety to be certain that fuel properties of primary concern are examined. Our effort involves experimental and calculational work.

1. Melting Temperatures in Fuel-Cladding Mixtures

Differential thermal analysis (DTA) tests have been performed on mixtures of U-10 wt% Zr and U-8 wt% Pu-10 wt% Zr fuel and the steel alloys HT9, D9, and type 316 stainless steel (316SS). Compositions of the three alloys are given in Table I-2. The overall compositions of the six fuel-cladding samples are given in Table I-3. The amounts were chosen to yield an approximately constant fuel atom fraction of 0.5 in the mixture. These experiments were intended to help clarify the effect of Pu on fuel-cladding compatibility. Details of our tests are given below.

Each fuel-cladding mixture was heated at 10 K/min to about 1540°C in a yttria crucible, after which several cooling/heating cycles at 1, 2, or 10 K/min were obtained. Similar results were obtained with the three steels with each of the fuel alloys, but distinctly different results were obtained with the two fuels. Overall, initial heating revealed the expected solid-state transitions for the fuel in the

Table I-2. Composition of Stainless Steels

	Weight Percent		
	HT9	D9	316SS
Ni	0.5	15.5	12.1
Cr	12.0	13.5	17.1
Mn	0.2	2.0	1.6
Mo	1.0	2.0	2.4
Si	0.25	0.75	0.4
Ti		0.25	
C	0.2	0.04	0.9
W	0.5		
V	0.5		
Cu			0.1
Co			0.1

Table I-3. Composition of Fuel-Steel Mixtures

	Atom Fraction		
	HT9	D9	316SS
Sample 1			
U	0.38	0.41	0.39
Zr	0.11	0.12	0.11
Fe	0.43	0.30	0.31
Cr	0.06	0.07	0.09
Ni	0.00	0.07	0.06
Sample 2			
U	0.35	0.35	0.36
Pu	0.034	0.034	0.035
Zr	0.11	0.11	0.11
Fe	0.42	0.32	0.31
Cr	0.064	0.071	0.088
Ni	0.00	0.072	0.055

range 600-700°C. In the neighborhood of 1200°C, a large exothermal peak appeared, which we attribute to formation of a relatively stable intermetallic, most likely Fe_2Zr , in which other components of the mixture are dissolved. Typical cooling curves are shown in Figs. I-1 and -2 for mixtures of HT9 with the binary and ternary fuels, respectively. On cooling, primary precipitation is indicated at about 1220°C, but the exact temperature depends on the steel alloy used. At about 700°C, there is a marked DTA peak, which appears to indicate an eutectic. The increased width of this peak for the ternary fuel alloy suggests, however, that it may not be a true eutectic. The melting temperatures are summarized in Table I-4 for the binary fuel and in Table I-5 for the ternary fuel. The melting temperature is very close for all three steels with a given fuel.

Fig. I-1.

Cooling Curve for U-10 wt % Zr with HT9

Fig. I-2.

Cooling Curve for U-8 wt % Pu-10 wt % Zr
with HT9

Table I-4. DTA Melting Temperatures for U-10 wt % Zr

Steel	Melting Temp., °C $\pm$ 1 σ	
	Heating	Cooling
HT9	723 $\pm$ 1	708 $\pm$ 5
D9	708 $\pm$ 2	707 $\pm$ 3
316SS	708 $\pm$ 1	713 $\pm$ 2

Table I-5. DTA Melting Temperatures for U-8 wt% Pu-10 wt% Zr

Steel	Melting Temp., °C $\pm$ 1 σ	
	Heating	Cooling
HT9	694 $\pm$ 1	683 $\pm$ 1
D9	675 $\pm$ 1	682 $\pm$ 1
316SS	682 $\pm$ 2	688 $\pm$ 3

A decrease in the melting temperature of about 25-30°C resulted from addition of 8 wt% Pu to the fuel. It is anticipated from phase diagram calculations that the general trend in melting temperatures observed would be from the 725°C eutectic in the U-Fe system downward toward the 410°C eutectic in the Fe-Pu system. Our next series of DTA experiments will be with a 19 wt% Pu fuel alloy.

The residues from these tests have been submitted for scanning electron microscope (SEM) examination to determine the composition of the phases which formed during freezing. Results have been obtained from examination of the binary fuel experiments and the findings are summarized below. Further study of these results and their interpretation is in progress. Refined phase diagram calculations for the U-Fe-Zr system will also be performed.

2. Examination of DTA Residues

Scanning electron microscope examinations were performed with residues from DTA experiments with U-10 wt% Zr and four cladding alloys HT9, D9, 316SS, and 304SS. All of the samples had a very similar microstructure of large, rod-like precipitates in a matrix. High magnification micrographs showed that the rod-like precipitates consisted of two phases. The innermost phase was the darkest in backscattered images, indicating that it had the lowest atomic number of the phases present and was the first to freeze during cooling. The dark phase was surrounded by a medium-gray phase that appeared to be the same material that was present as a dendritic precipitate in the matrix. The other phase in the matrix was the lightest phase present in the samples. The light phase did not show significant variations as a function of position within a sample. The variations in the composition of the dark and medium-gray phases indicate that the sample was not in a true equilibrium condition.

We have previously speculated on the behavior of these complex systems based on our analysis of the U-Fe-Zr ternary. In that simple system, assuming no ternary solubilities, one would expect primary precipitation of Fe₂Zr, secondary precipitation of Fe₂U, and finally formation of a Fe₂U-FeU₆ eutectic. The matrix found in the SEM examination of these samples has a eutectic-like appearance and the light phase has a very high U content. The compositions of the three phases, however, do not correspond to the rudimentary predictions, which in such complex systems should not be too surprising.

Work on simpler systems and additional phase diagram calculations are needed to define the phase relations involved.

3. Effect of Chromium on Fuel-Cladding Compatibility

Differential thermal analysis tests performed on mixtures of U-10 wt% Zr fuel with the steel alloys HT9 and D9 and with 316SS are described above. There were indications in heating tests with irradiated fuel that 316SS showed apparently improved compatibility with fuel. To help clarify that observation, DTA tests were performed on mixtures of U-10 wt% Zr fuel with pure Fe and an Fe-Cr mixture.

Experiments were performed on two mixtures of U-10 wt% Zr fuel with cladding components. In the first (sample I), pure Cr was used; in the second (sample II), Fe was added to yield a Cr/Fe ratio of about 4. The exact fuel-cladding compositions are given in Table I-6. As in previous experiments, the amounts were chosen to yield a nearly constant fuel atom fraction in the mixture of about 0.5. Each fuel-cladding mixture in yttria crucibles was heated in the DTA system at 10 K/min to about 1570°C, after which several cooling/heating cycles at 2 and 10 K/min were obtained.

The DTA results for these two mixtures were strikingly different. On initial heating of sample I, only a minor indication was seen of an exothermal reaction, in contrast to what was observed in sample II. The Fe-Zr and Cr-Zr phase diagrams shown respectively in Figs. I-3 and -4, however, appear to be quite similar, and Cr_2Zr would be expected to be fairly stable. A typical cooling curve for sample I is shown in Fig. I-5, and the Cr-U phase diagram is shown in Fig. I-6. Primary precipitation, indicated in Fig. I-5 at about 1327°C, is probably due to formation of a Cr_2Zr phase in which other components may be soluble. Calculations of the U-Cr-Zr phase diagram led to an estimate of about 1550°C for precipitation of Cr_2Zr , clearly too high. A similar problem was seen with the Fe-Zr-containing ternary systems and reflects an overestimate of the stability of the $(\text{Fe,Cr})_2\text{Zr}$ intermetallics. If we assume that all the Zr was removed as Cr_2Zr , we would expect the liquidus in the Cr-U system to be reached at about 1100°C, at which point essentially pure Cr would begin to precipitate. Actually, the next DTA peak was seen at about 1127°C. These two events were not shown very well on heating, but good agreement was found on cooling at rates of 2 and 10 K/min. The next peak, at a mean temperature of 873°C, appears to correspond to the Cr-U eutectic at 860°C. At this temperature a mixture of Cr and U(γ) with some Cr in solution would form. Residual Zr could be responsible for the difference between the DTA result and the Cr-U phase diagram. This peak was very reproducible and good agreement was found on heating and cooling at both 2 and 10 K/min. The final two peaks can be identified as solid-state phase transitions in U, which would be expected from the Cr-U diagram. Cooling curves gave temperatures significantly below those found for the peaks on heating and are probably less reliable. On heating, we found 757°C for $\text{U}(\beta) \rightarrow \text{U}(\gamma)$ and 661°C for $\text{U}(\alpha) \rightarrow \text{U}(\beta)$. The Cr-U phase diagram gives 738 and 630°C, respectively, for these transitions.

Table I-6. Composition of Fuel-Cladding Component Mixtures

	Atom Fraction	
	I	II
U	0.40	0.36
Zr	0.12	0.11
Fe	0.00	0.10
Cr	0.48	0.43

Fig. I-3. Zr-Fe Phase Diagram

Fig. I-4. Zr-Cr Phase Diagram

Fig. I-5.

Typical Cooling Curve for Sample I (U-10 wt % Zr with Cr)

Fig. I-6. Cr-U Phase Diagram

Sample II, which contained about 10 at.% Fe, behaved quite differently. On the initial heating a distinct exothermal peak was seen. A typical cooling curve is shown in Fig. I-7. Primary precipitation, at 1309°C, probably corresponds to formation of an $(\text{Fe,Cr})_2\text{Zr}$ phase. It is difficult to decide, without analytical data, what the Fe/Cr ratio in such a phase would be. The next event, at 1182°C, should correspond to precipitation of Fe-Cr solid solution. Preliminary calculations of the U-Fe-Cr phase diagram have been performed. If we assume that all the Zr precipitates with Fe and Cr in the same ratio as was originally present, then we would predict precipitation of a Cr-rich Fe-Cr solid solution at about 1200°C. This good agreement with the DTA result may be fortuitous. The final DTA peak appears to be due to eutectic freezing and is seen at 756°C on heating and about 726°C on cooling. The heating value is probably more reliable. Because of the absence of lower temperature U transitions, this event is different from what was found with sample I. The calculated U-Fe-Cr phase diagram predicts a ternary eutectic at about 710°C; however, this would involve a U-Cr solid solution. Because no lower temperature solid-state U phase transitions are observed, this phase probably does not form. It is possible that the melting corresponds to formation of a $\text{U}_6\text{Fe-UFe}_2$ eutectic in which Cr is dissolved. Analytical data are needed to understand what is happening at this stage.

Fig. I-7.

Typical Cooling Curve for Sample II (U-10 wt % Zr with Cr/Fe)

A summary of the melting temperatures found is given in Table I-7 along with the value previously reported for the HT9 experiment with this fuel alloy. It is clear from these results that addition of only 10 at.% Fe markedly changed the results and lowered the melting temperature by over 100°C. It appears unlikely that Cr additions to steel cladding alloys (short of using pure Cr cladding) will significantly raise the melting temperature.

Table I-7. Melting Temperatures Found in DTA Experiments

	Melting Temp., °C $\pm$ 1 σ	
	Heating	Cooling
HT9	723 $\pm$ 1	708 $\pm$ 5
I: U/Zr/Cr	872 $\pm$ 1	873 $\pm$ 0.5
II: U/Zr/Cr/Fe	756 $\pm$ 1	726 $\pm$ 8

C. Adsorption, Dissolution, and Desorption Characteristics of LiAlO₂-H₂O(g) System (A. K. Fischer)

1. Introduction

Adsorption of H₂O(g), dissolution of OH⁻, and rates of H₂O(g) evolution are being measured for the LiAlO₂-H₂O(g) system. The thermodynamic and kinetic data for these processes relate to the tritium retention and release and, hence, to concerns about tritium inventory in ceramic tritium breeder materials for fusion reactors. The information will enable (1) comparison of candidate breeder materials, (2) calculation of operating conditions, and (3) elucidation of the principles underlying the behavior of tritium in breeder materials.

Analysis of adsorption isotherms for the LiAlO₂-H₂O(g) system has defined a range of heats of adsorption from 80 to 360 kJ/mol in the region of 873 K; these heats are dependent on the fraction of surface coverage, by adsorbate, which ranges from 0.1 to 0.001. Desorption activation energies follow these values closely and are also dependent on coverage. Our estimates of adsorption activation energies confirmed the earlier report (ANL-90/15, Sec. I.D.) of two differently activated adsorption processes.

Modeling tritium release from irradiation tests requires accurate values for desorption activation energies. Though such information can be derived from the adsorption isotherm measurements, a technique specifically suited for desorption activation energy measurements is available: temperature programmed desorption (TPD). Apparatus for such measurements has been constructed, and the first measurements with the LiAlO₂-H₂O(g)-H₂ system will be made. The H₂ concentration in the helium purge gas is important to evaluate because it increases tritium release in irradiation tests.

2. Data Analysis

Further analysis of the adsorption isotherms presented in the last report (ANL-90/15, Sec. I.D.) provided estimates of the heats of adsorption of H₂O(g) on LiAlO₂ in the region of 873 K. As discussed in that report the data indicate that two adsorption processes with different activation energies operate in this system. In most of the 573 to 873 K temperature range, they contribute together to the adsorption process. Only at the ends of this range can one isotherm be clearly identified with each process (the 573 and the 873 K isotherms). Consequently, calculation of heats of adsorption by the Clausius-Clapeyron equation cannot be pursued rigorously. However, the shapes of the isosteres [plots, at constant coverage, of the partial pressure of H₂O(g) as a function of temperature] suggest minimum values for the heat of adsorption in the region of 873 K. The values are 80, 150, 220, 290, and 360 kJ/mol, respectively, for log(θ) values of -1, -1.5, -2, -2.5, and -3 (where θ is the fraction of surface covered by adsorbate.) The values follow the trend for the heat of adsorption to increase as the surface coverage decreases.

Unfortunately, a similar range of estimates is not possible at the lower temperature end of the range; measurements would be needed for temperatures below 573 K. However, the isostere for

relatively high coverage at $\theta = 0.1$ does suggest that the heat of adsorption is about 40 kJ/mol for these conditions.

For the conditions where heats of adsorption may be estimated, values of the activation energies of desorption may also be estimated. This is possible because the activation energy of desorption is equal to the sum of the heat of adsorption and the activation energy of adsorption. Because the activation energy of adsorption is usually small, even nearly zero, it is a useful approximation to take the activation energy of desorption as about equal to the heat of adsorption. It follows that the desorption activation energy is also dependent on the degree of surface coverage.

Though not designed as kinetic experiments, the adsorption measurements were analyzed further to extract information on the rates of adsorption. Figure I-8 shows the rate of adsorption as a function of temperature for a selected $\text{H}_2\text{O}(\text{g})$ partial pressure of 15 Pa. In the regions where this rate increases with temperature, the slopes allow an estimate to be made of the activation energy of adsorption. Confirming the earlier deduction that two different adsorption processes with different adsorption activation energies are involved in different temperature ranges, these curves suggest a 3 kJ/mol adsorption activation energy in the 573 to 623 K range and a 15 kJ/mol adsorption activation energy in the 673 to 773 K range. The high-temperature adsorption process is probably dissociative chemisorption, and the low-temperature process is perhaps low-activation-energy chemisorption or unimolecular physisorption. This figure also illustrates the possibility that observed net rates of adsorption decrease with increasing temperature when there are different processes which have different activation energies and different dependencies on coverage.

Fig. I-8.

Rates of Adsorption of $\text{H}_2\text{O}(\text{g})$ on LiAlO_2 at a Partial Pressure of 15 Pa

The coverage-dependent values of the desorption activation energy indicated in this work are the result of surface heterogeneity with respect to chemical differences between adsorption sites, crystallographic differences for exposed crystal planes, and defects on the surface. Multiple types of sites are involved in adsorption and desorption. This is consistent with our earlier evidence for site-dependent

evolution (desorption) of $\text{H}_2\text{O}(\text{g})$ from LiAlO_2 obtained from a TPD experiment.² It is also consistent with reports on other materials revealing the same complexity. For example, a theoretical analysis of the types of OH^- sites possible on the surface of alumina, characterized in terms of the number of O^{2-} nearest neighbors, showed five types to be present. These were related to experimentally measured infrared spectra.³

3. Implementation of Temperature Programmed Desorption Measurements

Recent work on modeling tritium release from irradiation tests on ceramic breeder materials has emphasized the need for data on surface properties to analyze dynamic inventory; for this the activation energies of desorption are of primary importance. These activation energies can be supplied directly by the TPD technique, which can also give information on quantities of adsorption, though not as well as the frontal analysis technique that was used for deriving the adsorption isotherms discussed above. Both TPD and frontal analysis are complementary approaches to studying surface processes.

In essence, the TPD technique consists of measuring the rate of desorption of a given species (i.e., in the form of the evolved species, not necessarily the surface species) into a sweep gas during an upward ramp of the sample temperature. The evolution rate goes through a maximum, giving a peak in the curve. A number of theoretical treatments for analyzing the data exist and require either single or multiple TPD curves, at fixed or variable initial coverages, and for single or multiple heating rates. Depending on treatment, the outputs provide values for various combinations of the preexponential factor in the activation energy equation, the activation energy for desorption, and the order of the evolution reaction.

A schematic diagram of the TPD apparatus is shown in Fig. I-9. The valves F, K, and L are high-temperature gas chromatographic switching valves so that all gas trains carrying $\text{H}_2\text{O}(\text{g})$ can be maintained at 473 K to eliminate holdup of this species. Not shown is a quadrupole mass spectrometer that samples effluent gas between valves K and L. This instrument is an important feature because data are needed not only for $\text{H}_2\text{O}(\text{g})$ evolution but also for $\text{H}_2(\text{g})$ adsorption and evolution. This is because H_2 in the purge stream of irradiation tests facilitates release of tritium. It is believed that adsorbed H_2 blocks energetic sites that would otherwise retain OH^- and impede evolution of $\text{H}_2\text{O}(\text{g})$. Data are needed for a quantitative evaluation of this process.

4. Future Work

Following proof-testing and calibration of the TPD apparatus, measurements will be made to obtain activation energies for desorption of $\text{H}_2\text{O}(\text{g})$ - $\text{H}_2(\text{g})$ from LiAlO_2 . Substrates to be studied after LiAlO_2 include Li_4SiO_4 , Li_2O , and Li_2ZrO_3 .

D. Tritium Transport Modeling (J. P. Kopasz)

1. Introduction

The modeling effort for this period has focused on the desorption process in candidate tritium-breeder ceramics for fusion reactors. The desorption process consists of a surface reaction and desorption of surface-bound tritium in the form of HTO , T_2O , HT , or T_2 . Of concern are the order of the surface reaction, the activation energy for the surface reaction, and the desorption step. In most of our previous work, desorption of tritium was considered to be first order due to the expected excess of hydrogen in the system. Equations for desorption which are second order in tritium were derived for situations where the hydrogen concentration on the breeder surface would be low and comparable to

Fig. I-9.

Schematic Diagram for Temperature Programmed Desorption Measurements

the expected tritium concentration. Expressions for tritium inventory were derived, and calculations were performed to determine the grain radius regimes where desorption would be expected to be the rate-controlling release process (Sec. I.D.2). In our previous work, we found evidence that the desorption energetics change as a function of surface coverage. We believe that this is due to the presence of multiple sites for desorption of tritium from the ceramic. To support this view, we have analyzed literature data from tritium release experiments performed at constant heat rate. This analysis allowed us to determine the number of desorption sites and to obtain estimates of the desorption activation energies (Sec. I.D.3). Estimates of activation energies for desorption of tritium from Li_2O and Li_4SiO_4 are reported in Sec. I.D.4.

The desorption process is considered to be the combination of surface reactions leading to a surface-bound molecule and desorption of the surface-bound molecule into the gas phase. These processes are not handled separately due to the difficulties in separating the processes experimentally. Our current modeling efforts are concerned with determining (1) the kinetic order of the surface reactions leading to desorption under various conditions and (2) the energetics of the surface reactions and the desorption step.

The reactions which we consider as likely candidates for desorption of tritium from the surface are:

and

Of these, the reactions on the left are first order in tritium, while those on the right are second order in tritium. Previously, our models were based on a desorption reaction which was first order in tritium since we believe that, due to the presence of hydrogen and water in the purge stream, the hydrogenic species on the surface will be present at a much higher concentration than the tritium species at the surface.

In this case, the inventory (I) due to desorption would be given by

$$I = (4/3)\pi a^3 [Ga / K_{d(1)}] \quad (I-2)$$

where G = generation rate, a = grain radius, and $K_{d(1)}$ = first-order desorption rate constant. For pure second-order desorption

$$I = (4/3)\pi a^3 [Ga / (3K_{d(2)})]^{1/2} \quad (I-3)$$

We have now performed some calculations to determine the release equations and inventory due to desorption under conditions where release would be second order in tritium or a combination of first and second order:

$$I = (4/3)\pi a^3 [C_H + (C_H^2 + 4Ga / 3K_d)^{1/2}] / 2 \quad (I-4)$$

where C_H is the hydrogen concentration. If $C_H = 0$, then Eq. I-4 becomes the same as Eq. I-3; and if $C_H > C_T$, then

$$I = (4/3)\pi a^3 [Ga / (3K_d C_H)] \quad (I-5)$$

This equation is the same as Eq. I-2 if $K_{d(1)} = K_d C_H$.

To determine where diffusion is the dominant release mechanism, plots of the fraction of the total inventory which is due to diffusion versus the factor aK_d/D (D = tritium diffusivity) were derived. For first-order release, the inventory is given by

$$I = (4/3)\pi a^3 G \{ a^2 / 15D + a / (3K_d C_H) \} \quad (I-6)$$

with values for aK_d/D of less than 0.5, diffusion accounts for less than 10% of the inventory, while with values for aK_d/D of greater than 20, diffusion accounts for 90% of the inventory. For second-order release, the inventory is given by

$$I = (4/3)\pi a^3 \{ Ga^2 / 15D + [Ga / (3K_d)]^{1/2} \} \quad (I-7)$$

In this case, the term aK_d/D is of little value in determining the rate-controlling mechanism. One must use the value of $(a^3 K_d G)^{1/2} / D$ to obtain the same type of relationship. For values of $(a^3 K_d G)^{1/2} / D$ of less than 0.5, diffusion accounts for less than 10% of the inventory, while for values of $(a^3 K_d G)^{1/2} / D$ greater than 50, diffusion accounts for over 90% of the inventory.

We believe that the hydrogen surface concentration on the ceramic will be much larger, in most cases, than the tritium surface concentration. This will result in pseudo-first-order kinetics and tritium release will be first order in tritium. This belief stems from the difficulties in obtaining an oxidic ceramic free of hydroxide impurities and in obtaining a high purity helium purge gas that has water contamination near the parts per million range. Even for experiments employing ultra-high-purity helium as a purge gas, desorption is likely to be first order in tritium. Commercially available ultra-high-purity helium contains from 1 to 10 ppm of water. In addition to this amount of water in the purge stream, there

will be water present from desorption of the water adsorbed on the transport lines. Finally, hydroxides will be present in the ceramics as a result of their preparation in impure atmospheres whose moisture concentrations are expected to be around the order of 0.01 wt %. One would expect the combination of these effects to result in hydrogen concentrations at the surface greater than the tritium concentration.

2. Evidence for Multiple Desorption Sites

Desorption has been determined to be the rate-limiting process in some tritium release experiments. Despite the importance of tritium desorption in determining the merits of candidate breeder materials, little is known about the tritium desorption process. Tritium desorption has been treated as occurring from one site with one desorption activation energy in most cases. However, recent experiments suggest that there are several sites for desorption, each with a corresponding activation energy.⁴⁻⁶

a. LiAlO₂

In some of the experiments on the adsorption-solubility relationships for H₂O(g)-LiAlO₂,⁷ the sample was heated to a high temperature in a helium stream and the evolution of water vapor was recorded. During the temperature ramp, the rate of evolution of H₂O(g) was observed to go through several maxima. This was interpreted as showing that evolution proceeded from several types of sites. Isotherms and isobars derived from these data revealed two adsorption processes with different activation energies for adsorption.⁷ Furthermore, the heats of adsorption were found to depend on the degree of surface coverage. Because the activation energy for desorption is equal to the sum of the heat of adsorption and the activation energy of adsorption, the desorption activation energy will exhibit the same trend as observed for the heat of adsorption. Earlier work on alumina also indicated several types of adsorption/desorption sites.⁸

Supporting evidence for multiple desorption sites on LiAlO₂ was obtained in the tritium release from the LILA-1 experiment.⁹ For several runs, an increase in temperature resulted in a small decrease in tritium release followed by an increase to a maximum then a decrease to steady state.¹⁰ Similar tritium release curves were observed for release from Li₂O in the CRITIC experiment.¹¹

b. Li₂O

A constant-rate heating experiment was performed by Tanifuji et al.⁴ on irradiated Li₂O. This experiment is, in essence, a temperature-programmed desorption (TPD) study. In TPD, a sample containing adsorbed material is heated at a specified rate, and the quantity of desorbed species is measured as a function of temperature. For a constant heating rate, a peak will be observed in a plot of the amount desorbed versus temperature. The position of the peak is indicative of the desorption activation energy. The presence of more than one peak indicates multiple desorption processes. Tanifuji et al. interpreted their results based on the presence of one broad desorption peak for each sample⁴; however, if the data are examined more closely, one can recognize several overlapping peaks. An analysis of these peaks indicates five types of sites for desorption of tritium from Li₂O.

Supporting evidence for the presence of multiple desorption sites in Li₂O was also obtained in the CRITIC in-pile tritium release experiment. In this experiment, an increase in sample temperature resulted in a sharp decrease in tritium release followed first by an increase to maximum release and then decay to steady state.¹¹ This behavior was successfully modeled using a desorption activation energy which varied with surface coverage; it could not be modeled by a diffusion-desorption model with a single desorption activation energy.¹²

c. Li₄SiO₄

Evidence for multiple types of desorption sites in Li₄SiO₄ has been observed in several out-of-pile tritium release experiments.^{5,6,13} The first suggestion of multiple desorption sites in this material came from attempts to fit tritium release data from out-of-pile annealing studies. Breitung et al.¹³ found that the best fit to their data was obtained for a desorption model with two types of desorption sites. More conclusive data have recently been reported. Two separate studies describing tritium release and water release from TPD experiments indicate multiple desorption activation energies.^{5,6} In the first of these experiments, pre-irradiated samples of doped and undoped Li₄SiO₄ were heated at a rate of 4.8°C/min, and the amount of tritium released was measured as a function of temperature.⁵ Multiple desorption peaks were observed in the TPD curve for all the samples, with six desorption peaks present for the pure silicate. The second study investigated the desorption of water from Li₄SiO₄.⁶ The TPD curve for water desorbed from Li₄SiO₄ powder stored in air showed what appear to be six overlapping peaks, indicating six types of desorption sites. Both of these studies on Li₄SiO₄ are consistent with the presence of up to six different desorption activation energies.

3. Calculations of Activation Energies of Desorption

a. Method

The mathematics governing desorption in TPD or constant-rate heating experiments have been covered in detail elsewhere.^{14,15} A brief description of the relevant equations follows.

For first-order desorption into a vacuum (or into a rapidly flowing purge stream), the pressure of the desorbing species in the purge stream from one site with desorption activation energy E_a can be calculated as follows:¹⁴

$$P = (v/C) \exp\{-v\beta (E_a/R)I - E_a/RT\} \quad (I-8)$$

where

$$\begin{aligned} I &= \exp(-\varepsilon) [1 - (2!/\varepsilon) + (3!/\varepsilon^2) - (4!/\varepsilon^3) + \dots] / \varepsilon^2 \\ v &= \text{desorption preexponential term} \\ \beta &= \text{heating rate} \\ E_a &= \text{desorption activation energy} \\ C &= \text{initial concentration} \\ T &= \text{temperature} \\ R &= \text{gas constant} \\ \varepsilon &= E_a/RT \end{aligned}$$

Second-order desorption gives the pressure as:¹⁴

$$P = \frac{v \exp(-E_a/RT)}{C(E_a/R) (1 + v\beta I E_a/R)^2} \quad (I-9)$$

The total release at any time would be the sum of the release over all the active desorption sites. Using these equations, one can calculate the tritium release profile as a function of time or temperature given the desorption activation energies, preexponential terms, and the heating rate.

Using the data from constant-rate heating experiments, one can estimate the desorption activation energies from the temperatures at which the maxima in plots of tritium release versus temperature occur. For experiments where the flow rate and heating rate are such that readsorption does not interfere, an estimate of the activation energy for a first-order desorption can be obtained from the following:¹⁵

$$E_a = RT[\ln(v T/\beta) - 3.46] \quad (I-10)$$

Using an estimate of 1×10^8 for the desorption preexponential (a value in agreement with tritium release measurements from Li_2O and kinetic studies of the decomposition of $\text{LiOT} + \text{LiOH}$),¹⁶ we obtained estimates for the activation energies of desorption of tritium from Li_2O from the Tanifuji et al. data.⁴ We also estimated the activation energies for desorption from Li_4SiO_4 using $v = 1 \times 10^8$ and the Skokan et al.⁵ and Schauer and Schumacher data.⁶ These estimates were then used as input to a computer program calculating the tritium release as a function of temperature using Eq. I-8 or -9. The initial concentrations and activation energies for each site were then varied to optimize the fit to the data.

b. Li_2O Calculations

Our analysis of the data obtained by Tanifuji et al.⁴ for their constant heating rate experiment suggests that there are six different sites for desorption of tritium from Li_2O . The estimates of the activation energies from the first-order desorption equation are 140.6 ± 0.4 , 149.4 ± 1.7 , 162.8 ± 1.7 , 178.2 ± 3.8 , and 186.2 ± 1.7 kJ/mol (33.6 ± 0.1 , 35.7 ± 0.4 , 38.9 ± 0.4 , 42.6 ± 0.9 and 44.5 ± 0.4 kcal/mol). The desorption peak corresponding to the highest activation energy, 186.2 kJ/mol (44.5 kcal/mol), was of low intensity and was not always seen. Examples of the calculated tritium release curves are illustrated in Fig. I-10 for 10 K/min, Fig. I-11 for 1 K/min, and Fig. I-12 for 5 K/min. The relative populations of the sites responsible for the different desorption peaks were dependent on the history of the sample and the heating rate. For experiments with a heating rate of 1 K/min, the major desorption peak was due to the process with an activation energy of 149.4 kJ/mol (35.7 kcal/mol), while the peak corresponding to an activation energy of 140.6 kJ/mol (33.6 kcal/mol) was dominant when the heating rate was 10 K/min. This suggests that there is a redistribution in the population of the sites as the sample is heated. In part, a low heating rate allows the most active sites to remain filled longer.

Fig. I-10.

Tritium Released from Li_2O as Observed from Tanifuji et al. Data and Calculated from Multiple Desorption Site Model with Heating Rate = 10 K/min

Fig. I-11.

Tritium Released from Li_2O as Observed from Tanifuji et al. Data and Calculated from Multiple Desorption Site Model with Heating Rate = 1 K/min

Fig. I-12.

Tritium Released from Li_2O as Observed from Tanifuji et al. Data and Calculated from Multiple Desorption Site Model with Heating Rate = 5 K/min

The tritium released from Li_2O and collected as HT was also determined as a function of temperature by Tanifuji et al.⁴ These curves were compared with calculations using our model with multiple desorption activation energies. The desorption activation energies were estimated to be 139.7, 148.5, 159.4, 175.7, and 187 kJ/mol (33.4, 35.5, 38.1, 42.0, and 44.7 kcal/mol). These energies are in good agreement with those determined from the curves of total tritium released. The amount of released tritium detected as HT was found to be of the order of 1% of the total tritium released.⁴ The agreement between the desorption activation energies for the tritium detected as HT and the total tritium released (detected as mostly HTO) suggests that tritium collected as HT and as HTO is released by the same mechanism. Thus, the form of tritium detected downstream is probably not determined by the form in which it is released from the solid, but by the gas phase chemistry.

It is of interest to compare our estimates of desorption activation energies with some reported in the literature. The first in the sequence of desorption processes, with an estimated activation energy of 140.6 kJ/mol (33.6 kcal/mol), is expected to be for desorption from a surface with a relatively high surface coverage. This value is in good agreement with the desorption activation energy reported by Kudo and Okuno of 129.7 kJ/mol (31 kcal/mol),¹⁶ as well as with the activation energies reported by Quanci (for tritium release into a helium purge stream containing 0.1 to 1.0% added hydrogen) of 130.6 kJ/mol (31.2 kcal/mol).¹⁷ The second energy (149.4 kJ/mol, 35.7 kcal/mol) is expected to correspond to desorption from a slightly more energetic type of site. Desorption from this site would begin to dominate when the population of a previously active site is diminishing. This activation energy is in excellent agreement with that reported by Quanci (for desorption into a pure helium purge) of 152.2 kJ/mol (36.4 kcal/mol).¹⁷ Bertone has reported lower activation energies than our estimates (118.8 kJ/mol, 28.4 kcal/mol),¹⁸ as has Quanci (102.0 kJ/mol, 24.4 kcal/mol, for a purge gas of He plus 4.82% H_2).¹⁷ There may be sites for desorption from Li_2O with even lower activation energies than those we estimated, but these are expected to correspond to samples with a higher surface coverage than the samples studied by Tanifuji et al. As a possible limiting case for high surface coverage, we note that Kudo and Okuno reported the activation energy for thermal decomposition of LiOH as 123.4 kJ/mol (29.5 kcal/mol).¹⁶ However, additional depression of the activation energy might result from radiation effects or reaction of the surface with H_2 in the purge gas.

The degree of surface coverage present at any particular time determines which activation energy will control the desorption process at that time. Unfortunately, we could not obtain estimates of surface coverage from the Tanifuji et al. data⁴; thus, we can not determine what surface coverages our estimated activation energies relate to. However, because these experiments were performed with pure helium purge gas, the results should be comparable with and relevant to tritium release experiments that were also performed with pure helium purge streams. A detailed experimental study is needed to quantitatively relate the hydrogen/tritium surface coverage to the desorption activation energies.

c. Li_4SiO_4 Calculations

Using Eq. I-10 and an estimated value of the desorption preexponential term of 1×10^8 , we derived approximations for desorption activation energies for Li_4SiO_4 from the data of Skokan et al.⁵ and Schauer and Schumacher.⁶ Activation energies of 73.6, 96.7, 110.9, 143.1, 178.2, and 215.9 kJ/mol (17.6, 23.1, 26.5, 34.2, 42.6, and 51.6 kcal/mol) were obtained from the Skokan et al. data.⁵ Values of 83.3, 97.9, 112.1, 146.9, 171.1, 193.3, and 218.8 kJ/mol (19.9, 23.4, 26.8, 35.1, 40.9, 46.2, and 52.3 kcal/mol) were obtained from the Schauer and Schumacher data.⁶ The expected first-order release was calculated and compared to the observed release of H_2O in the Schauer and Schumacher experiment.⁶ The positions of the calculated peaks were found to agree well with the experimental data; however, the peak widths for the calculated curves were narrower than the experimental peak widths. Calculations

based on second-order desorption using activation energies of 83.3, 97.9, 112.1, 144.3, 171.5, and 194.1 kJ/mol (19.9, 23.4, 26.8, 34.5, 41.0, and 46.4 kcal/mol) provided a much better fit to the observed data. The agreement between the activation energies calculated from the Skokan et al.⁵ and Schauer and Schumacher⁶ data is quite good, with a maximum deviation of less than 10 kJ/mol. One additional peak was observed in the tritium release curve from the Schauer paper.⁶ This peak may be masked by other, more intense peaks in the curves of Skokan et al.⁵

Our estimates of these desorption activation energies can be compared with values calculated by Breitung et al.¹³ from a fit of LISA data to a two-site desorption model with activation energies of 53.6 and 90.9 kJ/mol (12.8 and 21.7 kcal/mol). The energy we calculated, 97.9 kJ/mol, is in good agreement with the second of their energies, suggesting that we made a reasonable choice for the preexponential term. Again, it is not possible to determine the surface coverage from the data given in the Schauer and Schumacher paper⁶; thus, the surface coverages which correspond to our estimates of desorption activation energies are unknown.

Skokan et al.⁵ also studied the tritium release from several doped samples of Li_4SiO_4 . These doped samples showed different release characteristics than the pure silicate. The materials studied had the compositions $\text{Li}_{4.05}\text{Si}_{0.95}\text{Al}_{0.05}\text{O}_4$, $\text{Li}_{3.7}\text{Al}_{0.3}\text{SiO}_4$, $\text{Li}_{3.9}\text{Si}_{0.9}\text{P}_{0.1}\text{O}_4$, and $\text{Li}_{3.3}\text{P}_{0.7}\text{Si}_{0.3}\text{O}_4$.

The material creating lithium vacancies by doping with aluminum, $\text{Li}_{3.7}\text{Al}_{0.3}\text{SiO}_4$, exhibited better tritium release than pure Li_4SiO_4 . The TPD release curve shows a new desorption peak at low temperature (near room temperature), and the peak at 73.6 kJ/mol is increased in intensity relative to that for the pure silicate, while the peak at 96.7 kJ/mol in the pure silicate is no longer visible. The other peaks appear to be the same as for the pure silicate. The overall result is to introduce a new low-activation-energy desorption mechanism, improving the tritium release calculation.

The material doped with phosphorus to form $\text{Li}_{3.9}\text{Si}_{0.9}\text{P}_{0.1}\text{O}_4$ showed poorer tritium release than the pure silicate. The low-temperature peak observed in the aluminum-doped, lithium-deficient material is also present for this material; however, the peak at 73.6 kJ/mol is decreased in intensity relative to the pure silicate, and the peaks at 96.7 and 110.9 kJ/mol are no longer visible. The peak at 178.2 kJ/mol is increased in amplitude relative to the pure silicate and has a long tail to the high-energy side of the peak. The overall result is to shift the tritium release to processes with higher activation energies. A similar effect was seen for $\text{Li}_{3.3}\text{P}_{0.7}\text{Si}_{0.3}\text{O}_4$ and $\text{Li}_{4.05}\text{Si}_{0.95}\text{Al}_{0.05}\text{O}_4$. For the phosphorus-doped material, desorption peaks are observed at 73.6, 110.9, and 143.1 kJ/mol. The peak at 143.1 kJ/mol is the most intense peak and has a long trailing tail. Again, the tritium release is shifted to higher activation processes. For the aluminum-doped material, the peaks at energies of 73.6 and 96.7 kJ/mol are decreased in intensity relative to the pure silicate, while the peaks at energies of 178.2 and 215.9 kJ/mol are increased in intensity. The effects of doping based on the most likely defects formed are as follows:

1. Creating a lithium vacancy leads to the availability of a new low-activation-energy tritium desorption process and improves tritium release.
2. Creating silicon vacancies decreases the availability of low-activation-energy desorption mechanisms and leads to poorer tritium release.
3. Creating lithium interstitials decreases the availability of low-activation-energy desorption mechanisms and leads to poorer tritium release.

d. Future Work

The current estimates of desorption activation energies will be used to calculate the observed tritium release from in-pile release experiments. Relationships between purge gas chemistry, surface coverage, and desorption activation energies will be derived from laboratory experiments, in-pile experiments, and modeling efforts.

E. Thermal Conductivity of Sphere-Pac Bed (S. W. Tam and J. F. Wright)

1. Introduction

Various configurations have been considered for the solid breeder (e.g., Li_2O) plus neutron multiplier (e.g., Be) to be used in fusion reactor technology.¹⁹ One option is the sphere-pac configuration, which consists of the solid component in the form of small particles (ideally as spheres) put together in a bed in a close-packed manner. To achieve high packing density, particles of several different sizes need to be used. The interstitial spaces between particles of a given size are packed with particles of the next smaller size and so on in a hierarchical manner. The packing process can be achieved by vibratory compaction.²⁰ Much experience has been gained on this configuration in fission-reactor technology.²⁰ In particular, extensive data on the thermal conductivities (K_{sp}) of sphere-pac systems have been gathered through fission-related research, as well as from work on development of thermal insulation technology.²¹ The heat conduction properties of these systems possess unusual characteristics owing to the interweaving nature of the spheres combined with open pores. For example, with sphere-pac beds immersed in a gas (e.g., He or Ar), the thermal conductivities, K_{sp} , are dependent on the gas pressure. Typically, K_{sp} increases rapidly by 50-100% when the gas pressure is raised by as little as 1 MPa and then changes much more slowly thereafter (see Fig. I-13). It may be thought that such behavior may be exploited to the advantage of blanket technology if a sphere-pac configuration is utilized in the breeder-plus-multiplier component. However, straightforward extrapolation from experience with fission and thermal insulation technology to a fusion blanket environment should be done with care, since quite different materials characteristics are involved. A careful analysis on a physical basis revealed that a gas-pressure-sensitive thermal conductivity has a much less prominent effect than suggested from experiences with other technology. To understand this, one needs to first appreciate the reasons why such pressure effects are so dramatic in fission and thermal insulation materials.

2. Physical Basis

The pressure dependence of K_{sp} arises from its dependence on the gas conductivity (K_g). In fact, the materials utilized for the solid component in fission and thermal insulation experiments all have low K_{sp} , as low as only 5-10 times larger than K_g .^{20,21} The heat flux density is expected to be reasonably uniform, and a substantial fraction of the heat flux lines passes through the gas phase. This gives rise to a critical dependence of K_{sp} on K_g . In fact, several of the theories²²⁻²⁴ that have been successfully applied to describe K_{sp} in related systems have exploited the simplification resulting from this uniform flux approximation.

Although K_g is well-known to be pressure independent under ordinary conditions, this is not true when the gas is confined to a bounded region whose linear dimension is comparable or smaller than the mean free path of the gas.²⁵ In that case, heat transfer does not occur via intermolecular collision, as in the bulk, but rather through gas-molecule/solid-surface scattering. The relative inefficiency of the heat conduction process gives rise to a temperature difference between the solid surface and the gas phase region immediately above the surface. It is this factor which leads to the unusual pressure dependence of K_g (in a confined region) and, ultimately, K_{sp} .

Fig. I-13.

Thermal Conductivity for UO_2 Sphere-Pac Bed in Helium Gas as Function of Pressure. (Dashed curve calculated with bed particles of one size. Solid curve calculated with bed particles of three sizes. The squares show literature data from Moore et al.²⁰)

The critical parameters here are the ratio K_s/K_g (the solid-to-gas thermal conductivities) and the smoothness of the contact surfaces between solid particles. To maximize the influence of K_g on K_{sp} , one needs a small ratio of K_s/K_g to, in part, ensure a high flux density through the gas. Smooth spherical surfaces for the solid particles would lead to only point contacts between particles and, thus, would minimize direct heat conduction between solid microspheres. The low conductivity solids (e.g., UO_2 , ThO_2) utilized in fission technology²⁰ satisfy such criteria, and one should not be surprised at the gas pressure dependence of K_{sp} observed in both experiments^{20,21} and theoretical calculations.²²⁻²⁴

3. Sphere-Pac Bed with Beryllium Particles

For a sphere-pac system whose major solid component is a high-conducting metal, previous experience from fission and thermal insulation technologies may well be misleading. This is the case for a bed with mainly beryllium particles as a neutron multiplier for fusion blanket application. In this case, the ratio K_s/K_g is easily of the order of 500 or more.²⁶ The heat flux lines are far from uniform, with most of them passing directly from one solid particle to the next through the limited area of contact between the particles (thus bypassing the gas phase).

In practice, an inevitable degree of roughness of the particle surfaces must give rise to finite contact areas, not the point contacts assumed in ideal systems. The effects of flux constriction and interfacial roughness acting in concert would enhance direct heat conduction between solid particles and thereby reduce the effect of K_g (and, hence, the gas pressure) on K_{sp} .

To verify such physical considerations we have constructed simple models that include the effect of flux constriction and interfacial roughness on K_{sp} . In particular, we have used the models to estimate the effects of gas pressure on K_{sp} once these two factors are taken into account.

A complete theory of K_{sp} , including the effect of interfacial roughness, would require detailed microstructural information in the vicinity of the contact region. However, an upper and lower bound to the effect of gas pressure on K_{sp} due to roughness can be estimated using two simple models with a sound physical basis. The first model uses the equation:

$$1/K_{sp} = 1/K_s + 1/(K_c + K_g) \quad (I-11)$$

where K_s is the effective conductivity of the solid component, K_g is the the effective conductivity of the gas phase, and K_c is the conductivity due to the contact between particles with surface roughness.

While both K_s and K_g include geometrical factors, one expects their value to be of a similar order of magnitude as the conductivity of the pure solid and gas phases. Only K_g depends on the gas pressure. We have estimated the contact conductivity, K_c , using the equation²⁶:

$$K_c = h_{\text{contact}} \pi \delta \quad (I-12)$$

where

$$h_{\text{contact}} = K_s / R_1 \left[\frac{(R_1/R_2)^2}{\tan^{-1}[R_2/R_1 - 1]} \right] \quad (I-13)$$

Here, the interfacial roughness is modeled as a group of cylindrical protrusions with height δ , base radius R_1 , and the centers of adjacent cylinders spaced R_2 apart. Thus, $(R_1/R_2)^2$ measures the fractional surface area of the solid particles covered by the protrusions. Small values of δ/R_1 (e.g., <1) describe pillbox-like structures; larger values of δ/R_1 (e.g., >1) give more elongated cylindrical protrusions. We have evaluated K_c (for Be) at 500 K for $\delta/R_1=1$ and 4 for various $(R_1/R_2)^2$. The results are shown in Table I-8. Since the K_g value for He would be in the range of 0.1-0.2 W/(m·K),²⁷ one can deduce that, in general, $K_c \gg K_g$. In this case, the pressure-dependent effect from K_g is completely overwhelmed by K_c . According to this model, one would expect very little pressure effect. Because of flux constriction, the whole system conducts heat between solid particles via the contact resistance, with the heat bypassing most of the gas phase.

Table I-8. Calculated Values for Interfacial Contact Conductivity

δ/R_1	$(R_1/R_2)^2$	Contact Conductivity, W/(m·K)	
		T=400 K	T = 500K
1	0.04	15.3	13.2
	0.02	7.3	6.3
	0.01	3.5	3.0
4	0.04	61	52.7
	0.02	29.4	25.3
	0.01	13.8	12.0

The second model uses a different approach. It seeks to give an upper bound to the effect of the gas phase. The sphere-pac system is assumed to conduct heat by two parallel pathways: via the bulk solid in series with the gas phase or via the bulk solid in series with the interfacial contact resistance region. In the second pathway, the conductance is essentially controlled by K_c . Thus,

$$K_{sp} = K_c + K_{sp}^o \quad (I-14)$$

where K_{sp}^o is the initial sphere-pac conductivity without contact resistance being considered, and K_{sp} is the sphere-pac bed conductivity when the assumptions of uniform heat flux and interparticle point contact both hold. Figure I-14 shows the percent change in K_{sp} for $T = 500$ K and a pressure change of 0.5 to 2 atm in a Be/He sphere-pac system.²⁸ The horizontal axis represents the fractional surface area covered by the protrusions. For point contact, the percent change is about 86%, a significant increase. However, with the inclusion of the contact resistance, the change in K_{sp} becomes significantly less for as little as 2-3% of particle surface area covered with protrusions. This illustrates the drastic effect of interfacial roughness on the gas pressure dependence of K_{sp} . It should be noted that the present estimate already gives an upper bound on the pressure effect of K_{sp} for the conditions considered. The first model leads to practically a null pressure effect as a lower bound. The actual behavior is likely to be somewhere in between. Thus, one would expect that, for a sphere-pac bed with a high-conductivity solid component with roughness at a few percent surface coverage, the sensitivity of K_{sp} to gas pressure variation is significantly less than a bed with a thermal insulator as the solid component.

Fig. I-14.

Changes in Thermal Conductivity as Function of Fraction Surface Area Covered by Protrusions (temperature of 500 K; pressure change from 0.5 to 2 atm)

4. Conclusion

In considering the sphere-pac bed configuration for the blanket component in fusion technology applications, care must be exercised in extrapolating experience from previous technologies. The high thermal conductivity of the metallic component (i.e., Be as neutron multiplier) gives rise to serious heat flux constriction and indirectly increases the importance of interfacial roughness in the solid contact region. Both factors, in conjunction, significantly reduce the sensitivity of the thermal conductivity of a sphere-pac bed to variations in the gas pressure.

F. Design Studies for International Thermonuclear Experimental Reactor (P. A. Finn, D. K. Sze, and R. G. Clemmer)

Two breeder blanket options are being considered for the International Thermonuclear Experimental Reactor (ITER) design, an aqueous lithium salt blanket (containing either 2 M LiNO₃ or 2 M LiOH) and a solid oxide breeder blanket. Important design issues are radiolysis and electrolytic decomposition for an aqueous salt blanket in a magnetic field, while they are radiolysis of the water coolant and tritium recovery for the solid oxide breeder blanket.

Because of the large amount of gas generated during radiolysis, the ITER design was changed from a low-pressure to a high-pressure design. The higher pressure will retain the radiolytic gases in solution, thereby maintaining a single phase system. For the aqueous salt blanket, we determined the corrosion products and calculated the amount of electrolytic decomposition expected. For the solid oxide breeder, we examined the effects of radiolysis and electrolytic decomposition on the water coolant and also defined the blanket tritium recovery system.

1. Aqueous Salt Blanket

a. Corrosion Products

The species present in one liter of a 2 M LiOH aqueous solution at 60°C circulated in 316 stainless steel pipes were estimated using the thermodynamic code FACT.²⁹ To assess the amount of metal in the solution due to corrosion, we assumed a corrosion rate of 50 μm/yr, a surface area of 18000 m², a fluid volume of 280 m³, and on-line purification processing every three hours. The steady-state amount of iron and chromium in solution is 2×10^{-6} mol/L and $<1 \times 10^{-6}$ mol/L, respectively. Due to radiolysis, 0.05 mol hydrogen was also assumed to be present in the system.

This system consists of a gas phase, an aqueous phase, and two solids. Our FACT calculations yielded the following results. The gas phase contains most of the hydrogen and some water (0.034 and 0.00032 mol, respectively). In a liter of aqueous solution, there are 1.02 mol LiOH, 0.98 mol Li⁺ and OH⁻, 0.016 mol H₂, 4.87×10^{-11} mol FeOH⁺, and 9.2×10^{-14} mol H⁺. Metal species present at levels of 10^{-18} to 10^{-63} mol were ignored. The two solid species were 5×10^{-7} mol FeO•(Cr₂FeO₄) and 5×10^{-7} mol Fe₃O₄.

If the aqueous salt system behaves as this thermodynamic calculation suggests, nearly all of the corrosion products are expected to circulate through the system as particulates. Thus, extensive filters will be necessary to stop tube plugging.

b. Electrolytic Decomposition

Electrolytic decomposition for a 2 M LiOH blanket was examined to obtain an estimate on the extent of steel dissolution.

The circulation of a concentrated salt solution in a magnetic field results in the generation of a potential gradient in the salt solution. The magnitude of this potential gradient, or voltage (V), is equal to

$$V = B v l$$

where B is the magnetic field (3 T), v is the linear velocity of the salt solution (4 m/s), and l is the blanket thickness (0.01 m) perpendicular to the magnetic field and the direction of salt flow.

The net voltage is 0.1 V for these conditions. This voltage is the maximum available to overcome the resistive losses in the salt solution and the overvoltage associated with steel dissolution. Because the resistive losses of a 2 M salt solution are extremely small, the calculated voltage is equal to the overvoltage. Iterative calculations were done to match 0.1 V to anodic and cathodic polarization curves of stainless steel, the structural material for ITER, from which the corresponding current density was determined. From this current density, one can determine the potential for metal dissolution.

For a 2 M LiOH solution, the current density was determined to be 0.15 mA/cm². This current density corresponds to 4.7 x 10⁻⁴ cm/d of the wall's dissolution, an amount of dissolution which may be acceptable. However, if dissolution occurs nonuniformly, holes may appear in the walls.

2. Solid Breeder Blanket

a. Water Coolant System

The chemistry of the water coolant in a solid breeder blanket was defined. This water is to have low conductivity (i.e., 3 x 10⁻⁶ mho/cm), be neutral (i.e., pH ~7), and contain no additives. A hydrogen overpressure of ~0.06 MPa is needed to minimize water radiolysis. Maintenance of this water quality during reactor operation, i.e., over ten years of operation, will require continuous use of a purification system containing filters and ion-exchange resins and careful attention to the conductivity. Specific ions (such as chloride) which increase corrosion will have to be maintained below strict limits, <15 ppb.

The quality of the water coolant in a fusion reactor is influenced by four factors: the purity of the feedwater and/or makeup water introduced into the system, the coolant purity maintained during reactor operation, the effect of products from radiolysis, and the effect of the reactor's magnetic field on the electrolytic decomposition of the coolant.

High quality water coolant has an ion concentration of 10⁻⁷ M and an equivalent conductance of 1 x 10⁻⁶ mho/cm. The conductance of water coolant systems in fission reactors cannot be maintained at this level because gases and residual impurities originally in the metal pipes dissolve in the water. The recommended water quality standard for water added and/or maintained in a commercial fission reactor is an ion concentration of 10⁻⁵ M, which corresponds to an equivalent conductance of 3 x 10⁻⁶ mho/cm.

The ion concentration can increase as a result of metal corrosion during reactor operation; therefore, a purification system containing filters and mixed cation-anion exchange resins is used on a continuous basis to remove any ions which enter the water coolant. However, significant amounts of sulfur (<1 ppm by weight) can be introduced from decomposition of the resins³⁰ due to the presence of activated corrosion products in the water. Periodic replacement of the resin will minimize resin breakdown, which has deleterious effects other than sulfur introduction, i.e., increased metal

impurity concentrations resulting in higher water conductivity, as well as increased activation, CO_2 concentration, and radiolysis rates with an associated increase in hydrogen in the off-gas stream.³¹

In fission reactors, boric acid is added to flatten the radial power distribution. The presence of the boric acid produces a slightly acidic solution so that lithium hydroxide is added to bring the pH of the water back to a neutral pH. In a fusion reactor, these additives would not only change the pH but would also contribute to gas production by radiolysis and electrolytic decomposition. Their use, therefore, should be carefully studied.

(1) Water Radiolysis

Radiolysis of pure water increases the ion concentration an order of magnitude, to 10^{-4} M, which corresponds to an equivalent conductance of 10^{-5} mho/cm. The ions from water have a much higher conductance than metal ions. The ion concentration does not increase further because the ionic species produced, an aqueous electron and a proton, have a lifetime of $<100 \mu\text{s}$. Therefore, within the blanket, the water's conductance is three times that in other parts of the fusion plant. (In other parts of the reactor, water radiolysis due to gamma radiation occurs but at a dose much lower than that in the blanket; thus, the water coolant conductance is unaffected by this radiolysis.) The amount of radiolysis which occurs in the water coolant can be suppressed by the addition of hydrogen in the cover gas of the coolant. The addition of hydrogen has two effects: it reduces the ion concentration and the amount of oxygen gas present in the water. This latter effect is also important since the presence of oxygen can increase metal substrate corrosion. In both boiling water and pressurized water reactors, hydrogen gas is added to suppress the amount of oxygen gas and hydrogen peroxide arising from water radiolysis.

The radiolysis of the water coolant was calculated by two methods. In the first method, a simple model of the blanket was used. The dose was assumed to be that at the first wall and the heat load was averaged over the blanket. The average gamma and neutron doses were estimated to be 0.8 and 3.2 W/cm^3 , respectively. The maximum dose, which is at the first wall, is about a factor of three higher. The radiation yield, $G(\text{H}_2)$, for gamma rays and neutrons is a maximum of 0.43 and 1.1, respectively. The volume of water irradiated at the first wall is $2 \times 10^6 \text{ cm}^3$. The total moles of hydrogen gas generated per second is 2.4. Assuming a power of 1000 MW electrical (1200 MW thermal) and a coolant temperature rise of 35°C , $4.75 \times 10^5 \text{ mol}$ water would be flowing. The pressure required to keep the hydrogen in solution at $<80^\circ\text{C}$ at the first wall would be 0.06 MPa. Thus, to minimize water radiolysis, a minimum hydrogen pressure of $\sim 0.06 \text{ MPa}$ is needed.

In the second method, a recent (more complex) solid oxide design for the ITER was used to calculate the heat load borne by the first wall. The total heat load which the first wall coolant handles arises from several sources: (1) $q(\text{rad})$, the radiation from the plasma which reaches the first wall ($\sim 10\%$ of the total fusion power); (2) $q(\text{fw})$, the thermal load from the first wall itself (stainless steel for the outboard region and carbon plus stainless steel for the inboard region); (3) $q(\text{H}_2\text{O})$, the thermal load from the neutron and gamma dose in the water; and (4) $q(\text{breed})$, the thermal load from the first 45% of the blanket section between the first wall coolant channel and the next coolant channel. Thus, the total heat load, Q , is given by

$$Q = q(\text{rad}) + q(\text{fw}) + q(\text{H}_2\text{O}) + q(\text{breed}) \quad (\text{I-15})$$

The hydrogen produced due to radiolysis is equivalent to the relative fraction of the first wall coolant in the outboard and inboard regions. These regions are considered as single units in this calculation and were not considered sectors.

The following information was used to calculate each component of Q:

Heat Flux	
Carbon	6.9 W/cm ³ , at the first wall
Stainless Steel	11 W/cm ³ , at the first wall
Beryllium	7.8 W/cm ³ , at the first wall
Li ₂ O*	45 W/cm ³ , average
Fusion Power	850 MW
Power to Divertor	85 MW
Thermal power	1020 MW
Surface Area at First Wall	748 m ²
Delta Temperature (outboard)	6°C
Delta Temperature (inboard)	7°C
Energy Multiplication Factor	1.366

With these conditions, the total thermal load was determined to be 303 MW for the outboard first-wall coolant channel and 198 MW for the inboard first-wall coolant channel. The hydrogen produced in the first wall on the outboard side is 1.8 mol/s; that on the inboard side is 0.9 mol/s. The mole fractions (H₂/H₂O) for the outboard and inboard regions are those listed below; the needed overpressure for hydrogen is also listed.

	H ₂ /H ₂ O mole fraction	Overpressure, MPa
outboard	2.57 x 10 ⁻⁶	0.02
inboard	2.25 x 10 ⁻⁶	0.02

An overpressure of 0.02 MPa is lower than the 0.06 MPa estimated by the first method. This lower estimate is due to (1) the lower delta temperature (6-7°C) compared with the 35°C assumed earlier and (2) the large fraction of the blanket which is cooled by the first wall coolant channel. To better define the actual pressure, a heat transport calculation for the blanket is needed.

(2) Electrolytic Decomposition

In a magnetic fusion reactor, a moving ionic fluid generates an induced voltage, which can result in additional corrosion if the induced voltage is greater than the resistance losses of the fluid. The induced voltage is proportional to the product of the magnetic field (3 and 8 T, respectively, in the outboard and inboard sections of a fusion reactor blanket), the fluid's linear velocity, and the thickness of the channel through which the fluid is flowing. For a water coolant moving with a linear velocity of 3 m/s through a 0.01 m channel, the induced voltage is 0.1 and 0.2 V for the outboard and inboard, respectively. However, the resistance loss of water with a conductance of 10⁻⁵ mho/cm is 1 V, an order of magnitude greater than the induced voltage. Thus, for a water coolant in which the water quality specifications are met, the presence of a magnetic field is not expected to increase corrosion.

(3) Water Purification System

To produce feedwater and/or makeup water with a conductance of 3 x 10⁻⁶ mho/cm, a water purification system similar to that shown schematically in Fig. I-15 is needed.

*For Li₂O, heat loads drop a factor of three for each 10-cm radial distance into the inboard or outboard regions.

Each component has a specific function to remove impurities; however, other impurities can be added in each processing step:

1. Chlorination destroys organics but adds chlorine.
2. The aluminum hydroxide used for coagulation traps particulates but adds aluminum.
3. The sand filter removes aluminum hydroxide and the trapped particulates but adds silica.
4. The charcoal filter removes the chlorine and organics but adds carbon.
5. The oxidizing filter removes iron but adds manganese.
6. The cation exchange resins exchange hydrogen for cations (i.e., calcium, magnesium) but add sulfonic acid when the resin breaks down.
7. The vacuum deaerator removes dissolved gases, CO_2 , N_2 , O_2 .
8. The anion exchange resins exchange hydroxide for sulfates and carbonates but add sulfonic acid when the resin breaks down.
9. The mixed cation-anion exchange resins remove remaining ions.
10. Hydrazine and/or sulfite is added as an oxygen scavenger and remains as an impurity if excess is added.
11. The ultrafilter removes residual particulates, including those from resin breakdown.

Fig. I-15. Schematic for Water Purification System

b. Tritium Recovery System

A proposed tritium recovery system for the ITER solid breeder blanket has been developed based on ANL's work with Los Alamos National Laboratory on mating the Breeding Blanket Interface (BBI) to the Tritium Systems Test Assembly (TSTA). (See Sec. I. G.) In Table I-9, the calculated volume, capital cost, and tritium inventory of each component are listed.

The basic components of the tritium recovery systems for the two candidate blankets for ITER (solid and aqueous) are compared in Table I-10. A major difference between the two systems is the high hydrogen and water flow rates in the aqueous salt blanket system. A second difference is the low tritium enrichment factor (100) required for the solid breeder system versus the high factor (10^5) required for the aqueous salt system.

Table I-9. Calculated Volume, Cost, and Tritium Inventory for Components of ITER Solid Breeder Tritium Processing System

	Operating Temp., °C	Vol., ^a m ³	Capital Cost ^b , \$M	Tritium Inventory ^c
Li ₂ O Mol. Sieves (2)	-196	8	4.4	74
Be Mol. Sieves (2)	-196	0.2	0.4	<9
Cold Trap (2)	-100	0.4	0.4	4
Electrolysis (1)	600	0.1	0.2	--
Getter (2)	450	0.4	0.4	35
Waste Recovery (1)	450	0.1	0.2	1
Isotope Separation		9	3.2	60
Total		18.2	9.2	183

^aSystem was sized on basis of 100:1 hydrogen to tritium ratio, 10-s residence time, and one-hour regeneration.

^bBased on algorithms developed at TSTA for similar systems (1986 costs).

^cUnits which are cycled every 6 h contain 34 g of tritium plus residual inventory in unit.

G. Design of Breeding Blanket Interface

(P. A. Finn, R. G. Clemmer, D. K. Sze, and L. R. Greenwood)

The objective of this program is to incorporate a BBI as an integral part of the TSTA at Los Alamos National Laboratory. Los Alamos National Laboratory (LANL), Japan Atomic Energy Research Institute (JAERI), and Argonne National Laboratory (ANL) are partners in the BBI study. Joint technical work has been in progress since June 1987.

There are five phases in the BBI program. In Phase 1, concept definition, which was completed last year, the output stream conditions from different blankets were defined. This year in Phase 2, conceptual design, the BBI components are being defined for two ITER candidate blankets (aqueous salt and Li₂O solid). Phase 3 is engineering design. Phase 4 is hardware procurement and installation. Phase 5 is operation and testing of the BBI at TSTA.

The results of work in Phase 2 are summarized below.

1. Aqueous Salt Solution

The design of the tritium recovery system for an aqueous salt blanket was changed from a LiNO₃ solution to a LiOH solution to reflect the current tritium recovery system for the ITER design.

Spreadsheets were developed and used to track all flows through the different processing steps, including isotopics and impurities.

Table I-10. Comparison of Blanket Tritium Processing for Aqueous Salt and Solid Breeder Blankets^a

Process Step	Solid Breeder	Aqueous Salt
Tritium Recovery	Molecular Sieves (-196°C) 5 kg/d - H ₂	Flash Evaporator 5 x 10 ⁵ kg/d - H ₂ O
T ₂ O Conversion	Electrolysis <0.5 kg/d - HTO	VPCE 2 x 10 ² kg/d - H ₂ O 2 x 10 ² kg/d - H ₂
Tritium Purification	Getter	Ion Exchange + Driers + Filters
Tritium Enrichment	H ₂ Distillation Factor (100)	H ₂ O Distillation Factor (100) H ₂ Distillation Factor (1000)
Process Mode	Batch, 6-hour	Continuous
Operation	On with Reactor	On All Year, 24 h/day
BBI Test	Full to Half Scale	0.01 Scale

^aAssumptions: fusion power, 850 MW; breeding ratio, 1.0; assumed processing-system capacity, 0.3 for aqueous salt and 1.0 for solid; assumed availability, 1.0 for aqueous salt and 0.3 for solid.

When assembled, the BBI will include all components from the point at which molecular tritium is extracted. The components will include a blanket stream mockup system composed of a vapor phase catalytic exchange unit (VPCE) and a tritiated water circulation system, a fuel cleanup unit (BFCU) to remove impurities, a tritiated waste treatment unit (BTWT) to dispose of impurities, and an isotope separation unit (BISS), which is a cryogenic unit.

The H/T ratio for the aqueous salt BBI is the same as in ITER, 10³:1; however, the total hydrogen flow is reduced a factor of 100 in order to incorporate a BISS into TSTA. (The physical size, cryogenic cooling capacity, and the tritium inventory in the BISS necessitate this.)

The individual components are described further below.

The blanket stream mockup unit simulates the expected tritium and impurity source flows; a tritiated water stream with expected impurities and a hydrogen stream are included. The tritiated (1000 Ci/L) water circulation system simulates the tritiated water flow from a distillation unit. Subsystems include one to produce tritiated water, one to add expected impurities, one to evacuate the lines, one to recycle water, and one to purge with helium. The VPCE is a composite unit which contains a heater, a superheater, a catalyst bed, and a condenser. The tritiated water from the condenser is cycled back to a tritiated water circulation system.

The fuel cleanup unit (BFCU) contains four components, a cold trap which operates at -100°C, 4A molecular sieves which operate at -196°C, 5A molecular sieves which operate at -196°C, and a palladium diffuser. The first two components remove entrained water; a small amount of hydrogen is also removed in the 4A sieves. These two components are warmed to room temperature to recycle the tritiated water. The 5A molecular sieves at -196°C adsorb all impurities in the hydrogen stream (Cl, inerts, etc.) and a significant amount of hydrogen. The 5A sieves are warmed to 20°C, and the evolved

hydrogen is recycled past a palladium diffuser. The waste disposal unit (BTWT) is composed of two components, a 5A molecular sieve at 20°C and an activated carbon trap at -196°C.

The material remaining on the BFCU's 5A sieves after the 20°C hydrogen recycle is moved to the BTWT's 5A sieve bed by heating the former bed to 200°C. This material is retained on the latter bed as waste. Any material which is not stopped at the BTWT 5A sieve bed is passed to the cold activated carbon bed.

The purified hydrogen stream goes to a cryogenic distillation unit (BISS). There, a small stream of HT is passed to the TSTA and the rest of the hydrogen is recycled to the VPCE.

2. Solid Oxide

The U.S. ITER solid breeder lithium oxide (Li₂O) blanket has a beryllium (multiplier) mass that is ten times the Li₂O mass. Independent helium sweep streams remove tritium and impurities from the Li₂O and the beryllium.

A key attribute of the current blanket design is that the ten-fold excess of beryllium in the blanket results in beryllium being the major source of chemical and radionuclide contaminants in the blanket product streams. Summarized below are results obtained from our design analysis of the Li₂O breeder blanket.

The Li₂O contains 39 elemental impurities at a total of ~1000 ppm by weight. The major radionuclides are ²⁴Na, ²²Na, ¹²²Sb, ¹²⁴Sb, ⁵⁸Co, ⁶⁴Cu, and ³³S.

The beryllium contains 37 elemental impurities. Impurities include oxygen at 4500 ppm by weight; iron, carbon, silicon, magnesium, aluminum, and calcium at 100-500 ppm by weight; and sodium, chlorine, chromium, manganese, nickel, nitrogen, and lead at 10-60 ppm by weight. The major radionuclides plus their sources (in parenthesis) are ⁶⁴Cu (Cu,Zn), ⁵⁴Mn (Mn,Fe), ⁵¹Cr (Cr,Fe), ⁵⁵Fe (Fe), ⁵⁸Co (Ni,Co), ³⁵S (Cl,S), ³²P (Cl,S,P), ²⁴Na (Mg,Al,Na), and ²²Na (Na).

To recover tritium from the solid oxide blanket, the protium/tritium ratio must be 100 (number from recent design activities). Since the tritium level in the helium sweep gas is 10 ppm, the helium/tritium ratio is 10⁵, and the helium/protium ratio is 10³. The T₂O/T₂ ratio is assumed to be 1. Thus, a major task is the removal of tritium and impurities from the helium sweep streams.

The purge stream from a fusion reactor blanket is simulated by the blanket stream mockup unit. The purge flowing at 660 L/s is 99.9% He gas. The tritium product, along with hydrogen isotopes and impurities, is separated from the helium by sorption on 5A molecular sieves at -196°C. Upon regeneration of the molecular sieves, the HT stream is purified and isotopically enriched.

The helium sweep gas mixture (~99.8 at. % He, 0.2 at. % H, 20 ppm T, impurities) is blended to simulate the composition of the blanket stream in the blanket stream mockup. The tritium product (in the forms HT and HTO) is separated from the large volume of He gas by sorption in 5A molecular sieve beds at -196°C. The H₂ plus impurities are sorbed and removed from the helium gas stream. Tritiated water is separated from the stream by a set of cold traps operating at -100°C. The HT product plus H₂ and most impurities are not removed from the product stream by the cold traps. The tritiated water is reduced to the molecular (HT) form by an electrolyzer and returned to the product stream. (An electrolyzer has been developed by JAERI and tested at the TSTA.)

Hydrogen plus the tritium is absorbed on a Zr/Zr alloy getter bed. Sorption would occur at 350 to 450°C and regeneration would occur at 600 to 700°C. Impurities are not absorbed, and the waste stream is processed. Upon regeneration of the getter, the purified hydrogen/tritium stream is sent to the isotope separation system. The tritium is separated from the 100-fold excess of hydrogen isotope by cryogenic distillation. The tritium product is sent to the TSTA. The H₂ is recycled to the blanket system. The BTWT subsystem is designed to process impurities and recover tritium for recycle. The present design involves oxidation, and thus, the tritium recycle is in the oxide (HTO) form.

H. Dosimetry and Damage Analysis

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 Dosimetry and Damage Calculations for the ORR-MFE-7J Experiment (L. R. Greenwood and A. Intasom)

Neutron fluence and energy spectral measurements and damage calculations have been completed for the ORR-MFE-7J experiment in the Oak Ridge Research (ORR) Reactor at Oak Ridge National Laboratory (ORNL). This experiment was conducted jointly with Japanese experimenters and used a variety of specimens used for transmission electron microscopy and tensile tests.³² The specimens were irradiated at temperatures between 300 and 400°C in core position C3 from June 28, 1983, to March 26, 1987. The total exposure was 341,806 megawatt-hours (MWh) or 475 full-power days (FPD) at 30 MW. Twelve dosimetry capsules were placed throughout the sample area. Four capsules measuring 7 cm in length were placed in level 1, and two capsules measuring 4.5 cm were placed in level 3 for each temperature region. Each capsule measured 1.6-mm OD and contained wires of Fe, Ti, and 0.1% Co-Al. Due to required cooling times and shipping delays, the specimens were not received for analysis until September 1988.

Each capsule was opened in a hot cell at ANL and individual wires were segmented, weighed, and mounted for gamma spectroscopy. Because of the long decay time, we were only able to analyze the specimens ⁴⁶Sc, ⁵⁴Mn, and ⁶⁰Co. The measured activation rates are listed in Table I-11. The activities were corrected for burnup of target and product activity, decay during and after irradiation, and gamma self-absorption. The values in the table represent averages of several different samples at each level. In all cases, these radial flux gradients were less than 5%. A more detailed radial flux map was not determined since all measured values deviated by less than 3% from the averages in Table I-11. All of the data are well fit by the equation

$$A(x) = A(0) (1 + bx + cx^2) \quad (\text{I-16})$$

where A is the activity at height x. The average values of the parameters b and c for the three different reactions are $b = -1.015 \times 10^{-2}$ and $c = -7.614 \times 10^{-4}$. The maximum activity position was determined to be at about -6.7 cm below midplane.

The maximum activities were used as input to the STAY'SL least-squares adjustment computer code to adjust the flux spectrum. The input spectrum was taken from previous spectral measurements in ORR.³³ The resultant neutron fluences are listed in Table I-12. Damage parameters were then calculated with the SPECTER³⁴ computer code, and resultant dpa and helium values are listed for various elements in Table I-13. The values in Tables I-12 and I-13 are given at the maximum flux position. To obtain values at other heights, simply use Eq. I-16. The only exception to this prescription is

for nickel or 316SS. The thermal effect in nickel depends nonlinearly on the thermal neutron fluence.³⁵ Helium and dpa values for 316SS are listed as a function of height in Table I-14.

The MFE-6J experiment was run at the same time as the 7J experiment. Dosimetry samples were also received from this run, and they are now being analyzed. These experiments were the final runs in ORR since this reactor has now been decommissioned.

Table I-11. Measured Activation Rates for ORR-MFE 7J (values normalized to 30 MW; accuracy $\pm 2\%$)

Height, cm	Activation Rate, ^a atom/atom-s		
	⁵⁹ Co(n, γ) ⁶⁰ Co ($\times 10^{-9}$)	⁵⁴ Fe(n, p) ⁵⁴ Mn ($\times 10^{-11}$)	⁴⁶ Ti(n, p) ⁴⁶ Sc ($\times 10^{-12}$)
2.3	6.38	-	-
0.4	6.77	1.30	1.70
-0.8	7.07	1.30	1.72
-1.0	6.87	1.31	1.73
-1.5	-	-	1.74
-3.2	6.87	1.33	1.73
-5.5	6.87	1.35	1.73
-9.5	6.94	1.36	1.76
-11.8	6.62	1.33	1.74
-14.0	6.52	1.29	1.70
-18.8	6.12	1.22	1.61
-21.6	5.51	1.15	1.50

^aValues represent averages of radial flux monitors; radial gradients are $< 5\%$.

Table I-12. Neutron Fluences for ORR-MFE 7J (maximum values at -6.7 cm below midplane)

Energy	Fluence, 10^{21} n/cm ²	Uncertainty, %
Total	27.0	7.0
Thermal (< 0.5 eV)	8.07	7.0
0.5 eV-0.1 MeV	9.46	12.0
> 0.1 MeV	9.47	10.0
> 1 MeV	5.14	12.0

2. Production of ⁴⁹V, ⁹³Mo, and ^{93m}Nb near 14 MeV (L. R. Greenwood, D. L. Bowers, and A. Intasorn)

Measurements have been completed for the production of several long-lived isotopes at neutron energies near 14 MeV. Such data are needed to predict the activation of fusion reactor materials, especially for waste material evaluations. Similar experiments have been reported previously.³⁶⁻³⁸ The samples were irradiated at the Rotating Target Neutron Source II at Lawrence Livermore National Laboratory. Details of the neutron flux and energy distributions have been published.³⁶ The metallic samples of V, natural Mo, and ⁹⁴Mo enriched Mo were pressed into discs measuring 3-mm OD by 1-mm thick. The samples were irradiated over many months to fluences as high as 10^{18} n/cm². We have already published results for the production of ^{91m}Nb (650 y) and ⁹⁴Nb (20,300 y).³⁶

Table I-13. Damage Parameters for ORR-MFE 7J (maximum values at -6.7 cm; use gradients for other heights)

Element		dpa	He, appm
Al		12.6	5.7
Ti		8.0	4.3
V		8.9	0.21
Cr		8.0	1.4
Mn		8.5	1.2
Fe		7.1	2.4
Co		8.1	1.2
Ni	Fast	7.5	34.0
	Thermal	1.3	736.0
	Total	8.8	770.0
Cu		6.8	2.1
Nb		6.8	0.45
Mo		5.0	-
316SS ^a		7.4	102.0

^a316 SS: Fe(0.645), Ni(0.13), Co(0.18), Mn(0.019), Mo(0.026).

Table I-14. Damage Parameter Gradients for 316 SS in ORR-MFE 7J

Height, cm	dpa	He, appm
0	7.19	97.0
-4	7.40	101.0
-8	7.43	102.0
-12	7.28	99.0
-16	6.95	91.0
-20	6.45	80.0
-24	5.77	66.0

Following the irradiation, samples were analyzed for the presence of long-lived activities by a combination of chemical separations, X-ray counting, and liquid scintillation counting. Ion-exchange separations of Mo and Nb and Mn and V were performed. Details of the Mo-Nb separation were published in a previous report.³⁹ Thin samples were then deposited for X-ray counting relative to a ⁵⁵Fe standard.

Table I-15 lists the results for ⁴⁹V (331 d), ^{93m}Nb (16 y), and ⁹³Mo (3500 y). The measured cross sections of 258 mb for ⁴⁹V, 550 mb for ⁹³Mo, and 0.75 mb for ^{93m}Nb were then used to calculate the production of these radioisotopes in a fusion first-wall material with the STARFIRE reactor design. The results show that we will produce about 2.8 mCi/cm³ of ⁴⁹V in vanadium, and 28 mCi/cm³ of ⁹³Mo and 106 mCi/cm³ of ^{93m}Nb in molybdenum. None of these reactions has been measured previously; hence, our data are the only reliable determination of these activities in fusion materials. Table I-15 also summarizes our work on other long-lived isotopes.

Table I-15. Production of Long-Lived Isotopes Near 14 MeV

Reaction	Cross Section, mb	Half-Life, y	Activity, ^a mCi/cm ³
⁵⁰ V(n,2n) ⁴⁹ V	258 ± 39	0.90	2.8
⁵⁶ Fe(n,2n) ⁵⁵ Fe	454 ± 35	2.7	25,000
⁶³ Cu(n,p) ⁶³ Ni	54 ± 4	100	1795
⁶⁴ Ni(n,2n) ⁶³ Ni	958 ± 64	100	227
⁶⁰ Ni(n,2n) ⁵⁹ Ni	104 ± 25	7.5 × 10 ⁴	1.0
⁹⁴ Mo(n,p) ⁹⁴ Nb	55 ± 6	2.0 × 10 ⁴	---
⁹⁴ Mo(n,x) ⁹⁴ Nb	7.8 ± 0.8	2.0 × 10 ⁴	0.77
⁹² Mo(n,2n) ⁹¹ Nb	603 ± 119	350.0	243
⁹⁴ Mo(n,2n) ⁹³ Mo	550 ± 136	3500.0	28
⁹⁴ Mo(n,x) ^{93m} Nb	5.7 ± 0.9	16.1	---
⁹⁵ Mo(n,x) ^{93m} Nb	1.36 ± 0.27	16.1	---
⁹⁴ Mo(n,x) ⁹³ mNb	0.75 ± 0.11	16.1	106

^aSTARFIRE reactor; first wall spectrum; 21.6 MW-y/m²; 3000-day cooling; production from natural element.

Work is continuing on the production of other long-lived isotopes such as ¹⁴C (5730 y), ⁹³Zr (1,500,000 y), and ⁹²Nb (3,700,000 y).

3. Nuclear Reaction Cross-Section Calculations at 50-200 MeV (A. Intasorn and L. R. Greenwood)

We have previously reported on foil activation measurements for strategic defense initiative (SDI) applications.⁴⁰ Experiments were conducted at the ANL Intense Pulsed Neutron Source (IPNS) using 50, 113, and 256 MeV protons stopped in thick aluminum and uranium targets. Various activation products, which were produced by secondary neutron emission from the targets, were measured by gamma spectroscopy. The resultant activities were then used to determine the neutron yields and energy distributions with the STAY'SL computer code. Our ability to interpret these integral activity measurements depends on our knowledge of the energy-dependent activation cross sections. Unfortunately, these cross sections are not well-known and very difficult to directly measure with neutrons. Hence, we have used a combination of proton measurements⁴¹ and computer calculations to determine the activation cross sections. Previously, these calculations were done with semiempirical models of the nuclear spallation process. However, such calculations were found to not agree very well with measurements. Consequently, we decided to evaluate other computer codes which might provide a better estimate of the desired cross sections.

We recently obtained a copy of the ALICE/LIVERMORE 85 computer code.^{42,43} This code includes pre-equilibrium effects and has a variety of nuclear model options. To test the validity of the calculations, we have calculated the cross sections for proton-induced activation of copper, since the results can be directly compared to our earlier measurements taken at the IPNS.⁴¹ ALICE is based on a compound nucleus evaporation model with some particles in a precompound or pre-equilibrium condition. The decay of these excited particles is described by a hybrid model. We have chosen to use this model with an exciton number of three and a mean free path multiplier of two. The compound nucleus is described by a Fermi gas model with level density parameters. Nuclear masses are calculated from the Myers-Swiatecki-Lysekil mass formula, including shell corrections and pairing effects. Required inverse cross sections were calculated with an optical model. Other options (such as a geometry-dependent hybrid model, a sharp cutoff instead of the optical model for inverse reactions, mass tables, and normal pairing energy shifts) were found to only weakly affect the calculated reaction cross sections.

Calculations for proton-induced activation in copper are compared with our measurements in Figs. I-16 to I-19. The ALICE calculations generally predict the approximate shape of the cross section vs. proton energy curve; however, the absolute cross-section values often disagree by a factor of two or more. Hence, some renormalization may be required. One of the questions which we wanted to answer is whether or not there is any difference between proton- and neutron-induced reactions. Above about 100 MeV one would expect reactions to be charge independent, and spallation computer codes often make this assumption. This question is crucial to the determination of some of our activation cross sections since, if true, we can use proton measurements to estimate neutron data. Figures I-18 and I-19 compare the neutron and proton results for ^{51}Cr and ^{60}Co , respectively. As can be seen, there is no difference between neutron and proton results for ^{51}Cr ; however, the neutron results are about a factor of three higher for ^{60}Co . This difference is not unexpected since ^{60}Co is a favored reaction product from the $^{63}\text{Cu}(n,\alpha)$ reaction, which has a threshold at about 3 MeV and reaches about 50 mb at 10 MeV. Reactions which depend mainly on the spallation process, such as ^{51}Cr , show no preference for neutrons or protons, confirming our assumptions.

Although the absolute results from ALICE are somewhat disappointing, the code still does a better job of describing the energy-dependent cross section than previous semiempirical spallation models. Hence, we plan to explore further calculations for other targets and energies to see if we can improve on our activation cross-section libraries. For example, we could renormalize the calculations for reactions where some proton data are available and then use the results for other unmeasured reaction products. Eventually, we expect to receive time-of-flight measurements of the neutron spectra which are now in progress at Los Alamos National Laboratory. Such data could then be used to further test and adjust our cross section libraries above 50 MeV.

Fig. I-16.

Measured and Calculated (ALICE) Proton-Induced Activation of Copper to ^{52}Mn

Fig. I-17.

Measured and Calculated Activation of
Copper to ^{56}Co

Fig. I-18.

Measured and Calculated Activation of
Copper to ^{51}Cr . Note that the curves for
proton- and neutron-induced reactions are
nearly identical.

Fig. I-19.

Measured and Calculated Activation of Copper to ^{60}Co . The cross sections for the neutron-induced reactions are higher than proton-induced reactions due to a favored $^{63}\text{Cu}(n,\alpha)$ reaction at lower energies.

4. Dosimetry and Damage Calculations for the ORR-MFE 4A/4B Experiments

The MFE 4A and 4B experiments (1,077 and 995.5 FPD, respectively) in the ORR reactor used spectral-tailoring techniques to obtain a desired fusion reactor-like helium-to-dpa ratio in stainless steel. Initially, the experiments produced helium via the two-stage thermal neutron reactions on ^{58}Ni . After a lengthy exposure, the samples were placed in a hafnium core piece. This had the effect of reducing the thermal neutron flux by about 50%, thereby limiting further production of helium while permitting continued displacement damage. A brief summary of the exposure histories is as follows:

MFE-4A			MFE-4B		
Dates	Exposure, MWD	Core Piece	Dates	Exposure, MWD	Core Piece
6/12/80-4/26/82	12,189	Al, H ₂ O	4/22/81-10/20/82	12,720	A, H ₂ O
9/23/82-12/7/82	1,866	Al, H ₂ O	7/29/83-12/31-84	13,492	Al, Solid
12/8/82-5/1/84	11,562	Al, Solid	2/5/85-6/26/85	3,654	Hf Sleeve
5/1/84-1/20/85	6,693	Hf Sleeve	Total	29,866	
Total	32,310				

The 4A experiment was in the E3 position, while 4B was at E7. The complete, more detailed irradiation histories were used to correct for decay of activities during irradiation and to determine helium production. Some of the dosimeters were removed from the 4A experiment in January 1981 after 5471 MWD and in April 1982 at 12,189 MWD. Some of the dosimeters in 4B were removed in October 1982 at 12,720 MWD. These results were all reported previously.⁴⁴⁻⁴⁶ As each dosimeter was removed, a new one was inserted to take its place. For both experiments, some of the dosimeters remained with the samples for the entire exposure history.

Each dosimeter consisted of a stainless steel tube, 0.16-cm OD by 6.98-cm long (1/16 in. by 2.75 in.), and contained small samples of Fe, Ni, Co-Al, Ti, Nb, Cu, and 80% Mn-Cu, along with helium monitors from Rockwell International. All of the samples were gamma counted, and the corrected activation rates are shown in Tables I-16 to I-19. Dosimeters were located on both the upper and lower levels and inside and outside of a stainless steel capsule which contained the NaK and experimental samples. Exact locations are given for each sample in Tables I-16 to I-19. Some of the dosimetry wires were lost because some of the stainless dosimetry tubes had burst or the welds had failed, thereby allowing extreme oxidation of some materials. In particular, many of the Co-Al alloy, Ti, and Mn-Cu alloy wires were lost. Nevertheless, we were able to analyze adequate samples from all of the runs to determine the required activation rates for spectral analysis.

To determine the effect of hafnium on the activities, a special experiment was run at lower power on February 25-26, 1984, the results of which were published.⁴⁷ In that experiment, the Co and Fe captive gamma reactions were about 56% lower when covered with 0.040 in. (0.102 cm) of hafnium. Assuming a similar reduction in the present experiment, irradiation history corrections were generated for all reactions. The results, as listed in Tables I-16 to I-19, are in good agreement with previous experiments,⁴⁴⁻⁴⁶ indicating that the corrections are appropriate.

Table I-16. Activation Rates for ORR-MFE 4A3^a

Reaction	Ht, in.	(cm)	Activity, at./at.-s	
			Inner	Outer
⁵⁸ Fe(n,α) ⁵⁹ Fe	-0.63	(-1.60)	1.74 x 10 ⁻¹⁰	1.90 x 10 ⁻¹⁰
	-2.53	(-6.43)	1.76 x 10 ⁻¹⁰	1.76 x 10 ⁻¹⁰
	-3.69	(-9.37)		1.82 x 10 ⁻¹⁰
	-3.94	(-10.0)	1.65 x 10 ⁻¹⁰	
	-5.84	(-14.8)	1.57 x 10 ⁻¹⁰	1.67 x 10 ⁻¹⁰
⁵⁹ Co(n,γ) ⁶⁰ Co	-4.25	(-10.8)		4.41 x 10 ⁻⁹
⁹³ Nb(n,γ) ⁹⁴ Nb	-1.00	(-2.54)	3.08 x 10 ⁻¹⁰	
	-1.81	(-4.60)	2.96 x 10 ⁻¹⁰	2.74 x 10 ⁻¹⁰
	-4.44	(-11.3)		3.03 x 10 ⁻¹⁰
	-5.13	(-13.0)	2.73 x 10 ⁻¹⁰	2.85 x 10 ⁻¹⁰
⁵⁴ Fe(n,p) ⁵⁴ Mn	-0.63	(-1.60)	1.10 x 10 ⁻¹¹	1.18 x 10 ⁻¹¹
	-2.53	(-6.42)	1.11 x 10 ⁻¹¹	1.14 x 10 ⁻¹¹
	-3.69	(-9.37)		1.21 x 10 ⁻¹¹
	-3.94	(-10.0)	1.09 x 10 ⁻¹¹	
	-5.84	(-14.8)	1.01 x 10 ⁻¹¹	1.15 x 10 ⁻¹¹
⁴⁶ Ti(n,p) ⁴⁶ Sc	-1.59	(-4.04)	1.58 x 10 ⁻¹²	1.67 x 10 ⁻¹²
	-4.91	(-12.5)	1.46 x 10 ⁻¹²	1.64 x 10 ⁻¹²
⁶³ Cu(n,α) ⁶⁰ Cu	-2.06	(-5.23)	7.29 x 10 ⁻¹⁴	7.21 x 10 ⁻¹⁴
	-4.06	(-10.3)		0.02 x 10 ⁻¹⁴
	-5.38	(-13.7)	6.85 x 10 ⁻¹⁴	7.33 x 10 ⁻¹⁴
⁵⁵ Mn(n,2n) ⁵⁴ Mn	-0.81	(-2.06)	3.32 x 10 ⁻¹⁴	3.61 x 10 ⁻¹⁴
	-3.88	(-9.85)		4.66 x 10 ⁻¹⁴
	-4.13	(-10.5)	3.21 x 10 ⁻¹⁴	

^a1078 FPD (entire run); 30 MW.

Table I-17. Activation Rates for ORR-4A-Mod^a

Reaction	Ht, in.	(cm)	Activity, at./at.-s	
			Inner	Outer
⁵⁸ Fe(n,α) ⁵⁹ Fe	-0.53	(-1.35)	1.75 x 10 ⁻¹⁰	1.87 x 10 ⁻¹⁰
	-2.56	(-6.50)	1.80 x 10 ⁻¹⁰	
	-3.84	(-9.75)	1.76 x 10 ⁻¹⁰	
	-5.88	(-14.9)	1.47 x 10 ⁻¹⁰	
⁵⁹ Co(n,γ) ⁶⁰ Co	-0.69	(-1.75)	4.07 x 10 ⁻⁹	4.34 x 10 ⁻⁹
⁹³ Nb(n,γ) ⁹⁴ Nb	-2.19	(-5.56)	2.86 x 10 ⁻¹⁰	2.99 x 10 ⁻¹⁰
	-5.28	(-13.4)	2.746 x 10 ⁻¹⁰	
⁵⁴ Fe(n,p) ⁵⁴ Mn	-0.53	(-1.34)	1.09 x 10 ⁻¹¹	1.17 x 10 ⁻¹¹
	-2.56	(-6.50)	1.09 x 10 ⁻¹¹	
	-3.84	(-9.75)	1.06 x 10 ⁻¹¹	
	-5.88	(-14.9)	0.97 x 10 ⁻¹¹	
⁴⁶ Ti(n,p) ⁴⁶ Sc	-2.06	(-5.23)		1.65 x 10 ⁻¹²
⁶³ Cu(n,α) ⁶⁰ Cu	-2.31	(-5.87)		8.20 x 10 ⁻¹⁴

^a672 FPD (9/23/82 to 1/20/85); 30 MW.Table I-18. Activation Rates for ORR-MFE 4B/2^a

Reaction	Ht, in.	(cm)	Activity, at./at.-s	
			Inner	Outer
⁵⁸ Fe(n,α) ⁵⁹ Fe	-0.72	(-1.83)		1.60 x 10 ⁻¹⁰
	-2.41	(-6.12)		1.75 x 10 ⁻¹⁰
	-4.03	(-10.2)	1.74 x 10 ⁻¹⁰	1.84 x 10 ⁻¹⁰
	-5.72	(-14.5)	1.63 x 10 ⁻¹⁰	1.65 x 10 ⁻¹⁰
⁵⁹ Co(n,γ) ⁶⁰ Co	-4.20	(-10.7)	4.31 x 10 ⁻⁹	4.42 x 10 ⁻⁹
⁹³ Nb(n,γ) ⁹⁴ Nb	-5.37	(-13.6)	2.96 x 10 ⁻¹⁰	
	-4.88	(-12.4)	2.74 x 10 ⁻¹⁰	2.79 x 10 ⁻¹⁰
⁵⁴ Fe(n,p) ⁵⁴ Mn	-0.72	(-1.83)		1.16 x 10 ⁻¹¹
	-2.41	(-6.12)		1.24 x 10 ⁻¹¹
	-4.03	(-10.2)	1.11 x 10 ⁻¹¹	1.25 x 10 ⁻¹¹
	-5.72	(-14.5)	1.05 x 10 ⁻¹¹	1.16 x 10 ⁻¹¹
⁴⁶ Ti(n,p) ⁴⁶ Sc	-4.63	(-11.8)	1.48 x 10 ⁻¹²	1.67 x 10 ⁻¹²
⁶³ Cu(n,α) ⁶⁰ Cu	-5.38	(-13.7)	7.11 x 10 ⁻¹⁴	7.82 x 10 ⁻¹⁴
⁵⁵ Mn(n,2n) ⁵⁴ Mn	-1.81	(-4.60)	3.06 x 10 ⁻¹⁴	
	-5.13	(-13.0)	3.17 x 10 ⁻¹⁴	3.54 x 10 ⁻¹⁴

^a996 FPD (entire run); 30 MW.

There are two other conclusions which can be made comparing the modified (solid Al and Hf) portion of the run. In the hafnium experiment we observed a reduction of 5-10% in the fast reaction rates, which is not evident in the present data. There are two possible explanations. First, the reactor may have operated at higher flux to offset the hafnium effect in order to maintain a 30 MW power level. Second, although parts of the modified runs were conducted using a solid aluminum core piece, this seems to have had little effect on the activities inside the assembly, although a small effect (5-10%) is apparent in the outer dosimeters.

Table I-19. Activation Rates for ORR-MFE 4B/Mod*

Reaction	Ht, in.	(cm)	Activity, at./at.-s	
			Inner	Outer
$^{58}\text{Fe}(n,\alpha)^{59}\text{Fe}$	-0.53	(-1.35)	1.87×10^{-10}	1.83×10^{-10}
	-2.63	(-6.68)	1.89×10^{-10}	1.83×10^{-10}
	-3.84	(-9.75)	1.76×10^{-10}	1.95×10^{-10}
	-4.94	(-12.5)	1.79×10^{-10}	
	-5.94	(-15.0)	1.56×10^{-10}	1.73×10^{-10}
$^{59}\text{Co}(n,\gamma)^{60}\text{Co}$	-4.00	(-10.2)	3.94×10^{-9}	4.27×10^{-9}
$^{93}\text{Nb}(n,\gamma)^{94}\text{Nb}$	-2.19	(-5.56)	2.95×10^{-10}	3.04×10^{-10}
	-2.88	(-7.31)	2.75×10^{-10}	
	-4.19	(-10.6)	2.70×10^{-10}	3.08×10^{-10}
	-5.50	(-14.0)	2.72×10^{-10}	3.01×10^{-10}
$^{54}\text{Fe}(n,p)^{54}\text{Mn}$	-0.53	(-1.35)	1.09×10^{-11}	1.15×10^{-11}
	-2.63	(-6.68)	1.09×10^{-11}	1.14×10^{-11}
	-3.84	(-9.75)	1.09×10^{-11}	1.20×10^{-11}
	-4.94	(-12.5)	1.07×10^{-11}	
$^{46}\text{Ti}(n,p)^{46}\text{Sc}$	-5.94	(-15.0)	1.00×10^{-11}	1.10×10^{-11}
	-2.06	(-5.23)	1.48×10^{-12}	1.56×10^{-12}
	-4.44	(-11.3)	1.41×10^{-12}	
$^{63}\text{Cu}(n,\alpha)^{60}\text{Cu}$	-5.38	(-13.7)	1.39×10^{-12}	1.56×10^{-12}
	-2.31	(-5.87)	7.21×10^{-14}	7.79×10^{-14}
	-4.69	(-11.9)	6.95×10^{-14}	
	-5.63	(-14.3)	6.92×10^{-14}	8.12×10^{-14}

*572 FPD (7/29/83 to 6/26/85); 30 MW.

The activities given in Tables I-16 to I-19 can all be fit by a polynomial, as follows:

$$f(Z) = f(\text{max}) [1 + C (X - X_o)^2] \quad (\text{I-17})$$

where X_o is the position of the flux maximum -3 in. (-7 cm) below midplane, $f(\text{max})$ is the maximum activity, and C is a constant. For the present results $X_o = -2.3$ in. (-5.8 cm), $C = -5.40 \times 10^{-3}$ for MFE 4A and $X_o = -3.1$ in. (-7.9 cm), $C = -1.4 \times 10^{-2}$ for MFE 4B. This equation can be used in general to describe fluence and damage rates within the assembly. The inner rates are of most interest since they represent the materials locations.

The neutron spectrum was determined at the maximum flux location [-3 in. (-7 cm)] by using the STAY'SL least-squares adjustment code. The adjustments to the spectrum were generally small (<20%), and the results are in good agreement with previous measurements.⁴⁴⁻⁴⁷ The initial spectra were calculated by R. A. Lillie (ORNL).⁴⁸ The adjusted fluences are listed in Table I-20. Damage calculations were performed for the net exposure in both the 4A and 4B irradiations, and the results are given in Table I-21. Since the hafnium liner appears to have had little effect on the fast neutron flux, the damage rates (dpa and helium production) were nearly constant throughout the entire irradiation histories. However, the helium accumulation rate in nickel was reduced by about a factor of 0.2 during the hafnium-covered exposure. This assumes the hafnium effect which we measured,⁴⁷ as discussed previously. Helium in nickel was thus computed assuming a reduced net thermal fluence. Although there is some uncertainty in this procedure, our results are not very sensitive to the exact hafnium reduction factor. This is true because most of the helium was generated during the uncovered exposure. Hence, we estimate that the helium data for nickel are accurate to about $\pm 10\%$. Helium data will also be available later from Rockwell International. We should also mention that previous calculations for nickel agreed very well with the helium measurements.⁴⁴⁻⁴⁵ The helium and dpa gradients for 316 stainless steel are indicated by the data in Table I-22.

Table I-20. Neutron Fluences for ORR-MFE 4A/4B (values inside the assembly at maximum flux)

	Fluence, 10^{22} n/cm ²	
	MFE 4A ^{a,b}	MFE 4B ^{a,c}
Total	4.23	3.96
Thermal (<0.5 eV)	1.28	1.24
0.5 eV-0.11 MeV	1.33	1.26
>0.11 MeV	1.62	1.46
>1 MeV	0.91	0.83

^aValues assume 223.1 FPD under Hf for 4A and 121.8 FPD for 4B.

^bExposure, 1078.4 FPD.

^cExposure, 995.5 FPD.

Table I-21. Damage Parameters for ORR-MFE 4A/4B (values at maximum flux location, -2.3 in. for A, -3.1 in. for B)

Element		MFE 4A		MFE 4B	
		He, appm	dpa	He, appm	dpa
Al		9.95	21.80	8.84	19.90
Ti		7.75	14.00	7.06	12.82
V		0.35	15.50	0.31	14.17
Cr		2.49	13.94	2.23	12.76
Mn ^a		2.07	14.79	1.84	13.53
Fe		4.34	12.40	3.88	11.34
Co ^a		2.06	14.01	1.83	12.81
Ni	Fast	63.03	13.01	56.84	11.89
	⁵⁹ Ni	<u>1781</u>	<u>3.14</u>	<u>1580</u>	<u>2.79</u>
	Total	1844	16.15	1637	14.68
Cu	Fast	3.04	11.92	2.81	10.89
	⁶⁵ Zn	<u>0.49</u>	<u>--</u>	<u>0.46</u>	<u>--</u>
	Total	3.53	11.92	3.27	10.89
Zr		0.38	12.85	0.33	11.73
Nb		0.82	11.85	0.73	10.82
Mo		--	8.69	--	7.93
Ta		--	5.99	--	5.48
316SS ^b		243	13.12	216	12.00
He/DPA		18.5		13.0	

^aThermal neutron self-shielding may reduce damage (dpa).

^b316SS: Fe(0.645), Ni(0.13), Cr(0.18), Mn(0.019), Mo(0.026).

Samples have been received from the 60°C region of the ORR-MFE7J experiment and analysis is in progress. Samples from the 200°C region should be received shortly. We are also expecting samples from the CTR 49-56 experiments in the High Flux Isotopes Reactor.

Table I-22. Helium and Damage Gradients in 316SS for ORR-MFE 4A/4B

Height, in. (cm)	MFE 4A		MFE 4B	
	He, appm	dpa	He, appm	dpa
0	232	12.7	170	10.3
-1 (-2)	235	13.0	194	11.2
-2 (-5)	243	13.1	210	11.8
-3 (-8)	242	13.1	216	12.0
-4 (-10)	237	12.9	212	11.8
-5 (-13)	228	12.6	198	11.4
-6 (-15)	214	12.1	176	10.5

5. Activation of Long-Lived Activities in Rare-Earth Materials

A joint project has been initiated with Don Smith (Engineering Physics, ANL), Bob Haight (LANL), and Y. Ikeda (JAERI) to measure the production of long-lived isotopes in the rare-earth materials Tb, Hf, and Eu. Four identical packets of material have been assembled, each measuring 1-in. (2.5-cm) OD by 5/8-in. (1.6-cm) thick. Each packet contains plastic containers of HfO_2 , Tb_4O_7 , and Eu_2O_3 , as well as Ag and Ni, Cu, Fe, and Ti dosimetry foils.

Two packets have already been irradiated at accelerator neutron sources, one in the broad-spectrum Be(d,n) field at the ANL fast neutron generator and the other in a 10 MeV H(p,n) neutron field at LANL. The other packets have been sent to Japan for irradiation in the 14 MeV T(d,n) field at the Fast Neutron Source (FNS) facility at JAERI. All of the samples will then be gamma counted at Argonne, with a duplicate count in Japan.

The long-lived activities which we plan to measure include $^{108\text{m}}\text{Ag}$ (127 y) from Ag; $^{178\text{m}}\text{Hf}$ (31 y) from Hf; $^{150\text{m}}\text{Eu}$ (36 y), ^{152}Eu (13.3 y), and ^{154}Eu (8.8 y) from Eu; and ^{158}Tb (150 y) from Tb. We can also measure ^{63}Ni (100 y) from Cu. The dosimetry foils will be used to determine the neutron fluence and energy spectra from the $^{54}\text{Fe}(n,p)^{54}\text{Mn}$, $^{54}\text{Fe}(n,\alpha)^{51}\text{Cr}$, $^{63}\text{Cu}(n,\alpha)^{60}\text{Co}$, $^{58}\text{Ni}(n,p)^{58}\text{Co}$, $^{58}\text{Ni}(n,pn)^{57}\text{Co}$, $^{58}\text{Ni}(n,2n)^{57}\text{Ni}$, $^{46}\text{Ti}(n,p)^{46}\text{Sc}$, $^{47}\text{Ti}(n,p)^{47}\text{Sc}$, and $^{48}\text{Ti}(n,p)^{48}\text{Sc}$ reactions.

For the two irradiations at ANL and LANL, we have already measured the long-lived reactions on Eu. In all of the other cases, we must wait at least six months for shorter-lived activities to decay prior to looking for the longer-lived isotopes of interest.

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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 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 cell, or canyon facility. The development of centrifugal contactors for feed- and site-specific applications is also an important part of the effort.

Two other projects are underway: one to determine the feasibility of substituting low-enriched uranium for the high-enriched uranium currently used in producing fission-product ^{99}Mo , and another to develop a separation process for red water treatment.

A. Generic TRUEX Model Development (J. M. Copple)

The first-generation Generic TRUEX Model for the Macintosh computer is complete. The model has the capability to calculate distribution ratios for the important components of acidic nitrate-based TRU-containing waste and high-level waste streams in TRUEX-process flowsheets for either the TRUEX-TCE or the TRUEX-NPH solvent. All calculations are based on an operating temperature of 25°C . The GTM also calculates the concentration profile of feed components in flowsheets that are designed by the user and generated by the model. Results are displayed in tabular and graphical form. The space and cost requirements for installing a solvent extraction process using an Argonne-design centrifugal contactor in a canyon, shielded cell, or glovebox are estimated by the model. All these calculations are performed in a user-friendly mode that allows persons with limited computer knowledge to use the model. Help commands are available during the input of information to explain the necessary form of the input.

There are several limitations to this version of the GTM. Using the model outside the bounds of these limitations will detract from the usefulness of the information calculated by the model. Future versions of the model are expected to mitigate these limitations.

The major limitation of the first-generation GTM is its inability to handle solvent-loading effects. Distribution ratios, except for nitric acid, assume tracer concentrations of the extractable species, and inaccurate results occur if the model is used to calculate distribution ratios and flowsheets where the concentrations of extractable species are high enough to reduce significantly the concentration of CMPO due to its complexation of these species. For example, if the concentration of total extractable rare earth elements (REE) in the TRUEX-NPH solvent were 0.02M, 30% of the CMPO would be complexed $[(3 \text{ mol CMPO/mol REE}) \times 0.02\text{M} = 0.06\text{M}; 0.06\text{M CMPO}_{\text{complexed}}/0.2\text{M CMPO}_{\text{total}} = 30\%]$. Due to the third-order dependence of the CMPO concentration on the distribution ratio of americium, extraction of americium by the solvent would be reduced to $(0.7)^3 = 34\%$ of the value without loading of the solvent by rare earth elements.

A second limitation is that distribution ratios are only calculated at 25 °C. In general, distribution ratios increase as temperature decreases. For example, raising the temperature from 25 °C to 50 °C decreases the distribution ratios of HTcO_4 by a factor of 3.2 at low acidities and 1.2 at high acidities. Over the same temperature range, the distribution ratios of rare earth and actinide elements decrease by a factor of -1.5 at low and -2.6 at high nitric acid concentrations.

A third limitation is that the model has been designed to calculate flowsheets run with centrifugal contactors only. The Argonne-design centrifugal contactor limits the contact time between the aqueous and organic phases to ~3 s. This limitation is a problem for the extraction of two metal ions, iron and ruthenium, both of which have time-dependent extraction behavior. (Because the extraction of uncomplexed zirconium by the TRUEX solvents is substantial, we have allowed for calculating an addition of oxalic acid to the feed to complex zirconium so that its distribution ratios are dropped to ≤ 0.01 . This addition allows us to neglect its time-dependent extraction behavior.) The extraction behavior of all other species reaches equilibrium in very short contact times. We have found the transformation rates of aqueous-phase ruthenium species to be low enough that, in the short contact times of the centrifugal contactor, the aqueous phase speciation can be assumed to be constant. Because the only ruthenium species that appears to be extractable by the TRUEX solvents is $\text{RuNO}(\text{NO}_3)_3$, we have modeled ruthenium extraction behavior in terms of two components: extractable $[\text{RuNO}(\text{NO}_3)_3]$ and nonextractable $[\text{RuNO}^{3+}, \text{RuNONO}_3^{2+}, \text{RuNO}(\text{NO}_3)_2^+, \text{ and oxalate complexes}]$. This approximation would not be valid for equipment where the contact time can be minutes to hours. Iron partitioning is calculated based on a kinetic model that assumes short contact time; the equations are not valid for contact times greater than 10 s.

A fifth limitation is that the distribution ratio calculations are based on only two solvent options: the TRUEX-NPH solvent (0.2M CMPO and 1.4M TBP diluted by a NPH) or the TRUEX-TCE solvent (0.25M CMPO and 0.75M TBP diluted by TCE). Variations in the concentrations of CMPO and/or TBP are not accounted for in this version of the model.

Limitations in available thermodynamic data have, in some cases, limited the accuracy in calculating the distribution ratio values with GTM. This is especially true in aqueous-phase complexation equilibria, where, for example, thermodynamic activity coefficients for oxalate and bisulfate are not available. When activities are not available, equilibria are calculated on the basis of concentrations of species and are, therefore, less accurate over wide variations in aqueous-phase composition. Limitation in the data base of thermodynamic quantities is expressed in the front end of the GTM in the form of alert statements.

In future versions of the GTM, the above limitations will be either eliminated or reduced.

The conversion of the Macintosh version of the GTM to an IBM-PC version is underway. The model is being converted because of the many IBM-PC users and because Microsoft Excel, the software package on which the GTM is based, recently became available for the IBM-PC compatible computer. The majority of the Macintosh code can be transported to IBM-PC code with minor revisions. The user interface for the Macintosh version is written in HyperCard; a similar software package does not exist for the IBM-PC, so it will be recoded using Excel. The IBM-PC version of the model will have the same capabilities as the completed Macintosh version.

B. Density Correlation at Elevated Temperatures (I. R. Tasker)

Densities of aqueous solutions are necessary to convert from molar concentration (the scale commonly used to describe feed solutions) to molal composition (the scale upon which most solution physical chemistry is based). One of the improvements required in the GTM is an ability to treat changes in density resulting from changes in temperature. Whatever method is adopted must be easily formulated into current methods of density calculations.

1. Theory

The equation used for the estimation of density of an ionic multicomponent solution, $d^{(ref)}$, at 25 °C is

$$d^{(ref)} = d_o^{(ref)} + \sum_i \frac{[M_i - [d_o^{(ref)} \cdot V_{\phi,i}^{(ref)}]] \cdot c_i^{(ref)}}{1000} \quad (II-1)$$

where $d_o^{(ref)}$ = density of pure water (g/mL)

M_i = molar mass of species i (g/mol)

$V_{\phi,i}^{(ref)}$ = apparent molar volume at infinite dilution of species i (mL/mol)

$c_i^{(ref)}$ = molarity of species i (mol/L)

The superscript "(ref)" indicates a value at reference temperatures, $T^{(ref)}$, which in this case is 25 °C, but applies equally at any temperature.

For convenience in the correlation we have used the infinite dilution value of the apparent molar volume ($V_{\phi,i}^{\infty}$) to represent the apparent molar volume ($V_{\phi,i}$) under all conditions of solution composition. At temperature T the density, $d^{(T)}$, is

$$d^{(T)} = d_o^{(T)} + \sum_i \frac{[M_i - [d_o^{(T)} \cdot V_{\phi,i}^{(T)}]] \cdot c_i^{(T)}}{1000} \quad (II-2)$$

where all terms have their previous meanings.

For pure water, $d_o^{(T)}$ has been well tabulated. A convenient relationship is one based upon the work of Sohnel and Novotny¹:

$$d_o^{(T)} = 0.99965 + (2.0438 \times 10^{-4}T) - (6.1744 \times 10^{-5} T^2) \quad (\text{II-3})$$

where T is the temperature in degrees Celsius, and the function is valid in the interval 5-100°C. In Eq. II-2, $V_{\phi,i}^{(T)}$ may be evaluated by the normal methods²⁻⁷ from density measurements as a function of temperature. Of apparent molar volumes for the 43 ionic species used in the GTM, only a little over half (24) are taken from the literature; ten are estimated; while nine are set equal to zero in the absence of any data. This lack of data at 25°C becomes even more of a problem as one moves away from the standard temperature.

In Eq. II-2, $c_i^{(T)}$ presents an interesting problem. Molarity, being a concentrational scale (as opposed to the compositional scale of molality), varies with temperature since density, and hence volume, vary with temperature. Given the concentration in molar terms at one temperature, the molarity at another temperature can be calculated if we know the respective densities. However, this is exactly what we seek to determine from the equation employing the molarities.

Suppose we have a solution of some solute which was analyzed at a temperature T1 and found to have a solute concentration of $C^{(T1)}$ molar and a density of $d^{(T1)}$. If the solution is heated to temperature T2 and has a measured density of $d^{(T2)}$, we may calculate its new concentration, $c^{(T2)}$, as follows. Assuming appropriate units, at temperature T1

$$c^{(T1)} = \frac{\text{mol}^{(T1)}}{\text{liters}^{(T1)}} \quad (\text{II-4})$$

and at temperature T2

$$c^{(T2)} = \frac{\text{mol}^{(T2)}}{\text{liters}^{(T2)}} \quad (\text{II-5})$$

Obviously,

$$\text{mol}^{(T1)} = \text{mol}^{(T2)} \quad (\text{II-6})$$

Rearranging and equating Eq. II-4 and II-5 give

$$c^{(T2)} = c^{(T1)} \cdot \left[\frac{\text{liters}^{(T1)}}{\text{liters}^{(T2)}} \right] \quad (\text{II-7})$$

Since

$$\text{density} = \text{mass}/\text{volume} \quad (\text{II-8})$$

we have

$$\text{liters}^{(T1)} = \frac{\text{mass}^{(T1)}}{\text{density}^{(T1)}} \quad (\text{II-9})$$

and

$$\text{liters}^{(T2)} = \frac{\text{mass}^{(T2)}}{\text{density}^{(T2)}} \quad (\text{II-10})$$

Similarly to Eq. II-6,

$$\text{mass}^{(T1)} = \text{mass}^{(T2)} \quad (\text{II-11})$$

Rearranging and equating Eqs. II-9 and II-10 give

$$\frac{\text{liters}^{(T2)}}{\text{liters}^{(T1)}} = \frac{\text{density}^{(T1)}}{\text{density}^{(T2)}} \quad (\text{II-12})$$

Substituting Eq. II-12 into Eq. II-7 yields

$$c^{(T2)} = c^{(T1)} \cdot \left[\frac{\text{density}^{(T1)}}{\text{density}^{(T2)}} \right] \quad (\text{II-13})$$

Introducing Eq. II-13 into Eq. II-2 gives

$$d^{(T)} = d_o^{(T)} + \left[\frac{d^{(T)}}{d^{(ref)}} \right] \cdot \sum_i \frac{\left[M_i - [d_o^{(T)} \cdot V_{\phi,i}^{(T)}] \right] \cdot c_i^{(ref)}}{1000} \quad (\text{II-14})$$

Rearranging Eq. II-14 gives

$$d^{(T)} = \frac{1000 \cdot d_o^{(T)} \cdot d^{(ref)}}{\left[1000 d^{(ref)} \right] + \left[\sum_i \left[\left[d_o^{(T)} \cdot V_{\phi,i}^{(T)} \right] - M_i \right] \cdot c_i^{(ref)} \right]} \quad (\text{II-15})$$

Substituting Eq. II-1 into Eq. II-15 gives:

$$d^{(T)} = \frac{d_o^{(T)} \cdot \left[\left[1000 \cdot d_o^{(ref)} \right] + \left[\sum_i \left[M_i - \left[d_o^{(ref)} \cdot V_{\phi,i}^{(ref)} \right] \right] \cdot c_i^{(ref)} \right] \right]}{\left[\left[1000 d_o^{(ref)} \right] + \sum_i \left[M_i - \left[d_o^{(ref)} \cdot V_{\phi,i}^{(ref)} \right] \right] \cdot c_i^{(ref)} \right] + \left[\sum_i \left[\left[d_o^{(T)} \cdot V_{\phi,i}^{(T)} \right] - M_i \right] \cdot c_i^{(ref)} \right]} \quad (\text{II-16})$$

Using Eq. II-16, one can calculate solution density at a desired temperature (subject to assumptions in the model) based on given values of c_i at a reference temperature and d_o and $V_{\phi,i}$ as a function of temperature. In this case, no calculation of $d^{(ref)}$ is necessary. However, a separate calculation of $d^{(ref)}$ can be

advantageous; if the true solution density is available from analytical measurements, then the calculated $d^{(ref)}$ can be checked against it. Moreover, the availability of an experimental density value at $T^{(ref)}$ (or for that matter any other temperature) may help overcome some of the model limitations. This is because the equations used here and those used at present in GTM approximate the value for $V_{\phi,i}$ by the infinite dilution value $V_{\phi,i}^{\circ}$ and, hence, take no account of the concentrative variation of $V_{\phi,i}$. By having one experimentally obtained density reading, we could assume empirically that

$$\left[\frac{d(T)}{d^{(ref)}} \right]^{calculated} = \left[\frac{d(T)}{d^{(ref)}} \right]^{experimental} \quad (II-17)$$

and so obtain a better estimate of the desired density.

Inspection of Eq. II-1 shows that the density estimation now depends upon obtaining for each species i

$$V_{\phi,i} = f(T) \quad (II-18)$$

$V_{\phi,i}$ is readily obtained from density measurements as

$$V_{\phi,2} = \frac{1000 (d_o - d)}{C_2 d_o} + \frac{M_2}{d_o} \quad (II-19)$$

where the subscript 2 indicates a salt; $V_{\phi,2}^{\circ}$ is obtained from Eq. II-19 and the relationship⁸:

$$V_{\phi,2} = V_{\phi,2}^{\circ} + S_v \sqrt{C_2} \quad (II-20)$$

where S_v is a constant. Subsequently, the ionic partial molar volumes at infinite dilution are obtained from the additivity principle⁹⁻¹⁴:

$$V_{\phi,MX}^{\circ} = V_{\phi,M^+}^{\circ} + V_{\phi,X^-}^{\circ} \quad (II-21)$$

Data used in our work have come from three sources. Millero³ and Hovey¹⁵ have presented $V_{\phi,i}^{\circ}$ data directly. Sohnle and Novotny have produced an extensive compilation of density data, much of it as a function of temperature. Since considerable use has been made of Sohnle and Novotny's fitting of data, a brief discussion of their method is warranted.

It should be noted that Sohnle and Novotny use the international standard units. Rewriting Eq. II-19, we have

$$V_{\phi,2} = \frac{d_o - d}{C_2 d_o} + \frac{M_2}{d_o} \quad (II-22)$$

where the terms have their prior meaning, but the units are now $V_{\phi,2}$, m^3/mol ; C_2 , mol/m^3 ; d , d_o , kg/m^3 ; M_2 , kg/mol . Combining Eq. II-22 with II-20 (which retains its form in standard units) gives

$$d = d_o + \left[\alpha C_2 \right] - \left[\beta C_2^{1.5} \right] \quad (\text{II-23})$$

where

$$\alpha = M_2 - (d_o V_{\phi,2}^\circ) \quad (\text{II-24})$$

and

$$\beta = S_v d_o \quad (\text{II-25})$$

The terms α and β are functions of temperature; the forms of their functions are not known, but Sohnel and Novotny¹ found it convenient to use

$$\alpha(T) = A + (B T) + (C T^2) \quad (\text{II-26})$$

$$\beta(T) = -[D + (E T) + (F T^2)] \quad (\text{II-27})$$

where T denotes temperature in degrees Celsius. Combination of Eqs. II-23, II-26, and II-27 gives

$$\begin{aligned} d(T) = d_o(T) &+ (A C_2) + (B C_2 T) + (C C_2 T^2) \\ &+ (D C_2^{1.5}) + (E C_2^{1.5} T) + (F C_2^{1.5} T^2) \end{aligned} \quad (\text{II-28})$$

When data are available at only a given temperature, Sohnel and Novotny¹ use

$$d = d_o + \left[G C_2 \right] + \left[H C_2^{1.5} \right] \quad (\text{II-29})$$

where $G = \alpha$ and $H = -\beta$.

For appropriate solutes, Eq. II-3 and the coefficients from the fits are substituted into Eq. II-23 at a series of temperatures to yield densities. These densities are converted from kg/m^3 to g/mL by multiplying by 0.001. They are then used in Eq. II-19 to yield values of $V_{\phi,2}$ as a function of concentration at the various temperatures; $V_{\phi,2}^\circ$ is obtained from a plot of $V_{\phi,2}$ against $(C_2)^{1/2}$, and then the additivity relation (Eq. II-21) is appropriately applied to yield $V_{\phi,i}^\circ$ as a function of temperature. The $V_{\phi,i}^\circ(T)$ data are finally fitted to a small order polynomial in (T). Details of the calculations are given below for each of the species of interest.

2. Results

Table II-1 gives the parameters for determining the apparent molar volume of ions at infinite dilution as a function of temperature. The coefficients A, B, and C listed in the table relate to the equation

$$V_{\phi,i}^\circ = A + B T + C T^2 \quad (\text{II-30})$$

where T is the temperature in degrees Celsius.

Table II-1. Coefficients^a Used in Determining the Apparent Molar Volume of Ions at Infinite Dilution

Ion	Source Species ^b	A	B	C	Notes
Ag ⁺	Ag(NO ₃)	-4.67	0.1961	-0.00185	
Cd ²⁺	Cd(NO ₃) ₂	-3.88	-0.521	0.00374	
Ni ²⁺	NiSO ₄	-33.2	0.0359	0.000052	
Sm ³⁺	SmCl ₃	-43.07	-0.0485	-0.000601	
Pr ³⁺	PrCl ₃	-42.37	-0.073	+0.00077	
La ³⁺	LaCl ₃	-36.42	-0.097	0.00086	
Nd ³⁺	NdCl ₃	-43.69	-0.066	0.00075	
Cu ²⁺	CuCl ₂	-36.79	0.472	-0.00265	c
	CuSO ₄				
TcO ₄ ⁻	NaMnO ₄	36.23	-0.0746	0.005044	d
Gd ³⁺	GdCl ₃	-39.94	-0.0642	0.000577	
Y ³⁺	YCl ₃	-40.94	-0.097	0.00086	
Ce ³⁺	g	-39.39	-0.0852	0.00081	
Pm ³⁺	h	-43.38	-0.057	0.00068	e
Eu ³⁺	i	-41.51	-0.0561	0.000586	e
Ba ²⁺	Various	-15.97	0.181	-0.00104	
Ca ²⁺	Various	-18.95	0.02632	0.000433	
Mg ²⁺	Various	-21.84	0.04538	-0.000624	
Sr ²⁺	Various	-20.47	0.0965	-0.000707	
Na ⁺	Various	-3.85	0.117	-0.000709	
Cs ⁺	Various	19.79	0.0628	-0.00027	
Rb ⁺	Various	12.33	0.0828	-0.00072	d
F ⁻	Various	-2.39	0.0600	-0.00076	
Cl ⁻	Various	16.55	0.061	-0.00065	
SO ₄ ²⁻	Various	10.88	0.179	-0.001727	
NO ₃ ⁻	Various	25.84	0.153	-0.00093	
HSO ₄ ⁻	H ₂ SO ₄	32.64	0.206	-0.000162	f
UO ₂ ²⁺	UO ₂ (ClO ₄) ₂	-6.46	0.00589	-0.00056	f
Fe ³⁺	Fe(ClO ₄) ₃	-39.89	0.461	-0.00938	f
Am ³⁺	SmCl ₃	-43.07	-0.0485	0.000601	
Cm ³⁺	GdCl ₃	-39.94	-0.0642	0.000577	

^aCoefficients of Eq. II-30. Determined from literature data.

^bSource species is species from which V_{ϕ} for ion of interest was obtained using the additivity principle.

^cOnly valid in the interval 0-70°C.

^dOnly valid in the interval 0-50°C.

^eOnly valid in the interval 0-80°C.

^fOnly valid in the interval 0-55°C.

^gLimited, poor-quality data available. Ce³⁺ was estimated as the average of Pr³⁺ and La³⁺.

^hNo data available. Pm³⁺ was estimated as average of Nd³⁺ and Sm³⁺.

ⁱLimited, poor-quality data available. Eu³⁺ was estimated as the average of Gd³⁺ and Sm³⁺.

Certain aspects of the data presented in Table II-1 are worthy of note:

- For NiSO_4 a plot of V_ϕ° vs. $T/^\circ\text{C}$ was nontypical, showing a linear increase of V_ϕ with T . Thus, there is some doubt associated with these data. Alternative data using NiCl_2 and $\text{Ni}(\text{NO}_3)_3$ were examined and rejected due to nonagreement with literature data at 25°C .
- For CuCl_2 and CuSO_4 each data set was examined at 25°C . Though neither set individually agreed with literature values, the average of the two did. Thus, it was decided to calculate V_ϕ for Cu^{2+} from each data set separately, and then average the results.
- No experimental data of any kind are available for TcO_4^- . In the GTM, V_ϕ was approximated by the similar ion ClO_4^- ; however, this value (22.83 mL/mol) was experimentally determined by A. Lao (CMT Division) and does not agree with the accepted literature value (44.12 mL/mol).³ Upon inspection of available data, we felt that MnO_4^- would be a better analog for TcO_4^- . Manganese occurs one place above technetium in the periodic table and should thus approximate the properties of technetium better.
- Only limited data are available for Y(III) . Sohnle and Novotny¹ give fits for YCl_3 at 0°C and 25°C ; in each case the data source listed is Habenschuss and Spedding.¹⁶ Based upon data for Cl^- used in the additivity principle, the fits yielded $V_\phi^\circ(\text{Y}^{3+})$ values of -40.94 and -42.85 mL/mol at 25 and 0°C , respectively.

To calculate $V_\phi^\circ(\text{Y}^{3+})$, we assumed that the temperature dependence for Y^{3+} was the same as for La^{3+} . The corresponding values for $V_\phi^\circ(\text{La}^{3+})$ are -38.32 and -36.42 mL/mol at 25 and 0°C .

The difference in V_ϕ° between the two ions is almost the same: 4.52 mL/mol for 0°C and 4.53 mL/mol for 25°C . Therefore, we used

$$V_{\phi, \text{Y}^{3+}}^\circ = -40.94 - (0.0975 T) + (0.00086 T^2) \text{ mL/mol} \quad (\text{II-31})$$

- For Ce^{3+} , data are very limited. Sohnle and Novotny¹ give fits for CeCl_3 at 25°C and $\text{Ce}(\text{NO}_3)_3$ at 15°C . Data sources for both are listed in Timmermans.¹⁷ These data were analyzed and yielded $V_\phi^\circ(\text{Ce}^{3+})$ values of -51.5 and -37.5 mL/mol at 15 and 25°C . When compared with the previously estimated value of -40.8 mL/mol and the values of other lanthanides, these data were questionable. Therefore, we decided to estimate the value of Ce^{3+} as the average of Pr^{3+} and La^{3+} , the adjacent elements in the periodic table. The data are shown in Table II-2, and the resulting equation is

$$V_{\phi, \text{Ce}^{3+}}^\circ = -39.39 - (0.0852 T) + (0.00081 T^2) \text{ mL/mol} \quad (\text{II-32})$$

- No data are available for Pm^{3+} ; we decided to estimate $V_\phi^\circ(\text{Pm}^{3+})$ as the average of $V_\phi^\circ(\text{Nd}^{3+})$ and $V_\phi^\circ(\text{Sm}^{3+})$, the neighboring elements in the periodic table. The data used are shown in Table II-3, and the resulting equation is

$$V_{\phi, \text{Pm}^{3+}}^{\circ} = -43.38 - (0.057 T) + (0.00088 T^2) \text{ mL/mol} \quad (\text{II-33})$$

- Only limited data are available for Eu(III). Sohnel and Novotny¹ give fits at 25 °C for EuCl₃ (data source listed as Ref. 18) and Eu(ClO₄)₃ (data source listed as Ref. 19). These data were analyzed and yielded $V_{\phi}^{\circ}(\text{Eu}^{3+})$ values at 25 °C of -41.69 mL/mol (from EuCl₃ data) and -45.60 mL/mol [from Eu(ClO₄)₃ data], with an average value of -43.65 mL/mol. In the absence of other data, we decided to estimate $V_{\phi}^{\circ}(\text{Eu}^{3+})$ as the average of $V_{\phi}^{\circ}(\text{Gd}^{3+})$ and $V_{\phi}^{\circ}(\text{Sm}^{3+})$, the neighboring elements in the periodic table. The data used are shown in Table II-4, and the resulting equation is

$$V_{\phi, \text{Eu}^{3+}}^{\circ} = -41.51 - (0.0561 T) + (0.000586 T^2) \text{ mL/mol} \quad (\text{II-34})$$

This equation predicts that $V_{\phi}^{\circ}(\text{Eu}^{3+})$ at 25 °C is -42.53 mL/mol, in good agreement with the other average value [from EuCl₃ and Eu(ClO₄)₃ data] of -43.65 mL/mol.

Table II-2. Data Used in Estimating Apparent Molar Volume of Ce³⁺

T, °C	$V_{\phi}^{\circ}, \text{mL/mol}$		
	La ³⁺	Pr ³⁺	Ce ³⁺
20	-38.03	-43.52	-40.77
30	-38.57	-43.86	-41.22
40	-38.95	-44.05	-41.50
50	-39.15	-44.09	-41.62
60	-39.19	-43.97	-41.58
70	-39.05	-43.70	-41.38
80	-38.74	-43.28	-41.01

Table II-3. Data Used in Estimating Apparent Molar Volume of Pm³⁺

T, °C	$V_{\phi}^{\circ}, \text{mL/mol}$		
	Pm ³⁺	Sm ³⁺	Pm ³⁺
20	-44.72	-43.80	-44.26
30	-45.00	-43.98	-44.49
40	-45.14	-44.05	-44.59
50	-45.13	-43.99	-44.56
60	-44.96	-43.82	-44.39
70	-44.65	-43.52	-44.08
80	-44.18	-43.10	-43.64

Table II-4. Data Used in Estimating the Apparent Molar Volume of Eu^{3+}

T, °C	V_{ϕ}° , mL/mol		
	Gd^{3+}	Sm^{3+}	Eu^{3+}
20	-41.00	-43.80	-42.40
30	-41.35	-43.98	-42.67
40	-41.59	-44.05	-42.82
50	-41.71	-43.99	-42.85
60	-41.72	-43.82	-42.77
70	-41.61	-43.52	-42.57
80	-41.39	-43.10	-42.25

C. Modeling of Extraction Behavior

1. Plutonium/TRUEX-TCE Modeling (I. R. Tasker)

The plutonium/TRUEX-TCE model was presented in the previous semiannual (ANL-90/15, Sec.II.E.6). The model treated solutions containing sulfuric acid in terms of speciation into the bisulfate ion, and it treated solutions containing oxalic acid in terms of total oxalic acid. However, the remaining sulfate data in the GTM were treated in terms of concentrations of SO_4^{2-} rather than HSO_4^- .

The reason for treating sulfate data as HSO_4^- was that under TRUEX conditions (and, in fact, even in the simple binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ system) H_2SO_4 behaves as a 1:1 electrolyte, yielding H^+ and HSO_4^- upon dissociation. Thus, although the rationalization for choosing HSO_4^- as the predominant species still stands, for the sake of consistency, the model has been reworked in terms of formal sulfate concentration.

The revised equation for the Pu(IV) distribution ratio with TRUEX-TCE is

$$D = \frac{K_o \{\text{NO}_3^-\}^2}{1 + B_1^N \{\text{NO}_3^-\} + B_2^N \{\text{NO}_3^-\}^2 + B_1^F [\text{HF}] + B_2^F [\text{HF}]^2 + B_1^{SN} [\text{SO}_4^{2-}] \{\text{NO}_3^-\} + B_1^S [\text{SO}_4^{2-}] + B_1^P \frac{[\text{H}_3\text{PO}_4]}{\{\text{H}^+\}} + B_2^P \left[\frac{[\text{H}_3\text{PO}_4]}{\{\text{H}^+\}} \right]^2 + B_1^{Ox} \frac{[\text{HOx}^-]_{\text{free}}}{\{\text{H}^+\}} + B_2^{Ox} \left[\frac{[\text{HOx}^-]_{\text{free}}}{\{\text{H}^+\}} \right]^2} \quad (\text{II-35})$$

Values assigned to the constants are:

$$K_o = 14746.796$$

$$B_1^N = 0.408$$

$$B_2^N = 3.782$$

$$B_1^F = 39,410$$

$$B_2^F = 27,960$$

$$B_1^{SN} = 190.2$$

$$B_1^S = 0.001283$$

$$B_1^P = 2,378$$

$$B_2^P = 0.0001346$$

$$B_1^{Ox} = 277896$$

$$B_2^{Ox} = 2008456$$

Equation II-35 is essentially the same as that given in the previous semiannual with the exceptions that $[HSO_4^-]$ is $[SO_4^{2-}]$, and the total oxalate concentration is replaced by concentration of free bioxalate (HOx^-). This second change was introduced to maintain integrity with other calculation methods in the GTM. Given below are the oxalate acid equilibria along with their equilibrium constants:

$$K_{a1} = \frac{[H^+][HOx^-]}{[H_2Ox]} \quad (II-37)$$

$$K_{a2} = \frac{[H^+][Ox^{2-}]}{[HOx^-]} \quad (II-39)$$

Rearranging Eq. II-37 and II-39 gives

$$[HOx^-] = \frac{K_{a1}[H_2Ox]}{[H^+]} \quad (II-40)$$

$$[Ox^{2-}] = \frac{K_{a2}[HOx^-]}{[H^+]} \quad (II-41)$$

Combining Eq. II-40 and II-41 gives

$$[\text{Ox}^{2-}] = \frac{K_{a1} K_{a2} [\text{H}_2\text{Ox}]}{[\text{H}^+]^2} \quad (\text{II-42})$$

The total oxalate concentration is given by

$$[\text{total oxalate}] = [\text{H}_2\text{Ox}] + [\text{HOx}^-] + [\text{Ox}^{2-}] \quad (\text{II-43})$$

Substituting Eqs. II-40 and II-41 into II-43 yields

$$[\text{H}_2\text{Ox}] = \frac{[\text{total oxalate}] [\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2}} \quad (\text{II-44})$$

and

$$[\text{HOx}^-] = \frac{[\text{total oxalate}] K_{a1} [\text{H}^+]}{[\text{H}^+]^2 + K_{a1} [\text{H}^+] + K_{a1} K_{a2}} \quad (\text{II-45})$$

Thus, calculation of free oxalic acid and free bioxalate requires knowledge of total formal oxalate concentration, free hydrogen ion concentration, and the appropriate values of K_{a1} and K_{a2} .

Total bioxalate concentration is immediately available from solution compositions. Free hydrogen ion concentration is more of a problem. Our experiments have been conducted so that hydrogen activity can be calculated using Bromley's model²⁰; free hydrogen ion concentrations have not been reported. Recalculation of all data would be a considerable task and has no guarantee of success. It would thus seem expedient to continue calculations in terms of $\{\text{H}^+\}$. The values of K_{a1} and K_{a2} are more readily obtained. Smith and Martell²¹ give the following equilibrium constants for zero ionic strength at 25°C:

$$[\text{HOx}^-] / [\text{H}^+] [\text{Ox}^{2-}], \log K_1 = 4.286$$

$$[\text{H}_2\text{Ox}] / [\text{H}^+] [\text{HOx}^-], \log K_2 = 1.252$$

Since $K_{a1} = 1/K_2$ and $K_{a2} = 1/K_1$, $K_{a1} = 0.05598$ and $K_{a2} = 5.42 \times 10^{-5}$. These values properly apply to stoichiometric equilibria constants but have here been used as the basis of hydrogen activity.

The above approximations used in calculations of oxalate speciation should be noted.

2. Acid Extraction (D. J. Chaiko)

The effect of varying TBP and CMPO concentrations on acid and metal extraction in the TRUEX process remains to be incorporated into the GTM. In both the TRUEX-TCE and TRUEX-NPH solvents. The most complete set of extraction data collected thus far is for americium and nitric acid. The modeling of solvent effects, therefore, will be based primarily on the accumulated extraction data for these two species.

The addition of TBP to CMPO solutions has the effect of simultaneously lowering Am^{3+} extraction at low nitric acid concentrations ($<1\text{M HNO}_3$) and increasing Am^{3+} extraction at high nitric acid concentrations ($>1\text{M HNO}_3$).

The influence of [TBP] on Am^{3+} extraction at low nitric acid concentrations is believed to be a result of the following: (1) because the extent of $\text{Am}(\text{NO}_3)_3$ extraction by TBP alone is equivalent to about only 1% of that observed for CMPO alone, extraction of americium by TBP is insignificant and can be ignored, (2) the formation of a mixed TBP-CMPO- HNO_3 complex reduces the concentration of free CMPO available for metal extraction at low acid concentrations, (3) at high nitric acid concentrations ($>1\text{M}$), it is assumed that TBP solvates HNO_3 in the metal complex $\text{Am}(\text{NO}_3)_3(\text{CMPO})_3(\text{HNO}_3)_n$, with TBP then being located in the outer coordination sphere.²²

In the acid extraction model for the TRUEX solvent, the separate acid extraction models developed for CMPO and TBP are combined and all extraction constants are fixed at the values for the individual extractants.²³ To improve the fit of the combined model to the data, a mixed complex term was added to the TRUEX model. The best-fitting model was obtained by using the species $\text{CMPO} \cdot \text{HNO}_3 \cdot \text{TBP}$.

Previously, HNO_3 extraction data and modeling results were presented for the TRUEX-TCE solvent in which the [CMPO] was held constant at 0.25M while the [TBP] was varied from 0.25 to 1.0M .²⁴ Additional data were collected in which the [CMPO] was adjusted to 0.40M with 0.75M TBP. No change occurred in the extraction constant K_M (current value = 1.91), and no additional extraction equilibria were required to fit the new data at 0.4M CMPO. Therefore, small variations in the compositions of the TRUEX-TCE solvent can be handled quite effectively with the current extraction model.

Nitric acid extraction data for various CMPO/TBP concentration ratios were modeled with the following species: $(\text{CMPO})_2 \cdot \text{HNO}_3$, $\text{CMPO} \cdot \text{HNO}_3$, $\text{CMPO}(\text{HNO}_3)_2$, $(\text{TBP})_2 \cdot \text{HNO}_3$, $\text{TBP} \cdot \text{HNO}_3$, and $\text{CMPO} \cdot \text{HNO}_3 \cdot \text{TBP}$. The organic phase nitric acid concentration is calculated from:

$$\begin{aligned}
 [\overline{\text{HNO}_3}] = & [\overline{\text{CMPO}}]_{\text{free}} \left[K_{C1} \{ \text{H}^+ \} \{ \text{NO}_3^- \} + 2 K_{C2} \{ \text{H}^+ \}^2 \{ \text{NO}_3^- \}^2 + K_{C3} \{ \text{H}^+ \} \{ \text{NO}_3^- \} [\overline{\text{CMPO}}]_{\text{free}} \right] \\
 & + [\overline{\text{TBP}}]_{\text{free}} \left[K_{T1} \{ \text{H}^+ \} \{ \text{NO}_3^- \} + K_{T2} \{ \text{H}^+ \} \{ \text{NO}_3^- \} [\overline{\text{TBP}}]_{\text{free}} \right] \\
 & + K_M \{ \text{H}^+ \} \{ \text{NO}_3^- \} [\overline{\text{CMPO}}]_{\text{free}} [\overline{\text{TBP}}]_{\text{free}}
 \end{aligned} \tag{II-46}$$

The fit of the model to the extraction data for aqueous acid concentrations of $10^{-2}\text{M} \leq [\text{HNO}_3] \leq 10\text{M}$ is shown in Fig. II-1. A total of 40 different aqueous and organic phase compositions are represented in the calculated line for this figure. The CMPO concentration was varied between 0.25 and 0.40M , while the TBP concentration was simultaneously varied between 0.25 and 1.0M . Similar data will be collected for the TRUEX-NPH solvent.

Fig. II-1. Calculated and Measured Nitric Acid Extraction by TRUEX-TCE Solvents at 25°C

3. Extraction Models for Miscellaneous Metals (L. Reichley-Yinger)

During this report period, the TRUEX-NPH and TRUEX-TCE extraction models for the miscellaneous metals listed in Table II-5 were included within the SASPE section of GTM. The models for these metals assume that the distribution ratios are all equal to 10^{-3} .

Table II-5. Miscellaneous Metals Included in SASPE

Fission Products	Alkali and Alkaline Earths	Transition Metals
Sr	Na	Cr
Rh	Mg	N
Pd	Ca	Cu
Ag	Rb	
Cd		
Sn		
Cs		
Ba		

Based on available literature data,²⁵⁻²⁷ the accuracy of the TRUEX-NPH model for Sr, Ba, Mg, Ca, Cr, Ni, and Cu is expected to be good to an order of magnitude, i.e., the distribution ratios for these seven metals could be as high as 10^{-2} . The model is also expected to be accurate to an order of magnitude for Cs, Na, and Rb, although no data are available, since these metals behave similarly to Sr, Ba, Mg, and Ca. In the absence of oxalic acid in the feed, the accuracy of the model is expected to be poor for Rh, Pd, Ag, and Cd because the distribution ratios measured for these metals are as high as 10^0 . However, the data also show that the presence of oxalic acid can markedly decrease the distribution ratios for these metals.

Based on our own experimental data and the literature,²⁸ the accuracy of the TRUEX-TCE model for Ag, Cd, Mg, and Ca is expected to be good to an order of magnitude, i.e., the distribution ratios for these four metals could be as high as 10^{-2} . The model is also expected to be accurate to an order of magnitude for Sr, Cs, Ba, Na, and Rb, although no data are available, since these metals behave similarly to Mg and Ca. The accuracy of the model is expected to be poor for Rh, Pd, Cr, Ni, and Cu because the distribution ratios measured for these metals are as high as 10^0 . However, the data also show that the presence of oxalic acid can decrease the distribution ratios for these metals.

Due to the lack of information, the expected accuracy of the TRUEX-NPH and TRUEX-TCE model for tin is unknown.

More accurate models could be obtained for some of the miscellaneous metals if more distribution data were available. Distribution data are needed for Rh, Pd, Ag, Cd, Cr, Ni, and Cu since the available data indicate that these metals will have distribution ratios above 10^{-2} . In particular, distribution data measured in the presence of oxalic acid, which can decrease the distribution ratios for these metals, should be informative. Distribution data are also needed for tin since it does not behave similarly to the metals that have been studied. Other metals for which there are no distribution data include Cs, Na, and Rb with TRUEX-NPH and Sr, Cs, Ba, Na, and Rb with TRUEX-TCE. However, these metals behave very similarly to Mg and Ca, so distribution data are probably not needed for them.

D. Modeling of Solvent-Loading Effects (M. C. Regalbuto)

1. Introduction

The early GTM version successfully treated the nitric-acid loading of the solvent but did not account for the effect of solvent loading by metal salts on species extraction. Since TRUEX is a waste treatment process dealing with dilute solutions of actinides, the effects of solvent loading will be, in most instances, small. But when the concentration of rare earth fission products is high, solvent loading by a combination of these species together with iron, uranium, and TRU elements can lead to solvent-loading effects. In these situations, the solvent is not loaded with only one species (e.g., uranium in the PUREX process) but by a combination of more than ten species. The calculations of solvent-loading effects on the extraction of all components are fairly straightforward but time-consuming. A mathematical algorithm that decreases the complexity of the calculations is included in the new GTM version.

A new macro "LOADING_EFFECT_MULT" has been added to the GTM in order to account for the loading of the solvent by metal salts on the extraction of species. Concentration values for every component affected by the loading and the extractant are found by the solution of a set of simultaneous nonlinear equations given by the stage-wise mass balance for every species and the extractant and from the tracer distribution ratio equation. The solution to these equations is done by a Newton-Raphson technique. Computation time is reduced by averaging components that behave in similar fashion.

2. Mathematical Model

For any particular number of components and stages, SASSE can be used to calculate the steady-state organic and aqueous concentration for any component in any given stage by using distribution ratio (D) values calculated in SASPE. However, since SASPE does not account for the solvent loading by metal salts, these D values must be corrected, and then new concentrations in both organic and aqueous phases calculated in SASSE. Therefore, an iteration process is needed among SASPE, the loading-effect module, and SASSE (see Sec.II.D.4).

In calculating D values that reflect solvent loading, the loading module uses the new organic and aqueous phase compositions for a given stage i at steady state determined by SASSE, which computes the total number of moles present in stage i for every component, i.e.,

$$m_j = m_{j,o} + m_{j,a} = f_o C_{j,o} + f_a C_{j,a} \quad (\text{II-47})$$

where m_j is the total moles of component j in stage i; $m_{j,o}$ and $m_{j,a}$ are moles of component j in the organic and aqueous phase, respectively; $C_{j,o}$ and $C_{j,a}$ are the concentrations of component j in the organic and aqueous phase, respectively (given by SASSE); and f_o and f_a are the flow rates for the organic and aqueous phase, respectively. The application of Eq. II-47 to component j will generate an equation of the form

$$(O/A) C_{j,o} + C_{j,a} = (O/A) C_{j,o}^o + C_{j,a}^o \quad (\text{II-48})$$

where (O/A) is the organic-to-aqueous flow rate for stage i, and $C_{j,o}^o$ and $C_{j,a}^o$ represent the initial concentration in both organic and aqueous phases given by SASSE, respectively. The total number of components that are affected by the loading in stage i is N.

A relation between the organic and aqueous concentrations for every component can be obtained from the tracer distribution ratio, D_j , in any given stage i:

$$D_j = k_j E^{n_j} \quad (\text{II-49})$$

where E is the extractant available, and n_j is given by the stoichiometry of the reaction between the extractant and component j. Also, from the definition of the distribution ratio in a given stage i,

$$D_j = \frac{C_{j,o}}{C_{j,a}} \quad (\text{II-50})$$

Using the distribution coefficients given by SASPE (D_j^o), the value of the constants for every j component (k_j) in Eq. II-49 can be calculated as

$$k_j = \frac{D_j^o}{\left[\frac{C_{j,o}^o}{C_{j,a}^o} \right]^{n_j}} \quad (\text{II-51})$$

where E^o is the initial extractant concentration. Now combining Eq. II-49 and II-51 gives

$$\frac{C_{j,o}}{C_{j,a}} = \frac{D_j^o}{\left[\frac{C_{j,o}^o}{C_{j,a}^o} \right]^{n_j}} \cdot E^{n_j} \quad (\text{II-52})$$

Application of Eq. II-52 to every component generates a total of N equations. The only value left to compute is the final extractant concentration E , which can be obtained in terms of the organic and aqueous compositions for the extractable components. The mass balance for the total extractant in the organic phase is given by:

$$E = E^0 - \sum_{j=1}^N n_j C_{j,o} \quad (\text{II-53})$$

3. Numerical Analysis

Equations II-48, II-52, and II-53 will yield a total of $2N + 1$ nonlinear equations, whose numerical solution can be obtained by applying a Newton-Raphson technique. Table II-6 gives the components included in the loading-effect module, along with values for n_j in Eqs. II-52 and II-53.

Table II-6. Components Included in the Loading-Effect Module and the Exponential Dependence of the Extractant for Each Component

Component	Exponential Dependence ^a
Americium	3
Plutonium (III)	3
Plutonium (IV)	2
Neptunium (IV)	2
Neptunium (V)	2
Uranium	2
Curium	3
Yttrium	3
Lanthanum	3
Cerium	3
Praseodymium	3
Neodymium	3
Promethium	3
Samarium	3
Europium	3
Gadolinium	3
Iron	3

^aValue for n_j in Eqs. II-52 and II-53.

To simplify the calculations, the variable X can be introduced and defined as follows:

X_{2j-1} = the organic composition of component j ($C_{j,o}$)
 X_{2j} = the aqueous composition of component j ($C_{j,a}$)
 X_{2N+1} = concentration of the extractant

Also we can introduce the variable I as follows:

I_{2j-1} = initial concentration in the organic phase for component j
 I_{2j} = initial concentration in the aqueous phase for component j
 I_{2N+1} = initial concentration of the extractant

In the above definitions, $j = 1, \dots, N$. Using these definitions, Eqs. II-48, II-52, and II-53 can be rewritten as:

$$F_j = X_{2j} + (D/A) X_{2j-1} - I_{2j} - (D/A) I_{2j-1} = 0 \quad j = 1, \dots, N \quad (\text{II-54})$$

$$F_{j+N} = X_{2j-1} - X_{2j} - \frac{D_j \left[X_{2N+1} \right]^{n_j}}{\left[I_{2N+1} \right]^{n_j}} = 0 \quad j = 1, \dots, N \quad (\text{II-55})$$

$$F_{2N+1} = X_{2N+1} - I_{2N+1} + \sum_{j=1}^N n_j X_{2j-1} = 0 \quad (\text{II-56})$$

The iterative Newton-Raphson solution to these three equations is given by:

$$\begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_{2N} \\ X_{2N+1} \end{bmatrix}^{k+1} = \begin{bmatrix} X_1 \\ X_2 \\ \vdots \\ X_{2N} \\ X_{2N+1} \end{bmatrix}^k - \Phi_k^{-1} \begin{bmatrix} F_1 & (X_1, X_2, \dots, X_{2N}, X_{2N+1}) \\ F_2 & (X_1, X_2, \dots, X_{2N}, X_{2N+1}) \\ \vdots & \\ F_{2N} & (X_1, X_2, \dots, X_{2N}, X_{2N+1}) \\ F_{2N+1} & (X_1, X_2, \dots, X_{2N}, X_{2N+1}) \end{bmatrix} \quad (\text{II-57a})$$

where k is the iteration index, and Φ_k^{-1} represents the inverse of the Jacobian Φ , defined as follows:

$$\Phi_k = \begin{bmatrix} \frac{\partial F_1}{\partial X_1} & , & \frac{\partial F_2}{\partial X_2} & , & \dots & , & \frac{\partial F_1}{\partial X_{2N}} & , & \frac{\partial F_1}{\partial X_{2N+1}} \\ \frac{\partial F_2}{\partial X_1} & , & \frac{\partial F_2}{\partial X_2} & , & \dots & , & \frac{\partial F_2}{\partial X_{2N}} & , & \frac{\partial F_2}{\partial X_{2N+1}} \\ \vdots & & & & & & & & \\ \frac{\partial F_{2N}}{\partial X_1} & , & \frac{\partial F_{2N}}{\partial X_2} & , & \dots & , & \frac{\partial F_{2N}}{\partial X_{2N}} & , & \frac{\partial F_{2N}}{\partial X_{2N+1}} \\ \frac{\partial F_{2N+1}}{\partial X_1} & , & \frac{\partial F_{2N+1}}{\partial X_2} & , & \dots & , & \frac{\partial F_{2N+1}}{\partial X_{2N}} & , & \frac{\partial F_{2N+1}}{\partial X_{2N+1}} \end{bmatrix} \quad (\text{II-57b})$$

Once the system has converged, i.e.,

$$\left| \frac{X_j^{k+1} - X_j^k}{X_j^{k+1}} \right| \leq 0.001 \quad \text{for } j = 1, \dots, 2N+1 \quad (\text{II-57c})$$

the values of both organic- and aqueous-loaded concentrations would be known. With these new concentrations, new distribution coefficients can be calculated for every component. The D values for every component are given by:

$$D_j = \frac{X_{2j-1}}{X_{2j}} \quad j = 1, \dots, N \quad (\text{II-58})$$

The solution for Eqs. II-54 to II-56 converges readily. The only disadvantage is that a $(2N + 1)$ matrix inversion must be done (see Eq. II-57a). For a large number of components, this inversion is time-consuming. To avoid the $2N + 1$ inversion, all species that have the same exponential dependence on the extractant ($n_j = 3$ from Table II-6) and similar D values (tripositive actinides and lanthanides) can be grouped as one pseudocomponent. This pseudocomponent will possess the same characteristics as all the other species and, therefore, will behave in a similar fashion. Representing a large number of components as one pseudocomponent enables us to write one mass balance and distribution ratio equation instead of one for every component. Also the Newton-Raphson solution will require fewer equations and variables than before.

The species that were grouped and represented as one pseudocomponent are given in Table II-7.

Table II-7. Components Grouped as One Pseudocomponent to Decrease Computational Time

Am	Nd
Pu (III)	Pm
Cm	Sm
La	Eu
Ce	Gd
Pr	

The initial concentration ($C_{RE,o}^o$ and $C_{RE,a}^o$) for the pseudocomponent RE in the organic and aqueous phases is given by

$$C_{RE,o}^o = \sum_{p=1}^{NRE} C_{p,o}^o \quad (\text{II-59})$$

$$C_{RE,a}^o = \sum_{p=1}^{NRE} C_{p,a}^o \quad (\text{II-60})$$

where NRE is the total number of components whose organic and aqueous concentration are being combined as those of a pseudocomponent.

The initial distribution ratio can be calculated as:

$$D_{RE}^o = \frac{\sum_{p=1}^{NRE} D_p^o m_p}{\sum_{p=1}^{NRE} m_p} \quad (\text{II-61})$$

where m_p is the mass of the p 'th component in Table II-7. The total number of components (NT) in the solution for a system under study is given by

$$NT = N - NRE + 1 \quad (\text{II-62})$$

If NT is substituted for N in Eqs. II-54 to II-58, the resulting equations can be used to solve Eqs. II-48, II-52, and II-53. Note that any component belonging to Table II-7 will be described by the pseudocomponent RE.

Once the solution to Eqs. II-48, II-52, and II-53 has converged, concentrations and distribution ratios for the components represented by RE are calculated. To calculate the distribution ratio, we assume that the change in the ratio of the initial and calculated distribution ratios between every component p and RE is constant, i.e.,

$$D_p = \frac{D_p^{\circ} D_{RE}}{D_{RE}^{\circ}} \quad (\text{II-63})$$

Since the mass of every component p is constant,

$$C_{p,a} = \frac{C_{p,a}^{\circ} (O/A) + C_{p,o}^{\circ}}{D_p (O/A) + 1} \quad (\text{II-64})$$

and

$$C_{p,o} = C_{p,a} D_p \quad (\text{II-65})$$

Solution of Eqs. II-54 to II-56 using the RE pseudocomponent converges readily; computational time is significantly diminished with no loss in accuracy.

4. Implementation of Numerical Solution

The interaction among SASSE, the loading module, and SASPE is schematically shown in Fig. II-2. After the loading module recalculates the D values obtained from SASPE, SASSE will recalculate and pass concentrations of all components to SASPE for a given stage. In turn, SASPE will generate new distribution coefficients. The new distribution coefficients and concentrations are again given to the loading module, and this cycle is continued until the D values generated in the loading module remain constant. When the D values generated by the loading module remain the same in every cycle, convergence among the three has been achieved. It is important to note that SASSE can solve for N stages simultaneously, while SASPE and the loading module can only solve one stage at a time.

An Excel macro has been written to implement the numerical solution given in Sec.II.D.3. The general layout of the loading module is given in Fig. II-3. This macro has five major sections. The first section calculates the total number of components used in the solution of the system, i.e., total number of components minus number of components to be averaged plus one. The one is added to account for pseudocomponent RE. Calculations are performed to obtain the initial organic and aqueous concentrations and the distribution ratios for pseudocomponent RE (Eqs. II-59 to II-61). Also, initial aqueous and organic concentrations as well as D values for components not included as a pseudocomponent are obtained from SASSE and SASPE.

Fig. II-2. Interaction among SASSE, SASPE, and the Loading Module

The second section sets up the matrix that contains the equations describing the system and the Jacobian needed for the Newton-Raphson solution. (Eqs. II-54 to II-56 and Eq. II-57b). In the third section, new organic and aqueous concentrations are obtained by solving Eq. II-57a. An iterative procedure between sections two and three is performed until the organic and aqueous phase concentrations for all components remain unchanged. After convergence, section four calculates the D values for all the components present in the solution, including RE (Eq. II-58). Section five computes the organic and aqueous concentrations and the D values for the extractable components by using Eqs. II-59 to II-60. All new D values are passed to SASSE, and the iteration between the modules continues.

Fig. II-3. LOADING_EFFECT_MULT Macro Layout

E. Worksheet Development

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

1. Spreadsheet Algorithm for Stagewise Solvent Extraction

a. Introduction

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 whether or not each effluent will reach its specified composition, the SASSE worksheet (spreadsheet) can be used to identify key points for process monitoring and control.

Two Excel macros have been written to support SASSE. The one macro, "SASSE_generate," generates a new SASSE worksheet for a given number of (1) sections, (2) stages in each section, and (3) components in feed solution. This macro, included in the GTM, sets up the worksheet needed to calculate the specified TRUEX flowsheet in conjunction with distribution coefficients supplied by SASPE. The other macro, "SASSE_report_generator," developed as a part of the current effort and discussed below, takes the final results in the SASSE worksheet and generates (1) tabular reports for the concentration of the various components in the input and output streams and (2) tabular and graphical reports of the stage-to-stage concentration profiles for the various components. This macro allows the user to review the reports and graphs on the computer screen and to print them out. While the two SASSE macros are a part of the GTM, they can also be used independently.

The output from joint SASSE/SASPE calculations is combined with plant-specific information in a separate worksheet, called SPACE, where equipment size, plant space, and capital costs are calculated (Sec.II.E.2).

As the GTM is tested and upgraded, the SASSE_generate and the SASSE_report_generator are reviewed and modified as needed. In addition, the SASSE worksheet itself is being revised so that it can be used for modeling pulsed columns and will accommodate time-dependent chemical reactions in either phase. Once the layout of the modified SASSE worksheet has been developed and tested, the two SASSE macros will be revised accordingly.

b. Progress

The SASSE worksheet and the macro which generates it, SASSE_generate, are being modified so that they work smoothly with the rest of the GTM. Other work is being done on improving convergence of the SASSE worksheet to steady state. Finally, we are looking at ways to expand the capability of the SASSE worksheet to include time effects and pulsed column operation.

(1) SASSE Modifications

In working with the GTM, we found that the SASSE worksheet often converged to a steady-state solution while the D values being calculated in SASPE had not converged. As the GTM convergence criterion only checked the concentrations of the various components on the SASSE worksheet to see that they had reached steady state, the GTM sometimes stopped too soon. The GTM convergence criterion has now been revised to avoid this problem. When the SASSE worksheet is being set up with the SASSE_generate macro under the GTM, the previous D value returned from SASPE is now saved on the SASSE worksheet. This value is then compared with the new (last) D value returned

from SASPE. Thus, the last set of D values from the GTM can be checked with the previous set. Convergence of the D values occurs when no D value changes by more than 1% from the previous iteration with SASPE.

As reports are generated by SASSE_report_generator, those components which have complex parts in the SASSE worksheet, for example, Pu(III) and Pu(IV), are combined to give a single value for the component in each phase, and then an effective D value for the component is calculated.

It was estimated that, with 1 megabyte of RAM, the Generic TRUEX Model can handle up to 17 components with 27 contactor stages. If fewer components (C) are included in the model, the number of stages (S) can be increased so that the product (S•C) of stages times components does not exceed 460. No more than 17 components should be used at one time. This worksheet leaves 100 kilobytes of RAM for the worksheet calculations. The GTM was found to work well in test runs with 17 components and 27 contactor stages. Thus, it appears that the above estimate is realistic and perhaps even conservative. In running this test on a Macintosh II, we found that each iteration between SASSE and SASPE for the 27 stages took 48 minutes. Typically, six or more iterations will be required between SASSE and SASPE.

The SASSE worksheet was modified so that it now shows not only the aqueous-phase concentration for each component at each stage, $x(\text{last})$, but also the organic-phase concentration for each component at each stage, $y(\text{last})$. Thus, $x(\text{last})$ and $y(\text{last})$ are calculated with the same distribution coefficient. Previously, $y(\text{last})$ was calculated within the material-balance equations. Because of this, it used the new distribution coefficient for the component at that stage. During the iteration process, the difference between the prior distribution coefficient and the new distribution coefficient is usually small, and the creation of a separate row of cells for $y(\text{last})$ is not important. However, in the initial iterative cycle between SASSE and SASPE, the change in the distribution coefficient can be quite large. The net result is that, without $y(\text{last})$, material can appear to be created in a stage. This error disappears as the GTM calculations approach steady state. However, in some cases, the intermediate component concentrations become so high that the density worksheet in the SASPE calculations will not work. This difficulty is circumvented by calculating $y(\text{last})$ with the same D value as for $x(\text{last})$. Even without the problems in the SASPE calculations, the use of $y(\text{last})$ is desirable because it can speed up the convergence of the SASSE worksheet. Other work on the convergence of the SASSE worksheet is discussed next.

(2) Convergence of SASSE Worksheet

In the current structure of the SASSE worksheet, the concentration of a component in stage i , x_i , is a function of x_{i-1} and x_{i+1} . This function results in the double-diamond nature of the SASSE calculation, discussed elsewhere,²⁹ where two independent sets of calculations are simultaneously underway. The calculation is such that, on each iteration, a new estimate must be made for the component concentration at each stage. The number of times that a worksheet must be iterated to reach steady state for a component is proportional to the amount of time that the physical process itself must take to reach steady state for that component.

An alternative SASSE worksheet structure was explored where the worksheet iteration is based on successive approximations of the component concentration in the first process stage. As mentioned above, at steady state, the concentration of a component in stage i , x_i , is a function of x_{i-1} and x_{i+1} . One can get a value for x_2 if one guesses at a value for x_1 by using appropriate values for the distribution coefficients and the flow rates. This is possible since $x_0 (=x_{i-1})$, being nonexistent, is zero. Then, with values for x_1 and x_2 , one can calculate x_3 and so on through to x_m for the final stage, m . After this series of calculations, an overall material balance for the component is used to get the next estimate

for x_1 , and x_2 through x_m are recalculated in a second iteration. While a number of iterations is required for a worksheet to reach steady state, this number is no longer proportional to the amount of time that the process itself takes to reach steady state. Exploratory calculations using the modified SASSE worksheet showed that it reduced the number of iterations to reach steady state. It also eliminated the double-diamond structure of the calculations and the need for initial values for each component at each stage. The feasibility of implementing this procedure will be reviewed as the SASSE worksheet capabilities are expanded to include high values for other-phase carryover.

(3) Expanded SASSE Capabilities

The SASSE worksheet is to be modified so that (1) it can handle large amounts of other-phase carryover, that is, amounts greater than 2 to 5%, (2) the residence time of each phase in each stage is explicit rather than implicit, and (3) the volume of each phase in each stage can be specified. The modified worksheet will be used for modeling pulsed columns and will accommodate time-dependent chemical reactions in either phase. The residence time of each phase in each stage will be calculated and will be available for use in the SASPE worksheets.

As a first step, we attempted to derive a series of overall equations to accommodate large amounts of other-phase carryover. However, these equations quickly became very complex and were abandoned. Instead, the basic SASSE approach of focusing on an individual stage will be retained. Each of the two internal streams into this stage and each of the two internal streams out of it are assumed to carry some of the other phase. The fraction (f) of the other-phase carryover in each stream leaving a stage (i) will be specified by the user. Also, at each stage, an aqueous and organic feed and an aqueous and organic effluent will be permitted. They will not contain any other-phase carryover; however, this carryover can be modeled by appropriate additions or increases in the other feed or in the other effluent. Finally, by specifying the total volume (V) for each phase (A or O) in each stage (i), the residence time for each phase in that stage can be calculated.

The desired SASSE worksheet is now being laid out, and it will be tested upon completion. Then, the SASSE_generate macro will be revised to generate the revised worksheet.

2. Space and Cost Estimation Section Development (L. Chow and R. A. Leonard)

a. Introduction

The worksheet SPACE (Size of Plant And Cost Estimation) was developed to determine the size and cost of a TRUEX processing plant. This development work was completed in October 1988. This worksheet can be used as part of the GTM calculations or independently. In both methods, the user can enter input data through HyperCard and/or enter data to the appropriate cells of the worksheet and thus interact directly with the worksheet. After the calculation is completed, the user can view on the screen and print a summary and/or a full report of the size and cost calculations.

Figure II-4 shows the flowsheet of a basic TRUEX processing 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 using the centrifugal contactors. 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. (The water source and the related piping systems are not shown in Fig. II-5.)

Fig. II-4. Schematic of Typical TRUEX Flowsheet

Components and equipment outside the boundary of the hot area (see Fig. II-5) can be located in an open area. Components and equipment within the hot boundary have to be in a glovebox, shielded cell, or remote canyon. In practice, the solution wash raffinate and acid rinse raffinate should be cold. They are located in a hot area as a safety precaution.

b. General Approaches of SPACE Worksheet

The layout of the SPACE worksheet is shown in Fig. II-6. The first part of the worksheet is used for entering data. To account for a wide variety of factors such as design criteria, operating conditions, processing requirements, and plant characteristics and location, the SPACE worksheet is programmed such that all input data can be readily specified by the user. Moreover, all but four of the input parameters are provided with default values: (1) the number of contactor stages, (2) the diluent (TCE or NPH) used in the TRUEX process, (3) the type of hot processing location (canyon, shielded cell, or glovebox), and (4) the feed rate to the extraction section. Data for these four parameters can be entered by the use of HyperCard or can be directly entered into the worksheet. The input parameters that are provided with default values (such as the year for cost estimate, the relative flow rates, the space and cost factors, and storage tank and process vessel information) can be modified and overridden by users when they are directly interacting with the worksheet.

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

Fig. II-6. Flow Diagram of the SPACE Worksheet

Following the Input Section is the Output Section, which consists of primary and additional output data. The primary output data summarize the contactor stage requirements; the floor space needed in the hot and cold processing area; and the fixed capital cost of the contactor stages, tanks and equipment, CMPO, and the entire TRUEX processing plant. The additional output gives a breakdown of the space and cost requirements for each system under study. This section allows the user to review the calculated results and to make appropriate changes in the design by adjusting the input data.

The calculations part of the worksheet contains the correlations used to obtain the calculated results in the Output Section. These calculations include information related to the chemicals for the source tanks, the maximum contactor throughput, rotor diameter, tank size, floor area for hot and cold processing, sizing and cost factor for process pumps, inflation index, and purchased and fixed capital costs for the equipment. This part of the worksheet is for reference only.

The constants (bottom of Fig. II-6) include the direct-cost to equipment-cost ratio, the indirect-cost to equipment-cost ratio, and the clearance between adjacent tanks. A table lists the Marshall and Swift equipment cost index from years 1976 to 2000 (values between years 1988 and 2000 are obtained by extrapolation). Finally, a table of default values is given. Since the user can always override

the default values, changes to this part of the worksheet are not recommended unless a permanent change to a default value is desirable.

c. Spacing Calculations

In the SPACE worksheet, the spacing calculation is divided into two parts: (1) the spacing for hot processing, which includes the floor area to house the contactor stages and the tank and pump systems in the hot area, and (2) the spacing for cold processing, which includes the floor area to install the tanks and pumps in the cold area and also room to control and maintain the equipment in both the hot and cold area. The required floor area in each processing location is the product of the floor area occupied by the equipment and a space factor that allows extra room for installation, control, maintenance, and future expansion.

The total fixed capital cost of the entire TRUEX processing plant is the sum of the total fixed capital cost of contactor stages and conventional equipment and the purchased costs of CMPO for the TRUEX solvent. The purchased cost of CMPO is included because CMPO, which is very costly, is recycled back to the process continuously without the need for significant replenishment.

The calculations of the fixed capital cost of contactor stages and conventional equipment are based on the following general relationship:

$$C = L_f I_f [D_r + I_r] C_p \quad (\text{II-66})$$

where

- C = fixed capital cost of the equipment (installed), \$
- L_f = location factor that would affect the cost
- I_f = inflation factor, depending on the year for the cost estimate and the year that the equipment cost is obtained
- D_r = direct-cost to equipment-cost ratio
- I_r = indirect-cost to equipment-cost ratio
- C_p = purchased cost of the equipment for the year that it is determined, \$

The location factor, L_f is chosen as 1, 1.2, 1.4, and 1.5, respectively, when the equipment is located in an open area, glovebox, shielded cell, or canyon area. This implies that equipment installed in a glovebox, shielded cell, or canyon is 1.2, 1.4, and 1.5 times that in an open area, in that order.

The inflation factor is the ratio of the Marshall and Swift equipment cost index^{30,31} at the year for the cost estimate to the index at the year the equipment cost is obtained. The cost indexes from year 1976 to 2000 are listed near the end of the SPACE worksheet. In this table, the values from 1988 to 2000 are obtained by extrapolation from the values of the preceding 10 years. When the user enters the year for cost estimate in the input data, the worksheet searches this table and obtains the corresponding value for the cost index.

3. Summary

The development work for the SPACE worksheet is completed. This worksheet can be used to determine the size and cost of a TRUEX processing plant. In the input section of the worksheet, the

user has the options of using the default values provided or entering appropriate data to account for various design criteria, operating conditions, processing requirements, plant characteristics and location, etc.

In the report section, the user can request the displaying (on the screen) and/or printing (on the printer) of a summary and/or a full report of the cost and size calculations. The summary report includes the information about contactor stages; the total floor space requirements, including the requirements of the hot and cold processing area; and the fixed capital cost of an entire TRUEX processing plant, including the costs of contactor stages, tanks and equipment, and CMPO. The full report includes the input data, the primary output, and the additional output. The information listed in the primary output is similar to that listed in the summary. The additional output lists the results of the cost and size calculations in more detail.

F. 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 into a data base using the software package 4th Dimension on a MacIntosh computer. The design of the data base will place strong emphasis on various modes of data retrievability and anticipated report formats useful to the project.

The data base is intended to be useful to at least four customer types: program managers, 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 greater part, now functional. Debugging continues, and further improvements to facilitate use is 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.

G. Distribution Ratio Measurements

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

In the previous report (ANL-90/15, Sec.II.F.2), distribution ratio (D) data were given for ^{88}Zr and ^{88}Y extraction [forward (F) and back (B)] by TRUEX-NPH over a range of HNO_3 concentrations (0.1-6M). This experimental series has been repeated with the same solution, and the data obtained are shown in Table II-8. For comparison, the previous data are shown in Table II-9. It should be noted that the D_{Zr} values have decreased with time (4 months), while D_{Y} values are about the same. The same type of measurements was made for the first time with TRUEX-TCE, and the data are shown in Table II-10.

To determine if more than one zirconium species is being extracted and to measure the species D values with the TRUEX-NPH, a multiple extraction series was done with four consecutive forward extractions of the aqueous phase by fresh, pre-equilibrated organic phases and four back extractions of the organic phase with fresh aqueous solutions; results are given in Table II-11. The results of this study point to the existence of at least two zirconium species--one more extractable than the other.

Table II-8. Recent Data^a for ⁸⁸Zr and ⁸⁸Y Extraction by TRUEX-NPH (0.20M CMPO, 1.4M TBP) and Various HNO₃ Concentrations at 25 °C and 60-s Contact Time

[HNO ₃], M	D _{Zr} (F)	D _{Zr} (B)	D _Y (F)	D _Y (B)
0.1	1.08	5.82	0.08	0.08
0.5	4.74	12.9	0.99	1.02
1	8.06	18.2	1.90	1.91
2	14.3	25.6	2.91	2.93
3	17.0	32.2	3.80	3.80
4	21.6	35.9	4.68	4.42
5	24.4	42.0	5.37	5.26
6	27.7	50.6	6.66	6.66

^aData obtained during October 1988 with ⁸⁸Zr and ⁸⁸Y tracer in 0.5M HNO₃.

Table II-9. Previous Data^a for ⁸⁸Zr and ⁸⁸Y Extraction by TRUEX-NPH (0.20M CMPO, 1.4M TBP) and Various HNO₃ Concentrations at 25 °C and 60-s Contact Time

[HNO ₃], M	D _{Zr} (F)	D _{Zr} (B)	D _Y (F)	D _Y (B)
0.1	1.60	4.32	0.08	0.08
0.5	6.66	15.1	1.00	0.95
1	13.1	24.3	1.89	1.81
2	21.8	35.6	2.90	2.81
3	28.6	51.0	3.76	3.69
4	38.8	64.1	4.67	4.58
5	46.1	73.5	5.29	5.24
6	53.6	91.8	6.52	6.77

^aData obtained during June 1988 with ⁸⁸Zr and ⁸⁸Y tracer in 0.5M HNO₃.

Table II-10. Recent Data^a for ⁸⁸Zr and ⁸⁸Y Extraction by TRUEX-TCE (0.25M CMPO, 0.75M TBP) and Various HNO₃ Concentrations at 25 °C and 60-s Contact Time

[HNO ₃], M	D _{Zr} (F)	D _{Zr} (B)	D _Y (F)	D _Y (B)
0.1	1.01	3.90	0.15	0.14
0.5	5.51	15.2	1.77	1.81
1	8.18	19.8	2.35	2.35
2	11.3	17.7	1.88	1.88
3	9.78	21.6	1.33	1.49
4	12.2	22.6	1.49	1.43
5	12.3	21.5	1.53	1.36
6	13.2	24.6	1.71	1.69

^aData obtained during October 1988 with ⁸⁸Zr and ⁸⁸Y tracer in 0.5M HNO₃.

Table II-11. Data for ^{88}Zr and ^{88}Y Extraction by TRUEX-NPH (0.20M CMPO, 1.4M TBP) with HNO_3 or HNO_3 Plus Salt at 25 °C

	D_{Zr}			
	F-1	F-2	F-3	F-4
0.5M HNO_3	4.58	1.29	1.60	0.60
0.5M HNO_3 + 2.7M NaNO_3	14.5	1.95	1.48	0.03
	B-1	B-2	B-3	B-4
	F-1	F-2	F-3	F-4
0.5M HNO_3	11.3	14.9	19.1	18.4
0.5M HNO_3 + 2.7M NaNO_3	104.4	110.9	120.8	123.4
	D_{Y}			
	F-1	F-2	F-3	F-4
0.5M HNO_3	0.99	0.95	0.99	0.98
0.5M HNO_3 + 2.7M NaNO_3	20.7	16.9	--	--
	B-1	B-2	B-3	B-4
	F-1	F-2	F-3	F-4
0.5M HNO_3	1.00	0.99	1.10	1.01
0.5M HNO_3 + 2.7M NaNO_3	20.2	19.6	20.3	19.8

Another tracer-containing solution was obtained from Los Alamos National Laboratory, with an isotopic mix of 5.0 mCi ^{88}Zr and 2.6 mCi ^{88}Y in HCl (0.67 mL). This mixture is 10 times hotter in ^{88}Zr than the previous sample. The chloride solution was converted to nitrate by successive evaporations (three) with 2M nitric acid (final volume 1 mL). A further dilution of this solution (100 μL to 1 mL in 2M nitric acid) was made to obtain the working solution. The higher acid concentration (2M vs. 0.5M HNO_3 previously) was chosen to avoid hydrolysis of zirconium, which was evident by loss of material from solution in 0.1M HNO_3 .

The new sample was used to repeat the acid extraction series with TRUEX-NPH. Two forward and two back extractions were completed at each acid concentration. All extractions (F-1, F-2, B-1, B-2) were completed on the same day. Results are given in Table II-12. It should be noted that hydrolysis of zirconium was high at 0.1M nitric acid, as evidenced by the fact that re-sampling phases and gamma counting them showed a significant loss in counts. This loss amounted to 30% after 4 h for the aqueous phase, and 10% for the organic phase. This loss became much less at 0.5M HNO_3 (<4%). It appears that the loss of counts in the aqueous phase (0.1M HNO_3) happens quickly (<30 min). Two zirconium species were also evident in the extraction data from the new tracer solution.

Table II-13 shows the effect of oxalic acid and its complexes on ^{88}Zr and ^{88}Y extraction with the new tracer-containing solution at 50 °C. Similar data were obtained for the effect of HF; all samples were held in polypropylene ware. Results appear in Table II-14.

To establish if the zirconium polymer (assumed to be formed in aqueous stock solution over a period of months) can be destroyed by the addition of oxalic acid or hydrofluoric acid, we performed a series of extractions in which the ^{88}Zr and ^{88}Y tracer was kept in the aqueous phase for varying times before the extraction. For this study, a solution of 0.5M HNO_3 , 0.3M oxalic acid, and 2.7M NaNO_3 was used. Results are given in Table II-15 for stand times of 15 min, 4 h, 20 h, and 5 days. Similar experiments were run with four different HF solutions. These results, which are given in Table II-16, and those in Table II-15 show that the polymer is not attacked over short periods of time by either complexant.

Table II-12. Data for ^{83}Zr and ^{88}Y Extraction^a by TRUEX-NPH (0.20M CMPO, 1.4M TBP) and Various Acid Concentrations at 25°C and 60-s Contact Time

[HNO ₃], M	D _{Zr}				D _Y			
	F-1	F-2	B-1	B-2	F-1	F-2	B-1	B-2
0.1	6.73	0.64	6.64	8.26	0.08	0.08	0.09	-
0.5	17.0	2.13	16.9	20.3	1.02	1.00	0.98	-1
1	30.2	2.61	35.3	35.8	1.88	1.85	1.87	1.92
2	43.7	3.02	59.6	61.1	2.95	2.90	2.91	2.86
3	64.2	2.45	91.1	105.7	3.73	3.75	3.60	3.73
4	80.3	2.40	111.5	130.9	4.70	4.50	4.64	4.49
5	90.8	2.09	127.8	149.3	5.33	5.08	5.01	5.02
6	109.0	2.03	156.5	174.7	6.59	6.29	6.45	6.21

^aData obtained during October 1988 with ^{88}Zr and ^{88}Y tracer in 2M HNO₃.

Table II-13. Effect of Oxalic Acid and its Complexes on ^{88}Zr and ^{88}Y Extraction^a by TRUEX-NPH (0.20M CMPO, 1.4M TBP) at 50°C and 60-s Contact Time

	Conc., M				D _{Zr}				D _Y			
	[H ₂ C ₂ O ₄]	[HNO ₃]	[NaNO ₃]	[Al(NO ₃) ₃]	F-1	F-2	B-1	B-2	F-1	F-2	B-1	B-2
A-1	0	0.5	2.7	-	114.1	1.54	175	186	13.4	13.4	12.8	13.5
A-2	0.1	0.5	2.7	-	0.052	0.007	6.87	6.80	6.76	5.80	6.72	6.76
A-4	0.3	0.5	2.7	-	0.046	0.009	4.26	4.66	4.34	3.65	4.22	4.66
C-1	0	0.5	1.8	0.3	104.6	0.83	239	304	16.0	15.8	15.3	17.6
C-2	0.1	0.5	1.8	0.3	--	0.012	--	--	--	8.22	9.76	10.72
C-4	0.3	0.5	1.8	0.3	0.056	0.009	5.31	5.88	5.45	4.85	5.42	5.84

^aData obtained during October 1988 with ^{88}Zr and ^{88}Y tracer in 2M HNO₃.

Table II-14. Effect of HF and Salt on ^{88}Zr and ^{88}Y Extraction^a by TRUEX-NPH (0.20M CMPO, 1.4M TBP) at 50°C and 60-s Contact Time

	Conc., M			D _{Zr}				D _Y			
	[HF]	[HNO ₃]	[NaNO ₃]	F-1	F-2	B-1	B-2	F-1	F-2	B-1	B-2
H-1	0.1	0.5	2.7	0.062	0.010	4.95	10.2	8.88	7.34	8.82	10.1
H-3	0.5	0.5	2.7	0.054	0.013	3.00	3.34	3.29	3.12	3.07	3.34

^aData obtained during October 1988 with ^{88}Zr and ^{88}Y tracer in 2M HNO₃.

Table II-15. Effect of Stand Time on ^{88}Zr and ^{88}Y Extraction by TRUEX-NPH, Oxalic Acid, and Its Complexes at 50°C and 60-s Contact Time

Time ^a	D_{Zr}				D_{Y}			
	F-1	F-2	F-3	B-1	F-1	F-2	F-3	B-1
15 min	0.046	0.009	--	4.26	4.34	3.65	--	4.22
4 h	0.069	0.011	0.002	4.12	4.19	4.10	3.90	4.07
20 h	0.056	0.011	0.002	4.31	4.13	3.73	3.30	4.28
5 days	0.057	0.011	0.002	4.30	4.01	3.67	3.64	4.22

^aAll samples were 0.5M HNO_3 , 0.3M oxalic acid, 2.7M NaNO_3 .

Table II-16. Effect of Stand Time on ^{88}Zr and ^{88}Y Extraction by TRUEX-NPH, Hydrofluoric Acid, and Its Complexes at 50°C and 60-s Contact Time

Composition	Time	D_{Zr}		D_{Y}	
		Forward	Back	Forward	Back
a	15 min	0.159	7.21	8.98	9.22
	68 h	0.157	7.38	8.94	9.25
b	15 min	0.133	5.09	4.68	5.14
	68 h	0.163	5.30	5.25	5.15
c	15 min	0.117	3.17	2.91	3.14
	68 h	0.122	3.18	2.94	3.11
d	15 min	8.32	9.16	11.9	13.5
	68 h	8.69	9.15	12.4	12.2

^a0.5M HNO_3 ; 0.1M HF; 2.7M NaNO_3 .

^b0.5M HNO_3 ; 0.3M HF; 2.7M NaNO_3 .

^c0.5M HNO_3 ; 0.5M HF; 2.7M NaNO_3 .

^d0.5M HNO_3 ; 0.1M HF; 2.4M NaNO_3 ; 0.1M Al^{3+} .

2. Iron Extraction (D. R. Fredrickson)

The extraction of ^{59}Fe by the TRUEX-NPH solvent has been studied to measure the effect of (1) nitric acid, (2) oxalic acid, and (3) hydrofluoric acid, all with a constant nitrate concentration of 3.2M and at 25°C . Since the extraction is rate dependent, varying contact times from 15 to 300 s were used.

The influence of HNO_3 on the extraction of ^{59}Fe (tracer levels) from TRUEX-NPH (0.20M CMPO, 1.4M TBP in NPH) was determined at 15, 60, and 300 s. The results for three acid concentrations (0.5, 1.0, and 2.0M HNO_3) are shown in Table II-17. An equilibrium condition is readily achieved at 300 s, where the rates for forward and back extraction are similar.

The influence of oxalic acid on the extraction of ^{59}Fe from TRUEX-NPH was determined at 15 s and 300 s and over a range of oxalic acid concentrations (0.01 to 0.3M). The results for two nitric acid concentrations (0.5 and 1.0M) are shown in Table II-18. Again, it should be noted that at 300 s a near equilibrium condition exists.

Table II-17. Effect of Nitric Acid on Distribution Ratio for Forward and Back Extractions of Iron with TRUEX-NPH at 25°C

Aqueous Composition	15 s		60 s		300 s	
	D _f	D _b	D _f	D _b	D _f	D _b
0.5M HNO ₃ 2.7M NaNO ₃	0.199	6.60	0.581	1.84	1.10	1.05
1.0M HNO ₃ 2.2M NaNO ₃	0.100	7.12	0.379	2.05	0.66	0.71
2.0M HNO ₃ 1.2M NaNO ₃	0.043*	11.9	0.155	3.16	0.47	0.70
	0.052*	13.5	0.173	2.89	0.46	0.67

*Duplicate extractions.

Table II-18. Effect of Oxalic Acid on Distribution Ratio for Forward and Back Extractions of Iron with TRUEX-NPH at 25°C

Aqueous Composition, M			15 s		300 s	
[Oxalic acid]	[HNO ₃]	[NaNO ₃]	D _f	D _b	D _f	D _b
0.01	0.5	2.7	0.048	0.690	0.061	0.065
0.02	0.5	2.7	0.029	0.557	0.035	0.037
0.05	0.5	2.7	0.013	0.305	0.012	0.017
0.1	0.5	2.7	0.0055	0.168	0.0049	0.0072
0.2	0.5	2.7	0.0029	0.084	---	---
0.3	0.5	2.7	0.0034	0.120	0.0032	0.0031
0.3	0.5	2.7	0.0042	0.124	0.0028	0.0021
0.1	1.0	2.2	0.018	0.389	0.021	0.027
0.2	1.0	2.2	0.010	0.218	---	---
0.3	1.0	2.2	0.0064	0.103	0.0058	0.0058

The influence of hydrofluoric acid on the extraction of ⁵⁹Fe from TRUEX-NPH was determined at 15 and 300 s. All extractions and transfers were carried out in polypropylene ware. The range of HF concentrations was 0.01 to 0.5M. The results for two nitric acid concentrations (0.5 and 1.0M) are shown in Table II-19. The 300-s contact again indicates a near equilibrium condition.

Table II-19. Effect of Hydrofluoric Acid on Distribution Ratio for Forward and Back Extractions of Iron with TRUEX-NPH at 25°C

Conc., M			15 s		300 s	
[HNO ₃]	[HF]	[NaNO ₃]	D _f	D _b	D _f	D _b
0.5	0.01	2.7	0.142	3.33	0.468	0.474
0.5	0.03	2.7	0.098	2.16	0.233	0.252
0.5	0.1	2.7	0.060	1.09	0.094	0.100
0.5	0.3	2.7	0.027	0.304	0.029	0.031
0.5	0.5	2.7	0.015	0.123	0.016	0.016
1.0	0.1	2.2	0.052	2.19	0.122	0.122
1.0	0.3	2.2	0.031	0.563	0.050	0.052
1.0	0.5	2.2	0.024	0.329	0.031	0.032

The work has also been extended to cover TRUEX-TCE at nitric acid concentrations of 0.5, 1, and 2M with a constant nitrate concentration of 3.2M at 25 °C. The effect of adding oxalic acid was also measured for this solvent, as was varying contact times from 15 to 300 s. Results are given in Table II-20. An equilibrium condition exists at 300 s, where the rates for forward and back extraction are the same.

Table II-20. Effect of Nitric Acid on Distribution Ratio for Forward and Back Extractions of Iron with TRUEX-TCE at 25 °C

Solution	15 s		60 s		300 s	
	D_f	D_b	D_f	D_b	D_f	D_b
0.5M HNO ₃ 2.7M NaNO ₃	0.067	1.23	0.159	0.347	0.197	0.214
1.0M HNO ₃ 2.2M NaNO ₃	0.040	1.17	0.092	0.222	0.113	0.118
2.0M HNO ₃ 1.2M NaNO ₃	0.027	1.83	0.061	0.247	0.077	0.083
0.5M HNO ₃ 2.7M NaNO ₃ 0.1M H ₂ C ₂ O ₄	0.0011	--	0.0010	0.018	0.0010	--

In an effort to define iron extraction behavior at low nitric acid concentration, a series of ⁵⁹Fe extractions is underway using both TRUEX-TCE and TRUEX-NPH. Completed so far are tests with 0.02 and 0.05M HNO₃ for both solvents. Contact times were 15, 60, 300, and 900 s. A new sample of ⁵⁹Fe was used. In these experiments, radioactive ferric chloride in 0.1M HCl (as received from Amersham) is converted to nitrate by successive evaporation: with 1M HNO₃, to a final volume of 1.00 mL (1 mCi of ⁵⁹Fe). Results for 0.02 and 0.05M HNO₃ with TRUEX-TCE and TRUEX-NPH are given in Table II-21 and Table II-22, respectively. An equilibrium condition still does not seem to exist, even after 900 s.

Table II-21. Forward and Back Extractions of Iron with TRUEX-TCE and Nitric Acid at 25 °C

Solution	15 s		60 s		300 s		900 s	
	D_f	D_b	D_f	D_b	D_f	D_b	D_f	D_b
0.02M HNO ₃	0.00373	0.360	0.00950	0.237	0.0187	0.574	0.0342	0.196
0.05M HNO ₃	0.00258	0.175	0.00541	0.139	0.0174	0.364	0.0242	0.141

Table II-22. Forward and Back Extractions of Iron with TRUEX-NPH and Nitric Acid at 25 °C

Solution	15 s		60 s		300 s		900 s	
	D_f	D_b	D_f	D_b	D_f	D_b	D_f	D_b
0.02M HNO ₃	0.00612	0.527	0.00644	0.433	0.00995	0.238	0.0112	0.279
0.05M HNO ₃	0.00527	0.344	0.00492	0.247	0.00750	0.112	0.00842	0.155

3. Effects of Complexants on Noble Metal Extraction (F. C. Mrazek and J. B. Rajan)

Experimental work to determine the effect of iron, aluminum, oxalate, and fluoride ions on the extraction of noble metals is in progress. One liter of a concentrate solution (Table II-23) containing eight metal ions was prepared. Twenty groups of solutions were prepared from this concentrate by varying the amounts of iron, aluminum, oxalate, and fluoride ions present in the predominantly nitrate concentrate. Each group contains three to four samples whose composition varies by the concentration of HNO_3 , HF , and/or $\text{H}_2\text{C}_2\text{O}_4$.

Table II-23. Concentration of Metal Ions in Synthetic Concentrate Solution

Component	Chemical Used	Approximate Concentration, M
MoO_3	Ammonium molybdate	0.0018
Zr	Zirconium dinitrate oxide dihydrate	0.056
Rh	Rhodium nitrate	0.0057
Pd	Palladium nitrate	0.0055
Nd	Neodymium nitrate	0.027
Ru	Ruthenium nitroso-nitrate	0.021
Ni	Nickel nitrate	0.008
Mn	Manganous sulfate	0.045

Six groups of the twenty have been equilibrated with TRUEX-NPH at 50°C for one minute with equal volume of the organic and aqueous phases.* The aqueous phase was separated from the organic, and the organic phase stripped of its cations. Aqueous solutions from stripping the organic phase and diluting the aqueous phase were submitted for inductively coupled plasma/atomic emission spectroscopy (ICP/AES) by ANL's Analytical Chemistry Laboratory (E. Huff).

Analytical results for 27 of these solutions (six series, Nos. 1-4, 8, and 9) are presented in Appendix A. Conclusions will be delayed until more solutions are equilibrated.

Series eight and nine extractions were done in duplicate to compare two different methods of stripping the cations from the organic phase. The "old" stripping method, which was employed in the first four series, was accomplished by contacting 4 mL of organic phase twice with 12 mL of 0.05M oxalic acid/0.5M HNO_3 , twice with 2 mL of 5M HNO_3 , and three times with 4 mL water. The "new" stripping method involved contacting the 4 mL of organic phase once with 4 mL of 1.89M acetic acid/1.89M sodium acetate, twice with 4 mL of 0.05M 1-hydroxyethane 1,1-diphosphoric acid, and once with 4 mL of 0.05M HNO_3 . After the solutions were analyzed by ICP/AES, the distribution ratios for the metals were calculated, and no significant difference between methods was apparent. The "new" method, however, has a time advantage, requiring only four contacts versus seven contacts for the "old" method.

*The TRUEX-NPH was pre-equilibrated three times at 25°C with a solution containing all species but those in the concentrate.

The various individual stock solutions used in these extractions are stored in 4 oz. opaque plastic bottles. Removing the cover of these bottles and looking into the bottle (with a bright light beneath) while giving the liquid a gentle swirl showed the presence of a minor precipitate in some bottles (Table II-24). The elemental analyses results of all the stock solutions contained very little scatter between samples, except those with the observed precipitate and solutions IA to ID. The latter contained one-half the molybdenum as the other solutions.

Table II-24. Stock Solutions Containing Precipitated Material

Stock Solution Identification	Relative Amount of Precipitate ^a	Unusual Results in the Chemical Analyses
1C	3	Contained 1/4 and 1/3 the average amount of Ni and Nd, respectively.
1D	3	Contained 1/4 and 1/3 the average amount of Ni and Nd, respectively.
2C	1	Normal.
2D	1	Contained 1/2 the average amount of Nd.
3A	2	Not determined.
8B	2	Contained 3/4 and 1/2 the average amount of Nd and Zr, respectively.
8C	2	Not determined.

^aJudged on a scale of one to three, with three containing the most precipitate.

4. Plutonium Extraction

(L. Reichley-Yinger and K. Orlandini)

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 parts 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 scrubbing and stripping reagents.

One general area of concern in the determination of Pu(IV) distribution ratios has been obtaining and maintaining the IV oxidation state in an acidic nitrate stock solution. Before measuring Pu(IV) distribution ratios under scrubbing and stripping conditions, we studied the plutonium oxidation states present in existing stock solutions. By using anion exchange and LaF₃ precipitation in conjunction with alpha pulse-height analyses, we found that two Pu-HNO₃ stock solutions, which were suspected of containing significant amounts of Pu(VI), contained <1% Pu(VI), Pu(III), or Pu(IV) polymer. Analysis of a Pu-Cl stock, known to contain both III and IV states, showed that Pu(III) is not immediately oxidized to the IV state by 8M HNO₃ and can exist during the time it takes for the solution to pass through the ion exchange column. This suggests that the Pu(IV) found in the Pu-NO₃ stock is actually present in the stock solution and does not result from the oxidation of Pu(III) on the column. These results indicate that >98% of the plutonium present in a 2M HNO₃ stock solution exists in the IV state.

5. Neptunium Extraction (J. Sedlet)

During this report period, studies continued on the extraction of Np(IV) from nitric acid and from nitric/sulfuric acid solutions into TRUEX-NPH solvent. The experimental procedures, methods, and reagents were the same as those described in the previous report (ANL-90/15, Sec.II.F.3). As the neptunium isotopes, mixtures of ^{237}Np and ^{239}Np were used; the former was to provide mass and the latter to measure the neptunium concentration by counting its gamma rays. Experiments were also conducted on methods to improve the quantitative preparation of neptunium in the IV oxidation state and on the separation of the ^{233}Pa daughter from its ^{237}Np parent so that ^{237}Np alone could be used to determine distribution ratios by alpha-particle liquid scintillation counting or by gamma-ray counting with a germanium detector and multi-channel pulse height analyzer.

a. Distribution Ratio Measurements

A series of extractions was performed with a mixture of ^{237}Np and ^{239}Np that had been treated with ferrous ammonium sulfate to reduce the neptunium to the IV oxidation state. The ^{237}Np concentration was 10^{-5}M in the aqueous phase of the forward extraction.

The distribution ratio results for nitric acid are shown in Table II-25. Compared with earlier experiments of this type (ANL-90/15, Sec.II.E.3), the back-extraction distribution ratios are appreciably larger at acidities up to 1M HNO_3 . Moreover, the forward extraction ratios are appreciably lower than the back extractions at $<1\text{M HNO}_3$. Since the distribution ratios for Np(V) are much lower than those for Np(IV), both of these discrepancies can be explained by assuming that reduction to Np(IV) was initially incomplete, and that Np(IV) was partially oxidized to Np(V) at the lower acidities between the back extractions. At the higher acidities, Np(IV) may be stabilized as the nitrate complex.

Table II-25. Distribution Ratios for ^{239}Np - ^{237}Np between Nitric Acid and TRUEX-NPH^a

$[\text{HNO}_3], \text{M}$	Forward Extraction	Back Extraction	
		#1	#2
0.05	2.9	33.4	22.3
0.10	12.3	74.4	36.9
0.20	57.6	162	105
0.50	697	1.48×10^3	1.04×10^3
1.0	894	4.23×10^3	4.96×10^3
2.0	$(1.22 \pm 0.12) \times 10^4$	$(2.05 \pm 0.21) \times 10^4$	$(2.65 \pm 1.4) \times 10^4$
3.0	$(2.84 \pm 0.03) \times 10^4$	$(3.23 \pm 1.07) \times 10^4$	$(2.76 \pm 1.40) \times 10^4$
5.0	$(3.18 \pm 0.70) \times 10^4$	$(4.78 \pm 1.03) \times 10^4$	$(4.83 \pm 5.10) \times 10^4$

^aThe tracer mixture was treated with $0.25\text{M Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ in 0.5M HNO_3 for 40 min. Each aqueous layer was made 0.02M in $\text{Fe}(\text{NO}_3)_2$ and 0.02M in $\text{NH}_2\text{OH} \cdot \text{HNO}_3$ before contact with solvent. Each solvent layer was pre-equilibrated three times with HNO_3 of the same concentration used in the extractions. Extraction time was 1 min at 25°C , and the solvent/aqueous volume ratio was one. The solvent was prepared assuming that the CMPO was 98% pure.

The errors or uncertainties shown in Table II-25 for 2, 3, and 5M HNO₃ were calculated from the standard deviations (at the 1 sigma level) of the average counting rates of duplicate aliquots of the aqueous layers. The counting rates of these aliquots are very low, 10% to 20% of the counter background, and contribute the major portion of the total uncertainty in the distribution ratio at high acid concentrations. To lower this uncertainty, the above experiment was repeated using a volume ratio of solvent to aqueous phase of 1/3. This permits sampling a larger aliquot of the aqueous phase to obtain larger counting rates. The improvement in the uncertainties is shown in Table II-26.

Table II-26. Distribution Ratios for ²³⁹Np-²³⁷Np between Nitric Acid and TRUEX-NPH^a

[HNO ₃], M	Forward Extraction		Back Extraction	
	#1	#2	#1	#2
0.05	4.8	0.68	62	83
0.10	2.5	2.8	157	216
0.20	56.0	25	420	2.43x10 ³
0.50	1.55x10 ³	114	2.41x10 ³	4.53x10 ³
1.0	8.50x10 ³	24.6	1.27x10 ⁴	2.04x10 ⁴
2.0	(1.96±0.08)x10 ⁴	18.6±2.0	(2.50±0.03)x10 ⁴	(2.56±0.14)x10 ⁴
3.0	(2.43±0.01)x10 ⁴	10.8±1.2	(3.83±0.12)x10 ⁴	(3.26±0.39)x10 ⁴
5.0	(2.52±0.03)x10 ⁴	13.7±3.7	(3.24±0.17)x10 ⁴	(3.02±0.03)x10 ⁴

^aThe tracer mixture was treated with 0.34M Fe(NH₄)₂(SO₄)₂ in 0.33M HNO₃ for 30 min. Each aqueous layer was made 0.02M in Fe(NO₃)₂, 0.02M in NH₂OH·HNO₃, and 0.01M in sulfamic acid before contact with solvent. Each solvent was pre-equilibrated three times with nitric acid of the same concentration used in the extractions. Extraction time was 1 min at 25°C. Solvent/aqueous volume ratio was 1/3 except for the second forward extraction, for which equal volumes were used. The solvent was prepared assuming that the CMPO was 100% pure.

Several other changes were also made in the second experiment: (1) the Fe(II) concentration used to reduce the extracted neptunium tracer was increased from 0.25 to 0.34M since the differences between the forward and back extractions indicate that a poorly extractable species is present in the initial aqueous solution, perhaps Np(V); (2) sulfamic acid was added to each aqueous phase to remove any nitrite ion present since traces of nitrite catalyze the oxidation of Np(IV) to Np(VI), particularly at high nitric acid concentrations; and (3) a second forward extraction was added to determine the extractability of the neptunium that remained in the aqueous layer after the first forward extraction. As shown in Table II-26, the distribution ratios obtained in the second experiment are greater, usually by a factor of 2 to 4, in the range of 0.05 to 1.0M HNO₃. At 2M and above the ratios agree within the uncertainties.

A series of extractions was performed in which each aqueous phase contained 1M H₂SO₄ in addition to nitric acid. In all other respects the conditions were the same as for the extractions given in Table II-25. Since sulfate ion forms a complex with Np(IV), lower distribution ratios were expected. The results, given in Table II-27, show that the distribution ratios for technetium in the presence of nitric/sulfuric acid are lower and considerably more reproducible and consistent than those obtained with nitric acid solutions alone. This may be attributed to the greater stability of neptunium in the IV oxidation state when complexed by sulfate ion. Comparable results were obtained in a similar experiment without the addition of ²³⁷Np but with fewer sulfuric acid concentrations and additional forward and back extractions.

Table II-27. Distribution Ratios for ^{239}Np - ^{237}Np between Nitric/Sulfuric Acid Mixtures and TRUEX-NPH^a

Conc., M		Forward Extraction	Back Extraction	
[H ₂ SO ₄]	[HNO ₃]		#1	#2
1	0.05	2.3	2.8	2.9
1	0.10	5.8	6.0	5.7
1	0.20	8.6	10.9	10.8
1	0.50	21.9	40.0	28.0
1	1.0	142	128	114
1	2.0	--	677	618
1	3.0	1.89×10^3	1.17×10^3	2.18×10^3
1	5.0	7.98×10^3	8.52×10^3	7.59×10^3

^aThe conditions were the same as given in Table II-25.

b. Preparation of ^{239}Np Tracer

The usual procedure for preparing ^{239}Np tracer for the distribution ratio measurements is as follows: separate the ^{239}Np from its parent, ^{243}Am , by extraction from concentrated hydrochloric acid, into 5% triisooctylamine (TIOA) dissolved in xylene; back-extract the ^{239}Np into water (which becomes about 1.3M in HCl); evaporate the aqueous solution; evaporate twice with nitric acid to remove the hydrochloric acid; dissolve the tracer in dilute nitric acid; and add Fe(II) and hydroxylamine nitrate to reduce the neptunium to the IV oxidation state. Since the variations in the distribution ratios obtained thus far can be explained on the basis that evaporation with nitric acid oxidizes the neptunium partially to Np(V) and that the reduction to Np(IV) is incomplete, it was thought that extraction directly from nitric acid solution would eliminate this problem. Triisooctylamine extracts only Np(IV) from either nitric or hydrochloric acid solution. Published reports³² state that Np(IV) extracts well from 4-6M HNO₃ but back-extracts poorly into water unless NaNO₂ is present, apparently to oxidize Np(IV) to Np(V). This extraction was studied using a small aliquot of ^{243}Am stock solution. About 76% of the neptunium extracted into 10% TIOA in xylene in 1 min, but only 7% back-extracted into water after 1 min and 16% after 5 min of contact. By diluting the TIOA solution by a factor of six (to about 1.6% TIOA) to reduce the distribution ratio, 78% of the neptunium was back-extracted in 2 min of contact.

This procedure is not practical with the amount of ^{243}Am now available (1 mg), since the back-extracted solution would still need to be evaporated to a small volume to obtain a sufficiently concentrated tracer solution. Ten milligrams of ^{243}Am has been ordered, and this amount should provide sufficient ^{239}Np for the nitric acid separation to be practical.

c. Studies on the Use of ^{237}Np

The separation of ^{233}Pa from ^{237}Np on silica gel was examined as a method for obtaining ^{237}Np free from its daughter for counting the ^{237}Np alpha particles by liquid scintillation without interference from beta particles. The silica gel absorbed most of the ^{233}Pa , as expected since protactinium carries quite well on silica. The ^{237}Np in a ^{237}Np - ^{233}Pa mixture could also be counted with a germanium detector with little interference (perhaps 5-10%, before correction) from ^{233}Pa . With this method, the distribution ratio for protactinium could also be measured.

6. Technetium Extraction Behavior
(P.-K. Tse)

The aim of the present work is to study the extraction behavior of technetium with CMPO alone, TBP in TCE, and two TRUEX solvents (0.2M CMPO, 1.4M TBP in NPH and 0.25M CMPO,

0.75M TBP in TCE). These data were used to elucidate the possible stoichiometry for the extraction equilibrium reaction and the role of TBP in the TRUEX solvents.

a. Effect of HNO_3 Concentration

The values of the distribution coefficient of TcO_4^- as a function of HNO_3 concentration for 0.2M CMPO and 0.75M TBP are presented in Fig. II-7. The technetium distribution coefficient increases with increasing nitric acid concentration until a maximum is reached at approximately 0.5M HNO_3 . The maximum value of the technetium distribution coefficient is 0.71 for 0.25M CMPO. Above 0.5M HNO_3 , D_{Tc} falls off rapidly due to the competition between nitric acid and pertechnetonic acid for the free CMPO; extraction of HNO_3 reduces the amount of free CMPO available to extract technetium. For 0.75M TBP, the same trend of distribution coefficient curve is observed as that for the CMPO system, but the maximum technetium distribution coefficient is at 1M HNO_3 with the value of 0.058. These results indicate that CMPO is a more powerful extractant than TBP for technetium extraction in nitric acid media.

Fig. II-7. Distribution Ratios for TcO_4^- as Function of HNO_3 Concentration

In TRUEX solvents with TCE and NPH diluents, the maximum D_{Tc} value is observed at 0.5M HNO_3 (Fig. II-7), and the shape of these curves resembles that for CMPO alone. The maximum D_{Tc} values at 25°C are 1.89 and 9.94 for the TCE- and NPH-based solvents, respectively. The D_{Tc} values of TRUEX-TCE are higher than the combined values of CMPO and TBP in TCE diluent at any ambient nitric acid concentration. This implies that technetium is extracted by a synergistic combination of CMPO and TBP. Horwitz et al.³³ found that D_{CMPO} is lowest in aliphatic diluent and

highest in aromatic and chlorocarbon diluents. These trends are in agreement with results reported for TBP and other trialkylphosphates^{34,35} and can be explained by the interaction between the extractant and diluents. The stronger the interaction between the extractant and the diluent, the higher the extractant distribution ratio. Conversely, the stronger the interaction between the extractant and the diluent, the weaker the extraction power of the extractant. Therefore, the D_{Tc} values for NPH should be higher than those for TCE, and our experimental results agree with this hypothesis.

The D_{Tc} values decrease about 30% when the extraction temperature changes from 25 to 50°C.

b. Effect of TBP Concentration

Plots of D_{Tc} as a function of CMPO concentration with different TBP concentrations in contact with 1.0M HNO_3 are shown in Fig. II-8. The slopes of the lines change from 2.0 to 1.15 as the concentration of TBP is increased. Plotting the same data as a function of TBP concentration with different CMPO concentrations shows that the slope of the curves (Fig. II-9) changes from 0.4 to 1.3 when the concentration of CMPO is decreased from 0.5 to 0.1M. These results suggest that TBP takes part in the extraction process.

Fig. II-8.

Distribution Ratios for TcO_4^- in 1.0M Nitric Acid with CMPO in TCE at 25°C

Fig. II-9. Distribution Ratios for TcO_4^- in 1.0M Nitric Acid with TBP in TCE at 25°C

c. Extraction Stoichiometry

The variation of distribution coefficients of technetium from 1.0 and 6.0M HNO_3 as a function of CMPO concentration in TCE is shown in Fig. II-10. The slopes of the 1.0 and 6.0M HNO_3 curves are in agreement (slope = 1.96 and 1.80 , respectively), suggesting that the extraction stoichiometry is

Fig. II-10.

Distribution Ratios for TcO_4^- in 1 and 6M HNO_3 vs. CMPO Concentration in TCE at 25°C

To maintain electroneutrality, the extracted species is assumed to be HTcO_4 . This stoichiometry is different from that reported in recent studies of technetium extraction with dihexyl-N,N-diethylcarbamoylmethylphosphonate (DHDECMP) in diethylbenzene and TBP in n-dedocane from HNO_3 media. These studies show a third-order dependency on the extractant concentration^{36,37} This difference may be due to the steric hinderance in accommodating three CMPO molecules and HTcO_4 because the CMPO molecule is more rigid and larger in size than the other two extractants (DHDECMP and TBP).

An important consideration in explaining the extraction behavior of HTcO_4 is its strength as an acid. Rulfs et al.^{38,39} reported the pertechnetic acid dissociation constant. Their earlier results³⁸ indicated that pertechnetic acid is a weak acid with an acid dissociation constant of 0.5 ± 0.2 . However, in a later publication, they³⁹ determined HTcO_4 to be a very strong acid with an acid dissociation constant $>10^8$. The results of our extraction studies indicate that the acid association equilibrium of HTcO_4 is important in the range of HNO_3 concentrations studied and appears to be close to the Rulfs et al. earlier value. The following set of equations has been used to fit the experimental data:

Taking these equilibria into consideration leads to the following distribution coefficient equation for technetium in nitric acid media:

$$D = \frac{[\overline{\text{CMPO}}]^2_{\text{free}} \{ \text{H}^+ \} (K_0 + K_1 \{ \text{H}^+ \} \{ \text{NO}_3^- \} + K_2 \{ \text{H}^+ \} \{ \text{NO}_3^- \}^2 + K_3 \{ \text{H}^+ \}^3 \{ \text{NO}_3^- \}^3)}{1 + K_a \{ \text{H}^+ \}} \quad (\text{II-73})$$

The concentration of free CMPO in the organic phases and the hydrogen and nitrate activities in aqueous solutions are calculated according to the model developed by Chaiko et al.^{40,41}

The D_{Tc} values for 0.25M CMPO alone calculated from Eq. II-73 show good agreement to the measured D_{Tc} values (Fig. II-11), and equilibrium constants are displayed in Table II-28.

When K_a was set equal to zero in Eq. II-73, as would be the case for an acid dissociation constant $>10^8$, the calculated distribution ratio values were higher than experimental values, and an acceptable fit of calculated values to the measured D_{Tc} was not attained. To fit the data, K_a value for HTcO_4 of 2.54 (acid dissociation constant of 0.4) was necessary. This suggests that pertechnetic acid is a weak acid in nitric acid, and that the conclusion of Rulfs et al. in their first paper³⁸ is correct.

Fig. II-11.

Distribution Ratios for TcO_4^- in TCE or NPH Diluents at 25 °C (symbols, measured values; curves, calculated)

Table II-28. Calculated Equilibrium Constants for Extraction of HTcO_4^- with a 0.25M CMPO and TRUEX Solvent

	CMPO Only	TRUEX-TCE	TRUEX-NPH
K_a	2.54	2.54	2.54
K_0	9.66×10^1	3.4×10^2	1.61×10^3
K_1	4.73×10^1	1.07×10^3	9.87×10^3
K_2	5.30×10^{-1}	3.06×10^1	4.75×10^2
K_3	3.50×10^{-2}	2.54×10^{-2}	1.40×10^{-1}
K_4	---	3.90×10^{-4}	4.70×10^{-4}

d. Role of TBP in TRUEX Solvents

Figure II-12 shows the dependency of HTcO_4^- extraction on CMPO concentration in the presence of a constant TBP concentration. The slopes of the curves for 1.4M TBP/NPH and 0.75M TBP/TCE are 1.06 and 1.46, respectively. At $[\text{CMPO}] < 10^{-1}\text{M}$ in the 1.4M TBP/NPH solvent, the slope is horizontal, suggesting that CMPO does not take part in the technetium extraction at these low concentrations. At low nitric acid concentrations, the predominant extractant species is CMPO-TBP, and the extraction of technetium can be expressed by

Fig. II-12. Distribution Ratios for TcO_4^- in 1.0M Nitric Acid and 1.4M TBP/NPH or 0.75M TBP/TCE at 25°C

At medium and high nitric acid concentrations in aqueous solutions, the amount of nitric acid in the organic phase increases, and the following extraction equilibria become important:

Based on these equilibria, the technetium distribution coefficient expression is

$$D = \frac{\{ \text{H} \} [\text{CMPO}]_f^2 [\text{TBP}]_f (K_0 + K_1 \{ \text{H} \} \{ \text{NO}_3 \} + K_2 \{ \text{H} \}^2 \{ \text{NO}_3 \}^2) + K_3 \{ \text{H} \}^4 \{ \text{NO}_3 \}^4 [\text{CMPO}]_f [\text{TBP}]_f^2 + K_4 \{ \text{H} \}^4 \{ \text{NO}_3 \}^3 [\text{TBP}]_f^3}{1 + K_a \{ \text{H} \}} \quad (\text{II-79})$$

Figure II-11 shows the fit of Eq. II-79 to the extraction data for TRUEX-TCE and TRUEX-NPH. The values of K_0 , K_1 , K_2 , K_3 , and K_4 are given in Table II-28.

H. Thermodynamic Activity Measurements

(I. R. Tasker)

1. Introduction

One of the pressing needs for the improvement and extension of the TRUEX model is determining thermodynamic activities of certain species in the data base. Various techniques for obtaining these activities have been investigated and their limitations with respect to the needs and expediencies of our work evaluated. Only those techniques applicable to (primarily) aqueous solutions were considered. Techniques considered were:

- Isopiestic Method
- Freezing Point Depression
- Osmotic Pressure
- emf Cells with Transference
- emf Cells without Transference
- Bithermal Equilibration
- Boiling Point Elevation
- Solubility
- Solute Vapor Pressure
- Solvent/Solvent Distribution
- Sedimentation Rate
- Diffusion Rate
- Capillarity Measurements
- Conductivity Measurements
- Vapor Pressure Osmometry

For the purposes of our work, we need a method that is fast, not too experimentally complex, operates over a fairly wide temperature and concentration range, and has an accuracy appropriate to the models we are using (hence, not necessarily the highest quality). In addition, some added flexibility, such as the potential to measure organic phase activities and the ability to measure water activity (for verification), would be useful. In the light of these requirements, the only method that really addresses these needs is vapor pressure osmometry.

2. Vapor Pressure Osmometry

In vapor pressure osmometry, samples of solvent and solution are placed on temperature detectors in a chamber saturated with pure solvent vapor. The presence of solute in a solution requires that the solvent in that solution exerts a vapor pressure lower than that of pure solvent under the same conditions. In the vapor pressure osmometer, a consequence of this difference in vapor pressures is that solvent condenses from the vapor phase into the drop of solution on the thermistor. The enthalpy of condensation of the vapor causes the temperature of the solution to rise. This, in turn, increases the vapor pressure of solvent in the sample. Eventually, as the vapor pressure of the solvent in the solution approaches that of the pure solvent, a steady state is set up. The measured temperature rise is related to the vapor pressure of the solvent in the solution; this is related to the solvent activity, which in turn is related to the solute activity. The method has the advantages of being rapid, reasonably accurate, and operating over a wide temperature (0-100°C) and concentration range, as well as being amenable to any nonvolatile solute (ionic or neutral in character). The disadvantages are that it requires calibration,

requires excellent temperature control, is a steady-state rather than equilibrium method, and is not of the very highest accuracy. The commercial instrument chosen was a Wescan Model 233 (Wescan Instruments Inc., Alltech Associates Inc., San Jose, CA).

3. Aluminum Nitrate

Vapor pressure osmometer (VPO) measurements on aluminum nitrate systems have been completed. Data treatment has been started. Calibrations were performed using sodium chloride solutions. Concerns over hydrolysis of the Al^{3+} ion in aqueous solution require special precautions in purification of starting material and preparation of solutions. The method followed is that given by Hovey.¹⁵ Aldrich certified ACS aluminum nitrate nonahydrate was twice recrystallized from 0.02M HNO_3 by cooling slowly from 50°C to room temperature and then to 0°C. The crystals were stored wet with HNO_3 to prevent hydrolysis. Subsequent solutions prepared from this material will also contain varying amounts of HNO_3 to prevent hydrolysis. To determine the precise composition of the solutions, the stock will be standardized gravimetrically by homogeneous precipitation of aluminum with 8-hydroxyquinoline and the nitric acid content will be determined by pH measurements.

I. 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 chemistry of the TRUEX process, (2) test and verify process modifications, and (3) verify the results of the computer model being developed for predicting species extraction behavior and calculating flowsheets for the TRUEX process.

Three 4-cm centrifugal contactor units are available for completing these tests: a 16-stage unit for nonradioactive tests, a 16-stage unit located in a glovebox for radioactive tests, and a new 8-stage unit designed for remote operation. The latter can be used for either radioactive or nonradioactive experiments.

Although specific waste solution compositions will be used in these studies, the purpose of these tests is not to demonstrate flowsheets for specific waste streams, but to collect data to verify that the GTM predicts actual extraction behavior. Therefore, flowsheets have not been optimized. Three verification tests were completed this period with the TRUEX-TCE solvent. Only one of these tests will be discussed in detail since samples from the other two tests have not been analyzed. A discussion of the new system for radioactive tests is also included.

2. Verification Run 4

Verification Run 4 was completed without incident on February 2, 1989. The purpose of this run was to (1) evaluate the extraction of neodymium, nitric acid, and iron from a simplified acidic waste solution using the TRUEX-TCE solvent and (2) study the variability of the steady-state

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concentrations of various species. The TRUEX-TCE solvent consists of 0.25M CMPO, 0.75M TBP in TCE.

a. Flowsheet

The flowsheet used in this test is shown in Fig. II-13. The composition of each aqueous feed is shown in this figure. Only one scrub section is included in this flowsheet; its composition is 0.04M HNO_3 and 0.005M $\text{Fe}(\text{NO}_3)_3$. The purpose of the scrub section is twofold. First, some of the nitric acid that was extracted in the extraction section is stripped from the organic. By removing this nitric acid, the next strip section performs better. Second, 0.005M $\text{Fe}(\text{NO}_3)_3$ was added to remove any oxalic acid that was extracted into the organic phase.

Fig. II-13. Flowsheet for Verification Run 4

The purpose of the first strip section in the TRUEX process is to strip and recover americium from the organic phase. This stream is labeled EW in Fig II-13. In this test, americium was not added to the DF feed solution, but neodymium, a rare earth that behaves like americium, was present. By measuring the neodymium concentration in this test, the americium behavior can be inferred. The composition of the first strip solution was the same as in previous verification tests (0.04M HNO_3).

The purpose of the second strip section in the TRUEX process is to remove and recover plutonium from the organic phase. In this test, we did not have a metal that behaves similarly to plutonium. Therefore, we only concentrated on the nitric acid concentrations in this section and on any neodymium that was not stripped in the previous section. The composition of the second strip solution was changed from 0.1M HF to 0.04M HNO_3 plus 0.04M HF in this test.

Three solvent cleanup stages were also added for this test: two stages of carbonate wash (0.25M Na_2CO_3) and one stage of acid rinse (0.1M HNO_3). The purpose of the two carbonate cleanup stages is to remove acid degradation products from the organic phase and to remove any of the metals that were not recovered in the scrub and strip sections. The last stage, the acid rinse section, is used to reacidify the organic and neutralize any sodium carbonate that is carried over with the organic.

b. Sampling

Numerous samples were collected during the test. Approximately 16 min into the test, 55 samples from each of the raffinates were collected on an 8-min cycle. These samples were collected to determine how the various components approach their steady-state concentrations. The time was recorded when each of these samples was collected.

In addition, samples from the contactor stages were collected at the end of the test. These samples consisted of both the organic and aqueous phases that were contained in the contactor rotors. By measuring the concentrations in these samples, the concentration profile (both the organic and aqueous phase) for nitric acid and the metals in solution was determined. To collect accurate stage samples, the solution in the rotor (which is at steady state) and the solution in the mixing zone (which may not be at steady state) must be separated. This was accomplished by using a special shutdown procedure.

The shutdown procedure consisted of placing beakers underneath each stage drain valve, turning off all of the feed pumps, then quickly opening each drain valve. The rotors were left on during this operation to prevent solutions inside the rotors from draining. For this test, the pumps were shut off and all of the drain valves were opened within approximately 10 s. After the annular-region solutions were removed, sample bottles were placed beneath each stage, then the contactor motors were shut down. As the rotors spun down, the solution drained from the rotor and into the sample bottles.

Samples were then analyzed by aqueous titration, organic titration, and analysis by inductivity coupled plasma with atomic emission spectroscopy (ICP-AES). Some nitrate analysis was also performed.

c. Aqueous Acid Analysis

Acid analysis of the raffinates, the feeds, and the aqueous stage samples was completed by titrating a known aliquot with NaOH. When multiple endpoints were detected, the first endpoint was assumed to correspond to the hydrogen ion concentration (H^+). With solutions containing both HNO_3 and HF, the acid concentration from the titration was equal to the total H^+ concentration of the

solution ($\text{HNO}_3 + \text{HF}$). Titration of most of the samples was fairly straightforward, except for the extraction feed and extraction raffinate samples. Because of the number of components in these samples, four to seven endpoints were typically detected.

As discussed in the previous section, raffinate samples were collected to determine how the various components approach steady state and what the steady-state concentrations are. These concentrations are reported in Table II-29. These data can also be plotted versus the time that the sample was collected. To be consistent between tests, the sample collection times are adjusted; $t=0$ was set at the time when a color change was observed in the extraction section (DW) raffinate. This color change indicates that the extraction feed had passed through the extraction section and is exiting the contactor. A typical plot is shown in Fig. II-14. In this figure, the acid concentrations in the second strip (FW) raffinate are plotted versus time. In addition, the GTM prediction for the steady-state acid concentration in this stream is shown by the horizontal line. (The GTM cannot predict the approach to steady state, only the steady-state concentrations.) For the DW, EW, and FW samples, there was good agreement between the titration data and the GTM predictions. The current version of the GTM does not include the solvent cleanup stages, so predictions for the GW and FW raffinate streams are not available. A future version of the GTM will include these sections.

Fig. II-14. Acid Profile in the Second Strip Raffinate (FW) for Verification Run 4

The stage samples collected at the end of the run were also analyzed by aqueous titration. To analyze these samples, the aqueous and organic phases were separated by centrifugation, then an aliquot of the aqueous phase was collected and titrated. Titration results for the aqueous-phase stage samples are listed in Table II-30 and plotted in Fig. II-15. The GTM predictions are also included in this figure. For stages 10-13, the GTM predictions and the titration results include both the HNO_3 and HF concentrations. As shown previously for the raffinate samples, there is good agreement between the experimental results and the GTM predictions.

d. Organic Acid Analysis

All of the organic samples collected during the run were analyzed for H^+ by two different titration methods: (1) stripping the acid from the organic phase with water, then titrating the wash solutions, and (2) titrating the organic phase directly with tetrabutylammonium hydroxide (TBAOH). A reference electrode filled with aqueous-saturated KCl in both chambers was used in conjunction with an AgCl indicator electrode. Sample preparation involved the dilution of a known aliquot of the sample with isopropyl alcohol.

Table II-29. Aqueous Acid Titration Results for Verification Run 4

Sample	Sample Time, min	Meas'd. Conc., M		Calc'd. Conc., M	
		[H ⁺]	Average	[H ⁺]	[H ⁺] + [HF]
DW#1	4.00	0.995 1.012	1.004	1.19	1.19
DW#2	12.00	1.124 1.175	1.149	1.19	
DW#3	20.00	1.127 1.155	1.141	1.19	
DW#4	28.00	1.132 1.131	1.131	1.19	
DW#5	36.00	1.116 1.109	1.112	1.19	
DW#6	44.00	1.140 1.135	1.138	1.19	
EW#1	8.00	0.154 0.144 0.155 0.144 0.140	0.147	0.186	0.186
EW#2	16.00	0.154 0.145 0.143 0.152	0.148	0.186	0.186
EW#3	24.00	0.160 0.150 0.151 0.146	0.152	0.186	0.186
EW#4	32.00	0.164 0.154 0.154 0.159	0.158	0.186	0.186
EW#5	40.00	0.168 0.163 0.156 0.158 0.169	0.163	0.186	0.186
EW#6	48.00	0.172 0.163 0.173 0.159 0.161	0.165	0.186	0.186
FW#1	4.00	0.0500 0.0485	0.0492	0.0414	0.05029
FW#2	12.00	0.0465 0.0460	0.0462	0.0414	0.05029
(cond)					

Table II-29. (cond)

Sample	Sample Time, min	Meas'd. Conc., M		Calc'd. Conc., M	
		[H ⁺]	Average	[H ⁺]	[H ⁺] + [HF]
FW#3	20.00	0.0465			
		0.0461	0.0463	0.0414	0.0503
FW#4	28.00	0.0465			
		0.0462	0.0463	0.0414	0.0503
FW#5	36.00	0.0467			
		0.0467	0.0467	0.0414	0.0503
FW#6	44.00	0.0465			
		0.0437			
		0.0433			
		0.0446			
		0.0446	0.0445	0.0414	0.0503
HW#1	4.00	0.0795			
		0.0791	0.0793		
HW#2	12.00	0.0781			
		0.0769			
		0.0720			
		0.0723			
		0.0722			
		0.0744			
		0.0726	0.0741		
HW#3	20.00	0.0731			
		0.0728	0.0730		
HW#4	28.00	0.0698			
		0.0666			
		0.0691	0.0685		
HW#5	36.00	0.0612			
		0.0655			
		0.0610	0.0626		
HW#6	44.00	0.0630			
		0.0625	0.0628		

The organic acid concentrations from both titration methods and the values calculated by the GTM are tabulated in Table II-31 and plotted in Fig. II-16. Except for the low acid concentrations (<0.01M), the organic titration technique compares very well with values generated by the GTM. At the low acid concentrations, the differences may be due to analysis errors (because of the low concentrations), inaccuracies in the model, or small differences in the flowsheet that have yet to be analyzed (such as flow rates or differences in the feed compositions). The aqueous titration data do not agree with the GTM results for stages 7-13 due to the presence of HF in these samples. The direct organic titration method separates the HF from the nitric acid.

Table II-30. Aqueous Stage Sample Titration Results for Verification Run 4

Sample	Meas'd. Conc., M		Calc'd. Conc., M		
	[H ⁺]	Average	[H ⁺]	[HF]	[H ⁺] + [HF]
Stage #1	1.03				
	1.03				
	0.974				
	1.09	1.03	1.190	0.0003	1.19
Stage #2	1.30				
	1.35	1.33	1.490	0.0004	1.49
Stage #3	1.54				
	1.53				
	1.56				
	1.49				
	1.47				
	1.51	1.52	1.810	0.0004	1.81
Stage #4	1.00				
	1.01	1.00	1.230	0.0003	1.23
Stage #5	0.538				
	0.529				
	0.524				
	0.555	0.537	0.664	0.0002	0.664
Stage #6	0.173				
	0.172	0.173	0.344	0.0001	0.344
Stage #7	0.0651				
	0.0645	0.065	0.060	0.0000	0.060
Stage #8	0.0431				
	0.0437	0.043	0.043	0.0000	0.043
Stage #9	0.0410				
	0.0428				
	0.0432				
	0.0384	0.041	0.041	0.0000	0.041
Stage #10	0.0445				
	0.0449	0.045	0.041	0.0089	0.050
Stage #11	0.0496				
	0.0496	0.050	0.041	0.0173	0.058
Stage #12	0.0557				
	0.0620				
	0.0621				
	0.0546	0.059	0.040	0.0253	0.066
Stage #13	0.0649				
	0.0649	0.065	0.040	0.0328	0.073
Stage #14	0.177				
	0.173	0.175			
Stage #15	0.235				
	0.227	0.231			
Stage #16	0.0546				
	0.0567	0.056

Fig. II-15. Stagewise Acid Profile for Verification Run 4

Table II-31. Organic-Acid and Aqueous-Acid Titrations for Organic Stage Samples in Verification Run 4

Sample	Meas'd. $[H^+]$, M		Calc'd. Conc., M	
	Direct Organic Titration ^a	Stripped Organic (Aqueous Titration) ^b	$[H^+]$ ^c	$[H^+ + HF]$ ^{c,d}
Stage #1	0.480	0.480	0.472	
Stage #2	0.537	0.519	0.539	
Stage #3	0.384	0.382	0.410	
Stage #4	0.347	0.255	0.279	
Stage #5	0.121	0.121	0.133	
Stage #6	0.028	0.012	0.019	
Stage #7	0.0067	0.0018	0.0043	
Stage #8	0.0036	0.0066	0.0027	
Stage #9	0.0022	0.0023	0.0020	
Stage #10	0.0030	0.0047 ^{e,f}	0.0018	0.0060
Stage #11	0.0021	0.0045 ^{e,f}	0.0015	0.0097
Stage #12	0.0023	0.0068 ^{e,f}	0.0014	0.013
Stage #13	0.0024	0.0092 ^{e,f}	0.0014	0.017

^aOrganic titrated directly.^bOrganic stripped and the aqueous strip solution titrated.^cVersion 1.1c of the GTM was used to calculate these values.^dValues include the $[H^+]$ plus the $[HF]$.^eValue reported for the stripped organic titration includes stripped HF.^fValue reported does not include all of the organic HF because of an inadequate strip procedure.

Fig. II-16. Hydrogen Ion Concentrations Derived from Direct Organic Titration, Aqueous Wash Titration, and GTM Predictions for Verification Run 4

Two important advantages in the direct organic titration method include eliminating the organic stripping procedure and separating the organic nitric acid concentration from the hydrofluoric acid concentration. Future verification tests will use the direct organic titration method for determining organic nitric acid and hydrofluoric acid concentrations.

e. Nitrate Analysis

To measure the nitrate concentration in aqueous samples, we investigated a method using a specific ion electrode (Orion Nitrate Electrode Model #930700) and a pH meter. With this method, a calibration curve is generated by measuring standard nitrate concentrations of 0.1, 0.01, and 0.001M. These standards are prepared by adding Ionic Strength Adjustor (ISA) and Nitrate Interference Suppressor (NIS) to a solution of sodium nitrate. Two milliliters of ISA is added per 100 mL of sample; the NIS is added to suppress the activity of ions present in solution that affect the nitrate activity. The potential of each standard solution is measured by using the specific ion electrode, and a standard curve is prepared by plotting the log of the nitrate concentration versus the potential (read on the pH meter). To measure the nitrate concentration in another sample, the sample is prepared in the same way as the standards (by adding ISA and the NIS solutions), and then the potential is measured with the electrode. The potential is converted to a nitrate concentration by using the calibration curve.

To check the method, the concentration of a standard 0.05M HNO_3 solution was measured. Even though the concentration was well within the calibration range of 0.001 to 0.1M, an accurate reading of the nitrate concentration could not be measured; results were an order of magnitude different than expected. The method was checked using nitrate salts such as aluminum nitrate, sodium nitrate, and neodymium nitrate, and the measured nitrate concentrations agreed well with the expected values. Since the measurement of different nitric acid concentrations did not improve the accuracy of the method, the hydrogen ion seems to be the problem with measuring the nitrate in our solutions. Since all of the samples from the verification tests are acidic, an attempt was made to buffer the samples. However, the addition of the buffers prevented us from generating a standard curve of sufficient accuracy.

Another possibility that was briefly evaluated was adjusting the hydrogen ion concentration by titrating the samples to a known pH. This did not work because the samples contain metals that would precipitate if the solution were not acidic. Because of these problems, nitrate analysis using a nitrate electrode does not appear to be a viable method for determining nitrate concentrations in samples generated during verification runs.

f. Metals Analysis

Samples were measured for metals (Al, Ca, Fe, Zr, Nd, Na, Ni, and Mo) by ICP-AES. After sample preparation was completed, samples were submitted to E. A. Huff (ANL Analytical Chemistry Laboratory) for analysis. Aqueous sample preparation consisted of diluting aliquots. Preparation for organic samples was more complicated because the metals must be in an aqueous matrix for ICP-AES analysis. Metals were stripped from the organic phase by two different methods, summarized in Table II-32. The principal stripping agent used in Procedure #2 is 1 hydroxyethane, 1-1 diphosphonic acid (HEDP); HEDP is not used for stages 1-5 because a white precipitate forms on contact of the strip solution with the organic phase and is difficult to redissolve. A comparison of the two techniques has shown that both perform comparably in stripping metals from the organic samples.

Table II-32. Organic Stripping Procedure for ICP-AES Analysis in Verification Run 4

	Volume, mL	Number of Contacts
Procedure #1^a		
TRUEX Solvent	4	
0.5M Nitric Acid/ 0.05M Oxalic Acid	12	2
5.0M Nitric Acid	2	2
Water	4	3
Dilute Washings to 50 mL with 1.0M Nitric Acid		
Procedure #2^b		
TRUEX Solvent	4	
1.0M Na Acetate/Acetic Acid	4	1
0.05M HEDP in 0.25M Acetate Buffer	4	2
0.05M Nitric Acid	4	1
Dilute Washings to 50 mL with 1.0M Nitric Acid		

^aUsed for stage samples 1-5.

^bUsed for stage samples 6-16, as well as DX and HP samples.

The analysis results for the feed samples are shown in Table II-33. Based upon this analysis, the measured concentrations for all of the metal components in the extraction feed (DF) were less than expected. The last analysis results shown in this table are for the 1M HNO₃ used to prepare (dilute) samples for ICP-AES analysis. Low levels of Al, Ca, Fe, and Na were detected in the acid alone. This will adversely affect the results obtained in low level analysis of these metals.

Table II-34 contains the ICP-AES results for the aqueous raffinate streams and the aqueous stage samples. Also reported is an average concentration for each component in each stream,

Table II-33. Feed Sample ICP-AES Results for Verification Run 4

Sample	Conc., <u>M</u>							
	[Al]	[Ca]	[Fe]	[Zr]	[Nd]	[Na]	[Ni]	[Mo]
DF Feed	0.626	0.017	0.116	0.004	0.005	0.161	--	--
Expected	0.720	0.020	0.130	0.006	0.008	0.180	--	--
DS Feed	---	---	0.005	---	---	0.000	--	--
Expected			0.005					
GF Feed	---	1.72E-05	---	---	---	5.11E-01	--	--
Expected		0				0		
1.0M HNO ₃	5.19E-06	3.49E-06	1.25E-06	---	---	1.78E-05	--	--

which was calculated by averaging the last four samples in each series. Duplicate samples (one for each stream) were analyzed, and these results are included in the table. The last two metals listed in this table, Ni and Mo, were not added in the feed solution but are components of stainless steel. High concentrations of these metals would indicate a possible corrosion problem with the contactor. As shown in the table, nickel was only detected in the extraction section raffinate (DW) and at low concentrations ($2.5 \times 10^{-5} \text{ M}$). This is consistent with data collected in previous verification runs and indicates that corrosion is not a serious concern.

Table II-34 also includes the GTM predictions for the DW, EW, and FW streams. These values are based upon version 2.0 of the GTM (effect of solvent loading included). As shown in Table II-34, the data for the extraction raffinate (DW) are in fairly good agreement with the GTM results, except that they are generally too high. This supports the feed solution analysis (Table II-33), which indicates that lower concentrations of these metals were present in the feed.

The EW and FW raffinate concentrations measured for most of the metal components are greater than the GTM predictions. This finding is especially true for Ca, Zr, Fe, and Na. The measured metal concentrations are partially attributable to the presence of these components in the nitric acid solution used to prepare the samples for analysis (Table II-33), but in general, these concentrations are an order of magnitude greater than they should be if this is the only source of these metals. We suspect that these measured concentrations are due to contamination in the contactor from previous experiments. This has been a problem in the tracer experiments with the contactor designed for radioactive solutions.

Table II-35 contains the ICP-AES results and the average concentration for the organic stream and stage samples. Average values were calculated as described above. The first thing that is evident from these results is the high concentration of Na (1.5 M) and Ca (10^{-5} M) in these samples. These high concentrations are due to the HEDP-buffer solution used to strip the metals from the organic phase.

Figures II-17 to II-19 illustrate some of the ICP-AES data listed in the previous three tables. In Fig. II-17, the neodymium stage concentrations are plotted versus stage number. The fit between the measured concentrations and the GTM predictions is not very good and may be due to several reasons. First, the other-phase carryover has been estimated to be 0.5% for the 4-cm contactor. A lower value would move the GTM curves down in the two strip sections and make the fit better. Second, the organic flow rate was not checked during the run (because it is a recycle stream). A small change in this flow rate changes the organic-to-aqueous (O/A) ratio and, therefore, the extraction factor. Changing

Table II-34. Aqueous Phase ICP-AES Results for Verification Run 4

Sample	Time of Collection, min	Conc., M							
		[Al]	[Ca]	[Fe]	[Zr]	[Nd]	[Na]	[Ni]	[Mo]
DW#1	3.8	0.530	0.014	0.098	0.0029	5.48E-05	0.14	2.39E-05	---
DW#2	11.8	0.537	0.014	0.099	0.0029	7.00E-05	0.14	2.39E-05	---
DW#3	19.8	0.545	0.014	0.101	0.0030	6.93E-05	0.14	2.39E-05	---
DW#4	27.8	0.537	0.014	0.100	0.0030	6.72E-05	0.14	2.39E-05	---
DW#4	27.8	0.549	0.015	0.102	0.0030	6.72E-05	0.14	2.56E-05	---
DW#5	35.8	0.534	0.014	0.099	0.0029	6.45E-05	0.14	2.39E-05	---
DW#6	43.8	0.556	0.015	0.103	0.0030	6.52E-05	0.14	2.56E-05	---
AVERAGE (3 thru 6)		0.544	0.014	0.101	0.0030	6.67E-05	0.14	2.45E-05	
GTM Prediction ^a		0.617	0.017	0.112	0.0051	5.69E-05	0.15		
EW#1	7.8	---	8.26E-05	1.32E-03	1.34E-03	7.45E-03	1.09E-04	---	---
EW#1	7.8	---	8.89E-05	1.34E-03	1.31E-03	7.11E-03	1.09E-04	---	---
EW#2	15.8	---	8.26E-05	1.31E-03	1.36E-03	7.89E-03	1.01E-04	---	---
EW#3	23.8	---	8.43E-05	1.42E-03	1.45E-03	7.97E-03	5.44E-05	---	---
EW#4	31.8	---	8.11E-05	1.38E-03	1.41E-03	7.76E-03	5.17E-05	---	---
EW#5	39.8	---	8.42E-05	1.45E-03	1.50E-03	8.02E-03	9.52E-05	---	---
EW#6	47.8	---	8.42E-05	3.53E-03	1.52E-03	8.02E-03	5.44E-05	---	---
AVERAGE (3 thru 6)			8.34E-05	1.95E-03	1.47E-03	7.94E-03	6.39E-05		
GTM Prediction ^a		3.57E-08	1.39E-09	4.79E-05	4.87E-08	8.49E-03	1.25E-08		
FW#1	3.8	---	8.23E-05	1.43E-05	8.77E-06	---	6.09E-05	---	---
FW#2	11.8	---	6.74E-05	1.61E-05	6.36E-05	1.59E-05	4.78E-05	---	---
FW#2	11.8	---	7.24E-05	1.43E-05	7.34E-05	3.47E-05	4.78E-05	---	---
FW#3	19.8	---	6.74E-05	1.43E-05	5.59E-05	1.39E-05	4.78E-05	---	---
FW#4	27.8	---	6.24E-05	1.43E-05	5.04E-05	1.32E-05	3.91E-05	---	---
FW#5	35.8	---	5.74E-05	1.25E-05	4.82E-05	1.59E-05	3.91E-05	---	---
FW#6	43.8	---	8.98E-05	1.25E-05	4.93E-05	1.94E-05	3.48E-05	---	---
AVERAGE (3 thru 6)			6.92E-05	1.34E-05	5.10E-05	1.56E-05	4.02E-05		
GTM Prediction ^a			3.59E-18	5.07E-05	6.23E-08	6.82E-03	3.23E-17		
GW#1	7.8	---	1.72E-05	1.12E-05	4.11E-06	---	0.51	---	---
GW#2	15.8	---	1.87E-05	1.57E-05	2.19E-05	---	0.51	---	---
GW#3	23.8	---	1.25E-05	6.71E-06	---	---	0.51	---	---
GW#4	31.8	---	2.18E-05	7.83E-06	---	---	0.51	---	---
GW#5	39.8	---	1.40E-05	8.95E-06	---	---	0.51	---	---
GW#5	39.8	---	2.65E-05	6.71E-06	---	---	0.52	---	---
GW#6	47.8	---	2.03E-05	6.71E-06	---	---	0.52	---	---
AVERAGE (3 thru 6)			1.90E-05	7.39E-06			0.51		
HW#1	3.8	---	1.56E-05	1.12E-05	---	---	7.53E-04	---	---
HW#2	11.8	---	1.56E-05	1.12E-05	---	---	1.07E-03	---	---
HW#3	19.8	---	1.56E-05	6.71E-06	---	---	1.33E-03	---	---
HW#4	27.8	---	1.56E-05	6.71E-06	---	---	1.61E-03	---	---
HW#4	27.8	---	1.25E-05	8.95E-06	---	8.71E-05	1.55E-03	---	---
HW#5	35.8	---	1.56E-05	6.71E-06	---	---	1.79E-03	---	---
HW#6	43.8	---	1.56E-05	7.83E-06	---	---	2.09E-03	---	---
AVERAGE (3 thru 6)			1.50E-05	7.39E-06		8.71E-05	1.67E-03		
Stage #1		5.45E-01	1.45E-02	9.54E-02	2.13E-03	4.16E-05	1.43E-01	2.39E-05	---
Stage #2		5.41E-01	1.45E-02	9.69E-02	2.96E-03	4.34E-04	1.41E-01	2.56E-05	---
Stage #3		8.11E-04	4.55E-04	1.48E-02	1.07E-03	7.09E-04	4.78E-04	---	---
Stage #4		8.34E-05	5.30E-05	1.32E-02	6.66E-04	5.72E-04	1.74E-04	---	---

(cond)

Table II-34. (cond)

Sample	Time of Collection, min	Conc., M							
		[Al]	[Ca]	[Fe]	[Zr]	[Nd]	[Na]	[Ni]	[Mo]
Stage #5	---	---	3.43E-05	1.14E-02	3.37E-04	8.84E-04	9.79E-05	---	---
Stage #5	---	---	4.05E-05	1.16E-02	3.36E-04	8.93E-04	3.26E-05	---	---
Stage #6	---	---	1.12E-04	3.49E-03	1.07E-03	6.61E-03	4.35E-05	---	---
Stage #7	---	---	1.12E-04	9.24E-04	2.37E-03	1.25E-02	---	---	---
Stage #8	---	---	8.42E-05	1.28E-04	8.62E-04	7.13E-03	7.07E-05	---	---
Stage #9	---	---	1.03E-04	2.91E-05	1.66E-04	1.74E-03	5.98E-05	---	---
Stage #10	---	---	6.24E-05	2.69E-05	5.48E-05	1.19E-04	6.52E-05	---	---
Stage #11	---	---	6.65E-05	2.98E-05	---	---	4.35E-05	---	---
Stage #12	---	---	8.73E-05	3.28E-05	---	---	7.97E-05	---	---
Stage #13	---	---	8.73E-05	2.39E-05	---	---	5.07E-05	---	---
Stage #14	---	---	2.18E-05	1.34E-05	8.22E-06	---	5.12E-01	---	---
Stage #14	---	---	4.68E-05	3.36E-05	2.47E-05	---	5.23E-01	---	---
Stage #15	---	6.95E-05	2.81E-05	2.01E-05	---	---	5.17E-01	---	---
Stage #16	---	---	3.43E-05	---	---	---	2.41E-03	---	---

^aBased on expected feed composition shown in Table II-33; note discrepancy between as-made-up and as-analyzed compositions.

Fig. II-17. Comparison of Experimental Data for [Nd] with the GTM Predictions for Verification Run 4

Table II-35. Organic Phase ICP-AES Results for Verification Run 4

Sample	Time of Collection, min	Conc., M					
		Al	Ca	Fe	Zr	Nd	Na
DX#0	0.0	---	4.37E-05	1.79E-05	---	---	1.57E+00
DX#1	3.8	---	2.81E-05	2.46E-05	---	---	1.58E+00
DX#2	11.8	---	1.87E-05	---	---	---	1.55E+00
DX#3	19.8	---	2.50E-05	---	---	---	1.51E+00
DX#4	27.8	---	1.87E-05	---	---	---	1.56E+00
DX#5	35.8	---	1.56E-05	---	---	---	1.57E+00
DX#6	43.8	---	2.36E-05	---	---	---	1.54E+00
AVERAGE (3 thru 6)			2.07E-05				1.54E+00
HP#0	0.0	---	2.81E-05	---	---	---	1.54E+00
HP#1	7.8	---	1.75E-04	---	---	---	1.59E+00
HP#2	15.8	---	3.43E-05	---	---	---	1.60E+00
HP#3	23.8	---	3.12E-05	---	---	---	1.58E+00
HP#3	31.8	---	1.31E-04	---	---	---	1.41E+00
HP#4	31.8	---	2.18E-05	---	---	---	1.54E+00
HP#5	39.8	---	2.50E-05	---	---	---	1.56E+00
AVERAGE (3 thru 6)			5.22E-05				1.52E+00
Stage #1		---	1.37E-04	6.83E-03	2.58E-03	8.59E-04	2.12E-04
Stage #2		---	1.09E-04	7.61E-03	3.58E-03	8.01E-03	2.34E-04
Stage #3		---	5.30E-05	3.60E-04	6.50E-04	7.15E-03	1.59E+00
Stage #3		---	1.56E-05	3.85E-04	2.36E-04	7.58E-03	2.45E-04
Stage #4		---	4.05E-05	2.62E-04	5.04E-04	8.39E-03	1.61E+00
Stage #4		---	---	3.18E-04	1.95E-04	7.15E-03	2.17E-04
Stage #5		---	4.68E-05	3.38E-04	2.92E-04	7.43E-03	1.61E+00
Stage #5		---	---	4.19E-04	2.56E-04	7.48E-03	2.28E-04
Stage #6		0.00E+00	4.68E-05	4.48E-05	3.70E-04	1.35E-02	1.60E+00
Stage #6		---	---	4.16E-04	2.55E-04	7.55E-03	2.07E-04
Stage #7		---	3.12E-05	---	3.52E-04	8.52E-03	1.57E+00
Stage #8		---	4.05E-05	---	1.64E-04	2.56E-03	1.59E+00
Stage #8		---	3.12E-05	---	---	2.38E-03	1.61E+00
Stage #9		---	6.86E-05	---	4.93E-05	3.84E-04	1.58E+00
Stage #10		---	3.74E-05	---	---	---	1.58E+00
Stage #10		---	2.50E-05	---	---	---	1.56E+00
Stage #11		---	8.42E-05	2.01E-05	---	---	1.54E+00
Stage #12		---	3.74E-05	---	---	---	1.56E+00
Stage #13		---	5.30E-05	---	---	---	1.58E+00
Stage #13		---	2.18E-05	---	---	---	1.56E+00
Stage #14		---	2.81E-05	---	---	---	1.57E+00
Stage #15		---	2.81E-05	---	---	---	1.58E+00
Stage #16		---	2.50E-05	---	---	---	1.56E+00

the O/A ratio would move the GTM predictions closer to the experimental data. Lastly, the GTM program may be in error. Improvements planned for the GTM include the addition of complexation calculations for every stage and an improvement in some of the component models. These changes may improve the fit between the GTM predictions and the data.

In Fig. II-18, the zirconium concentrations are plotted versus stage number. Some of the deviation between the measurements and calculations may be due to the factors discussed for the neodymium data. However, the large material balance error in these data indicates that contamination of the contactor or inadequate stripping of the organic phase during sampling is significant. Some of the raffinate data are shown in Fig. II-19, where the ICP-AES results are plotted versus sample time for the first strip raffinate (EW). In general, the concentrations of all of the components for all of the raffinate streams were fairly level, indicating that steady-state operation was achieved.

Fig. II-18. Comparison of Experimental Data for [Zr] with the GTM Predictions for Verification Run 4

Fig. II-19. First Strip (EW) Raffinate ICP-AES Results for Verification Run 4

3. Glovebox Setup for Contactor

A 16-stage 4-cm centrifugal contactor and associated equipment were installed in a glovebox so that solvent extraction experiments with trace levels of radioactivity can be conducted. The unit, shown in Fig. II-20, is a CENHAM (Chemical Engineering Hood Alpha Modular) glovebox that is 120-in. (3-m) long, 63-in. (1.6-m) high, and 42-in. (1-m) deep. It consists of three modules in a row with one-half module on top of each. Glove ports are located on two sides of the box, as shown in Fig. II-20.

Fig. II-20. Glovebox Setup

The glovebox is maintained at a negative pressure (typically, 200 Pa) by the building ventilation system. Two HEPA filters are located in parallel at the north end of the box (right side of Fig. II-20) to filter air passing into the box, and two more HEPA filters (also in parallel) are located in the discharge duct to filter air before it is discharged to the building's ventilation system. A manually adjusted valve on the air discharge is used to adjust and maintain a negative pressure of 200 Pa.

Utilities to the box include electrical power, nitrogen, and deionized water. Electrical power (single phase, 110 V) is connected to the box to provide power for the contactors, pumps, mixers, and lights. The laboratory deionized water supply is connected to the glovebox through a special reservoir system to limit the volume of water that can be added to the box at one time (40 L).

Thirty-six gloves are installed on the east and west sides of the box. The majority of these gloves are constructed of Hypalon (chloro-sulfonated polyethylene) and are 15 mil (380 μm) thick. Several of the gloves located in front of the contactor are ambidextrous gloves and are rubber-lined Hypalon, 30 mil (760 μm) thick. Lead-loaded gloves that are 30 mil (760 μm) thick have also been purchased but have not been installed on the glovebox.

The 16-stage 4-cm centrifugal contactor has a maximum throughput of 600 mL/min (sum of both the aqueous and organic flow rate in each stage). Feed tanks and pumps supplying the nonradioactive solutions were located beneath the glovebox in a stainless steel drip pan, while the rest of the equipment was located inside the box. Figures II-21 to II-23 show the general layout of this equipment.

Fig. II-21. Nonradioactive Feed System

Fig. II-22. Equipment Installed in the Glovebox

Figure II-21 is a sketch of the nonradioactive feed system. The tanks and pumps for this system are located beneath the box. The feed lines, fabricated from 1/2-inch (1.3-cm) dia stainless steel and 1/2-inch (1.3-cm) dia Teflon FEP, enter the glovebox on the north end. One-half-inch ball valves isolate these lines from the inside of the box. After entering the box, these lines rise above the contactors and then drop down into each feed stage (as shown in Fig. II-21). Solution transfer rates are such that the down leg of these lines are never completely full of solution. The air in the line provides a siphon break, preventing solutions from siphoning out of the box.

Fig. II-23. Solution Transfer Line

Figure II-22 shows the layout of some of the equipment in the glovebox. The extraction section feed tank will contain all of the radioactive tracers. To reduce operator exposure, this tank is shielded with 1/8-in. (0.3-cm) thick lead plate. Most of the product tanks are located on a shelf above the contactor bank. Pumps are used to transfer the product solution from the contactors up to these vessels. One of the product tanks is located on the main floor of the glovebox. All of the tanks in the glovebox are shielded with 1/8-in. (0.3-cm) lead.

Figure II-23 shows the piping connecting the glovebox to a hood. This line is used to transfer the aqueous radioactive solutions from the glovebox to the hood for disposal. This transfer line eliminates the need for collecting 45 L of solution generated during a typical run. The line consists of a 20-ft (6-m) section of 3/8-in. (1-cm) dia stainless steel tubing running through a 1/2-in. (1.3-cm) dia stainless steel tube (to provide secondary containment). Both tubes do not have any breaks or connections located outside of the box or the hood. A Swagelok cap is located on the 1/2 in. (1.3-cm) tube in the hood to seal off both lines when it not in use. Although not likely, any leaks in the 3/8-in. (1-cm) dia tube would be contained by the larger, 1/2-in. (1.3-cm) dia tube and carried to the hood or back to the glovebox.

4. Verification Runs 5 and 6

In addition to the verification test described above, two verification tests were completed in the glovebox contactor system using the TRUEX-TCE solvent. The flowsheet for both tests was the same as Verification Run 4, with the exception of the extraction section feed. For Run 5, UO_2 was added to the feed solution, and in Run 6, ^{59}Fe , ^{239}Pu , and $^{99\text{m}}\text{Tc}$ were added at tracer levels. The ^{59}Fe was also added to the scrub feed (DS) in Run 6. The purpose of both runs was to (1) test and improve our sample collection and handling procedures, (2) check the operation of the contactor system, (3) measure the UO_2 , Fe, Pu and TcO_4^- concentration profiles, and (4) compare these data with concentrations calculated by the GTM. Verification Run 5 was completed on March 10, 1989, and Run 6 was completed on March 30, 1989. Data from these runs will be presented in future reports.

J. Centrifugal Contactor Development

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1. Introduction

The Argonne centrifugal contactor is modified as necessary to work with specific solvent extraction processes. To evaluate processes involving high alpha/beta activity levels (in a glovebox) and/or high gamma radiation (in a shielded cell facility), a 4-cm contactor was designed, built, and tested in remote-handling environments. The remote-handling design was used for the new 2-cm contactor ("minicontactor"), which was designed and built to minimize the amount of 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, modified 4-cm rotors have been built. In support of these various contactor development efforts, vibrational frequencies and amplitudes are being measured using 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. Minicontactors

To meet the need for a laboratory contactor that minimizes feed volume, a 16-stage 2-cm contactor (the minicontactor) was designed and built for testing solvent extraction flowsheets. For a typical flowsheet test, only 1 L of feed solution will be required since each stage holds less than 10 mL of liquid. Ten liters of feed solution is required for a 4-cm contactor. In addition, the minicontactor works well at all O/A flow ratios, just as the 4-cm and larger contactors do. Based on successful test results of a single-stage 2-cm contactor, a 16-stage 2-cm contactor was built. Fabrication of the 16-stage unit was completed in September 1988.

Laboratory evaluation of this 16-stage 2-cm contactor is reported here. This evaluation included (1) general tests, (2) stage-volume tests, (3) one-phase flow tests with water, and (4) two-phase flow tests with TRUEX-NPH and 0.01M HNO_3 . The results of the volume and flow tests were compared with computer model calculations. After some changes, the unit was found to be fully operational for flow rates of 40 mL/min at all O/A flow ratios.

a. General Tests

General tests included (1) mechanical tests and (2) observations of flow patterns in the mixing zone of the contactor.

(1) Mechanical

The first mechanical test was to turn on the rotors and see that all 16 stages ran quietly and smoothly. The second mechanical test was to repeat the first test with TCE in all the stages. The use of pure TCE gives a worst case for contactor vibrations because it is the most dense liquid that could possibly enter the contactor. Therefore, filling each stage with TCE results in the largest liquid mass that a contactor rotor will encounter. Only one stage, stage 8, was observed to run noisily. It did so when empty and when filled with TCE. It also did so when the rotor was removed so that the motor ran alone. Because of this, the motor was disassembled and inspected. The orientation of the washers and

*Co-op student from University of Cincinnati.

**Co-op student from University of Illinois at Chicago.

bearings, the armature condition, and the grease were checked. Nothing out of the ordinary was found and the motor was re-assembled. M. A. Slawewski, an electrical engineer in CMT, listened to the motor for stage 8 and thought that the noise was not excessive. However, it was much noisier than the other 15 motors. The other 15 stages ran very quietly both empty and filled with TCE.

The drawings for the 2-cm multistage contactor, ANL drawings CMT-E1155 entitled "2-CM CONTACTOR (HOT CELL)," have been revised so that they reflect the as-built contactors. Each of the rotors was given its own number, which was scribed on the side and the top surface of the rotor. Motor speeds for the rotors are 3583 ± 7 rpm. In one case during contactor setup, one rotor was not on the motor shaft far enough. This stopped the rotor from turning as it was binding on the housing. Although it took several minutes to discover this problem, the motor was not damaged. This motor, a totally enclosed synchronous motor with a capacitor, does not have a centrifugal startup switch.

(2) Flow Patterns in the Mixing Zone

A clear, single-stage housing made of Lucite was used to observe the flow patterns in the mixing zone. Rotor 0 was used in these single-phase tests. This housing and rotor were used in earlier single-stage tests to determine phase inversion behavior in the mixing zone of the 2-cm contactor. Of interest in these new tests is the relation between the changes in mixing zone flow patterns and the pulsing flows observed in the less-dense-phase exit at low flow rates. These pulsing flows were seen in single-phase tests of the 2-cm contactor using the stainless-steel 4-stage housings. One observation is that gas bubbles appear at the bottom of the rotor, which is usually free of bubbles, as a liquid pulse enters the lower collector ring from the rotor. In addition, this liquid pulse is usually accompanied by a drop of the liquid level in the annular mixing zone. However, this liquid pulse into the lower collector ring from the rotor does not necessarily result in a pulse out the less-dense-phase exit line. Typically, two or three pulses are required before a liquid pulse flows out this exit. The frequency of the pulse seems to depend on the orientation of the tube coming off the contactor housing. When this tube is oriented downward, the pulse frequency is higher, and the liquid level in the exit line tends to stay low. However, this level does not vary much.

The range of liquid heights in the annular mixing zone and the period of variation for each pump setting are shown in Table II-36. The range of the liquid height varies only slightly with the flow rate. For each flow rate, a minimum height occurs for a fraction of a second. This point was used to measure the period required for the liquid height to go through a complete cycle. When the feed pump was shut off, the liquid in the annular region was found to have a height of 1.4 cm above the bottom edge of the rotor. When this annular liquid was allowed to drain with the rotor still spinning, the annular liquid was found to have a volume of 3.6 mL. When the rotor was shut off, it contained a liquid volume of 6.1 mL.

Table II-36. Liquid Height in the Annular Mixing Zone during Water-only Tests

Pump ^a Micrometer Setting, mils (mm)	Flow Rates, mL/min	Range of Liquid Heights, ^b cm	Period of Variation, s
25 (0.6)	28.6	1.1-1.9	6-12
50 (1.3)	42.8	0.8-1.8	2-8
80 (2.0)	59.8	0.8-1.9	2-9
280 (7.1)	173	1.7	c

^aAn FMI pump, model RP-D with a 1/4-in. dia piston was used.

^bMeasured up from the bottom edge of the rotor.

^cLiquid height did not vary.

Based on these observations, it appears that the pulsing flow at the less-dense-phase exit from the contactor housing has a lower frequency than the liquid pulsing from the less-dense-phase exit in the rotor. This happens because an accumulation of liquid in the lower collector ring is required to produce flow out the exit line of the contactor housing. It is not clear if (1) the appearance of bubbles near the bottom entrance to the rotor causes liquid to surge into the rotor or (2) liquid surging into the rotor causes the bubbles. In any case, the net result is a high transient flow rate into the rotor. If the average flow rate is high enough, the liquid level in the separating zone of the rotor is close to the weir for the less-dense phase. For these cases, a high transient flow triggers flow over this weir and out the less-dense phase exit in the rotor. These pulses, in turn, accumulate in the less-dense-phase collector ring and result in subsequent pulses out the less-dense-phase exit in the contactor housing at the same or, more typically, a lower frequency.

b. Stage-Volume Tests

Initial stage-volume tests were done in the contactor housing. In these tests, water was fed to a stage with the rotor spinning at 3600 rpm until water was exiting out the more-dense-phase exit port of the housing. Then, the flow of water was stopped and the flow of water out the exit was allowed to decrease to zero. With the rotor still running, the liquid in the mixing zone was drained through the valve under the rotor and its volume measured. This gives the no-flow liquid volume in the mixing zone. Finally, the motor was switched off and the volume of liquid in the rotor drained and measured. Using our model to calculate rotor and mixing zone volumes gives 5.4 and 2.9 mL, respectively.

Results from this test procedure were erratic. In 4 of the 16 stages, the annular mixing zone would not drain completely with the rotor spinning. This was detected when liquid was heard sloshing around in the mixing zone. For these four stages (11, 13, 15, and 16), the apparent rotor volume ranged from 7.0 to 8.3 mL, while the apparent mixing zone volume ranged from 1.2 to 2.5 mL. In two other rotors (9 and 10), the rotor volume was also high, ranging from 7.0 to 7.2 mL, although no liquid sloshing in the mixing zone was reported. For these two cases, the mixing zone volume was also low, ranging from 1.5 to 2.9 mL. For the other rotors, including the single-stage rotor (rotor 0), the apparent rotor volumes were lower, ranging from 5.1 to 6.5 mL, while the apparent mixing zone volumes were higher, ranging from 3.2 to 5.7 mL. For all 17 rotors, the total no-flow volume in the contactor stages ranged from 8.0 to 12.5 mL.

One hypothesis on liquid sloshing in the mixing zone is that it occurs when the rotor is very close to the bottom vanes in the contactor housing. To test this, one of the sloshing rotors, rotor 11, was shimmed up in 0.2 mm increments. When the total shim reached 0.8 mm, the sloshing stopped. The specification on the gap between the rotor and the bottom vanes is 0.8 to 2.4 mm. The actual gap for this rotor was not measured. Before the rotor was shimmed, the rotor volume was 7.5 mL with a standard deviation of ± 0.4 mL. After the rotor was shimmed 0.8 mm so that the sloshing stopped, the rotor volume was 5.4 mL with a standard deviation of ± 1.0 mL. Thus, the allowable range for the gap between the rotor and the bottom vanes is enough to explain the erratic volume measurements.

To obtain more consistent volume measurements and ones that reflect the volume in the rotor itself, the rotor volume measurements were repeated outside the contactor housing. In these

tests, the bottom of the rotor was submerged in a beaker of water until water exited over the more-dense-phase weir. Vertical baffles were placed at the bottom of the beaker before the test to ensure that the water in the beaker would be able to enter the rotor. With the rotor still spinning, it was lifted out of the water and allowed to drain for 10 to 30 s. Then the rotor was moved over an empty beaker, turned off, and allowed to drain. From these tests, the liquid volume in rotor 11 at no-flow conditions was determined to be 6.1 mL. The standard deviation for this volume was low, ± 0.1 and ± 0.2 mL for waiting times of 30 and 10 s, respectively.

Based on these results, all the rotor volumes were measured outside the contactor housing. The results, given in Table II-37, are very consistent. Excluding rotors 0 and 13, the average rotor volume is 6.32 mL with a standard deviation of ± 0.15 mL. The standard deviation for the rotor volumes measured in the contactor housing had been much higher, ± 0.75 mL. Rotor 0 was excluded from the average because it was made before the other rotors and had a different, slightly smaller, radius for the upper weir. Rotor 13 was excluded from the average value because it had been reworked, based on single-phase flow tests reported next, giving it a slightly larger radius for the upper weir.

Table II-37. Liquid Volume in the 2-cm Rotors at No-Flow Conditions

Rotor No.	Average Volume, ^a mL
0 ^b	6.03
1	6.37
2	6.42
3	6.18
4	6.25
5	6.23
6	6.45
7	6.17
8	6.42
9	6.32
10	6.38
11	6.32
12	6.42
13	5.92
14	6.12
15	6.32
16	6.45

^aAverage of three or more trials. The standard deviation for the individual volumes is ± 0.15 mL.

^bThis rotor is from the single-stage 2-cm contactor that was built and tested before the multistage contactor was built.

c. Single-Phase Flow Tests

Single-phase flow tests allow one to evaluate each 2-cm rotor at typical liquid flow conditions without the complication of a liquid dispersion. In all the tests reported here, the liquid used

was water. Of particular interest in these tests was the zero point. The zero point is that flow rate at which, as the flow rate is increased, the liquid just starts to flow out the less-dense-phase exit. With two exceptions, the zero point gave an apparent radius for the upper (more-dense-phase) weir that was less than the measured radius. Because of this, we tested all the rotors and adjusted those that needed it, taking into account the two-phase flow tests reported in Sec. II.J.2.d. Also, erratic or periodic spurts from the less-dense-phase exit were observed from all the rotors near the zero point; for one rotor, the slope of the less-dense-phase flow vs. the total flow was low above the zero point; and significant variability was seen for the apparent radius of the more-dense-phase weir as determined using the zero point and the WEIR model. The WEIR model is discussed in more detail in Sec. II.J.3.a.

(1) Weir Adjustment

Results from the initial zero-point tests, shown in Table II-38, were lower than expected for almost all the 2-cm rotors. Only two rotors, rotors 1 and 3, were found to have an apparent radius for the upper weir that was within ± 0.08 mm of the actual weir radius. In terms of zero-point measurements, this means that the zero point could not vary from its expected value by more than ± 23 mL/min. With the exception of rotor 0, the prototype rotor used in the initial single-stage tests, all rotors were to have an upper weir radius of 6.09 mm. Rotor 3 was found to have an upper weir radius of 6.12 mm when the radii of all the rotors were rechecked.

Since the radius for the upper weir of the other 15 rotors all appeared to be low, it seemed logical to increase the radius of the more-dense-phase weir to correct the problem. Before this was done, two-phase flow tests, reported in Sec. II.J.2.d, were carried out to check whether the more-dense-phase weir radius was low for two-phase flow as well as for one-phase flow. This was indeed found to be the case, so the weir enlargements were started using electrical discharge machining (EDM).

The first rotor to have its upper weir enlarged was rotor 13. Since its apparent radius was 0.22 mm less than the desired actual radius, 0.20 mm was machined from the inside of the actual more-dense-phase weir to make it 6.29 mm. When this was done, the apparent radius and the actual radius were found to agree quite closely (see Table II-38). However, the radius for rotor 13 is too large to be used.

The second rotor to be have its upper weir enlarged was rotor 5. Although its apparent radius was 0.12 to 0.20 mm less than the desired actual radius, only 0.03 mm was machined from the inside of the actual more-dense-phase weir to make it 6.12 mm. When this was done, the apparent radius and the actual radius were found to agree quite closely (see Table II-38 and Fig. II-24), and the radius for rotor 5 is still in a range where it can be used.

Based on this successful test with rotor 5, all of the rotors whose actual upper-weir radii were less than 6.12 mm were machined to 6.12 mm by the EDM process. As can be seen in Table II-38, these rotors are now within ± 0.08 mm of 6.12 mm, except for rotors 0, 2, 11, 15, and 16. Two of these rotors, 2 and 15, are considered borderline acceptable as they are only 0.08 mm less than 6.09 mm, the original design goal. After some two-phase flow tests were made, we decided to increase the more-dense-phase radius of these five weirs by an additional 0.03 mm. The one-phase flow tests showed that rotors 0 and 2 are still borderline. However, the two-phase flow tests showed that these rotors will meet the design specifications, that is, they will be able to handle 40 mL/min of total throughput for all O/A flow ratios.

With these rotor modifications, the minicontactor was accepted as fully operational. However, we do not understand why the EDM process brought the apparent and actual

Table II-38. Zero-Point Results from Single-Phase Flow Tests

Rotor Number	Initial Tests			Final Tests			Notes
	Actual Weir Radius, ^a mm	Zero Point, ^b mL/min	Apparent Weir Radius, ^{a,c} mm	Actual Weir Radius, ^{a,d,e} mm	Zero Point, ^b mL/min	Apparent Weir Radius, ^{a,c,e} mm	
0	6.01	18.5		6.12, 6.15		6.00, 5.97	f, g
1	6.09	70	6.09	6.12		6.11	
2	6.09	17		6.12, 6.15		6.01, 6.01	g
3	6.12	85	6.14	6.12	107	6.22	h
4	6.09	24		6.12		6.06	
5	6.09	9, 23	5.89, 5.97	6.12	85	6.14	i
6	6.09	30		6.12		6.08	
7	6.09	19		6.12		6.13	
8	6.09	14		6.12		6.07	
9	6.09	28		6.12		6.09	
10	6.09	11		6.12		6.13	
11	6.09	24		6.12, 6.15		5.99, 6.04	g
12	6.09	17.5		6.12		6.07	
13	6.09	7	5.87	6.29 ± 0.02	124	6.28	
14	6.09	15		6.12		6.07	
15	6.09	9		6.12, 6.15		6.01, 6.03	g
16	6.09	10		6.12, 6.15		6.00, 6.03	g

^aMore-dense-phase weir.

^bWhen the more-dense-phase radius is 6.01 mm, the expected zero point is 43 mL/min; 6.09 mm, 69 mL/min; 6.12 mm, 79 mL/min; and 6.29 mm, 127 mL/min.

^cDetermined using WEIR model and measured zero-point value.

^dWhen final value (or values) for rotor differs from its initial value, electrical discharge machining was used to open up the radius.

^eLast two values are shown for rotors 0, 2, 11, 15, and 16.

^fSingle-stage prototype rotor.

^gThe two values for the apparent weir radius in the final tests correspond to the two values for the actual weir radius in the final tests.

^hRotor removed from motor shaft between initial and final test.

ⁱDifferent rotor housings for the two initial zero-point tests.

Fig. II-24. Comparison of WEIR Model Calculations with Results of One-Phase Flow Test for Rotor 5 after Electrical Discharge Machining

radius values together for some cases and not for others. We assume that, when it worked, something was wrong around the upper weir, and the EDM process was able to correct that problem. (A machining burr on the weir radius, a gap between the weir plate and the vanes in the liquid riser going to the weir, or riser vanes that do not extend all the way to the weir are three possibilities.) When it did not work, we assume that something was wrong elsewhere, probably around the lower weir. Since the lower (less-dense-phase) weir is located inside the rotor, its radius cannot be machined.

(2) Erratic Flow near Zero Point

We observed that flow out the less-dense-phase exit was erratic near the zero point. The flow would come out as one or more large drops of liquid every 10 to 60 s. This erratic flow was seen as much as 40 mL/min below the zero point. Table II-39 lists some flow rates starting from below the zero point. These data illustrate the erratic flow rates out the less-dense-phase exit. In Fig. II-24, one can see that the erratic flow region below the zero point lies above the WEIR model curve.

The maximum flow rate out the less-dense-phase exit for which erratic flow occurs is seen to vary from rotor to rotor in Table II-40. However, for these small 2-cm rotors, this maximum flow rate is always less than 40 mL/min. Thus, in using the WEIR model with the zero-point test to determine the apparent radius for the less-dense-phase weir, we used only those flows where the flow out the less-dense-phase exit was greater than 40 mL/min.

The source of the erratic low flows below the zero point is attributed to the mixing zone. When the flow patterns in the mixing zone changes, as noted above, the amount of liquid that can be held there will change. If the pattern changes in such a way that the liquid volume held is less, a sudden short increase will occur in the flow rate into the rotor. This will cause the liquid level in the separating zone of the rotor to rise, and liquid will momentarily flow out the less-dense-phase exit in the rotor. Based on the appearance of liquid in the less-dense-phase exit port at flow rates 20 to 40 mL/min below the zero point, it appears that the instantaneous flow rate into a rotor can be as much as 40 mL/min greater than the average flow rate. This factor will be considered in the design of future 2-cm contactor rotors.

Table II-39. Detailed Results for Several Single-Phase Flow Tests

Rotor Number	Radius of the More-Dense-Phase Weir, mm	Zero Point, mL/min	Flow Rate, mL/min		Notes
			Total Flow	Flow from Less-Dense-Phase Exit	
3 ^a	6.12	85	42.5	0	
			50.2	1.5	
			55.9	2.3	
			68.9	7.6	
			68.9	3.6	
			88.0	13.0	
			94.1	4.0	
			128.5	12.7	
			186.6	61.3	
3 ^b	6.12	107	7.7	0	
			31.9	0	
			55.6	0	
			70.7	0.9	c
			86.4	1.3	c
			101.2	2.0	c
			129	7.7	c
			162	25.4	
			194	48.9	
5	6.09	23	249	96.2	
			309	140	
			4.3	0	
			7.5	0	
			10.8	1	c
			14.1	1.2	c
			17.8	2.1	c
			20.9	2.8	c
			24.1	3.8	c
			28.3	4.7	c
			31.3	5.2	c
			34.0	5.7	c
			38.7	7.2	c
			41.0	8.9	c
			48.4	11.9	c
			60.0	17.6	
			71.6	26.3	
			82.5	28.6	
			92.2	30.0	

(contd)

Table II-39. (contd)

Rotor Number	Radius of the More-Dense-Phase Weir, mm	Zero Point, mL/min	Flow Rate, mL/min		Notes
			Total Flow	Flow from Less-Dense-Phase Exit	
5	6.12	85	24.2	3.7	c
			39.3	5.2	c
			51.6	9.1	c
			69.0	11.1	c
			82.2	6.8	c
			103.2	11.2	c
			132	22.9	c
			163	43.5	
			193	61.1	
			253	109	
			309	145	
13 ^a	6.29	124	97.8	0.5	
			103	0.7	
			108	1	
			114.3	2.5	
			124.7	4.5	
			128	3.5	
			144	7.7	
			158.1	22.1	
			173.9	29.5	
			174	32.8	
			186	33.7	
			189.3	33.3	
			217	55	
			246	78	

^aCyclic flow noted when flow from the less-dense-phase exit is low.

^bTest repeated after rotor weir for the more dense phase was measured and found to be 6.12 mm, not 6.09 mm.

^cFlow occurs in periodic spurts of varying duration.

(3) Low Slope above Zero Point

When the flow out the less-dense-phase exit is plotted against the total one-phase flow as shown for rotor 5 (Fig. II-24), the slope of the curve for the experimental results above the zero point approximately matches that obtained with the WEIR model. However, the slope for the experimental results with rotor 7 is low above the zero point up to ~40 mL/min flow out the less-dense-phase exit, as can be seen in Fig. II-25. One cause of this low slope might be a slight eccentricity between the diameter of the less-dense-phase weir and that of the hole in the coupling for the motor shaft. Such an eccentricity would allow flow out the less-dense-phase exit at lower one-phase flow rates than expected. A second cause of this low slope could be the erratic flow near the zero point, as discussed earlier. In fact, for rotor 7, Table II-40 shows that the experimental results were affected by erratic flow up to 136 mL/min of total flow. Above this flow rate, the experimental and model curves have nearly the same slope. Thus, this low slope above the zero point may also have its origin in the operation of the mixing zone.

Table II-40. Maximum Flow Rate for Erratic Flow out the Less-Dense-Phase Exit for Several Single-Phase Flow Tests

Rotor Number	Actual Rotor Radius, mm	Total Flow Rate, mL/min	Max. Flow Rate, ^a mL/min
0	6.12	90	29 ± 5
	6.15	51	14 ± 4
1	6.12	110	20 ± 4
	6.12	69	12 ± 4
2	6.12	70	14 ± 4
	6.15	111	29 ± 4
4	6.12	90	17 ± 5
	6.12	136	36 ± 8
6	6.12	88	16 ± 3
	6.12	84	10 ± 4
7	6.12	105	15 ± 5
	6.12	89	23 ± 7
8	6.15	69	12 ± 3
	6.12	130	39 ± 5
9	6.12	109	24 ± 7
	6.12	89	21 ± 8
10	6.15	70	12 ± 4
	6.12	72	14 ± 6
11	6.12	106	28 ± 4
	6.15		

^aFor flow out the less-dense-phase exit with the occurrence of erratic flow droplets of varying duration. These tests were made after the more-dense-phase weirs had been machined to 6.12 mm.

Fig. II-25. Comparison of WEIR Model Calculations with Results of One-Phase Flow Test for Rotor 7 after Electrical Discharge Machining

(4) Variability in Apparent Radius for More-dense-phase Weir

Determinations of the apparent radius for the more-dense-phase weir using the WEIR model and the zero-point data indicated that variability was in the range of 0.08 mm. For the initial measurements of the zero point for rotor 5, tests done in different housings gave apparent radii for the upper weir which differed by 0.08 mm (see initial rotor 5 tests in Table II-38). Between the initial and final measurements of the zero point for rotor 3, the rotor was removed from the motor. These test results also gave apparent radii for the upper weir which differed by 0.08 mm (compare initial and final tests for rotor 3 in Table II-38). This finding suggests that the position of the rotor in the housing relative to the stationary vanes at the bottom of the housing is more important than previously thought.

To explore this idea further, several tests were made by varying the gap between the bottom of the rotor and the top of the stationary vanes while keeping the total one-phase flow constant at 300 mL/min. The effect of this rotor/vane gap is shown in Fig. II-26. Not only is the scatter in the apparent radius ± 0.05 mm for a given rotor/vane gap, but also the apparent radius seems to decrease by 0.08 mm as the rotor/vane gap increases by 1.6 mm (0.06 in.). The scatter for a given rotor/vane gap seems to depend on whether a ruler or a feeler gage is used to determine the gap. However, the decrease in the apparent radius as the rotor/vane gap increases appears to be real.

Fig. II-26. Effect of the Rotor/Vane Gap on the Apparent Radius for Rotor 3

While varying the rotor/vane gap, we noted that some results had a time dependence. In these cases, the flow rate out the less-dense-phase exit (the total flow being constant) was high so that the apparent radius appeared to be low by as much as 0.08 to 0.10 mm. However, when successive flow measurements were made with the rotor operating continuously, the flow rate out the less-dense-phase exit decreased to a steady value that gave the same apparent radius as other tests with the same rotor/vane gap.

Overall, it appears that the standard deviation for the apparent radius is ± 0.04 mm if the rotor/vane gap is constant or ± 0.06 mm if the gap is allowed to vary slightly by ± 0.8 mm

($\pm 1/32$ in.). Thus, the design basis for the radius, which assumed that the apparent radius of the upper weir could vary by as much as 0.8 mm even though the actual radius has much closer tolerances, does not seem like an unreasonable choice. At two standard deviations (the 95% certainty level), the apparent radius should be within ± 0.12 mm of the design radius.

d. Two-Phase Flow Tests

The final step in rotor evaluation is the two-phase flow test, which evaluates rotor performance under actual operating conditions. In the previous semiannual (ANL-90/15, Sec.II.J.3), the single-stage prototype 2-cm rotor was evaluated with both 33.7% TBP in NPH (essentially PUREX-NPH, which has 30% TBP in NPH) and the TRUEX-NPH solvent. For both evaluations, the aqueous phase was 0.01M HNO_3 and O/A ratios were 0.33, 1.0, and 3.0. In these two-phase tests, the apparent radius of the prototype rotor, rotor 0, was less than the actual radius by 0.09 to 0.19 mm. The key solvent test was found to be TRUEX-NPH since its density is closer to the aqueous phase than that of PUREX-NPH. Based on these earlier results, the system chosen for the two-phase flow tests of the 16-stage minicontactor was the TRUEX-NPH solvent (density = 858 g/L) and 0.01 M HNO_3 (density = 997 g/L) at O/A ratios of 0.2, 1.0, and 5.0.

During these tests, the total throughput is increased for a given O/A flow ratio until the other-phase carryover in one of the effluent streams is $>1\%$. The flow rates as well as the mode of failure ("A in O" or "O in A") were recorded. Since the final design specification is for good contactor operation at 40 mL/min and all O/A flow ratios, the test criterion was good operation at 50 mL/min and the three O/A flow ratios used in the tests. While these flow results are sufficient to evaluate the contactor, this work was extended and tied in with the one-phase flow tests by comparing the experimental results with the ROTOR model calculations (Sec. II.J.3.a). This work was especially important because apparent radius of the more-dense-phase weir was so different from the actual radius in several cases. To use the ROTOR model, one must have a value for the dispersion number (N_{Di}). If no other number was available, we used a value of 8×10^{-4} , which is a reasonable value based on our earlier results. Typically, a batch dispersion test would be used to measure N_{Di} . The batch N_{Di} measured at an O/A ratio of 1.0 was also used as the value for an O/A ratio of 0.2. The flow N_{Di} for an O/A ratio of 5.0 is typically higher than that measured in the batch test. In this work, we used a compromise value that represents the minimum N_{Di} that could account for the high flow rates seen when the O/A flow ratio was 5.0. As the two-phase flow test is time-consuming, only a few key rotors were tested.

After the EDM process had been used to enlarge its upper weir radius, rotor 13 was subjected to the two-phase flow tests. Because the actual value for the upper weir radius of this rotor now fits the apparent radius calculated from the WEIR model using the single-phase flow tests, rotor 13 was tested to determine whether the apparent radius calculated from the ROTOR model using the two-phase flow tests also fits with the actual value. These tests, summarized in Table II-41, show good agreement between the actual and apparent radii. The average results for the three radii have a range of ± 0.05 mm, well within the ± 0.08 mm design range. However, because of its large radius, the operation of rotor 13 is unacceptable at low O/A flow ratios. Calculated results from the ROTOR model, compared with the experimental data (shown as the vertical line) in Fig. II-27, show that the more-dense-phase weir radius is above the region of satisfactory rotor operation. This radius location is confirmed in that the mode of failure is O in A. Thus, further increases in the upper weir radius of the rotor will only make operation worse. Because of this, rotor 13 was replaced by rotor 0 in the final 16-stage 2-cm contactor.

Rotor 5 was the second rotor subjected to the two-phase flow tests, which were done before and after the EDM machining of the upper weir in the rotor. As noted above, a much smaller change was made in the radius of the upper weir, increasing only from 6.09 mm to about 6.12 mm. The

Table II-41. Summary of Results from the Two-Phase Flow Tests

Rotor Number	Actual Weir Radius, ^a mm	O/A Flow Ratio	Apparent Weir Radius, ^a mm	Dispersion Number	Failure Mode ^b	Max. Flow Rate, mL/min
13	6.29	0.2	6.32	8.0×10^{-4}	A in O	168 ± 14
		1.0	6.24	8.0×10^{-4}	NM ^c	>50
		5.0	6.22	8.0×10^{-4}	O in A	10
			6.28 ^d	--	--	--
			6.26 ^e			
			0.05 ^f			
5 ^g	6.09	0.2	5.92	6.7×10^{-4}	A in O	32 ± 5
		1.0	5.93	6.7×10^{-4}	A in O	66 ± 5
		5.0	6.04	10.8×10^{-4}	O in A	209 ± 20
			5.93 ^d	--	--	--
			5.96 ^e			
			0.07 ^f			
5 ^h	6.12	0.2	6.04	6.9×10^{-4}	A in O	76 ± 4
		1.0	6.04	6.9×10^{-4}	A in O	108 ± 4
		5.0	6.04	13.0×10^{-4}	O in A	240 ± 20
			6.14 ^d	--	--	--
			6.04 ^e			
			0.01 ⁱ			

^aMore-dense-phase weir.^bEither >1% aqueous (A) in organic (O) or >1% O in A.^cNot measured.^dOne-phase flow test result, included here from Table II-38 for ease of comparison.^eAverage for two-phase flow tests for all three O/A flow ratios.^fStandard deviation for two-phase flow tests for all three O/A flow ratios.^gBefore EDM process used.^hAfter EDM process used to enlarge the upper weir radius.ⁱValue associated with individual O/A tests.

results, also summarized in Table II-41, show good agreement between the apparent radii for one- and two-phase flow before the EDM process. However, these radii are less than the actual radius by 0.05 to 0.17 mm. After the EDM process, the apparent radius for the one-phase flow test now agrees well with the actual radius. The apparent radius for the two-phase flow test, which only increased 0.08 mm, is still 0.08 mm less than the actual radius. However, because it is only 0.05 mm less than the desired 6.09 mm radius, rotor 5 is now acceptable. As can be seen from the data in Table II-41, the maximum total flow rate for rotor 5 is now well above 50 mL/min at all three O/A flow ratios.

Before rotor 5 was subjected to the EDM process, the rotor gave unsatisfactory operation at the lowest O/A flow ratio at flow rates less than the design value of 40 mL/min. As can be seen in Table II-41, the maximum total flow rate is only 32 mL/min at an O/A flow ratio of 0.2. Calculated results from the ROTOR model, compared with the experimental data (shown as the two vertical lines) in Fig. II-28, show that the more-dense-phase weir radius is at the low end in the region of satisfactory rotor operation. This radius location is confirmed in that the mode of failure is A in O. Thus, further increases in the upper weir radius of the rotor can be used to make operation better. That this was achieved is shown in Table II-41 by the maximum flow rates (both phases) for rotor 5 after the radius of its upper weir was enlarged 0.03 mm by the EDM process.

Fig. II-27. Comparison of ROTOR Model Calculations with Two-Phase Flow Test for Rotor 13 at an O/A Flow Ratio of 5

Fig. II-28. Comparison of ROTOR Model Calculations with Two-Phase Flow Test for Rotor 5 at an O/A Flow Ratio of 0.2

Based on the successful results with rotor 5, the 14 remaining rotors with an upper weir radius less than 6.12 mm (rotors 0-2, 4, 6-12, 14-16) had this radius enlarged to 6.12 mm by the EDM process. These rotors were again subjected to the single-phase flow test. The results, given in Table II-38 under the final tests, show that the apparent radius for most of these rotors was within the range of 6.09 ± 0.08 mm. However, five rotors (rotors 0, 2, 11, 15, and 16) were borderline or below this range. Because of this, these five rotors were subjected to the critical two-phase flow test at an O/A flow ratio of 0.2. The test results, given in Table II-42, show that rotors 2 and 16 failed this test, that is, their maximum flow rate was less than 50 mL/min. Following these results, all five rotors had the radius of their upper weir enlarged from 6.12 to 6.15 mm. As seen in Table II-38, the apparent radii from one-phase flow tests increased into the acceptable range for rotors 11, 15, and 16, remained the same for rotor 2, and decreased for rotor 0. Because the apparent radius for rotor 0 had decreased and because rotors 2 and 16 had not been acceptable, these three rotors were again subjected to the two-phase flow test at an O/A flow ratio of 0.2. These results, also given on Table II-42, show that these rotors are now acceptable.

Table II-42. Final Two-Phase Test Results for O/A = 0.2

Rotor Number	Actual Weir Radius, ^a mm	Total Flow Rate, mL/min	A in O, %	O in A, %	Appearance		Notes
					Organic	Aqueous	
0	6.12	52.6	<0.02	<0.02	Sl. Cldy	Sl. Cldy	b
	6.15	52.5	<0.02	<0.2	Clear	Sl. Cldy	b
2	6.12	30.7	0.1	0.1	Sl. Cldy	Sl. Cldy	
	6.12	40.5	1.7	0.2	Sl. Cldy	Sl. Cldy	
	6.12	51.4	3.8	<0.2	Sl. Cldy	Sl. Cldy	
	6.15	52.1	0.1	0.3	Clear	Sl. Cldy	b
11	6.12	51.7	0.1	<0.1	Sl. Cldy	Sl. Cldy	b
15	6.12	52.5	0.07	0.1	Sl. Cldy	Sl. Cldy	b
16	6.12	42.5	0.2	0.1	Sl. Cldy	Sl. Cldy	
	6.12	52.3	1.4	<0.1	Sl. Cldy	Sl. Cldy	
	6.15	51.5	0.1	0.3	Clear	Sl. Cldy	b

^aMore-dense-phase weir, that is, the upper weir in the rotor.

^bAcceptable; has less than 1% other-phase carryover when the flow rate is 25% above the design throughput of 40 mL/min.

With the conclusion of the two-phase flow tests, the 16-stage 2-cm contactor is now fully operational for both TRUEX-NPH and TRUEX-TCE solvents at all O/A flow ratios for flow rates up to 40 mL/min.

3. Contactor Design

Excel worksheets used for contactor design are discussed in this section. These worksheets were used to redesign the 4-cm contactors for use with TRUEX-NPH solvent. Other notes on general contactor design are also included here.

a. Worksheets

Two Excel worksheets, ROTOR and WEIR, have been developed for the design of centrifugal contactors. The ROTOR worksheet models two-phase flow through the contactor rotor. This

worksheet is used in the design of new rotors and the evaluation of the results from two-phase flow tests. The WEIR worksheet models one-phase flow through the contactor rotor. This worksheet is used in the evaluation of new rotors. Both worksheets are spreadsheet implementations of the earlier FORTRAN program called CCD (Centrifugal Contactor Design).

These two worksheets were revised so that they properly account for the air pressure inside the spinning rotor for two cases. The one case assumes that the inlet port at the rotor bottom has a liquid seal. The other case assumes that the liquid seal at the rotor bottom is broken. The difference between these two cases is small. Normally, it is assumed that a liquid seal is at the rotor bottom.

b. Rotors for TRUEX-NPH Solvent

After the first verification run, when some TRUEX-NPH solvent exited with the aqueous effluent from the second strip section, contactor operation was modeled with the ROTOR worksheet. We found that the appearance of 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. Using the ROTOR worksheet, we designed a new 4-cm rotor that would work at all O/A flow ratios over the density range that can be expected with this solvent. This new rotor, designated Rotor II, will work even though the density of the organic phase is only 11% lower than that of the aqueous phase.

In the design for Rotor II (marked "693"), the upper (more-dense-phase) weir diameter was reduced from 19.05 mm (0.750 in.) for Rotor I (the original rotor sometimes marked "750") to 17.60 mm (0.693 in.). With this smaller diameter for the upper weir, the contactor will be operable when the density of the organic phase is 11 to 29% lower than that of the aqueous phase. Over this density range, the maximum contactor throughput for all O/A flow ratios will be at least 340 mL/min for a solution pair that has a dispersion number of 8×10^{-4} . With the original rotor, Rotor I, the density of the organic phase must be 16 to 29% lower than that of the aqueous phase. Because of this narrower range of solvent density, the maximum throughput for Rotor I is higher, 620 mL/min. These Rotor-II rotors were fabricated in the CMT shops for all the 4-cm contactors except the earliest units which had rotors with removable upper weirs and removable bottoms.

c. General Notes

Some general ideas for improving the designs of future contactors are summarized here. They are based on our recent experiences with remote-handled 4-cm and 2-cm contactors (shown in drawings ANL number CMT-E1128 and ANL number CMT-E1155, respectively).

1. When remote-handling features are required, pin the motor mount bolts so that they cannot be screwed out. When remote-handling features are not required, use a simple cap screw and eliminate the pin. Watch to see that the support/contact surface area for the cap screw is large enough to keep the motor from becoming cocked.
2. If the motor/rotor coupling is threaded, have the threads treated by the Dicronite process (Dicronite of Chicago, Illinois) so that the use of a molybdenum disulfide lubricant on the threads is not necessary.
3. Make sure that the bottom of the rotor is 1/32 in. (~0.8 mm) above the bottom vanes when the slinger ring is just touching the upper collector ring.

4. Electrical Discharge Machining (EDM) can often be used to increase the diameter of the upper (more-dense-phase) weir. Design the rotor shaft so that the EDM technique can be used, if necessary, to enlarge the upper weir.
5. The use of a welding ring on the contactor housing simplifies contactor assembly. Make this ring hefty if a continuous weld is desired (see Fig. II-29). A hefty welding ring will prevent distortion of the contactor housing.
6. Be sure that the bottom drain is high enough for satisfactory operation.
7. Keep the same center-to-center spacing for the interstage lines of more-dense and less-dense phases so that the two sets of interstage lines are interchangeable.
8. Test the liquid level detector under actual running conditions.
9. Use helium leak test to verify that rotor welds are solid. Helium leak rate should be less than 10^{-6} cm³/s.
10. For removing a motor/rotor assembly from remote-handling contactors, the notch for the crane hook should be on the centerline of the contactor stage and perpendicular to the contactor bark.
11. If possible, make the legs for the support frame interchangeable.
12. Review design for the use of full-penetration welds and see if they are really needed.
13. To simplify machining, use a 1/2-inch NPT coupling as part of the mount for the liquid level detector.
14. In contactors for laboratory use, the liquid level detector can be simply a stainless steel tube with Teflon fluorinated ethylene polypropylene (FEP) tubing at the top. The translucent FEP tubing allows visual observation of a high liquid level. The tube should be high enough so that the liquid will not overflow unless it is almost to the motor.

Fig. II-29. Location of Continuous Weld between Contactor Housing and Box Beam Support Frame

4. Vibration Criteria

In this effort, we are developing a relatively simple vibration criterion that can be used for the design of rotating equipment such as the motor/rotor system for the centrifugal contactor. This criterion will be tested using the BEAM IV model on the VAX computer and the Zonic Real Time Spectrum Analyzer.

In this report period, the Zonic Real Time Spectrum Analyzer, which will be used to measure the vibrational characteristics of representative motors, was checked for general operation and found to have a problem with the monitor. The monitor was returned to the factory and a loaner has been sent out for our use until the original monitor is repaired.

5. Consultation with Westinghouse Hanford

We are consulting with Westinghouse Hanford on the final design of the 10-cm centrifugal contactor for plant processing of Plutonium Finishing Plant (PFP) wastes using TRUEX to remove the transuranic elements. The current 10-cm contactor design will be reviewed in light of ongoing Hanford tests and plant needs. Special attention will be given to (1) modifying the contactor so that a 124- to 248-W (1/6- to 1/3-hp) motor can replace the present 745-W (1-hp) motor and (2) specifying a new motor/rotor coupling which is self-tightening yet has good coupling stiffness. Detailed designing, fabricating, and testing would be done at Westinghouse Hanford. We will also review the new 10-cm contactor prints that will be drawn up at Westinghouse Hanford.

A second consulting task is to work with Westinghouse Hanford on the selection of an appropriate Argonne centrifugal contactor to use in a remote pilot plant at Westinghouse Hanford. Detailed designing, fabricating, and testing would be done at Westinghouse Hanford. As a part of this task, we would review the drawings for this remote-handled contactor. These drawings will be prepared by Westinghouse Hanford.

During this report period, R. A. Leonard visited with A. J. Naser and others at Westinghouse Hanford on March 28-29, 1989, as a first step in accomplishing this consulting task. Based on these talks, a new self-tightening coupling for the 10-cm contactor will be designed by Hanford based on sketches that we will provide. This new coupling will be tested with the existing 745 W (1 hp) motor. Its use on smaller motors, 124 to 248 W (1/6 to 1/3 hp), will be considered as time and money permit. It is expected that the face-mounting bell on the motor and the enclosed bearing will have to be replaced for these smaller motors to work. In any case, Westinghouse Hanford plans are to use three-phase motors in the plant.

After a review of the performance characteristics for both the 2- and 4-cm remote-handled contactors, we chose the 4-cm contactor for use in the planned Hanford pilot plant facilities. The Argonne drawings for these units will be converted to appropriate Hanford drawings and a four-stage unit will be built at Hanford for evaluation there.

K. Development of Pyrochemical Centrifugal Contactors (L. Chow, R. A. Leonard, and T. R. Johnson)

The objective of this work is to develop a conceptual design for a high-temperature centrifugal contactor (pyrocontactor) that operates with cadmium metal and chloride salts at temperatures around 500°C. The potential design problems for such a high-temperature contactor are (1) the corrosion of the contactor; (2) the cooling of the rotor shaft such that the interface temperature between the shaft and the

motor is below about 50°C ; (3) the liquid-liquid dispersion of the more dense phase (molten cadmium metal) with the less dense phase (chloride salts) in the Couette mixing zone, which is the annular space between the spinning rotor and the stationary housing; (4) the separation of the more dense phase from the less dense phase in the centrifugal separating zone inside the rotor; and (5) the vibration of the contactor rotor. Because neither cadmium metal nor the dry chloride salt at 500°C is corrosive toward low carbon steels and iron-chromium alloys, choosing a material for the contactor will not be a problem. Thus, the cooling of the rotor shaft, the mixing (dispersion) and separation characteristics of the molten cadmium metal with chloride salts, and the vibration of the rotor need to be investigated to produce a well-designed pyrocontactor.

The development work for a conceptual design of a pyrocontactor was started in January 1989. The initial effort was to determine the configuration of the rotor shaft such that the interface temperature between the shaft and the motor would be below 50°C . The second effort was to investigate the mixing (dispersion) and separation characteristics of the more dense phase with the less dense phase and the vibration characteristics of the rotor.

1. Determination of Rotor Shaft Configuration

A simple schematic of the rotor system for a centrifugal contactor is shown in Fig. II-30. Details such as the housing for the rotor, molten salt weir, metal weir, and housing for rotor shaft are not shown. The function of the rotor is to mix and then separate the cadmium metal and the chloride salts at temperatures around 500°C . Thus, the temperature at the interface of the rotor shaft and the rotor can be taken as 500°C . Heat moves by conduction from this end of the shaft to the other end, which is connected to the motor. Part of this heat will be transferred either to the housing around the rotor shaft by thermal radiation or to the gaseous coolant surrounding the rotor shaft by convection.

Fig. II-30. Simple Schematic for Rotor System of Centrifugal Contactor

Ordinary electric motors are designed to operate at ambient temperatures below 40°C. The motor bearing normally can operate at a temperature below 80°C, while the motor can operate at a temperature below 110°C. Because the motor will generate heat during operations, the interface temperature between the motor bearing and the motor shaft should be kept below about 50°C. (Remarks: With a special motor with Class F insulation and high temperature grease applied to the bearing, the motor can operate at a temperature up to about 170°C, while the bearing temperature can be up to about 120°C. With such a motor, the interface temperature between the motor bearing and the motor shaft can be as high as about 90°C.)

The design problem becomes the determination of a minimum total length for the rotor/motor shaft such that the surface temperature at the rotor end of the shaft contacting the molten salt is about 500°C, while the surface temperature at the motor end of the shaft is below the desired temperature (about 50°C for an ordinary motor and about 90°C for a special motor).

a. Heat Transfer Model

A two-dimensional axi-symmetric heat transfer model has been developed to calculate the temperature distributions along the motor/rotor shaft. The governing equation for the model is the conduction heat transfer equation in cylindrical coordinates, given as⁴²

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} + \frac{q''}{k_s} = 0 \quad (\text{II-80})$$

where $T(r,z)$ = temperature of the shaft in the radial and axial coordinates, °C

r = distance in radial direction, m

z = distance in axial direction, m

q'' = internal heat source, W/m³

k_s = thermal conductivity of the shaft, W/(m·K)

We next introduce the dimensionless parameters

$$\theta = \frac{T - T_c}{T_o - T_c} \quad (\text{II-81})$$

$$R = \frac{r}{r_1} \quad (\text{II-82})$$

$$Z = \frac{z}{L} \quad (\text{II-83})$$

$$\gamma = \frac{r_1}{L} \quad (\text{II-84})$$

$$P = q'' r_1^2 / [k_s (T_o - T_c)] \quad (\text{II-85})$$

where T_o = molten salt temperature (500°C)
 T_c = coolant temperature, $^\circ\text{C}$
 r_1 = radius of the shaft, m
 L = length of the shaft, m

Equation II-80 can be rewritten as:

$$\frac{\partial^2 \theta}{\partial R^2} + \frac{1}{R} \frac{\partial \theta}{\partial R} + \gamma^2 \frac{\partial^2 \theta}{\partial Z^2} + P = 0 \quad (\text{II-86})$$

Using the central difference method, an internal element in cylindrical coordinates (see Fig. II-31) can be expressed as:

$$\begin{aligned} \theta_{i,j} = \frac{1}{2(1 + \beta^2)} & \left[\left(1 + \frac{\Delta R}{2R_j} \right) \theta_{i,j+1} + \left(1 - \frac{\Delta R}{2R_j} \right) \theta_{i,j-1} \right. \\ & \left. + \beta^2 \left[\theta_{i+1,j} + \theta_{i-1,j} \right] + \left[\Delta R \right]^2 P \right] \end{aligned} \quad (\text{II-87})$$

where

$$\beta = \frac{r_1}{L} \left[\frac{\Delta R}{\Delta Z} \right] = \frac{\Delta r}{\Delta z} \quad (\text{II-88})$$

$$\Delta R = \frac{\Delta r}{r_1} \quad (\text{II-89})$$

$$\Delta Z = \frac{\Delta z}{L} \quad (\text{II-90})$$

Fig. II-31. Element in Cylindrical Coordinates

Here, Δr and Δz are grid sizes in the radial and axial directions, respectively.

Four boundary conditions are defined:

$$(1) \quad \text{At } Z = 0, \quad \theta = 1. \quad (\text{II-91})$$

(2) At $R = 0$, there is no heat transfer across the axis of symmetry. This condition can be numerically expressed as:

$$\theta_{i,j} = \frac{1}{(1 + 0.5\beta^2)} \left[\theta_{i+1,j} + 0.25\beta^2 (\theta_{i+1,j} + \theta_{i-1,j}) + 0.25 (\Delta R)^2 P \right] \quad (\text{II-92})$$

(3) At $R = 1$, heat is transferred by convection and radiation cooling. Numerically, this condition can be expressed as:

$$\begin{aligned} \theta_{i,j} = \frac{1}{[1 + \beta^2 + 0.5 (Nu_1 + Nu_2 - 1)]} & \left[(1 - 0.5\Delta R) \theta_{i,j-1} \right. \\ & \left. + 0.5\beta^2 (\theta_{i+1,j} + \theta_{i-1,j}) + 0.5 \Delta R [Nu_2 \theta_2] + 0.5 (\Delta R)^2 P \right] \end{aligned} \quad (\text{II-93})$$

where

$$Nu_1 = \frac{2h_c r_1}{k_s} \quad (\text{II-94})$$

$$Nu_2 = \frac{2h_r r_1}{k_s} \quad (\text{II-95})$$

$$\theta_2 = \frac{T_2 - T_c}{T_O - T_c} \quad (\text{II-96})$$

In the above equations,

h_c = convective heat transfer coefficient of the coolant, $W/(m^2 \cdot K)$

h_r = radioactive heat transfer coefficient between the shaft and housing surfaces, $W/(m^2 \cdot K)$

T_2 = surface temperature of the housing, $^\circ C$

(4) At $Z = 1$, there is no heat transfer across the interface between the motor/rotor shaft and the motor bearing. This condition in numerical form is given as:

$$\theta_{i,j} = \frac{1}{2(1+\beta^2)} \left[\left(1 + \frac{\Delta R}{2R_j} \right) \theta_{i,j+1} + \left(1 - \frac{\Delta R}{2R_j} \right) \theta_{i,j-1} + 2\beta^2 \theta_{i-1,j} + (\Delta R)^2 P \right] \quad (\text{II-97})$$

An initial estimate for the dimensionless temperature is assigned to each of the grid points. Then, Eq. II-87 with the above four boundary conditions can be solved by successive iterations. The convergence criterion is taken as:

$$\left| \frac{\theta(\text{new}) - \theta(\text{old})}{\theta(\text{new}) + \theta(\text{old})} \right| \leq 10^{-8} \quad (\text{II-98})$$

where $\theta(\text{new})$ and $\theta(\text{old})$ are the dimensionless temperatures of the latest and the previous iterations, respectively.

(1) Radiation Boundary Conditions

The radiation heat transfer between two concentric cylinders is given as:

$$q_{1-2} = \left[\frac{1}{\frac{1}{\epsilon_1} + \frac{A_1}{A_2} \left[\frac{1}{\epsilon_2} - 1 \right]} \right] A_1 \sigma (T_1^4 - T_2^4) \quad (\text{II-99})$$

where q_{1-2} = heat transfer from cylinder 1 to cylinder 2, W
 A_1, A_2 = surface areas of cylinders 1 and 2, respectively, m^2
 ϵ_1, ϵ_2 = emissivities of cylinders 1 and 2, respectively
 T_1, T_2 = temperatures of cylinders 1 and 2, respectively
 σ = Stefan-Boltzmann constant, $5.67 \times 10^{-8} \text{W}/(\text{m}^2 \text{K}^4)$

This radiation heat transfer between two cylinders can also be expressed as:

$$q_{1-2} = h_r A_1 (T_1 - T_2) \quad (\text{II-100})$$

Solving Eqs. II-99 and II-100 yields:

$$h_r = \left[\frac{\sigma}{\frac{1}{\epsilon_1} + \frac{A_1}{A_2} \left[\frac{1}{\epsilon_2} - 1 \right]} \right] \left[T_1^3 + T_1^2 T_2 + T_1 T_2^2 + T_2^3 \right] \quad (\text{II-101})$$

Substituting the value of h_r from Eq. II-101 into Eq. II-95 will provide the Nusselt number for thermal radiation. If part of the rotor shaft is not enclosed by any housing, then the radiation heat transfer for that part of the shaft is zero.

(2) Convective Boundary Conditions

When the rotor shaft is enclosed by a housing where a coolant is allowed to pass through axially, the rotor shaft is subjected to the convective cooling by the axial flow of the coolant and the circumferential flow of the coolant caused by the rotation of the shaft. With air or other gases as coolant, laminar flow is indicated by the Reynolds numbers being below about 500 for both the axial and circumferential flows.

For a laminar axial flow through an annulus, the correlation for heat transfer is given as⁴³

$$\frac{h_{ca} d_h}{k_c} = 1.86 (\text{Re Pr } d_h/L)^{0.333} (\mu_c/\mu_s)^{0.14} \quad (\text{II-102})$$

where h_{ca} = convective heat transfer coefficient for axial flows, $\text{W}/(\text{m}^2\text{K})$
 d_h = hydraulic diameter $(2r_2 - 2r_1)$, m
 k_c = thermal conductivity of coolant, $\text{W}/(\text{mK})$
 Re = Reynolds number for axial flow
 ρ_c = coolant bulk density, kg/m^3
 μ_c = coolant viscosity at bulk temperature, $\text{kg}/(\text{m}\cdot\text{s})$
 μ_s = coolant viscosity at stream temperature, $\text{kg}/(\text{m}\cdot\text{s})$
 Pr = coolant Prandtl number
 L = shaft length, m

The Reynolds number for axial flow is given by

$$\text{Re} = \rho_c u d_h / \mu_c \quad (\text{II-103})$$

where u = coolant bulk velocity, m/s

For a rotating inner cylinder and stationary outer cylinder in a laminar flow regime, the temperature across the gap is given as⁴⁴

$$\frac{T - T_s}{T_2 - T_s} = B_1 \left[1 - \frac{r_1^2}{r^2} \right] + B_2 \frac{\ln(r/r_1)}{\ln(r_2/r_1)} \quad (\text{II-104})$$

where T_s = surface temperature of inner cylinder, $^{\circ}\text{C}$
 T_2 = surface temperature of outer cylinder, $^{\circ}\text{C}$
 r_1, r_2 = radii of inner and outer cylinders, respectively, m
 r = radial distance, m
 T = temperature at radial distance r , $^{\circ}\text{C}$

$$B_1 = \frac{\mu_c r_1^2 r_2^4 \omega^2}{k_c (T_2 - T_s) (r_2^2 - r_1^2)^2} \quad (\text{II-105})$$

$$B_2 = 1 - B_1 \left[1 - \frac{r_1^2}{r_2^2} \right] \quad (\text{II-106})$$

In Eq. II-105, ω is the rotational speed in rads/s.

The convective heat transfer at the inner cylinder surface is calculated by

$$q = -k_c A \left. \frac{\partial T}{\partial r} \right|_{r=r_1} \quad (\text{II-107})$$

Differentiating Eq. II-107 with respect to r and evaluating at $r = r_1$ yield

$$q = \frac{k_c A (T_s - T_2)}{r_1} \left[2B_1 + \frac{B_2}{\ln(r_2/r_1)} \right] \quad (\text{II-108})$$

The heat transfer equation in terms of heat transfer coefficient can be written as

$$q = h_{cr} A (T_s - T_c) \quad (\text{II-109})$$

where h_{cr} is the convective heat transfer coefficient caused by rotation, $W/(m^2 \cdot K)$, and T_c is the coolant temperature, $^{\circ}C$. Thus, Eqs. II-108 and II-109 give

$$h_{cr} = \frac{k_c}{r_1} \frac{(T_s - T_2)}{(T_s - T_1)} \left[2B_1 + \frac{B_2}{\ln(r_2/r_1)} \right] \quad (\text{II-110})$$

The convective heat transfer coefficient, h_c , in Eq. II-94 is the sum of h_{ca} in Eq. II-102 and h_{cr} in Eq. II-110.

When there is no enclosure or housing surrounding the rotating shaft, the shaft is cooled (or heated) by the rotating action and natural convection by the surrounding fluid. The convection heat transfer by rotation is given by⁴⁵

$$\frac{h_{cr} r_1}{k_c} = 0.135 (2Re_r^2 \cdot Pr)^{0.333} \quad (\text{II-111})$$

where

$$Re_r = \rho \omega r_1^2 / \mu \quad (\text{II-112})$$

The average heat transfer coefficient for natural convection for a vertical cylinder of length L is given by⁴⁶

$$\frac{h_{cn} L}{k_c} = 0.555 (Gr_L Pr)^{0.25} \quad (\text{II-113})$$

where h_{cn} = heat transfer coefficient for natural convection, $W/(m^2 \cdot K)$

Gr_L = Grashof number

The Grashof number is given by

$$Gr_L = g \frac{(T_s - T_c) L^3}{(T_c + 273) (\mu/\rho)^2} \quad (\text{II-114})$$

where g is gravitational acceleration. Thus, at the portion of the shaft where there is no enclosure or housing, the convective heat transfer coefficient, h_c , in Eq. II-94 is the sum of h_{cr} in Eq. II-111 and h_{cn} in Eq. II-113.

b. Results and Discussion

Calculations with the heat transfer model were performed to study the effects of (1) shaft enclosure percent, (2) shaft length, (3) shaft diameter, (4) motor speed, and (5) radial gap size between shaft and enclosure on the temperature distributions of the shaft. The properties of the materials assumed in the calculations are:

shaft thermal conductivity (carbon steel)	= 51.9 W/(m·K)
shaft surface emissivity	= 0.8
molten salt temperature	= 500°C
enclosure temperature	= 30°C
average coolant temperature	= 30°C
coolant (air) density	= 1.14 kg/m ³
coolant (air) thermal conductivity	= 0.0267 W/(m·K)
coolant (air) viscosity	= 1.91 × 10 ⁻⁵ kg/(m·s)
coolant (air) Prandtl number	= 0.7

The base case for the calculations is

shaft length	= 12 in. (30 cm)
shaft diameter	= 1 in. (~2 cm)
motor speed	= 1800 rpm
axial velocity of coolant	= 1 m/s
radial gap between shaft and enclosure	= 1/16 in. (0.16 cm)

Then calculations were made by varying one of these five parameters while keeping the others constant.

Figure II-32 shows the effect of the shaft length on the shaft temperature at the center of the interface between the shaft and the motor. The solid line represents the results for the case that 100% of the shaft is enclosed with a housing. Air as coolant is introduced to the housing at a distance of 1/4 shaft length from the hot end with an axial velocity of 1 m/s (about 0.29 ft³/min of air). In this case, the entire shaft is cooled by radiant heat transfer to the enclosure, and 75% of the upper portion of the shaft is cooled by convective heat transfer by the axial flow and the rotational flow of the coolant. For these calculations, the average heat transfer coefficients for the axial flow, rotational flow, and radiation have a ratio of 2:1:1, approximately. As expected, the interface temperature between the shaft and motor decreases with an increase in the length of the shaft.

The broken line in Fig. II-32 represents the results for the case that 25% of the shaft has an enclosure where no coolant is introduced into the housing. In this case, 25% of the lower portion

Fig. II-32. Effect of Shaft Length on Shaft/Motor Interface Temperatures

of the shaft is cooled by radiant heat transfer to the housing, and the upper 75% of the shaft is cooled by convective heat transfer by the rotation and natural convection of the ambient air. For these calculations, the average heat transfer coefficients for the rotational flow, natural convection, and radiation have a ratio of 3:0.3:1, approximately. As shown in Fig. II-32, the cooling of the shaft between the cases with 100% enclosed shaft and 25% enclosed shaft is about the same, with the latter case slightly more efficient.

The effects of the shaft diameter on the shaft/motor interface temperature are shown in Fig II-33. The curves indicate that a shaft with 25% enclosure is cooled slightly more efficiently than that with 100% enclosure. The results also show that the smaller the shaft diameter, the lower the interface temperature (or the more efficient cooling effect).

The effects of motor speed on the shaft/motor interface temperature are shown in Fig. II-34. For the case of a 100% enclosed shaft, the calculated results are not affected by the motor speed. For these results, the Reynolds number for the axial flow remains constant while the Reynolds number for the rotational flow is below about 300, which indicates a laminar flow regime. In this case, B_1 and B_2 in Eq. II-108 are equal to 0 and 1, respectively, and Eq. II-108 reduces to

$$q = \frac{k_c 2\pi L (T_s - T_2)}{\ln(r_2/r_1)} \quad (\text{II-115})$$

These results suggest that, when the Reynolds number is low, the rotational heat transfer from an inner rotating cylinder to an outer stationary cylinder (housing) equals the conduction heat transfer across the radial gap.

As expected, the shaft/motor interface temperature for a 25% enclosed shaft decreases when the motor speed increases (broken line in Fig. II-34).

Fig. II-33. Effect of Shaft Diameter on Shaft/Motor Interface Temperatures

Fig. II-34. Effect of Motor Speed on Shaft/Motor Interface Temperatures

The effects of the size of the radial gap when the shaft is 100% enclosed are shown in Fig. II-35. The solid line represents the cases where the volume flow rate of the coolant remains constant while the axial velocity varies. The broken line represents the cases where the volume flow rate of the coolant can be varied to produce a constant axial velocity of 1 m/s. In both calculations, the shaft/motor interface temperature increases with an increase in the radial gap size.

Fig. II-35. Effect of Radial Gap on Shaft/Motor Interface Temperatures

c. Summary of Rotor Shaft Configuration

One of the problems in the design of a high-temperature centrifugal contactor is the possible overheating of the motor by conduction heat transfer along the shaft caused by the high temperature (500°C) of the cadmium metal and chloride salts. To assist in the design of such a contactor, a computer program was developed to calculate the temperature between the interface of the shaft and the motor. The calculated results indicate that the shaft/motor interface temperature is affected by the shaft length, shaft diameter, radial gap between the shaft and the housing (if one exists), the coolant velocity (or flow rate), the motor speed, and to a lesser degree, the length of the housing for the shaft. The calculated results suggest that an overheating of the motor would not occur if the following parameters are chosen:

shaft material	= low carbon steel
shaft diameter	= 1 in. (~2.5 cm) or smaller
shaft length	= 12 in. (30 cm) or longer
motor speed	= ~1800 rpm
radial gap between shaft and housing	= ~1/16 in. (~0.16 cm)
coolant axial velocity along housing	= ~1 m/s

Also, a short housing for the shaft is preferable.

2. Experimental Investigation of Mixing Characteristics

Experiments were made to investigate the mixing (dispersion) characteristics of the more dense phase (molten cadmium metal) with the less dense phase (chloride salts). Instead of using molten cadmium metal and chloride salts for the initial experiments, we employed a system of Wood's metal mixed with water containing an acetic acid/sodium acetate buffer. The densities of molten Wood's metal and acetate buffer solution are about 9.7 and 1.0 g/mL, respectively, while the densities of molten cadmium metal and chloride salts at 500°C are about 7.8 and 1.6 g/mL, respectively. Because the density difference between the two phases in the molten Wood's metal system is larger than that in the molten cadmium system, good mixing is more difficult to achieve in the molten Wood's metal system than in the molten cadmium metal system. Thus, from any indication of mixing of the two phases in the molten Wood's metal system, it can be inferred that mixing could also be obtained for the molten cadmium metal system.

The experiments were carried out in a Blickman hood after a safety review was completed. Experiments were made to investigate the dispersion of Wood's metal (more dense phase) with water buffered with acetate (much less dense phase). The setup of the apparatus for these experiments is shown in Fig. II-36. A dc motor with a variable speed control (0 to 2000 rpm) was made to simulate contactor rotors of various sizes. The solid shaft was immersed in a Pyrex beaker (simulating the rotor housing) containing a mixture of Wood's metal and acetate buffer solution and rotated over a range of speeds to about 2000 rpm. Clearance between the Pyrex beaker and the rotating shaft would be varied between 1/16 and 1/4 in. (0.16 and 0.6 cm) by changing the rotor diameter. The Pyrex beaker was held fixed by a beaker clamp. It was suspended in a water bath in a metal container with wide opening. The water bath was kept at about 90°C by a hot plate to maintain the Wood's metal in liquid form (the melting point for Wood's metal is 65.5°C). The metal container also served as a backup should the Pyrex beaker containing the Wood's metal-water mixture break. The use of a Pyrex beaker for the mixture enabled us to determine the mixing characteristics of the mixture by observation.

Fig. II-36. Schematic of Experimental Setup for Mixing Tests

During the experiments, the rotor speed was calibrated with respect to the control dial setting of the variable speed motor by a stroboscope. The results of the calibration are shown in Fig. II-37. Then, tests were made using TCE and water as the mixture instead of Wood's metal/water mixture. The purpose of these tests was to gain some experience in the operation of the test apparatus. These tests showed the dispersion of the TCE/water mixture at various speeds.

Fig. II-37. Calibration Curve for Rotor Speed

After the preliminary investigation with TCE/water mixture, tests were made with Wood's metal and water (with acetate buffer). A Pyrex beaker (Corning 1140, 180 mL) was installed as the housing of the 1-3/8 in. (3.5 cm) dia rotor. The gap between the rotor and the housing was about 1/4 in. (0.6 cm). About 40 mL of the acetate buffer solution was poured into the housing with the rotor submerged into the solution. The solution and the submerged part of the rotor were heated by keeping the water bath inside the metal container to about 90°C. Wood's metal was put inside a 250 mL stainless steel beaker and was melted by a separate hot plate. With the rotor spinning at a very low speed, Wood's metal was gradually poured into the housing. It sank to the bottom of the housing, with the acetate buffer solution floating on the top. The rotor was stopped, and the line separating the two phases was marked on the beaker surface. Then the rotor speed was gradually increased to 1000 rpm. The rotor was allowed to spin at this speed for about 30 s. During this period, dispersion of Wood's metal was not observed while the swirling of the two phases was. The rotor was then stopped abruptly by turning the control knob to the brake position. Following this action, the two phases inside the beaker housing were observed to rest almost instantaneously. The interface line coincided with the initial marking of the interface. Then, the rotor control was reset to zero. The above test was repeated for rotor speeds of 1250, 1500, 1720, 1930, and 2000 rpm, respectively. The higher the rotor speed, the more turbulent the swirling of the mixture. However, the dispersion of Wood's metal was not obvious by observation from these tests, even at the highest rotor speed.

Later, four vanes were glued to the bottom of the Pyrex beaker (housing). The above tests were repeated, and similar results were obtained. Tests were then made replacing the above rotor system by a variable speed motor of 500 to 2500 rpm and centrifugal agitation (6.4-mm dia and 191-mm length for stem; and 20-mm dia and 23-mm length for agitator). The centrifugal agitator functioned as a propeller and produced rapid circulation of liquids. The test procedures were similar to the previous test except that the agitator speed ranged from 550 to 2500 rpm. Again, dispersion of Wood's metal into the acetate buffer solution was not assured by observation from these tests.

The finding that dispersion was not ascertained by observation from the above tests does not necessarily lead to the conclusion that dispersion of Wood's metal did not occur during the tests. First, Wood's metal is opaque; dispersion away from the beaker surface could not be seen. Second, Wood's metal density is about 10 times the density of the acetate buffer solution; the centrifugal force acting on a Wood's metal particle would be about 10 times that of a solution particle of the same size. Thus, the large centrifugal force acting on the dispersed particles of Wood's metal (if it ever occurred) would coalesce these particles almost instantaneously such that observation of dispersion is very difficult if not impossible under the test conditions. This second explanation was supported by the test described below.

A mixture of molten Wood's metal and acetate buffer solution of about 15 mL each was poured into a 50 mL centrifuge tube, which was later covered with a cap. An adhesive tape was wrapped around the cap to prevent spilling of the mixture out of the tube. The sample was then put on a vortex mixer. When the force pressing the centrifuge tube against the vortex mixer was not too high, particles of Wood's metal jumping up and down were observed. Upon further pressing the centrifuge tube against the vortex mixer, a swirling of the mixture occurred, but dispersion of Wood's metal was not obvious by observation from the swirl.

More tests are planned to investigate the dispersion of a more dense phase with a much less dense phase. In these tests, vertical baffles will be installed inside the housing (a Pyrex beaker), and vertical vanes will be added to the rotor surface. These baffles and vanes will provide energy to break up the Wood's metal. After confirmation that the molten Wood's metal had mixed with the acetate buffer solution, an existing 4-cm centrifugal contactor will be modified such that experiments to investigate the separation of the two phases can be conducted.

L. TRUEX-NPH Solvent Degradation

(L. E. Trevorrow, A. Crabtree, N. Simonzadeh, P.-K. Tse, and L. Reichley-Yinger)

Because the TRUEX-NPH solvent will be used to treat PUREX raffinates from the reprocessing of irradiated fuel, the solvent will undergo radiolytic and hydrolytic degradation. The purpose of this study is to (1) quantitate the effects of radiolysis and temperature on the degradation of the solvent and (2) develop solvent cleanup procedures to treat degraded TRUEX-NPH solvents.

The previous report (ANL-90/15, Sec. II.H) described results of experiments on degradation of TRUEX-NPH solvent by radiolysis and by hydrolysis. The extent to which these reactions had proceeded had been characterized by measuring the distribution ratio for americium between the treated solutions and nitric acid solutions. These data are to be used for determining rates of hydrolysis of the extractant, CMPO, contained in TRUEX-NPH solvent. Furthermore, the rate constants will be used, together with data previously obtained at 50-95 °C, to derive values of activation energies for the hydrolysis reaction. These values are expected to be useful in calculating a concentration of CMPO, corrected for changes caused by hydrolysis, that can be used in process calculations with the GTM.

Recently, additional distribution ratios were measured for solvent samples that had been subjected to controlled hydrolytic conditions and then washed with aqueous sodium carbonate. The products of solvent degradation are acidic compounds that act as powerful agents for extracting americium from aqueous solutions of low acid concentration, such as 0.01 and 0.05M HNO_3 . They do not show this power in equilibrations with higher acid concentrations, such as 2.0M HNO_3 . Consequently, D_{Am} values for degraded solvent equilibrated with 0.01 and 0.05M HNO_3 will be greater than the corresponding D_{Am} values for non-degraded solvent. Washing degraded solvent with aqueous sodium carbonate was tested

here as a means of removing those acidic extractants. Thus, if a carbonate wash is effective, the values of D_{Am} for degraded, washed solvent should not be greater than those for non-degraded solvent at the same conditions. Table II-43 permits such a comparison. Despite the scatter in the data, it is concluded that a carbonate wash is only partially effective in removing the powerful extractants that are present in degraded solvent.

Table II-43. Americium Distribution Ratios of Degraded, Carbonate-Washed TRUEX-NPH Samples

Hydrol. Acid, M	Hydrol. Temp., °C	Hydrol. Time, h	$(D_{Am}^{0.1})^a$	$(D_{Am}^{0.05})^b$
Non-degraded		0	1.15×10^{-2}	2.31×10^{-1}
2.5	50	28	9.00×10^{-3}	2.18×10^{-1}
2.5	50	126.3	1.07×10^{-2}	2.12×10^{-1}
2.5	50	220.6	1.00×10^{-2}	2.20×10^{-1}
6	70	24	9.18×10^{-3}	2.13×10^{-1}
6	70	98	9.21×10^{-3}	2.05×10^{-1}
6	70	193.5	3.68×10^{-1}	2.77×10^{-1}
6	70	268.4	8.67×10^{-1}	2.53×10^{-1}
6	70	436.7	1.02×10^0	2.39×10^{-1}
6	70	603.5	7.13×10^{-1}	1.78×10^{-1}
0.25	70	603.5	2.11×10^{-1}	5.83×10^{-2}
CAW ^c 1.6	70	24	1.36×10^{-1}	3.47×10^{-1}
CAW 1.6	70	98	2.12×10^{-1}	3.09×10^{-1}
CAW 1.6	70	193.5	6.87×10^{-2}	2.26×10^{-1}
CAW 1.6	70	268.4	1.49×10^{-1}	2.23×10^{-1}
CAW 1.6	70	436.7	3.25×10^{-1}	2.61×10^{-1}

^aEquilibrated with 0.01M HNO₃.

^bEquilibrated with 0.05M HNO₃.

^cCurrent acid waste stream generated at Hanford site.

M. Production and Separation of ⁹⁹Mo from Low-Enriched Uranium (W. E. Streets, J. D. Kwok, and G. F. Vandegrift)

1. Introduction

Generators furnish ^{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 has been developing reactor and reactor-fuel designs to accommodate the use of low-enriched fuel (LEU). The next goal is to reduce the ²³⁵U content of targets used to produce ⁹⁹Mo from HEU to LEU.

2. Fifth Janus Irradiation (U₃Si₂)

a. Experimental

In this report period, a sample of U₃Si₂ mixed with uranium powder was irradiated in the Janus reactor. The purpose of this irradiation is to investigate the fractional loss of ⁹⁹Mo from U₃Si₂ fuel particles to an aluminum matrix due to recoil as a function of fuel particle size.

Workers in the Materials and Components Technology Division prepared three compacts, each with a different U₃Si₂ fuel particle size range mixed with aluminum powder. Compact 1 had 1.00 g of U₃Si₂ particles with sizes of ~125-150 μ m mixed with 0.495 g of ALCAN 101 powder. Compacts 2 and 3 had the same weights of U₃Si₂ and ALCAN 101 powder with U₃Si₂ particle sizes of ~73-88 μ m and ~40-45 μ m, respectively. ALCAN 101 is "pure" aluminum powder with the following components (in weight percent): Cu, 0.003; Fe, 0.076; Si, 0.076; Mn, 0.002; Mg, <0.001; Zn, 0.01; Cr, <0.001; Ti, <0.004; Ga, 0.004; B, <0.001; Cd, 0.0028; Co, <0.001; and V, 0.013.

The irradiation was performed in the Janus reactor on December 12, 1988, for 80 min at 48.73 kW power. After irradiation, each compact was placed in a 150 mL beaker to which about 10 mL of 3M NaOH was added. Upon reaction, some black precipitate was observed, and the U₃Si₂ particles were released. The liquid and a very fine dark precipitate were removed with a plastic pipette. The remaining silicide particles were washed with water, and the washings were added to the supernatant. Final volumes of supernatant for samples from compacts 1, 2, and 3 were 10.5, 11.8, and 12.3 mL, respectively. These solutions, the Al-fraction samples, were analyzed by gamma spectroscopy.

One milliliter aliquots of the aluminum fractions were filtered through Whatman 41 paper, and solutions were reanalyzed for gamma activity.

The U₃Si₂ particles were dissolved in 1.5M NaOH/15% H₂O₂. Sample 3 required 80 mL and 3 h to dissolve; sample 2, 90 mL and 3.5 h; sample 1, 115 mL and 4.5 h. The peroxide was destroyed with heat and the precipitated uranium centrifuged. Supernate volumes (the precipitates were not washed) for samples 1, 2, and 3 were 69.5, 65.0, and 87.5 mL, respectively. The uranium precipitates were then dissolved in 4M HNO₃; sample volumes were 24.8, 22.5, and 23.9 mL for samples 1, 2, and 3, respectively.

The gamma activities of the various fractions were determined with a recently installed ND65 gamma spectroscopy system equipped with an intrinsic germanium well detector and sample changer under automatic control of an AST computer. The spectra were transferred to the CMT VAX computer for analysis of the gamma spectra by GAMANAL.⁴⁷

b. Results and Discussion

Calculation of the theoretical loss of ⁹⁹Mo from the U₃Si₂ particles into the aluminum matrix is based on the following equation⁴⁸:

$$f = 0.5 \left(3\lambda/D - \lambda^3/D^3 \right) \quad (\text{II-116})$$

where f is the fraction of fission products, D is the diameter of the particle (sphere), and λ is the fission fragment range. Thus, theoretically, ^{99}Mo recoil loss into the aluminum matrix from the U_3Si_2 fuel should be inversely proportional to the diameter of the U_3Si_2 particles.

Some discussion on how fission fragment ranges were determined is in order. For earlier calculations of ^{99}Mo , $9.4\ \mu\text{m}$ was used. This is the value for UO_2 for fission fragments in general, not specifically for ^{99}Mo in U_3Si_2 . To calculate the fission fragment ranges for ^{99}Mo and ^{131}I in U_3Si_2 , we used tabulated data⁴⁹ to determine the average energies for fission products with masses of 99 and 131 (98.2 and 76.1 MeV, respectively). Recoil ranges from ^{98}Mo and ^{127}I in U and Al at these average energies are also tabulated;⁵⁰ these data are presented in Table II-44. The recoil ranges (λ) of these nuclides in silicon were then estimated from the values in aluminum by a simple ratio of recoil range and atomic weight:

$$\lambda_x \text{ in Si} = \frac{\lambda_x \text{ in Al} \times \text{atomic wt. (Al)}}{\text{atomic wt. (Si)}} \quad (\text{II-117})$$

where x is the fission product of interest.

Table II-44. Fission Product Recoil Ranges in Various Materials

	Range, μm			
	U Metal	Al Metal	Si Metal	U_3Si_2
^{98}Mo	7.6 ^a	16.4 ^a	15.8	8.1
^{127}I	6.3 ^a	13.2 ^a	12.7	6.6
^{99}Mo	7.5		15.6	8.0
^{131}I	6.1		12.3	6.4

^a Values from tables in Ref. 50.

The values for ^{99}Mo and ^{131}I are similarly estimated by simple ratios from the behavior of ^{98}Mo . For ^{99}Mo , the equation is

$$\lambda[^{99}\text{Mo}] \text{ in Y matrix} = \frac{\lambda[^{98}\text{Mo}] \text{ in Y matrix} \times \text{atomic wt. } [^{98}\text{Mo}]}{\text{atomic wt. } [^{99}\text{Mo}]} \quad (\text{II-118})$$

The values of the recoil ranges of the various isotopes in U_3Si_2 are then calculated from weighted means based on the mass of its elemental components:

$$\lambda[^{98}\text{Mo}] \text{ in } \text{U}_3\text{Si}_2 = \lambda[^{98}\text{Mo}] \text{ in U} \left[\frac{g\text{U}}{g\text{U}_3\text{Si}_2} \right] + \lambda[^{98}\text{Mo}] \text{ in Si} \left[\frac{g\text{Si}}{g\text{U}_3\text{Si}_2} \right] \quad (\text{II-119})$$

Recoil loss calculations for both ^{99}Mo and ^{131}I are in good agreement with experimental values (Table II-45). Of course, the most important point demonstrated here is the strong dependence of ^{99}Mo loss on the U_3Si_2 particle size.

Table II-45. Calculated and Experimental Recoil Loss of ^{99}Mo and ^{131}I to Aluminum Fraction

U_3Si_2 Particle Size Range, μm	Calc. Loss (%) Recoil to Al Matrix ^b			Exp. Loss (%) to Filtered Al Fraction		
	^{99}Mo	^{131}I	^{239}Np	^{99}Mo	^{131}I	^{239}Np
125-150 (138)	8.8	7.2	0	10.4	6.7	0.7
73-88 (81)	15.0	12.2	0	18.2	12.7	1.7
40-45 (43)	28.3	23.0	0	30.1	19.8	2.2

^aSphere diameters for which the calculated losses were made are in parentheses.

^bAssumes a fission fragment range of 8.1 μm for ^{99}Mo and 6.6 μm for ^{131}I .

Because ^{239}Np is an activation rather than fission product, it will not recoil and should serve as a measure of loss due to the transfer of fines and dissolution from particle surfaces. In Table II-44, we see that about 4% of the ^{239}Np is lost to the unfiltered aluminum fraction for all three samples, irrespective of particle size. Of particular interest is a comparison of unfiltered and filtered aluminum fraction because any difference should be attributed to removal of fines or precipitations. Because there is no recoil loss, little neptunium should be dissolved into the aluminum fraction except for what is dissolved from the surface of the particles. Most of the neptunium is removed during filtration, indicating that it is probably present in the aluminum fraction as fines. The same amount of neptunium being lost from all fractions indicates that the same amount of fines is associated with each particle size range. It is interesting that about 3% ^{239}Np was also lost to the aluminum fraction during our first Janus irradiation, where the particle size range was 40-150 μm .

The ^{239}Np that was found in the filtered aluminum fraction increases with decreasing particle size (Table II-45). This ^{239}Np is probably what dissolved from the particle surface and would, therefore, be expected to increase with increasing surface area (or decreasing particle size). It is surprising that some neptunium is found in the filtered fraction since one would expect that any neptunium that did get dissolved would then precipitate out as the hydroxide. The importance of the ^{239}Np loss is in the estimation of the ^{99}Mo loss due to dissolution of U_3Si_2 in NaOH. Certainly, no more than 4% of the ^{99}Mo loss can be attributed to U_3Si_2 dissolution. Probably, this contribution to the loss is not greater than about 2%, the percentage of ^{239}Np found in the filtered aluminum fraction. The close agreement between ^{99}Mo experimental loss and that calculated from recoil supports this conclusion. Hence, dissolution of U_3Si_2 in NaOH is not an important factor in ^{99}Mo loss to the aluminum fraction.

Iodine-131 behaves similarly to ^{99}Mo and shows the same trend (Table II-45) of loss dependence on particle size. One might expect that some I and Mo would be filtered out along with the fines, as seen with ^{239}Np . However, neither nuclide has activity associated with the filtered material (Table II-44). This is probably because these fines are so small that essentially all of the fission products escape, while the activation products do not. (Theoretically, any particle with a diameter less than 8.1 μm would lose all of its ^{99}Mo .) This reasoning also holds for other fission products (depending on their

fission fragment range) such as Ba, Ce, and Nd. However, they are removed essentially completely by filtration. Because of their chemistries; these elements should precipitate from basic solution and thus be filtered out. Other nuclides (Te and Ru) show losses between that of these two groups of fission products, probably reflecting their more complex chemistries.

3. Batch Processing

Dissolution of the U_3Si_2 fuel particles is much different in a laboratory hood than in a ^{99}Mo processing facility, where work would be done in a shielded cell. We want to be able to provide a method for dissolution that is applicable on an industrial scale. The most important problem is advancing from the interval process we have used to a batch process. In a plant, one would not be able to use our laboratory method (i.e., adding dissolver solution, waiting for the reaction to subside, pouring off the spent solution, and adding more dissolver solution). The following is a modified procedure which is more amenable to plant use.

a. Dissolution of U_3Si_2 Only

A 250-mL Erlenmeyer flask was attached to a three-hole connecting tube with a condenser and a 25-mL buret. Depleted U_3Si_2 (0.33 g, mesh size -100/+325) was introduced to the flask with 20 mL of 3M NaOH. The buret dispensed 30% H_2O_2 . After rapidly adding 5 mL of H_2O_2 initially, a delivery rate of 1 mL/min was established and heat was applied ($\sim 70^\circ C$). After 40 mL of H_2O_2 had been added, the U_3Si_2 had dissolved. This amount of H_2O_2 appears about optimum since uranium hydroxide began precipitating about 10 min after dissolution, indicating that only a small excess of H_2O_2 was present at the end of dissolution for complexing the uranium. The rate of addition can be at least doubled without losing control of the reaction.

Using this procedure of continual H_2O_2 addition avoids the violent reaction that would occur if the H_2O_2 were added all at once, and maintains a vigorous reaction rate.

b. Dissolution of Unirradiated Target

A quarter of a Compatibility Study plate* (CS 118) was placed in the Erlenmeyer flask, and 3M NaOH was added to dissolve the Al6061 cladding. A great deal of black-grey precipitate formed. Once most of the aluminum was dissolved, 30 mL of H_2O_2 was added directly to the flask without removal of the precipitate or solution. The H_2O_2 was destroyed immediately upon addition, possibly due to the catalysis action of the precipitate. This result leads to the conclusion that a one-step batch process like this is not feasible. The cladding precipitate must be removed from the U_3Si_2 before H_2O_2 addition.

4. Extent of U_3Si_2 Dissolution in NaOH

A series of experiments was performed (1) to verify the results of earlier experiments indicating low solubility of U_3Si_2 in hot sodium hydroxide solutions, (2) to measure the effect of particle size on the dissolution rate of U_3Si_2 , and (3) to measure the effect of sodium hydroxide concentration on the dissolution rate.

*These small plates had been used by the RERTR program to test a variety of fuel plate designs as prototypes of fuel elements.

a. Experimental

In these experiments, we mixed 0.5 g uranium silicide particles (with diameters in the range of either 40-45 μm , 73-88 μm , or 125-150 μm) with 30 mL of 3 or 6M sodium hydroxide, with and without 0.2M sodium carbonate. These solutions were then heated to 70°C. Sample aliquots were withdrawn at various times during the dissolution.

In the first experiment, the U_3Si_2 samples were subjected to 3 and 6M NaOH solution. Because the uranium that dissolves can precipitate under these conditions, these results may be suspect.

b. Results and Discussion

The percentage of uranium silicide which had dissolved was calculated from the experimentally determined uranium ion concentration in the basic solutions for each sample aliquot.* A volume correction was made for any previous aliquots removed for analysis, but no correction was attempted to account for possible volume losses and increases in NaOH concentration due to evaporation. These results are illustrated in Figs. II-38 and II-39.

Fig. II-38. Effect of Particle Size on U_3Si_2 Dissolution in 3M NaOH with and without 0.2M Na_2CO_3 at 70°C

*Uranium loss fluorescence analysis was performed by Alice Essling, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory.

Fig. II-39. Effect of Hydroxide Concentration on U_3Si_2 Dissolution with and without $0.2M Na_2CO_3$ at $70^\circ C$

The following conclusions were drawn from these results:

1. The dissolution rate of U_3Si_2 is very low, and dissolution of the fuel by the basic solution used to dissolve the cladding material will be only a few tenths of a percent at most.
2. The effects of particle size on the rate of uranium silicide dissolution was imperceptible within experiment uncertainties.
3. Increasing the concentration of sodium hydroxide will increase the extent of fuel dissolution, but, even at $6M$ sodium hydroxide, dissolution of the fuel will be minimal.
4. The addition of sodium carbonate had a negligible effect on the dissolution process.

5. Future Work

Future work will look at the processing steps we have defined for separating ^{99}Mo from LEU silicide targets in terms of their use in a production-scale operation in a shielded-cell facility.

N. Separation Processes to Treat Red Water

(L. Reichley-Yinger, D. J. Chaiko, E. Van Deventer, and E. R. Orth*)

1. Introduction

This work is the first phase of a research project directed toward developing a new and cost-effective process for converting the hazardous red-water waste stream from TNT manufacture to forms that are readily disposable or acceptable for recycling. The conceptual process initially separates the red water, which has approximately the composition given in Table II-46, into its (1) inorganic and (2) organic water-soluble components. The stream containing the water-soluble organic constituents is treated biologically, while the inorganic stream is further processed to recover the sodium sulfite, which can be recycled back into the TNT manufacturing process. Our work focuses on developing the two separations in the process, (1) the separation of the inorganic and organic components of red water by foam fractionation or solvent extraction and (2) the recovery of sodium sulfite from the inorganic stream by solvent extraction. The development of the biotreatment for the organic stream will be done in the ANL Energy and Environmental Systems Division.

2. Characterization of Red Water

To compare the present sample of red water with samples which may be received in the future, physical properties such as acid-base behavior, density, UV-visible spectrum, and carbon-13 nuclear magnetic resonance (NMR) spectrum have been measured. For characterization and separations studies, 5 L of red water was received from Canadian Industries Ltd., Inc. The red water was transferred from the polypropylene shipping container, which was distended due to internal gas pressure, to a 4-L amber-glass bottle, which was stored lightly capped in a hood, and two pint bottles, which were refrigerated to minimize further degradation. During the transfer, we observed that the red water (1) has a very dark red color, (2) seems to be a monophasic liquid devoid of any solids, (3) has a viscosity similar to water, and (4) has an affinity for glass surfaces.

After several days of refrigeration ($T < 10^{\circ}\text{C}$), a cluster of very large monoclinic crystals was found in the red water. Analysis by X-ray diffraction identified these crystals as a mixture of thenardite (Na_2SO_4) and mirabilite, or Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

Samples of red water were titrated with 0.098M HNO_3 and 0.101M NaOH . Only one endpoint was observed during the titrations. This endpoint in the acid titration occurred at 0.1 eq/L of base.

The densities of the "as-received" red water and the red water which had been poured off the sodium sulfate crystals were determined to be 1.204 and 1.189 g/mL , respectively.

The UV-visible absorption spectra for diluted samples of red water were measured at wavelengths from 190 to 900 nm . Figure II-40 shows the spectrum for a $1:10^4$ dilution of red water. The absorbances of the peaks at 193 and 344 nm were found to be proportional to the dilution factor. The extinction coefficients for the two peaks are 2×10^4 and $3 \times 10^3 \text{ cm}^{-1}\text{mL}^{-1}$, respectively.

A carbon-13 NMR spectrum for red water was recorded by J. Rathke, CMT Division. The spectrum in Fig. II-41 shows the presence of three distinct environments for the carbons in red water: aromatic, aliphatic, and an intermediate environment, possibly a nitrated aliphatic.

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Table II-46. Typical Composition of Red Water^{a,b}

Chemical	Weight %
Inorganics	
Sodium sulfite/sulfate	8-12
Sodium nitrite	3-4
Sodium nitrate	0.3-0.5
Total Inorganics	11-17
Organics	
Sulfonate of 2,4,5-trinitrotoluene	6-8
2,4,6-TNT-sulfite complex	3-7
Sulfonate of 2,3,4-trinitrotoluene	2-4
Sulfonate of 2,3,6-trinitrotoluene	0.4-0.8
Trinitrobenzene-sulfite complex	0.3-0.5
Trinitrobenzaldehyde-disulfite addition compound	0.2-0.5
Trinitrobenzyl alcohol	0.2-0.5
2,4,6-trinitrobenzoic acid, sodium salt	0.1-0.5
White compound, sodium salt ^c	0.1-0.5
Sodium nitroformate	0.2
Dissolved 2,4,6-trinitrotoluene	0.1
Sulfonate of 2,3,5-trinitrotoluene	0.05
Dissolved 2,4-dinitrotoluene	0.03
3,4-dinitrobenzoic acid, sodium salt	0.03
2,3-dinitrobenzoic acid, sodium salt	0.03
Total Organics	13-23
Other	
Solids	30-32
Ash	14-16

^aAdapted from J. E. Eckenrode, C. G. Denzler, and J. Klein, in "Evaluation of TNT Red Water Pollution Abatement Technologies," Chemical Systems Laboratory, Aberdeen Proving Ground, MD, ARCSL-TR-80023 (April 1980).

^bDetermined for red water from the continuous process.

^cAlso known as 2,2'-dicarboxy-3,3',5,5'-tetranitroazoxybenzene or 1,9-dicarboxy-2,4,6,8-tetranitrophenazin-V-oxide.

3. Foam Fractionation for the Organic/Inorganic Separation

Work on the separation of the organic and inorganic components of red water by foam fractionation has consisted of two parts, (1) testing whether the concentration of the organic components can be monitored by UV-visible spectroscopy in order to determine an enrichment ratio ($[\text{organics}]_{\text{foamate}}/[\text{organics}]_{\text{raffinate}}$) and (2) determining under what conditions red water would form a stable foam. Spectrophotometric measurements made on solutions containing NaNO_3 , NaNO_2 , Na_2SO_4 , and Na_2SO_3 have indicated that these salts will interfere with determining the organics at 193 nm, because they have very high extinction coefficients ($10^2 \leq \epsilon \leq 10^4$) at that wavelength. However, it appears possible to monitor the concentration of the organics at 344 nm, where the extinction coefficients for these salts are <20 if the concentrations of these inorganic salts are similar to those given in Table II-46.

Foam fractionation experiments have been conducted with the "as-received" red water (pH ~ 8.5) and with acidified red water. Neither "as-received" nor highly acidified (pH < 1) red water forms stable foams. However, by adjusting the pH of the red water to 3, stable foams do form. In fact, a stable foam formed during acidification of red water due to the formation of NO_x and SO_x . A stable foam can also be generated by bubbling air through the acidified red water.

Fig. II-40. Ultraviolet Visible Spectrum for a 1:10⁴ Dilution of Red water

Fig. II-41. Carbon-13 NMR Spectrum of Red Water (5 mL)
in the Presence of D₂O (1 mL)

4. Sellite Recovery (D. J. Chaiko and E. Orth)

The use of solvent extraction as a means of separating and recovering sulfite from the inorganic fraction produced by a foam fractionation step has been investigated. Preliminary tests were performed in order to judge the compatibility of a proposed solvent extraction process for sulfite recovery with foam separation. Foam fractionation would involve the aeration of the red water to generate the foam used to concentrate surface active organics at the air/water interface. Of concern is the possible oxidation of sulfite to sulfate, since aeration is well known to be an effective means of lowering sulfite concentrations and, hence, chemical oxygen demand (COD) in aqueous waste streams.

Air oxidation trials were carried out with alkaline (pH = 8.5) and acidic (pH = 2.0) solutions of simulated red water. Under alkaline conditions, sulfite was oxidized to sulfate following a pseudo-first-order reaction rate with respect to sulfite concentration. At high pH, nitrate and nitrite concentrations were unaltered by aeration. Air oxidation at low pH, however, resulted in a very rapid and quantitative conversion of sulfite to sulfate accompanied by the complete loss of nitrite as gaseous NO_x . Nitrate concentrations were unaltered. Oxidation of synthetic and actual red water samples at pH = 2 in the presence of an oxidizing agent such as hydrogen peroxide resulted in the quantitative conversion of nitrite and sulfite to nitrate and sulfate, respectively. While peroxide prevents the unwanted production of a gaseous waste stream, these tests raise serious questions about the feasibility of sellite recovery from red water.

5. Other Technologies for Organic/Inorganic Separations (D. J. Chaiko and E. R. Orth)

We have also begun to investigate the use of high-molecular-weight flocculants for the selective flocculation of the organic materials from red water as either a preconditioning step before foam fractionation or as a stand-alone unit operation. Using flocculation as a preconditioning step has the potential of greatly reducing the amount of organics that must be removed by foam separation. This is advantageous since foam fractionation operates most efficiently on dilute streams. In addition, any residual flocculant remaining in solution has the potential for increasing the efficiency of the foam separation by acting as a collector for any non-surface-active organic components in the red water. Because the majority of the organics are negatively charged nitroaromatic sulfonates, the flocculant of choice would contain either neutral or cationic functional groups.

Two different types of flocculants have thus far been studied--a high molecular weight ($> 4 \times 10^6$ daltons) cationic polymer (magnafloc 1569CSP obtained from American Cyanamid) and the neutral poly(ethyleneamine). At a concentration of 250 ppm, the cationic flocculant was capable of producing an easily filtered precipitate. Under alkaline conditions, the neutral flocculant was much less effective. However, use of the neutral flocculant in conjunction with hydrous iron colloid produced a clear yellow supernatant.

Both types of flocculants studied thus far were capable of producing an easily filtered precipitate. The neutral flocculant, when used in conjunction with 5 mM hydrous iron colloid, appeared to be the most effective at removing the nitroaromatic sulfonates from solution as judged by the degree of color change in the supernatant. Flocculation was also very effective at removing organics from dilute red water samples.

Other technologies that will be examined include solvent extraction, a combined use of flocculants with ultra filtration for the selective removal biphasic systems. These are systems in which

high-molecular-weight polymers are used to generate two immiscible aqueous phases. Aqueous solutes and particulates can be separated using this form of solvent extraction.

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III. HIGH-LEVEL WASTE/REPOSITORY INTERACTIONS (J. K. Bates)

A. Yucca Mountain Project Glass Studies

(J. K. Bates, B. M. Biwer, W. L. Ebert, T. J. Gerding, and J. J. Mazer)

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 of ANL 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 analysis of the reacted surface using 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). Previous reports¹⁻³ have documented developments in the above five areas through September 1988.

1. The YMP Unsaturated Test Method

(J. K. Bates and T. J. Gerding)

The YMP Unsaturated Test Method (see ANL-90/15, Sec. III.A.1) is being used in the N2 and N3 test series. No new method development work has been done.

a. N2 Unsaturated Test

The N2 continuing tests (SRL 165 glass) have been completed through the 156-week sampling period. All the batch tests have been completed, and three continuous tests and one blank test are ongoing with samplings at 13-week intervals. The release of actinide elements and selected cations over a 120-week sampling period is shown in Figs. III-1 and III-2.

b. N3 Unsaturated Test

The N3 Unsaturated Test uses ATM-10 glass (simulated West Valley glass containing actinides plus ⁹⁹Tc) that was received from the Materials Characterization Center (MCC) and remelted to obtain the required form of the glass. This ongoing test was started July 6, 1987, according to the Unsaturated Test matrix³ and has been completed through the 91-week sampling period. The release of actinide elements and selected cations is shown in Figs. III-3 and III-4. The components from this test are being analyzed by surface analytical techniques to provide a more detailed description of the glass reaction over the first one-year period.

2. Parametric Experiments

(J. K. Bates and T. J. Gerding)

The YMP Unsaturated Test rigidly sets many of the test parameters; therefore, the effect that each parameter may have on the final radionuclide release needs to be studied. This is being done in

(a)

(b)

(c)

Fig. III-1. Cation Release from the N2 Test Series:
(a) N2-9, (b) N2-10, and (c) N2-12

(a)

(b)

(c)

Fig. III-2. Transuranic Release from the N2 Test Series:
(a) Np, (b) Pu, and (c) Am

(a)

(b)

(c)

Fig. III-3. Cation Release from the N3 Test Series:
(a) N3-9, (b) N3-10, and (c) N3-12

(a)

(b)

(c)

Fig. III-4. Transuranic Release from the N3 Test Series:
(a) Np, (b) Pu, and (c) Am

parametric experiments. A description, purpose, and status for the parametric experiments in progress are given in Table III-1. Each of the ongoing experiments has been discussed in detail previously^{1,4,5} and are continuing as scheduled.

The Unsaturated Test has been applied to glass in both the standard mode (0.075 mL of EJ-13 water injected every 3.5 days with a glass surface area of $\sim 13.5 \text{ cm}^2$ and use of presensitized 304L stainless steel) and the standard mode modified to study the effects of varying the volume of water contacting the waste, the interval between water injection periods, the ratio of glass surface area (as-cut or cast) in contact with water to the water volume (SA/V), and the condition of the stainless steel in contact with the glass. Details of the experiments listed in Table III-1 are presented elsewhere.^{3,6-8} The test has been performed with (1) glass based on the Savannah River Laboratory "black frit" modified to give the SRL 165 composition shown in Table III-2 and (2) remelted ATM-10 glass, which is a reference glass developed for use in testing for the West Valley Demonstration Project.

Of particular interest is determining the effect of the varied conditions on the glass performance and the identity of interactions of particular importance in the reaction process. The SRL 165 glass performance is measured by the release of Li, B, and U from the waste package assemblage, shown in Fig. III-5 for the continuous experiments. These elements provide evidence of glass reaction because they are significant constituents of the glass, not the water or other test components. The results are normalized to the glass composition and total surface area.⁶

The smallest elemental release is found in the test with the longest interval between water injection (test 6), the one with no metal retainer (test 3), and the one with the low carbon stainless steel (test 7). In each of these batch tests, the glass samples gained weight, and the top and bottom surfaces were covered with what appears to be products of evaporation (Fig. III-6), mainly calcite. Calculations indicated that a temperature differential of $\sim 0.1^\circ\text{C}$ between the glass and the container walls is large enough to evaporate the 0.075 mL injected in a 3.5 day period if the walls are cooler than the glass. Such temperature differentials will certainly exist in the repository for long periods of time and also in the laboratory tests.

More extensive reaction was observed in test 1, which was done with partially sensitized 304L stainless steel (i.e., 24 h at 550°C , followed by slow cooling to room temperature). Sensitization is a process of chromium depletion where chromium carbides are formed along the grain boundaries when the metal alloy is heated in the range $550\text{--}850^\circ\text{C}$ for short periods of time (hours to days) or at lower temperatures for longer times. Formation of these chromium-rich carbides can cause depletion of chromium (to $<12 \text{ wt } \%$) in the immediate vicinity of the grain boundaries. The depleted material is no longer "stainless" and is quite susceptible to attack at the grain boundaries. The extent of sensitization is also dependent on the amount of carbon in the steel.

In test 1, the 304L steel contained 0.022 wt % carbon, and by the first sampling period (6.5 weeks), extensive reaction between the metal, glass, and groundwater had occurred, resulting in the formation of metal (Fe, Cr, Mn, Ni) silicates and iron oxide-hydroxide reaction products⁷ (Fig. III-7). The glass samples lost weight, and the extent of reaction as measured by the release of Li, B, and U increased by about two times that of tests 6, 3, and 7, as well as previous parametric tests done using non-sensitized metal.⁶ With continued time, the effect of the sensitization may have abated somewhat, in that the amount of reaction products covering the top metal and glass surfaces remained fairly constant and the glass reaction rate slowed.

Table III-1. Description, Purpose, and Status of Glass-Related Unsaturated Tests

Test No.	Description	Purpose	Status
1	Regular-sized SRL 165 glass waste forms in presensitized 0.022 wt % carbon SS holders, 0.075 mL EJ-13/3.5 days, continuous and batch experiments.	To measure glass reaction and radionuclide release under standard conditions, SRL 165 type glass doped with Np, Pu, and Am.	Initiated 2/3/86. Batch experiments completed 2/2/87. Continuous experiments in progress.
2	Regular-sized ATM-10 glass waste forms in presensitized 0.022 wt % carbon SS holders, 0.075 mL EJ-13/3.5 days, continuous and batch experiments.	To measure glass reaction and radionuclide release under standard conditions, ATM-10 glass.	Initiated 7/5/87. Batch experiments completed. Continuous experiments in progress.
3	Regular-sized SRL 165 glass waste form, no SS holder, 0.075 mL J-13/3.5 days, continuous and batch experiments.	To study the release from glass only.	Initiated 2/20/84. Batch experiments completed 2/18/85. Continuous experiments in progress.
4	Half-sized SRL 165 glass waste form, SS holder, 0.075 mL EJ-13/3.5 days, continuous and batch experiments.	To study the effect of changing the waste form surface area by reducing the as-cast surface area by half.	Initiated 12/6/84. Batch experiments completed 12/5/85. Continuous experiments in progress.
5	Half-sized SRL 165 glass waste form, SS holder, 0.0375 mL EJ-13/3.5 days, continuous and batch experiments.	To study the effect of reducing the volume of water added per inject period with the as-cast surface area reduced by half.	Initiated 2/18/85. Batch experiments completed 2/17/86. Continuous experiments in progress.
6	Regular-sized SRL 165 glass waste form, SS holder, 0.075 mL EJ-13/14 days, continuous and batch experiments.	To study the effect of lengthening the time interval between water additions.	Initiated 6/10/85. Batch experiments completed through two years. Continuous and batch experiments in progress.
7	Regular-sized SRL 165 glass waste forms in presensitized 0.017 wt % carbon SS holders, 0.075 mL EJ-13/3.5 days, continuous and batch experiments.	To study the effect of presensitizing the SS waste form holder using low carbon SS.	Initiated 2/27/86. Batch experiments completed through two years. Continuous and batch experiments in progress.

Table III-2. Composition of Glasses Used in the Unsaturated Tests

Oxide Component	ATM-10 ^a		SRL 165	
	Oxide wt %	Element wt %	Oxide wt %	Element wt %
Al ₂ O ₃	6.65	3.52	4.08	2.16
B ₂ O ₃	9.17	2.85	6.76	2.09
BaO	0.05	0.04	0.06	0.05
CaO	0.60	0.43	1.62	1.16
CeO ₂	0.07	0.06	<0.05	<0.04
Cr ₂ O ₃	0.24	0.16	<0.01	<0.01
Cs ₂ O	0.07	0.06	0.07	0.07
Fe ₂ O ₃	11.53	8.06	11.74	8.20
K ₂ O	3.34	2.78		
La ₂ O ₃	0.03	0.02	<0.05	<0.004
Li ₂ O	2.88	1.34	4.18	1.94
MgO	1.15	0.70	0.70	0.42
MnO ₂	1.29	0.82	2.79	1.76
Na ₂ O	10.53	7.81	10.85	8.05
Nd ₂ O ₃	0.17	0.14	<0.05	<0.01
NiO	0.30	0.02	0.85	0.67
P ₂ O ₅	2.34	1.02	0.29	0.13
RhO ₂	0.01	0.01		
RuO ₂	0.06	0.05		
SO ₃	0.31	0.12		
SiO ₂	45.84	21.43	52.86	24.71
SrO	0.03	0.02	0.11	0.10
TiO ₂	0.86	10.51	0.14	0.08
Y ₂ O ₃	0.02	0.01		
ZnO	NA	NA	0.04	0.03
ZrO ₂	0.25	0.18	0.66	0.48
(Radioactive)				
AmO ₂	0.006	0.006		
NpO ₂	0.021	0.018	0.008	0.0239
PuO ₂	0.081	0.071	0.022	0.0198
Tc ₂ O ₇	0.003	0.002		<0.01
ThO ₂	3.29	2.89		
UO ₂	0.53	0.47	0.92	0.81
(Anions)				
Cl	NA ^b	NA		0.01
S	NA	NA		0.12

^aComposition reported by the MCC. The glass was remelted and cast prior to use in the Unsaturated Test.

^bNA - not analyzed.

Fig. III-5. Normalized Release of Li, B, and U in Glass Unsaturated Tests (SRL 165 Glass)

Fig. III-6. SEM Photomicrograph of a Reacted Surface of Glass from Test 3 (magnification, 100X; marker, 100 μm)

Fig. III-7. SEM Photomicrograph of Metal-Rich Reaction Products Formed in Test 1 (magnification, 150X; marker, 100 μm)

In test 7, the 304L steel contained 0.016 wt % carbon, and the extent of sensitization was measured to be less than that in test 1, although the sensitization process was the same for both tests (24 h at 550°C, followed by slow cooling to room temperature). The effect of the lesser degree of sensitization is quite evident in that only localized reaction of the metal and glass was observed, and the elemental release was less than that measured in test 1. The elemental release was also influenced by the evaporative processes that occurred in this test, as discussed earlier.

The greatest effect on glass reaction was found in test 4 and, especially, test 5. The larger elemental release is accompanied by a striking change in the appearance of the reacted glass surface. In all the batch samples examined, there was evidence that layers of reacted glass had spalled from the waste package assembly (WPA) during the test period and had been analyzed with the 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-8, regions of bare glass that exist on the surface and not in contact with metal are 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 tests, but these regions are much more extensive in test 5 and, to a lesser degree, in test 4. Surrounding the exfoliated regions are usually copious quantities of chlorine- and sulfur-bearing precipitates.

Fig. III-8. SEM Photomicrograph of a Bare Section of Glass from Test 4. (Section has undergone exfoliation of the reacted layer, followed by reprecipitation.)

While a definitive explanation of the exfoliation/reprecipitation process is not available, it is likely that the reduced amount of water injected in test 5 created conditions favorable for wet/damp cycling, with enough water 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.

The elemental releases from ATM-10 glass (test 2 in Table III-1) are shown in Fig. III-9. 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 ATM-10 tests was that, despite a pretreatment of the metal retainer as was done in test 1 for SRL 165 glass, no evidence of strong reaction between the metal and glass was

Fig. III-9. Normalized Release of Li, B, and U in Glass Unsaturated Tests (ATM-10 Glass). (The tests were run in triplicate and are identified as 2a, 2b, and 2c.)

observed. This may be due to the composition of ATM-10 glass, which was prepared with starting components that contained no S or Cl (the anionic composition was not reported for this glass). Further analysis of the reacted components from test 2 may be required to completely address the apparent lack of glass/metal reaction in test 2.

3. Vapor Hydration Experiments (W. L. Ebert)

The hydrology of the Topopah Spring tuff being studied by the YMP has been characterized as unsaturated. Heat generated by the waste is expected to maintain unsaturated conditions in the repository for several hundred years after closure, though the repository environment is expected to remain humid throughout the containment period and into the isolation period. Since breaching of the metal container may occur without liquid water accumulating in the repository, the waste glass may be exposed to humid atmospheres after emplacement.

To characterize the behavior of waste glass in a humid environment, a series of experiments was performed wherein an SRL 165 black frit based glass and WVCN 44 glass were reacted in steam at temperatures up to 200°C for reaction times up to several months. Samples were prepared as disks approximately 1 cm in diameter and 1-mm thick with the faces ground to a 600-grit finish. Samples were suspended by Teflon thread in sealed 304L stainless steel reaction bombs containing an appropriate amount of water to assure saturation of the vapor phase at the reaction temperature. Upon heating, steam forms and an equilibrium amount of water sorbs onto the sample surface. The reaction occurs in this thin film of sorbed water. The extent of reaction can be quantified by measuring the thickness of the depletion layer which forms on the glass surface due to selective leaching. The reaction can also be characterized by the secondary phases which form in addition to the depletion layer.

The results of experiments performed at 150, 175, and 200°C show that the depletion layer thickness increases with the reaction time, and the growth rate increases with the reaction temperature. However, there was significant scatter in the measured layer thicknesses and many samples failed to react. Samples having thick reaction layers always had a large inventory of secondary products. It had been observed previously that the formation of certain secondary phases concurred with an apparent acceleration of the reaction rate.^{9,10} We attribute the scatter in the measured layer thicknesses to nucleation kinetics. If the reaction rate is different when a specific phase is present, then the measured extent of reaction will depend on the fraction of the total reaction time that phase was present. This effect is illustrated in Fig. III-10, where the reaction rate is higher when phase A is present. If phase A forms at time t_1 on sample 1 and at t_2 on sample 2, and if the layer thickness is measured at time t , then the measured extent of reaction will be greater on sample 1 because it reacted longer at the higher rate. Thus, while both samples react by the same mechanism, differences in time required to precipitate a rate-controlling phase may lead to different apparent reaction rates. Samples which did not form precipitates reacted at the low rate for the entire reaction period and so developed layers too thin to measure.

Two sets of experiments were performed at 200°C, where special attention was paid to preparing a uniform glass surface in set II. The measured layer thicknesses for these samples are plotted vs. the reaction time in Fig. III-11. The scatter is similar in both sets of experiments, and all samples produced measurable layers (unless the water was lost due to vessel leakage). The curve shown in the figure assumes a $t^{1/2}$ dependence of the layer growth, though no mechanism is implied here.

Figure III-12 shows the profiles of Na, Al, and Si obtained by EDS analysis of a cross section of the depletion layer on sample 1020, which was reacted 15 days. Profiles are shown from the

Fig. III-10. Schematic Plot of Layer Thickness vs. Reaction Time Showing the Formation of a Precipitate A after Different Reaction Times (t_1 and t_2). The layer thickness at time t is different because the reaction rate changes with the formation of the precipitate.

Fig. III-11. Measured Layer Thickness vs. Reaction Time for SRL U Glass Reacted in Steam at 200°C. Different symbols represent different series of experiments: set I (●), set II (+). The cross symbols were fit with the equation, $\text{thickness} = 3.92 t^{1/2} + 2.79$.

mounting resin (left-hand side) through inner and outer zones of the reactor layer and into the unreacted bulk glass. A cross-section image revealed the layer to be comprised of two regions. The outer region has a striated appearance, which is oriented normal to the surface, while the inner region has an amorphous appearance similar to the unreacted glass. The Na and Al counts have been multiplied by five to better illustrate their profiles. Silicon has a similar concentration in the layer and the bulk, while sodium is completely depleted and aluminum is partially depleted in the layer compared to the bulk glass.

Scanning electron microscopy analysis of the surface revealed that a clay-like layer is formed on the outer surface of the depletion layer. Several precipitates were found on the surface in addition to the clay. The predominant mineral phase was identified as analcime, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$. Several calcium silicate phases and the sodium analog of weberite, a uranium silicate, are also precipitated. Current work is focused on identifying the secondary phases forming on this and other glass types during the hydration process in a steam environment.

Fig. III-12. Energy Dispersive X-Ray Spectroscopy (EDS) Line Profile across Alteration Layer of Sample 1020

4. Static Leach Experiments (B. M. Biwer)

Experiments are being conducted following a MCC-1 type format in support of the effort at LLNL to model the corrosion of nuclear waste glasses over extended time periods. They will also provide a basis for comparison with similar experiments performed by other workers. These experiments are to be performed at QA level 1 in FY 1990 and will use the new reference glass waste formulation designated as SRL 202, in addition to SRL 131 glass. Therefore, expertise in conducting MCC-1 type leach tests must first be acquired, and a suitable test plan must be formulated based on such experience.

The modeling effort, as currently understood, is concerned with predicting the long-term leach behavior of a nuclear waste glass after a steady-state equilibrium has been reached between glass

components and their corresponding species in solution. At this time, it is not clear which phase establishes the steady-state equilibrium between the glass and the solution. The solution concentration after any given time is dependent on the formation of a leached (reacted) layer of a given thickness and composition. The same steady-state conditions (solution species concentration) may not exist if saturation is attained at a different stage during the development of the reacted layer (the composition of the leached layer and precipitates present may vary with the extent of reaction). If steady-state conditions are different, each long-term prediction will only be applicable to the specific set of initial conditions used (glass composition, solution composition, SA/V ratio, etc.). If so, more information from LLNL will be required on the initial conditions desired for support experiments.

A series of experiments (the SVT matrix) based on the MCC-1P test method is in progress to investigate the effect of the SA/V ratio, as well as initial leachant silicon concentrations, on the final steady-state conditions of a static leach test. For these tests, SRL 131 glass is being used since it is one of the more reactive nuclear waste reference glasses under hydrothermal conditions and will attain steady-state conditions in shorter reaction times than other glasses. Reaction for 100 days is required to reach near, if not complete, solution saturation of most elements at the standard MCC-1 SA/V ratio of 10^{-1} m. Higher SA/V ratios of 50 and 100 m^{-1} reach saturation at earlier time periods. Table III-3 shows the reaction times to be used in the SVT matrix. In addition to SRL 131 glass, SRL 202 glass will be reacted to give an indication of the effect of this new glass composition on the rate of reaction and its effect on the steady-state equilibrium after saturation.

The leach tests are performed following MCC-1 procedures in 22-mL Teflon vessels with deionized water (DIW), a silicon-saturated solution with respect to silicic acid, and a 50% silicon-saturated solution. Glass reaction layers will be analyzed and solution concentrations will be determined at the conclusion of each experiment.

Varying the SA/V ratio will allow solution concentrations to saturate at various stages in the development of the reacted surface layer. The experiments at higher SA/V ratios should attain saturation of solution species faster than experiments at lower SA/V ratios and have a thinner reacted layer for the same reaction time because less glass need react. This has been observed for PNL 76-68 waste glass.^{11,12} If elemental release rates from the glass change before equilibrium is established, a different equilibrium reaction could become the controlling factor for a specific ion involved in other equilibria. Such a result would change the amount of one or more ions in solution and ultimately would affect the long-range results. Observation of the reacted layer composition and solution concentrations will give indications as to the controlling equilibrium reactions. Comparison of "equivalent" leach periods, $(\text{SA/V}) \cdot t = \text{constant}$, may show very similar results but could be different.¹¹ If the reacted layer becomes a barrier to diffusion, a difference in results might occur. Leaching samples at the same SA/V ratio for different periods of time will also give information on how the reacted layer develops and whether or not it is different (e.g., composition and structure as a function of thickness) for different SA/V ratios.

The case of the three different leachants will provide information in two areas. Owing to saturation effects, initial silicon concentrations in various solutions tend to suppress the leaching and glass dissolution of some of the proposed U.S. nuclear waste glasses. Hence, we will test the effect of initial silicon concentrations in solution (prepared with DIW and silicic acid without the initial presence of other ions found in the glass) on glass reaction. The second area of interest concerns the effect of the initial silicon concentrations on the final steady-state equilibrium values. One expects the steady-state values to have higher ratios of silicon to other elements if more silicon is present at the start, unless a pure $\text{Si}_x\text{-O}_y\text{-H}_z$ species equilibrium is controlling the silicon concentration.

Leach experiments involving the SRL 131 glass are underway. Those involving SRL 202 glass will be initiated after analysis of the SRL 131 results, which might indicate that modifications in the test matrix are necessary to obtain the desired information.

Table III-3. Reaction Time for the SA/V Ratios Employed in the SVT Matrix

SA/V, m ⁻¹	Time, days						
	(SA/V)•t=70 d/m	140 d/m	280 d/m	560 d/m	1000 d/m	2000 d/m	2500 d/m
10	7	14	28	56	100		
50			5.6	11.2	20	40	50
100			2.8	5.6	10	20	25

5. Relative Humidity Experiments (B. M. Biwer)

a. Introduction

The primary aging mechanism for glassified waste forms in an unsaturated environment is expected to be due to vapor phase hydration. Any liquid water present initially will be vaporized due to the heat generated by the waste package and will be driven to the cooler regions of the repository.

These experiments were designed to study the vapor phase aging/hydration of glass by comparing the reaction progress for waste and natural glasses of varying composition under different relative humidity (RH) conditions. The glasses under investigation are the nuclear waste glasses SRL 131, SRL 165, and PNL 76-68 along with the natural glasses obsidian and basalt. The compositions of these glasses and the experimental matrix for the relative humidity experiments have been given previously.³ Recent work includes the surface characterization of samples reacted for 365 days at 75 °C and 60, 95, or 100% RH and the addition of new samples to the test matrix.

b. Results

(1) General

Discussed below are the SEM/EDS surface analysis results (elements heavier than neon) of the 365-day samples of SRL 131, PNL 76-68, obsidian, and basalt. The results for the SRL 165 samples have already been reported.^{5,13,14} In general, the higher the humidity for a given glass sample, the greater the observed extent of reaction. The majority of the reaction products on all samples have a composition similar to that of the unreacted glass. We found Si-, Ca-, or Fe-dominated species on all samples. The presence of NaCl and Na-S formations was detected scattered across the surfaces of the samples subjected to 60% RH. The glass samples exposed to a 95% RH environment had the largest number of reaction products on their surfaces, easily observed by a visual inspection. The nuclear waste glass specimens subjected to the 100% RH environment had developed an open pore-like structure on their surfaces with fewer reaction products present. The initial development of such a structure was noted for the SRL 131 and SRL 165 samples at 95% RH. Many leached samples also form such a layer on the surface.

(2) SRL 131 Glass

The SRL 131 glass reacted at 75 °C in 60% RH for 365 days was designated V-129. An EDS examination of the surface yielded a spectrum identical to the unreacted glass, attesting to the small depth of its reacted layer. High magnification on the SEM did not bring out any well-defined

features or structure of the surface layer. Aside from NaCl and Na-S species, other precipitates observed were dominated by Ca, Si, Ti, Fe, or Ni; Cr-Ni and Cr-Fe-Ni species were also present. The SRL 131 sample subjected to 95% RH (V-109) was heavily reacted, the predominant species observed being one composed of silicon with minor amounts of other elements; NaCl and Na-S products were present to a small degree, in addition to other products consisting of varying amounts of Na, Si, S, Cl, and Ca in combination. Enrichment of Al, Ti, Ni, Zn, or La was noted in other reaction products. X-ray diffraction of one precipitate revealed the presence of a smectite-type phase and calcite. The surface layer had Si, Mn, and Fe at levels close to those of the bulk glass, but Ca was absent and S and Cl were evident. The 100% RH SRL 131 sample (V-144) exhibited large patches of white precipitate under visual observation. These patches are probably the remains of evaporated condensate which formed on the sample during reaction. Sodium and calcium were absent; Mn and Fe were diminished with respect to Si; Mg and S were enriched. In contrast, the general surface layer was enriched in Mn and Fe as well as Mg and S. A few Cr-Fe precipitates were also present.

(3) PNL 76-68 Glass

The EDS for the surface of the PNL 76-68 sample subjected to 365 days at 75 °C in 60% RH (V-130) showed a slight enrichment of iron. High magnification on the SEM showed no apparent structure for the surface layer. Chlorine and sulfur were found in many precipitates; Al-Si or Pb-enriched species were also present. This glass also appeared to have Cr-Fe-Zn spinels in different locations. The PNL 76-68 glass reacted at 95% RH (V-113) still had a few NaCl and Na-S compounds on the surface, in addition to precipitates rich in Cr-Ni, Cr-Fe, Pb, or La. At 60% RH, sample V-113 had no apparent structure to its surface and included Cr-Fe-Zn spinels. The PNL 76-68 sample at 100% RH (V-145) had a surface partially depleted in sodium. Otherwise, its porous network structure appeared to have a composition similar to the base glass.

(4) Obsidian

The majority of the relatively few reaction products on all of the obsidian samples had a composition similar to that of the bulk glass, with slightly different amounts of Al, K, Ca, Fe, and Si. A Si-Ca-Fe phase was observed on all samples and appears to be interspersed throughout the obsidian itself. As might be expected, due to its high SiO₂ and Al₂O₃ content, the obsidian samples had hardly reacted in comparison with the other glasses.

(5) Basalt

Up to this point, all the glasses, including SRL 165, followed the trend of higher surface sodium concentration with decreased humidity. The basalt is an exception. Large amounts of NaCl (some Na-S species) could be seen scattered across the 100% RH sample (V-147) surface; Ti- and Al- enriched reaction products were also present. Its surface layer was too thin for EDS to detect any compositional change from the unreacted glass. The 95% RH sample (V-121) had many reaction products enriched in a few of the 3d transition metals, such as Ti, Fe, Ni, Cu, and/or Zn. Magnesium and titanium were found to be highly enriched in a number of reaction products. All basalt samples had an enrichment of S and Cl in many species.

6. Basalt Analog (J. J. Mazer)

Hydrothermal leaching and vapor phase hydration experiments have been performed using two synthetic basalts and one SRL glass composition and deionized water. A discussion of these

experiments has been presented previously.¹⁵ While these experiments were completed under a different sponsor, they provide a wealth of samples and data that still require analysis and interpretation, where the synthesized information will be of use to the YMP program. For this reason, work has continued with these samples. This work has focused on determining the reaction kinetics and identifying the composition of the alteration layer as a function of the test method used. The conclusions from this work are presented below:

- (1) Under the hydrothermal leaching conditions used in this study, both Hawaiian basalt glass and SRL 165 glass experience layer growth that is best described as a function of time^{1/2}.
- (2) The layer composition of hydrothermally leached basalt glass samples was somewhat similar for all reaction times and temperatures examined for up to 364 days and between 90°C and 187°C. X-ray diffraction analysis identified the presence of a smectite clay in the layer formed at 187°C, while the layers produced at lower temperatures were completely amorphous. The composition of the layers which formed on leached basalt glass is not consistent with smectite, based on the cation-to-silicon ratios. This result suggests that the reacted layer may be a precursor to smectite. The completely amorphous layers were slightly enriched in Fe and depleted in Ca compared to the bulk glass. The measured amount of water in the reacted layers is similar to that found by others in both experimental and natural studies of smectites and palagonites.¹⁶⁻¹⁸
- (3) Under vapor reaction conditions, Hawaiian basalt glass experiences layer growth of uncertain kinetics. The layer composition is different from that formed on leached basalt glass, and the layer may be structurally more complicated. The layer growth of SRL 165 glass reacted in the present vapor phase experiments is best represented by a function of time^{1/2}.
- (4) The layer composition of hydrothermally leached SRL 165 glass is a complex mixture of at least three discernible phases. Each phase has a variable composition. Within the layer, sodium becomes more depleted and iron more enriched as the outer surface of the layer is approached. The layer formed on vapor-reacted SRL 165 has two discernible regions, though the appearance and composition of both regions are similar to the dominant (center) phase found on leached SRL 165 glass. The composition of the vapor-reacted layer has a cation-to-silicon ratio which is consistent with that of a smectite clay.
- (5) Leach tests and vapor phase tests conducted on the same glass type for identical lengths of time produce reaction assemblages which are different. On basalt glass, leach tests produce a reacted layer which contains smectite (or perhaps a kaolinitic) clay. The same glass reacted in a vapor phase environment produces a reacted layer which appears similar but is compositionally different from that observed in a leach test. In addition, vapor tests also produce zeolites, including analcime, thomsonite, and phillipsite overlying the reacted layer.
- (6) Layer growth follows an Arrhenius relationship for the leached samples. The activation energy of leached Hawaiian basalt glass (120-187°C) was 10 kcal/mol and is similar to what others have found for leached basalt glass^{17,19} and vapor-reacted nuclear waste glasses.⁵ The kinetics of the vapor-reacted samples is uncertain over the temperature range investigated.

- (7) Layer growth on SRL 165 glass is faster than that on basalt glass under leaching and vapor conditions at 187 °C.
- (8) The rate of layer growth in leaching experiments is faster than that of vapor experiments, although the phase assemblage is more mature in vapor experiments. The reacted layer which forms on the glass surface in each type of experiment is compositionally different. Each reacted layer is a smectite-bearing phase, similar to natural palagonites which contain crystalline phases.^{16,18}

The criteria to be used in determining an appropriate test acceleration method are ascertaining that (1) the experimental reaction kinetics and (2) the alteration products closely match those found on natural samples. Leaching tests produce a reaction layer whose formation is best described as a function of time^{1/2}. The reaction layer varies from a smectite-bearing phase to an amorphous, palagonite-like layer. Vapor tests produce a reaction layer whose growth kinetics is not able to be determined. The reaction assemblage includes a smectite-bearing layer and several zeolites. The reaction layer formed in each test is compositionally similar to what is found on naturally altered basalt glass; however, the reaction layers are not identical. It is clear that the vapor-phase-test alteration assemblage more closely duplicates what is found in natural environments.

The experiments performed on SRL 165 glass at various SA/V ratios suggest that vapor phase experiments are a form of leach test with a very high SA/V ratio. Differences in the dominant cation sink in leach and vapor phase tests result in reacted layers with compositions which cannot be directly compared as a function of (SA/V)^{•t}. The reaction layers formed on SRL 165 glass at different SA/V ratios in both leach and vapor phase tests are compositionally different and more complicated than those which form on basalt glass.

A basis for completely understanding the kinetics and mechanisms of vapor experiments still does not exist, but with the glasses and experimental conditions considered here, vapor tests appear to be the most appropriate method for accelerating glass reactions. The similarities which do exist between the interactions of vapor-reacted basalt glass and nuclear waste glass also strongly suggest that, eventually, naturally reacted glasses can be used as analogues to aid in the interpretation of processes that may occur to waste glass stored in a repository. Further studies are in progress to better characterize the basalt glass and SRL 165 reacted layers and determine the reaction kinetics of vapor phase tests.

7. Gamma Irradiation Experiments (W. L. Ebert)

An extensive series of experiments has been performed to determine the influence of penetrating gamma radiation on the reaction of simulated nuclear waste glass in tuff groundwater. Groundwater which may enter the repository during the isolation period (several hundred years after emplacement) will be subjected to low levels of gamma radiation generated by the decay of high-level nuclear waste. The air in the repository will have been irradiated at high doses and will also affect the groundwater chemistry. Because the primary means of radionuclide escape is via leaching and transport in the groundwater, the behavior of the waste glass and radionuclides in such an irradiated air/groundwater system must be characterized.

Experiments similar to the MCC-1 static leach test were performed at 90 °C under gamma radiation exposures of 2×10^5 , 1×10^4 , or 1×10^3 R/h; nonirradiated experiments were performed for

comparison. Repository reference groundwater J-13 was used as the leachant, and doped SRL 165 black frit, ATM-1c, and ATM-8 glasses were used to simulate the waste glass. The leachant and glass were placed in 304L stainless steel vessels; the amount of leachant was varied to achieve an SA/V ratio near 0.3 cm^{-1} and an air/leachant volume of about 0.3. The final leachates were analyzed for pH, for various anions and cations, and for released transuranics. The reacted samples were analyzed with SEM/EDS and SIMS.

The primary influence of radiation was acidification of the leachate by nitric and nitrous acid. The stability of the nitrite ion suggests that the leachate Eh was lowered by radiolysis as well. The results of experiments with nonradioactive glasses have been described previously,²⁰ where the behavior of most species associated with the frit glass was unaffected by radiation. This report highlights the influence of radiation on the behavior of the released transuranics from SRL 165 black frit doped with U, Np, Pu, and Am (referred to as SRL A) and ATM-8 glass which contains U, Pu, and Np.

The leachate pH reflects the relative rates of (1) acidification due to radiolysis and (2) basification due to the glass reaction. The tuff groundwater contains a high concentration of bicarbonate, which prevents the pH from dropping below about 6.4. The final leachate pH's are plotted vs. the reaction time at the different exposure rates for experiments with SRL A or ATM-8 glass in Fig. III-13. Nonirradiated experiments attained pH's near 9 for SRL A glass and 9.5 for ATM-8 glass, while irradiated experiments approached a pH near 7 for SRL A glass and near 7.5 for ATM-8 glass at long reaction times for all radiation exposure rates. The higher final pH's indicate that the extent of glass reaction is greater in experiments with ATM-8 glass than with SRL A.

The leachate was analyzed for transuranics using filtered ($50 \text{ \AA}$), unfiltered, and acidified samples to determine the fractionation of the released species between dissolved, colloidal, and sorbed phases. Neptunium was present only in the aqueous phase, in both dissolved and filterable (colloidal) form. Plutonium and americium were primarily sorbed or plated onto the stainless steel vessel surface. Uranium precipitates were present on several SRL A samples, but these precipitates were too small to identify further. No precipitates containing other transuranics were found. The total release of the transuranics from SRL A glass decreased as $\text{Np} > \text{U} > \text{Si} = \text{Pu} > \text{Am}$, where the silicon release represents the extent of etching. Plutonium is released with silicon, while neptunium and uranium are preferentially leached from the glass. The low solubility limit of americium at the experimental pH's results in an accumulation of americium on the glass surface. The concentration of neptunium released into the aqueous phase is shown plotted against the reaction time in Fig. III-14a. Although the low concentrations result in significant scatter, irradiation does not appear to have a large influence on the neptunium release, nor does irradiation appear to affect the release of any transuranic from SRL A glass.

In contrast, the normalized elemental mass loss of all transuranics from ATM-8 glass was affected by irradiation, with the release following the order $2 \times 10^5 \text{ R/h} > 1 \times 10^3 \text{ R/h} > 0 \text{ R/h}$ for all species. The release of species at each exposure followed the order $\text{Si}, \text{Np} > \text{Pu} > \text{Am}$. The silicon and neptunium results were similar, within analytical error. Figure III-14b shows the neptunium leachate concentration (dissolved plus colloidal) as a function of the reaction time for ATM-8 glass. The neptunium concentration correlates with the leachate pH in Fig. III-13b, where the concentration is low at the high pH attained in the nonirradiated experiments and high at the low pH of the experiments irradiated at $2 \times 10^5 \text{ R/h}$. After 56 days of reaction, the pH of the leachate from both the 2×10^5 and $1 \times 10^3 \text{ R/h}$ experiments is near 7.5, and the neptunium concentrations are similar. The release of uranium and plutonium in the $2 \times 10^5 \text{ R/h}$ experiments increases through 28 days, when pH is low, then decreases at 56 days when the pH is higher. This implies that the release of transuranics into the aqueous phase increases as the pH decreases due to higher solubility limits at low pH. Because the irradiated experiments with

SRL A glass attained similar pH at all exposure rates, the transuranic release was the same.

Fig. III-13.

Leachate pH vs. Reaction Time for SRL A Glass and ATM-8 Glass in EJ-13 Solution. (Filled circle, 2×10^5 R/h; filled triangle, 1×10^4 R/h; inverted filled triangle, 1×10^3 R/h; and open square, 0 R/h.)

These experiments have shown the primary effect of radiation to be the acidification of the leachate. The extent of acidification is limited (1) to a pH of 6.4 because of the high bicarbonate level in tuff groundwater and (2) by the glass reaction itself, which generates hydroxide ions during alkali release. The pH reached after long reaction times appears to be independent of the exposure rate, reaching values only about two pH units lower than those of nonirradiated experiments. The solubilities of some species may be significantly different at the different pH's and so may their releases into solution, even though the extent of glass reaction may be the same in both irradiated and nonirradiated environments.

B. Yucca Mountain Project Spent Fuel Studies (E. Veleckis and J. C. Hoh)

1. Dissolution of Mixed UO₂ Powder in J-13 Water under Saturated Conditions

Experimental work on the dissolution of mixed UO₂ powder in J-13 well water under saturated test conditions at room temperature has been completed, and the data interpretation is underway.

Fig. III-14.

Total Neptunium Concentration in Aqueous Phase vs. Reaction Time for SRL A Glass and ATM-8 Glass in EJ-13 Solution. (Filled circle, 2×10^5 R/h; filled triangle, 1×10^3 R/h; and open square, 0 R/h.)

One of the principal goals of the task was to develop an isotope dilution technique for measuring the reaction rate of the spent fuel UO_2 matrix in oxidizing aqueous solutions. Gaining experience and familiarity with the equipment and analytical procedures to be used in the SFL work was another important goal.

The use of a powdered UO_2 mixture in the experiment had a dual purpose: (1) to accelerate the uranium release rates and (2) to ease the preparation of a UO_2 specimen having an appropriate enrichment for the experiment (15 wt % ^{235}U). The specimen was prepared by blending 5.5 parts of depleted UO_2 powder (0.187 wt % ^{235}U) with 1 part of enriched powder (93.20 wt % ^{235}U). Both powder fractions had the same oxygen/uranium ratio (2.15/0.01), and SEM microphotographs taken of the mixed powder revealed no evidence of inhomogeneities, although this could not be fully confirmed because of the extremely small particle size ($<<0.1 \mu\text{m}$) and extensive cluster formation.

The experiment was conducted in two cycles. The first cycle was intended to stabilize the uranium release rates in pure J-13 water. For the second cycle, the leachate was replaced with J-13 water that had been spiked with a natural uranium salt at the steady-state concentration established during the first cycle. The isotopic imbalance between the solute and solid specimen created by the spike has caused brisk isotope exchange reactions that were monitored by measuring the isotopic makeup of the leachate samples with a mass spectrometric isotope dilution (MSID) technique. Exchange rate data are needed for a kinetic model used in estimating the UO_2 matrix dissolution rate. An expected trend was discovered in the MSID data. During the 93-day span of cycle 2, the ratio of the principal uranium isotopes ($^{238}\text{U}/^{235}\text{U}$) decreased from 25 to 2.3, the latter value being well below the ratio of the original powder itself (5.97).

This trend was verified by making MSID measurements on archived samples from the 161-day span of cycle 1. Here again, the $^{238}\text{U}/^{235}\text{U}$ ratio decreased from 5.97 to 2.2.

It is clear from these findings that the enriched powder had a significantly higher dissolution rate in J-13 water than the depleted powder, owing to some unknown morphological difference between the powders. For cycle 1, the dissolved uranium in the leachate solution can be thought of as being composed of two portions: one originating from the depleted powder, the other from enriched powder. The MSID data for this cycle were used to calculate the depleted/enriched weight ratio (X_d/X_e) in the solute of each leachate sample by using the following equation:

$$\frac{X_d}{X_e} = \frac{1}{100} \sum_{i=1}^4 C_m^i \cdot \frac{C_e^i - C_m^i}{C_m^i - C_d^i} \quad (\text{III-1})$$

where X_d and X_e are the weight fractions of the solute representing the depleted and enriched powder, respectively; i values of 1, 2, 3, and 4 correspond to ^{234}U , ^{235}U , ^{236}U , and ^{238}U isotopes, respectively; and C_d^i , C_e^i , and C_m^i are the concentrations (in g/100 g U) of the specified isotope in the depleted powder, the enriched powder, and the solution, respectively. Equation III-1 represents X_d/X_e values for a weighted average of all four isotopes. The knowledge of X_d and X_e allows an apportionment of each uranium isotope between its depleted and enriched portions for each sample by the equations:

$$C_d^i = X_d C_m^i \quad \text{and} \quad C_e^i = X_e C_m^i \quad (\text{III-2})$$

Results of such calculations are given in Fig. III-15 for ^{235}U and ^{238}U . For cycle 2, the uranium introduced with the spike has no relationship to the individual powders in the specimen, and the solution cannot be resolved into its depleted and enriched portions. Therefore, the isotopic distribution was calculated on the basis of X_d/X_e values that were extrapolated from the data of cycle 1. Because of the large mass of the solid specimen, the isotopic balance in the perturbed solution is eventually reestablished through isotopic exchanges, and the distribution becomes identical with that of cycle 1.

2. Leaching Action of EJ-13 Water on UO_2 Surfaces under Unsaturated Conditions at 90°C

Parametric experiments designed to investigate the leaching action of slowly dripping EJ-13 water on unirradiated UO_2 surfaces at 90°C have been in progress for 3.5 years. The experiments are being performed by the Unsaturated Test method, which has been extensively applied to the glass waste form.⁷ The purpose of these experiments is to simulate conditions in which a UO_2 -based waste form (e.g., light water reactor spent fuel) is contacted intermittently by groundwater under oxidizing conditions at a temperature anticipated in a high-level waste repository. The information expected from the results falls into two categories: (1) the changes in the concentration of dissolved species in fluids that contact UO_2 and collect in the bottom of the reaction vessel, and (2) the identification of secondary phases that form on the reacted UO_2 surfaces. The present report deals with results of the first category; those of the second category will be reported later.

The experimental apparatus, shown in Fig. III-16, consists mainly of a stainless steel vessel to contain the Zircaloy-clad UO_2 specimen and its Teflon stand. The vessel is sealed with a matching cap that has a built-in feedthrough connected to a water injection system. The EJ-13 water used in the experiments is groundwater from well J-13 (located near Yucca Mountain, NV) that has been equilibrated with the site-specific rock (Topopah Spring tuff) at 90°C. Water injection rates and other experimental

parameters are given in Table III-4. Of the original eight experiments, four are still in progress, while the other four have been terminated to assess the extent of surface reactions. The experiments are carried out in duplicate runs for three specimen configurations: (1) a stack of eleven UO_2 discs, (2) crushed UO_2 pellets (-60 +80 mesh) vertically sandwiched between two UO_2 discs, and (3) a stack of three UO_2 pellets. For configuration 3, which is represented in Fig. III-16, an additional pair of experiments is conducted at a lower water injection rate.

Fig. III-15. Distribution of ^{235}U and ^{238}U in the Depleted, Enriched, and Mixed (Total) Portions of Dissolved Uranium for Cycles 1 and 2

A semicontinuous leaching mode was adopted for the experiments, i.e., at predetermined intervals (approximately every 6.5, 13, or 26 weeks), an experiment was interrupted to collect the fluid accumulated in the vessel bottom. The vessel and the Teflon stand were then rinsed with acidified DIW to dissolve any plated-out uranium. For all samplings, the acid rinse was combined with the accumulated fluid and analyzed for the total released uranium and other cations. For some of the larger samples, however, there was enough fluid for direct samplings to determine the pH, carbon, and anions, as well as the portion of dissolved uranium that was not plated out on the vessel walls.

Fig. III-16. Schematic of Vessel Used for Unsaturated UO_2 Leaching Experiments

The combined mass of uranium released for each experiment after 180 weeks has provided some insight into the leaching process. For example, the differences in the release values observed between duplicate tests can be interpreted to mean that the degree of leaching is influenced by the variety of paths that water can take on its downward flow. Further observations can be made by considering the uranium release data, which were averaged for each duplicate pair: (1) there was no significant difference between the three- and eleven-pellet stacks, (2) changes in the water injection rate had no measurable effect, and (3) the crushed UO_2 granules released only about one-half of the uranium when compared to that determined for other configurations.

Other noteworthy observations made from the leachate data analyses are as follows: (1) only ~9% of the released uranium is actually associated with the leachate solution, the remainder is plated out on the vessel walls and is detected in the acid wash fraction, (2) the neutral pH values of EJ-13 water are retained in the leachate samples, (3) dissolved carbon is associated mainly with organic species (e.g., a typical sample contains ~20 ppm C, with 17 ppm organic and 3 ppm inorganic), and (4) the concentrations of Ca, Mg, and Si are significantly reduced during the leaching, probably because of their participation in the secondary phase formation.

Table III-4. Experimental Parameter Matrix for Leaching Studies of Unirradiated UO₂

Test Number	Specimen Configuration ^a	Weight of UO ₂ , g	Surface of UO ₂ , cm ²	Volume of UO ₂ , cm ³	Weight of Zircaloy, g	EJ-13 Water Injection Rate	
						Volume, mL	Interval, days
PMP8U-1	1	29.522	40.7	2.83	2.365	0.075	3.5
PMP8U-2	1	29.166	40.6	2.80	2.401	0.075	3.5
PMP8U-3	2	19.856	486	2.21	2.368	0.075	3.5
PMP8U-4	2	18.258	467	2.14	2.376	0.075	3.5
PMP8U-5	3	47.955	22.1	4.54	3.839	0.075	3.5
PMP8U-6	3	48.360	22.2	4.58	3.854	0.075	3.5
PMP8U-7	3	47.596	21.9	4.48	3.840	0.0375	7
PMP8U-8	3	47.773	22.1	4.54	3.850	0.0375	7

^aConfigurations defined in text.

C. Yucca Mountain Project Radiation Studies (D. T. Reed)

The YMP Organization 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 Mrad/h. The extent of radiolytic alteration of the gas phase present and the nature of the radiolytic products generated are an important consideration in evaluating waste package material performance during the early stages of repository history.

The radiation effects studies being conducted at Argonne National Laboratory consist of (1) establishing the extent and nature of radiolytic products generated under repository-relevant conditions; (2) experimentally addressing questionable or unusual results, relevant to this effort, that are reported in the literature; and (3) performing atmospheric corrosion studies of candidate container materials in an irradiated environment.

Work performed during the reporting period included (1) NO_x yield studies at 30-200°C; (2) a series of atmospheric corrosion experiments in an irradiated environment at 120°C; and (3) a study of nitrate formation due to the oxidation of dissolved nitrogen in aqueous media.

1. NO_x Yield Studies

The NO_x yield studies were performed in 150 mL stainless steel (304L) vessels with a ⁶⁰Co source at 30-200°C. Gamma dose rates were in the range of 0.1 to 0.4 Mrad/h and were measured with nitrous oxide gas as a dosimeter. Yields were measured at absorbed doses from 5 to 320 Mrad obtained by exposure from one day to three months. Experiments were performed in an oven in which temperature was controlled to ±3°C and monitored on a data logger.

Two types of samples were irradiated: a dry air sample (water vapor less than 10 ppm) and a moist air sample (water vapor saturated at room temperature). The purpose of the moist air sample was

to qualitatively establish the effect of water vapor on the radiation chemistry. A more systematic study of the effect of water vapor on the NO_x yield is in progress.

Radiolytically, these experiments represent a measurement of initial NO_x yields, although the results were obtained over relatively long times compared to typical initial yield studies (which are usually on the order of an hour or less in duration). Pulsed techniques are usually on the order of seconds or less. The current data, therefore, included an unavoidable contribution from the vessel wall via (1) catalysis of intermediate reactions on the vessel surface and (2) the removal of products from the gas phase due to a sorption reaction. The wall effect is important to YMP studies because NO_x formation under repository-relevant conditions will occur over long times and in the proximity of solid surfaces.

The yield of nitrous oxide at temperatures between 28 and 200°C is given in Table III-5. The yield of nitrous oxide as a function of absorbed dose was linear in the dry air experiments. Yields observed were greater than published homogeneous gas phase yields, reflecting contributions from the vessel wall.²¹ In the moist air experiments, nitrous oxide yields were not linear with absorbed dose. At low temperatures, initial yields were significantly lower than those in the dry air experiments and increased with absorbed dose. This difference became less apparent at the higher temperatures, and dry and moist air yields were essentially the same at 120°C.

Table III-5. Yield of Nitrous Oxide as a Function of Temperature

Temperature, °C	Nitrous Oxide Yield, molecules/100 eV	
	Dry Air	Moist Air ^a
28	0.83 ± 0.08	0.06 ± 0.02 ^b
90	0.81 ± 0.08	0.87 ± 0.05 ^b
120	0.57 ± 0.05	0.62 ± 0.06
150	0.69 ± 0.07	0.54 ± 0.05
200	0.74 ± 0.07	0.50 ± 0.05

^aAir saturated with water vapor at room temperature.

^bThese plots were nonlinear. The 28°C yield value was the initial yield (low dose); the yield at 90°C corresponded to the linear formation of nitrous oxide observed after a 50 Mrad "induction" period.

The nitrogen dioxide yield was, as expected, highly dependent on the moisture content of the initial air. In dry air systems, the nitrogen dioxide yield was linear with absorbed dose and comparable to the nitrous oxide yield observed. The addition of moisture converted the nitrogen dioxide generated to nitric acid, with most of the NO_x generated appearing in the vessel wall rinse. Nitric oxide was only present in trace amounts and did not show any increase with absorbed dose. This was also consistent with published literature results.²²

In all experiments, there was carbon dioxide buildup, which was somewhat correlated with absorbed dose and increased temperature. This was due to a combination of carbon dioxide desorption and reaction of oxygen with the vessel wall. Carbon monoxide was present along with carbon dioxide but in much lesser amounts. The buildup of both carbon dioxide and carbon monoxide had a minimal effect on the NO_x yields observed.

2. Corrosion Product Identification

Experiments were initiated to determine the nature and extent of corrosion product formation on candidate container materials in irradiated dry air and air-steam environments. Materials tested were 70/30 copper-nickel, oxygen-free copper, aluminum bronze, and Incoloy 825. Experiments were performed at 120°C as a function of moisture content.

Coupons of each material, polished to 600 grit, were placed in a 275 mL stainless steel vessel, filled with a water/gas mixture of appropriate composition, and irradiated in the ⁶⁰Co facility. Initial and post-irradiated gas phase composition was determined with gas chromatography. Following the experiment, the products formed were determined by XRD analysis, and both weight loss and weight gain measurements were made.

All copper-based materials showed measurable corrosion, the extent of which increased as the humidity of the experiment was increased. In the dry air experiment, a dulling of the material was noted with little uniform corrosion. Progressively greater corrosion was observed in the higher humidity experiments (100% RH at 23 °C and 15% RH at the test temperature). Copper nitrate phases were identified on all three materials. The Incoloy 825, in contrast, did not exhibit any discoloration or measurable corrosion in any of the environments tested.

3. Oxidation of Dissolved Nitrogen in Curium Sulfate Solutions

Work was completed to determine the formation of nitrate via oxidation of dissolved nitrogen in curium sulfate solution by alpha radiation. Nitrate yields were much lower than those published elsewhere²³ and were comparable to predictions based on gamma and beta (low linear energy transfer) interactions. Measurable contributions from the surface irradiation of liquid samples with high gas/liquid contact areas were observed. Improper accounting for this contribution was proposed as an explanation of the higher yields obtained elsewhere.

D. Product Consistency Test

(J. K. Bates, T. J. Gerding, and J. C. Hoh)

The Product Consistency Test (PCT) was developed by Savannah River Laboratory (SRL) to verify the consistency of radioactive glass produced by the Defense Waste Processing Facility (DWPF) glass melter. The test is performed by contacting glass with deionized water at 90°C for seven days and analyzing the leachate for selected elements. Comparison of element concentrations between tests is the basis for determining the product consistency. This short-lived leach test is designed to demonstrate the limited variability of successive batches of glass produced at the DWPF site. The data in the Waste Qualification Report will demonstrate that the baseline glass will meet the release criteria set by the Waste Acceptance Preliminary Specifications.

The SRL demonstrated the suitability of the PCT by conducting an internal laboratory testing program.²⁴ They were able to show that the PCT was sensitive to glass composition and homogeneity, and that a seven-day test was sufficient to produce precisions of 2-3% by an investigator and 5-8% between investigators. Test procedures were developed that could be adapted to remote operating conditions, and the testing of a radioactive glass was part of this initial demonstration.

To evaluate the leach test methodology, including the uncertainty associated with analytical methods, SRL sponsored a full-scale round robin conducted by the Materials Characterization Center (MCC) with nonradioactive glass. Argonne and six other laboratories, experienced in glass leach testing,

were selected to participate in the round robin. Each participant was provided equipment and materials to perform the test following the SRL-PCT Test Protocol.²⁴ After completion of the test, the test data from 32 samples and an inductivity coupled plasma spectroscopy (ICP) solution standard were submitted by each laboratory to the MCC for evaluation.

Examination of the results by the MCC indicated that sufficient disparity existed in the data to suggest separating the laboratories into two groups, Level A and Level B labs. The separation was based on within-lab standard deviations; the Level A labs had lower within-lab standard deviations than did the Level B labs. The Level A lab results were nearly identical to the precisions reported by SRL in their internal round robin.²⁴ Argonne was one of the three Level A labs. The detailed results of the round robin have been prepared by the MCC.²⁵

The ANL High-Level Waste/Repository Interactions Group consulted with SRL concerning the methodology of the SRL-PCT as it relates to radioactive glasses²⁶ and then produced a refined version of the SRL Test Protocol. Using the refined version of the PCT, ANL tested two highly radioactive glasses and one nonradioactive standard glass supplied by SRL. The radiation levels associated with the radioactive glasses required that many of the test-related operations be conducted in a shielded facility equipped with remote handling capabilities. The experience gained from conducting these tests in a fully remote configuration suggests that the refined version of the PCT will indeed improve the overall operational aspects of the test plan. A report was sent to SRL giving details of all changes made to the SRL procedure and a statistical analysis of the data, plus all the data obtained from these tests. The successful completion of these tests helps to establish the adaptability of the PCT to the fully remote-handling procedures needed to accommodate the highly radioactive glass from the DWPF melter.

E. Detection and Speciation of Transuranic Elements via Pulsed-Laser Excitation (D. T. Reed)

Laser photoacoustic spectroscopy (LPAS) and laser-induced fluorescence (LIF) are being used to spectroscopically detect and determine the speciation of actinides in condensed phase media. These techniques are complementary in that species with either a high fluorescent quantum efficiency or a high tendency toward radiationless de-excitation can be detected. The high sensitivity of these techniques permits the spectroscopic detection (oxidation-state specific) of actinide species to concentrations that are frequently of interest to nuclear waste management and related environmental concerns.

Past emphasis of the work at ANL was on the characterization of actinide species in the pH range of 6-12 for simplified groundwater-like systems. High sensitivities were achieved with the LPAS system (3×10^{-7} a.u./cm), corresponding to the detection of actinide concentrations in the low- to mid-nanomolar range. With the LIF system, concentrations two to three orders of magnitude lower were detected for those actinides, such as trivalent americium and curium, that had a high fluorescence efficiency. Both our LPAS and LIF systems were modified to work at temperatures up to 90°C. The LPAS sensitivity always increased as the temperature was increased, whereas the effect of temperature on LIF sensitivity was system dependent.

Current emphasis of the program is on the application of the LPAS system to a wider variety of condensed phase systems. Radionuclide speciation work in groundwater-relevant systems remains as the most important aspect of the work. Two other applications being investigated, however, are (1) LPAS spectroscopy of actinides in concentrated nitric acid systems, and (2) LPAS spectra of lanthanides and actinides in molten lithium chloride salts at elevated temperatures (350-500°C). In addition to these areas, continued improvement of LPAS signal reproducibility and sensitivity is being emphasized.

The application of LPAS/LIF to radionuclide speciation in groundwater-like systems has been already demonstrated at ANL²⁷ and elsewhere.^{28,29} Speciation of radionuclides and the factors that influence their migration in natural systems continue to be important information needed in DOE site-related waste management problems. The LPAS sensitivities were determined for Am(III), Pu(IV), U(VI), and Np(V) in high pH systems at up to a temperature of 90°C. The LIF studies emphasized Cm(III) and Am(III) systems, with a lesser emphasis on uranyl systems. A summary of "best case" detection limits at $21 \pm 2^\circ\text{C}$ is given in Table III-6. The current emphasis is a more detailed study of Pu and Np in groundwater-relevant systems.

Obtaining LPAS spectra of actinides in concentrated nitric acid systems is of importance to monitoring actinide concentrations in nuclear reprocessing streams. The influence of nitric acid concentration on the photoacoustic signal generated, the point at which signal saturation occurs, and an estimate of the sensitivity of the system to the concentration of the uranyl will be determined. From the results of this work, a preliminary evaluation of LPAS as an on-line monitor will be made.

The high-temperature (350-500°C) molten salt studies may be relevant to waste management problems associated with the Integral Fast Reactor being developed at Argonne. The objective of obtaining LPAS spectra in molten salts is to (1) demonstrate LPAS applicability to molten salt systems, (2) assess LPAS sensitivity relative to aqueous systems, (3) obtain molten salt spectra in the blue-green region of the spectrum, and (4) determine LPAS sensitivity to lanthanides and possibly actinides. Of interest is the potential for observing unusual oxidation states in the strongly reducing molten salt environment. Since the temperatures of interest in this system are considerably higher than those in past work that was performed at ANL, considerable effort is planned to modify the LPAS technique to work reliably at the elevated temperatures. Temperature stability is expected to be an important factor in long-term drift and noise problems associated with obtaining the spectra.

Table III-6. System-Specific Sensitivity of LPAS and LIF at $21 \pm 2^\circ\text{C}$

	Actinide Solution	Sensitivity	
		Demonstrated	Projected ^a
<u>LPAS</u>	UO ₂ ²⁺ in synthetic basaltic groundwater	$5 \times 10^{-8}\text{M}$	
	Am ³⁺ in carbonate	$3 \times 10^{-9}\text{M}$	
	Pu ⁴⁺ in carbonate	$3 \times 10^{-9}\text{M}$	
	NpO ₂ ⁺ in perchlorate	$1 \times 10^{-9}\text{M}$	
<u>LIF</u>	UO ₂ ²⁺ in synthetic basaltic groundwater	10^{-8}M	10^{-10}M
	Am ³⁺ in perchlorate	10^{-8}M	10^{-10}M
	Cm ³⁺ in dilute NaCl	10^{-11}M	10^{-13}M

^aSensitivity expected following modification of LIF system to use picosecond excitation pulse.

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IV. PLUTONIUM RECOVERY FROM RESIDUES

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The objective of this effort is to develop an effective pyrochemical process for the recovery of plutonium from intractable residues (PuRR). Lawrence Livermore National Laboratory (LLNL) is working jointly with ANL to (1) devise a single economical pyrochemical process capable of recovering plutonium from the various types of scrap and residue now being generated or stored from previous DOE weapons production operations, (2) remove and concentrate other transuranium materials from the wastes so that the bulk of the pyrochemical process effluents can be classified as nontransuranic (nonTRU) wastes, (3) recycle virtually all pyrochemical reagents to minimize the volume of material to be discarded, and (4) provide a basis for the upgrading of recycled weapons materials.

Savannah River Laboratory (SRL) is working with ANL in an adjunct effort to use a pyrochemical head-end step to convert intractable residues to a form that can be introduced into existing aqueous processes. The progress in both efforts is summarized here.

A. Reduction and Salt Extraction Experiments

The anticipated processes use liquid metals and molten salts at elevated temperature to effect the necessary separation and chemical conversion. Separations are possible because of the differing stabilities of compounds in the molten salt phase relative to those in the liquid metal phase. Several flowsheets are under consideration, but common to all is the reduction of PuO_2 from an oxide residue as an initial step. The current effort has concentrated on this reduction step because it is common to all the flowsheets and because the other steps of the processes have been or are part of existing production methods (e.g., electrorefining), have been demonstrated during process development work on other processes (e.g., salt and metal extractions), or have sufficiently sound theoretical bases to give confidence that they can be blended into successful production processes.

The reduction step requires a feed material, solvent/reductant, and a salt fluxing agent and produces salt and metal effluent streams. Feed material for the developed process can be any of 22 categories of weapons production residues; therefore, feed material for the current process development effort was selected to be representative of the most difficult to process residues. Acid-leached LECO analytical crucibles (ground) from SRL and incinerator ash heels from Rocky Flats (calcined and ground) are considered the most intractable of feed materials. These materials contain a wide spectrum of metals and have plutonium contents ranging from <1% to ~20% by weight.

In this report period, we performed scoping experiments with Cu-Mg-Ca, Zn-Mg, and Zn-Ca solvent/reductants, ZnCl_2 and CdCl_2 salt extraction experiments, and process design and developmental electrochemical activities for LLNL. In addition, we performed scoping experiments with Al-Mg and Al solvent/reductant for SRL.

The reduction and extraction were performed at 800°C in a furnace well of a high-purity argon-atmosphere glove box. The crucibles used were made of high-purity magnesia stabilized with yttria and were 62-mm OD and 140-mm high. The melts were stirred at ~900 rpm with 32-mm dia agitators made from tantalum or Mo-30 wt% W.

The cover salt combination used during the reduction experiments involving the Cu-Mg-Ca and Zn-Ca systems is 85 wt% CaCl_2 -15 wt% CaF_2 . This salt was chosen because of its low melting point and its ability to dissolve the CaO formed by the reduction of the metal oxides in the feed material. In

addition, the CaF_2 assists in the separation of the metal and salt after stirring of the metal/salt mixture has been terminated. The salt combination used for the Zn-Mg and Al-Mg systems is 55 wt% MgCl_2 -22 wt% NaCl -19 wt% KCl -4 wt% MgF_2 , which has been used extensively at ANL for reduction with magnesium alloys. These same salts (MgCl_2 , NaCl , KCl) were also used in various combinations as cover salts in the extraction of PuCl_3 from the reduction ingots.

Experimental results, presented in Table IV-1, indicate that good reduction of plutonium from the intractable residues can be expected; however, efforts at chemical extraction of plutonium from the reduction ingots have met with mixed success. The results of the reduction experiments also indicate that multiple countercurrent reductions or use of scrub stages may reduce the plutonium and other transuranic elements to nonTRU waste levels. Although results of the reduction experiments with Zn-10 wt% Ca were encouraging, those with 2 wt% of the metal charge of excess calcium indicated a poorer reduction of plutonium in the ash heel than expected. This reduction was 95.2 wt% in one stage and 98.9 wt% in two stages. For Zn-10 excess wt% Ca, the one-stage reduction was 99.4%.

The effort at chemical extraction of plutonium from the reduction ingots (using ZnCl_2 or CdCl_2) indicated that better than 94% recovery of plutonium in the extraction salt was achievable from the Zn-10 wt% Mg and some (Cu-40 wt% Mg) + Ca ingots. However, there were problems with extraction and material balance in the Zn-Ca and some Cu-Mg-Ca runs; extractions into the salt phase as low as 56% of the plutonium were obtained. The poor material balance and extraction of plutonium in the Zn-Ca and some Cu-Mg-Ca experiments may be the result of a greater interaction of the plutonium metal in the ingot and the tantalum components (stirrer and baffles); there appeared to be significantly more corrosion of the tantalum in the Zn-Ca and some Cu-Mg-Ca experiments.

Table IV-1. Plutonium Reduction and Recovery from Nuclear Waste
by Pyrochemical Process at 800°C

Reductant	Pu Reduction, %				Pu Extraction, ^a %
	Pure PuO_2	LECO Crucible	Raw Ash	Ash ^a Heel	
Zn-10 wt% ^b Mg	-	95	97.4	97.0 99.9 ^c	94
(Cu-40 wt% ^b Mg) + 5 wt% Ca	-	-	99.8	98.2	70-95
Al-10 wt% ^b Mg	99.5	91 ^d	-	-	
Al	99.2	92	-	-	
Zn-2 wt% ^b Ca				95.2 98.9 ^c	56 76
Zn-10 wt% ^b Ca				99.4	

^aBased on percent of reduced Pu in ingot; using ZnCl_2 or CdCl_2 extraction to PuCl_3

^bPercent of the total metal charge of excess reductant.

^cTwo stages.

^dCoarsely ground.

Other experimental results associated with the reduction systems indicate that the presence of a high concentration of silica in some of the feed materials will not be a problem in the Al-Mg system because silicon has a high solubility in aluminum and the low activity of plutonium in aluminum prevents formation of an insoluble plutonium-silicon intermetallic compound. The results also indicate that in the Zn-Mg system the silicon formed in the reduction step decreases the plutonium concentration in the solvent by a partial precipitation. This lowered plutonium concentration in the solvent is not expected to decrease its availability to subsequent extraction by electrolytic or chemical means. Also, for the Zn-Mg system, the presence of aluminum appreciably increases the plutonium concentration in the presence of silicon by reducing the activity coefficient for plutonium in the solvent. The experimental results obtained with the Cu-Mg-Ca system, however, indicated that the presence of ~2 wt% silicon in the solvent produces high melting solids ($>750^{\circ}\text{C}$) such that the reduction may have to be performed at temperatures greater than 800°C .

Our future research will concentrate on the zinc-based system, with special emphasis on the selective extraction of plutonium from the reduction alloy.

Problems were encountered in the Zn-Ca experiments. Initial attempts to use tantalum stirrers and flow baffles, proven to be useful in the Zn-Mg and Cu-Mg-Ca systems, resulted in rivet failures and collapse of these components. New flow baffles and stirrers of Mo-30 wt% W were built and tested to correct the problem. Analysis of the metal ingots indicated that molybdenum is below detectable limits (0.01 wt%) in the Zn-Ca melt. Analysis of the metal ingot has also indicated that a small amount (<0.1 wt%) of the MgO of the crucibles is being reduced to Mg in the experiments. As in the previous Zn-Mg and Cu-Mg-Ca systems, silicon, which reduces more slowly than plutonium, is also believed to be responsible for the removal of plutonium from the Zn-Ca melt because the plutonium concentration decreases with time.

B. Electrorefining Tests

Electrorefining is being considered for two applications in the PuRR process: (1) recovery of plutonium from the reduction ingots and (2) recycle of calcium from the reduction salt. A major reason for both applications is the minimization of wastes. The plutonium recovery is a solvent electrorefining step similar to that used in the current process under development at Argonne for the Integral Fast Reactor. The calcium recycle step was proposed and initial investigations made several years ago at ANL under the process development program for fast reactor fuels.

Two areas associated with electrorefining are being investigated to supply information needed for PuRR process application. The first area is the development of a reference electrode that can be used as a useful tool to accurately measure and control variables during electrorefining and chemical extraction. The second area is verification and measurement of performance parameters in electrowinning calcium from CaO into a zinc alloy.

Two types of reference electrodes were experimentally investigated: the $\text{Ag}:\text{Ag}^+$ electrode and an electrode with a more corrosion-resistant simple metal, zinc. Both electrodes were contained in 6.6-mm-dia porous MgO tubes. The porosity of these tubes was selected to contain the metal but allow the pores to fill with molten salt. A silver wire, inserted into the electrode tube, was discharged to create the silver ions in the $\text{CaCl}_2\text{-CaF}_2$ cover salt within the electrode. A tungsten lead wire was used in the simple zinc metal electrode.

With both reference electrode types, the potential differences were measured at different temperatures between the reference electrodes and a Zn-Ca melt alloy whose composition was varied by the addition of either pure zinc or zinc with a high concentration of calcium. The potential change with

calcium concentration was strong (>50 mV per 1% Ca concentration in the range of 3 to 7%Ca) with both electrode types and long-term drifting was a problem on both. Because of the simplicity of the use of a zinc reference electrode and the reductions in drifting that are expected with an improved reference electrode design, the development of the simple zinc-metal electrode will be continued.

Preparations were made for the verification and measurement of performance parameters in electrowinning calcium from CaO into a zinc alloy by fitting a furnace well in a helium glove box with a new liner and appropriate heat shields. Specialized crucibles, graphite secondary, etc., for the experiments have been ordered.

The activity coefficient of plutonium in liquid Zn-Ca solutions is an important parameter for the PuRR process. This activity coefficient was computed from data for the activity coefficient of plutonium in liquid zinc, extrapolated data on the activity coefficient of plutonium in liquid calcium, and the thermodynamic properties of liquid Zn-Ca alloys. Experiments were also initiated to determine the reduced-calcium equilibrium concentration in CaCl_2 - CaF_2 in contact with Zn-Ca solution. The results indicated a much higher reduced-calcium content in the salt than predicted for equilibrium with CaCl_2 alone. Since there was excessive CaO present in these experiments and since its effects on the experiment and analysis are unknown, additional experiments are planned.

APPENDIX.

EXPERIMENTAL RESULTS ON EFFECTS OF COMPLEXANTS
ON NOBLE METAL EXTRACTION

Given below are results from six series (Nos. 1-4, 8 and 9) of experiments to determine the effect of complexants on noble metal extraction (Sec. II.G.3).

Series One Experiments

Table A-1. Initial Solution Composition, Molar

Solution Designation	Oxalate	Al ³⁺	Fe ³⁺	HNO ₃	HF	NaNO ₃
1A	0	0	0	0.5	0	2.7
1B	0.1	0	0	0.5	0	2.7
1C	0.2	0	0	0.5	0	2.7
1D	0.3	0	0	0.5	0	2.7

Table A-2. Analytical Results of Sample 1A

Metal Ion	Typical ^a Feed, μg/mL	Aqueous, μg/mL	Organic, μg/mL	D	% Material Balance
Al	--	--	--	--	--
Mo	131.3	8.85	90.8	10.2	76
Mn	207.9	214	18.1	0.085	112
Ni	387.5	410	23.4	0.057	112
Nd	335.0	<5	300	>60	<87
Zr	238.8	39.4	189	4.79	96
Ru	163.8	55.0	28.2	0.51	51
Pd	43.88	15.5	10.6	0.69	60
Rh	43.38	42.8	3.0	0.07	106

^aSince the analyses of the starting feed solutions were so similar, this "Typical Feed" value is obtained by averaging all the analytical results.

Table A-3. Analytical Results of Sample 1B

Metal Ion	Typical Feed, μg/mL	Aqueous, μg/mL	Organic, μg/mL	D	% Material Balance
Al	--	--	--	--	--
Mo	131.3	118	6.50	0.055	95
Mn	207.9	192	12.0	0.063	98
Ni	387.5	362	14.4	0.040	97
Nd	335.0	<5	145	>29	45
Zr	238.8	239	8.75	0.037	104
Ru	163.8	149	6.88	0.046	95
Pd	43.88	35.1	<1.25	<0.04	83
Rh	43.38	40.4	1.38	0.034	95

Table A-4. Analytical Results of Sample 1C

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	--	--	--	--	--
Mo	131.3	121	6.63	0.055	97
Mn	207.9	173	14.4	0.083	90
Ni	387.5	111	56.5	0.51	43
Nd	335.0	30.1	111	3.65	42
Zr	238.8	241	9.25	0.038	105
Ru	161.3	153	6.63	0.043	99
Pd	43.88	31.8	<1.25	<0.04	<75
Rh	43.38	37.0	2.13	0.058	90

Table A-5. Analytical Results of Sample 1D

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	--	--	--	--	--
Mo	131.3	121	2.38	0.020	94
Mn	207.9	152	9.00	0.059	77
Ni	387.5	25.0	39.0	1.6	17 ^a
Nd	335.0	20.4	52.9	2.6	22
Zr		242	1.75	0.0072	102
Ru	163.8	156	1.88	0.012	96
Pd	43.88	31.6	<1.25	<0.04	<73
Rh	43.38	35.1	<1.25	<0.04	<84

^aAnalysis of starting stock solution contained one fourth typical amount.

Series Two Experiments

Table A-6. Initial Solution Composition, Molar

Solution Designation	Oxalate	Al ³⁺	Fe ³⁺	HNO ₃	HF	NaNO ₃
2A	0	0	0	0.5	0	2.3
2B	0.1	0	0	0.5	0	2.3
2C	0.2	0	0	0.5	0	2.3
2D	0.3	0	0	0.5	0	2.3

Table A-7. Analytical Results of Sample 2A

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	2813	2720	16.9	0.0062	97
Mo	131.3	6.15	90.4	14.7	74
Mn	207.9	202	6.9	0.034	100
Ni	387.5	385	3.6	0.0094	100
Nd	335.0	<5	240	>50	73
Zr	238.8	18.3	198	10.8	90
Ru	163.8	39.0	27.2	0.70	40
Pd	43.88	14.8	12.6	0.85	62
Rh	43.38	40.3	<0.1	<0.0025	93

Table A-8. Analytical Results of Sample 2B

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	2813	2640	1.5	0.0006	94
Mo	131.3	119	5.25	0.044	95
Mn	207.9	198	5.13	0.026	98
Ni	387.5	371	0.63	0.0017	96
Nd	335.0	<5	225	>45	<69
Zr	238.8	246	1.0	0.004	103
Ru	163.8	155	1.50	0.0097	96
Pd	43.88	32.7	<1.25	<0.04	75
Rh	43.38	40.9	<1.25	<0.03	<97

Table A-9. Analytical Results of Sample 2C

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	2813	2610	107	4.1×10^{-2}	97
Mo	131.3	120	9.13	$>7.6 \times 10^{-2}$	99
Mn	207.9	195	13.75	7.1×10^{-2}	100
Ni	387.5	372	17.0	4.6×10^{-2}	98
Nd	335.0	<5	143.8	>28.8	<43
Zr	238.8	243	11.25	4.6×10^{-2}	106
Ru	163.8	156	7.63	4.9×10^{-2}	100
Pd	43.88	34.9	<1.25	$<3.6 \times 10^{-2}$	<82
Rh	43.38	42.1	1.50	3.6×10^{-2}	100

Table A-10. Analytical Results of Sample 2D

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	2813	2790	21.25	0.0076	100
Mo	131.3	124	3.75	0.030	97
Mn	207.9	198	6.38	0.032	98
Ni	387.5	376	3.25	0.0086	98
Nd	335.0	30.9	178.75	5.8	63
Zr	238.8	247	3.75	0.015	105
Ru	163.8	160	1.86	0.012	99
Pd	43.88	34.8	<1.25	<0.04	<84
Rh	43.38	41.3	<1.25	<0.03	<98

Series Three Experiments

Table A-11. Initial Solution Composition, Molar

Solution Designation	Oxalate	Al^{3+}	Fe^{3+}	HNO_3	HF	NaNO_3
3A	0	0.3	0	0.5	0	1.7
3B	0.1	0.3	0	0.5	0	1.7
3C	0.2	0.3	0	0.5	0	1.7
3D	0.3	0.3	0	0.5	0	1.7

Table A-12. Analytical Results of Sample 3A

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	8250	8000	181	0.023	99
Mo	131.3	5.65	85.62	15.1	70
Mn	207.9	201	10.88	0.054	102
Ni	387.5	385	10.00	0.026	102
Nd	335.0	<5	245	>49	<73
Zr	238.8	8.45	205	24.3	89
Ru	163.8	35.6	24	0.67	37
Pd	43.88	13.5	19.8	1.47	76
Rh	43.38	39.5	1.5	0.038	94

Table A-13. Analytical Results of Sample 3B

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	8250	8000	444	0.056	102
Mo	131.3	111	20.7	0.19	100
Mn	207.9	202	17.6	0.087	106
Ni	387.5	385	12.5	0.037	103
Nd	335.0	<5	178.8	>35.8	<58
Zr	238.8	249	17.0	0.068	111
Ru	163.8	157	10.9	0.069	102
Pd	43.88	28.7	7.8	0.27	83
Rh	43.38	41.0	2.3	0.056	100

Table A-14. Analytical Results of Sample 3C

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	8250	7680	76.75	0.010	94
Mo	131.3	116	8.5	0.073	95
Mn	207.9	196	7.5	0.038	98
Ni	387.5	374	4.25	0.011	100
Nd	335.0	5.1	225	44	69
Zr	238.8	245	3.25	0.013	104
Ru	163.8	154	2.88	0.019	71
Pd	43.88	32.0	3.38	0.11	81
Rh	43.38	41.8	<1.25	<0.03	<99

Table II-A-15. Analytical Results of Sample 3D

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/L}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	8250	7790	53.5	0.0069	95
Mo	131.3	119	5.25	0.044	95
Mn	207.9	198	6.50	0.033	98
Ni	387.5	381	3.00	0.008	99
Nd	335.0	(5.5)	167.5	30	52
Zr	238.8	249	2.00	0.008	105
Ru	163.8	158	1.88	0.012	98
Pd	43.88	34.4	<1.25	<0.04	<81
Rh	43.38	41.6	<1.25	<0.03	<99

Table A-16. Initial Solution Composition, Molar

Solution Designation	Oxalate	Al ³⁺	Fe ³⁺	HNO ₃	HF	NaNO ₃
4A	0	0.7	0	0.5	0	0.5
4B	0.1	0.7	0	0.5	0	0.5
4C	0.2	0.7	0	0.5	0	0.5
4D	0.3	0.7	0	0.5	0	0.5

Table A-17. Analytical Results of Sample 4A

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	19375	19,600	205	0.010	102
Mo	131.3	4.7	81.6	17.4	66
Mn	207.9	203	11.75	0.058	103
Ni	387.5	396	5.23	0.013	103
Nd	335.0	<5	211.3	>42.3	64
Zr	238.8	1.2	215	179.2	90
Ru	163.8	41.2	32.1	0.78	45
Pd	43.88	14.0	18.6	1.33	74
Rh	43.38	40.3	1.25	0.03	96

Table A-18. Analytical Results of Sample 4B

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	19375	19,800	459	0.023	104
Mo	131.3	86.0	37.6	0.44	95
Mn	207.9	197	12.6	0.064	101
Ni	387.5	380	10.1	0.027	101
Nd	335.0	<5	211.3	>42.3	<65
Zr	238.8	226	24.3	0.11	105
Ru	163.8	151	7.3	0.048	96
Pd	43.88	25.9	6.1	0.24	73
Rh	43.38	41.2	<1.3	<0.03	<98

Table A-19. Analytical Results of Sample 4C

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	19375	19,100	143.8	0.0075	99
Mo	131.3	106	15.75	0.15	92
Mn	207.9	194	8.75	0.045	97
Ni	387.5	375	3.50	0.0093	97
Nd	335.0	8.5	212.5	25	65
Zr	238.8	242	5.38	0.022	103
Ru	163.8	154	3.00	0.019	95
Pd	43.88	30.6	2.38	0.078	75
Rh	43.38	41.4	<1.25	0.03	92

Table A-20. Analytical Results of Sample 4D

Metal Ion	Typical Feed, $\mu\text{g/mL}$	Aqueous, $\mu\text{g/mL}$	Organic, $\mu\text{g/mL}$	D	% Material Balance
Al	19375	19,300	287.5	0.015	101
Mo	131.3	113	10.88	0.096	94
Mn	207.9	197	8.50	0.043	98
Ni	387.5	378	6.38	0.017	99
Nd	335.0	14.1	182.5	12.9	58
Zr	238.8	248	5.00	0.02	105
Ru	163.8	158	3.62	0.023	98
Pd	43.88	33.6	<1.25	<0.04	73
Rh	43.38	41.9	<1.25	<0.03	93

Series Eight Experiments

Table A-21. Initial Solution Composition, Molar

Solution Designation	Oxalate	Al^{3+}	Fe^{3+}	HNO_3	HF^a	NaNO_3
8A	0	0	0	0.5	0.1	2.7
8B	0	0	0	0.5	0.1	2.7
8C	0	0	0	0.5	0.1	2.7

^aThese solutions were handled in plastic containers due to the presence of HF.

Table A-22. Analytical Results of Sample 8A

Metal Ion	Concentration, $\mu\text{g/mL}$			D	% Material Balance
	Typical Feed	Aqueous	Organic ^a		
Al	--	--	--	--	--
Mo	131	31.8	95.9	3.01	97
		26.8	97.2	3.62	95
Mn	206	182	17.7	0.097	97
		185	11.4	0.062	95
Ni	388	342	6.38	0.017	99
		357	8.3	0.023	94
Fe	--	--	--	--	--
Nd	332	3.83	302	78.7	92
		3.83	52.8	13.8	17
Zr	237	131	116	0.89	100
		118	7.3	0.062	53
Ru	161	88.7	24.8	0.28	70
		84.5	24.5	0.29	67
Pd	43.6	17.5	19.5	1.12	84
		17.7	13.9	0.79	72
Rh	42.2	40.3	2.65	0.066	101
		41.2	1.87	0.045	102

^aThe "new" organic metal ion stripping method uses HEDP and is listed as the second experiment in each series.

Table A-23. Analytical Results of Sample 8B

Metal Ion	Concentration, $\mu\text{g/mL}$			D	% Material Balance
	Typical Feed	Aqueous	Organic ^a		
Al	<6.25	2.00	<1.56	<0.78	<5.81
		<1.67	<1.56	<0.93	<9.48
Mo	131	42.2	95.9	2.27	105
		36.8	83	2.25	91
Mn	206	178	12.5	0.07	147
		173	11.3	0.65	89
Ni	388	342	12.0	0.35	91
		330	11.3	0.34	87
Fe	--	--	--	--	--
Nd	332	6.33	256	40.5	79
		3.5	92.3	26.4	28
Zr	237	23.5	203	8.64	95
		118	7.3	0.062	22
Ru	162	84	25	0.30	67
		83.5	21.9	0.26	65
Pd	43.6	18.8	16.9	0.90	81
		19.8	23.3	1.17	98
Rh	42.2	39.5	1.56	0.39	97
		38.8	1.88	0.26	96

^aThe "new" organic metal ion stripping method uses HEDP and is listed as the second experiment in each series.

Table A-24. Analytical Results of Sample 8C

Metal Ion	Concentration, $\mu\text{g/mL}$			D	% Material Balance
	Typical Feed	Aqueous	Organic ^a		
Al	<6.25	<1.67 <1.67	<1.56 <1.56	-- --	<9.48 <9.48
Mo	131	47.8 46.3	66.9 76.7	1.40 1.66	87 93
Mn	206	188 183	10.8 13.3	0.057 0.072	96 95
Ni	388	363 357	10.2 13.8	0.03 0.0385	96 95
Fe	--	-- --	-- --	-- --	-- --
Nd	332	3.67 1.00	93.3 79.5	25.4 79.5	29 17
Zr	237	61 15.8	95.2 32.0	1.56 2.02	65 20
Ru	162	96.7 94.7	22.0 22.3	0.23 0.23	73 72
Pd	43.6	22 20.8	16.7 20.8	0.76 1.00	88 95
Rh	42.2	40.8 40.7	1.56 2.03	0.038 0.05	100 101

^aThe "new" organic metal ion stripping method uses HEDP and is listed as the second experiment in each series.

Series Nine Experiments

Table A-25. Initial Solution Composition, Molar

Solution Designation	Oxalate	Al ³⁺	Fe ³⁺	HNO ₃	HF ^a	NaNO ₃
9A	--	0.1		0.5	0.1	2.3
9B	--	0.1		0.5	0.3	2.3
9C	--	0.1		0.5	0.5	2.3

^aThese solutions were handled in plastic containers due to the presence of HF.

Table A-26. Analytical Results of Sample 9A

Metal Ion	Concentration, $\mu\text{g/mL}$			D	% Material Balance
	Typical Feed	Aqueous	Organic ^a		
Al	2113	2417	136	0.056	120
		2433	107	0.044	120
Mo	131	16.2	106	6.33	93
		17.8	105	5.86	93
Mn	206	187	21.7	0.12	101
		187	18.9	0.10	99
Ni	388	337	21.4	0.064	92
		363	18.3	0.050	98
Fe	--	--	--	--	--
Nd	332	4.33	184	42.59	56
		4.50	256	56.96	78
Zr	237	17	234	13.79	105
		15.3	225	14.68	101
Ru	162	83.4	30.6	0.37	70
		78.0	27.3	0.35	65
Pd	43.6	20.3	13.6	0.67	77
		20.0	18.0	0.90	87
Rh	42.2	42.2	3.00	0.070	107
		42.3	3.00	0.070	107

^aThe "new" organic metal ion stripping method uses HEDP and is listed as the second experiment in each series.

Table A-27. Analytical Results of Sample 9B

Metal Ion	Concentration, $\mu\text{g/mL}$			D	% Material Balance
	Typical Feed	Aqueous	Organic ^a		
Al	2113	1834	484	0.26	109
		1700	208	0.12	90
Mo	131	26.7	87.0	3.26	86
		22.0	95.2	4.32	89
Mn	206	183	21.7	0.12	99
		172	28.9	0.17	97
Ni	388	357	26.3	0.074	98
		335	40.2	0.12	96
Fe	--	--	--	--	--
Nd	332	8.00	223	27.9	69
		8.84	140	15.8	44
Zr	237	172	70.6	0.41	102
		156	68.9	0.44	94
Ru	162	92.9	23.0	0.24	71
		86.7	25.6	0.30	69
Pd	43.6	22.0	20.2	0.92	96
		19.8	15.0	0.76	79
Rh	42.2	40.8	3.13	0.077	104
		38.0	4.84	0.13	104

^aThe "new" organic metal ion stripping method uses HEDP and is listed as the second experiment in each series.

Table A-28. Analytical Results of Sample 9C

Metal Ion	Concentration, $\mu\text{g/mL}$			D	% Material Balance
	Typical Feed	Aqueous	Organic ^a		
Al	2113	848	237	6.28	51
		806	--	--	--
Mo	131	27.5	91.1	3.31	90
		24.0	--	--	--
Mn	206	185	14.5	0.079	96
		185	--	--	--
Ni	388	365	8.91	0.024	96
		365	--	--	--
Fe	--	--	--	--	--
		--	--	--	--
Nd	332	6.83	222	32.5	68
		6.33	--	--	--
Zr	239	200	39.8	0.20	100
		197	--	--	--
Ru	162	101	20.2	0.20	124
		99.9	--	--	--
Pd	43.6	23.5	16.7	0.71	106
		23.0	--	--	--
Rh	4.42	41.3	1.41	0.034	196
		41.7	--	--	--

^aThe "new" organic metal ion stripping method uses HEDP and is listed as the second experiment in each series.