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NUCLEAR TECHNOLOGY PROGRAMS
SEMIANNUAL PROGRESS REPORT

April - September 1991

Chemical Technology Division

J. E. Battles, Director

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April 1989-September 1989	ANL-91/26

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EP

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	1
 I. APPLIED PHYSICAL CHEMISTRY	 8
A. Liquidus-Solidus Temperatures and Viscosities of Core-Concrete Mixtures	 8
1. Differential Thermal Analysis Experiments	8
2. Viscosity Experiments	11
B. Metal Fuel Property Studies	13
1. Thermal Conductivity Studies	13
2. Behavior of Actinide and Lanthanide Alloys	14
C. Fusion-Related Research	15
1. Temperature-Programmed Desorption from LiAlO_2	15
2. Lithium Vaporization Behavior of Lithium Ceramics	20
3. Tritium Release Studies	22
D. Support Studies for New Production Reactor	25
1. Fission Product Release from Fuels and Targets	26
2. Shielded-Cell Modifications to Handle Tritium	27
 REFERENCES	 28
 II. SEPARATION SCIENCE AND TECHNOLOGY	 30
A. Model Enhancements	30
1. General Improvements	30
2. Development of Loading Module	31
B. Development of Data Base	33
1. Distribution Ratio Measurements for Phosphate	33
2. Distribution Constant Measurements for Cadmium	34
3. Distribution Ratios for Thorium between TRUEX Solvents and Aqueous Solutions	 35
C. Development of Spreadsheet Algorithm for Stagewise Solvent Extraction	39
1. New SASSE Features	39
2. Simple Section Rules	40
3. TRUEX Flowsheet for Rocky Flats Plant	46
D. Centrifugal Contactor Development	50
1. Super High-Throughput Centrifugal Contactor	50
2. Annular Contactor	56

TABLE OF CONTENTS (contd)

	<u>Page</u>
E. Monitoring and Controlling of TRUEX Processes	57
F. Processing of Plutonium Waste Solution	59
1. Reprocessing of Raffinate from TRUEX Processing of Batch 1 Waste	61
2. Acidified Carbonate Waste Processing	64
3. New Plutonium Strip Reagents	67
4. TRUEX Solvent Cleanup	72
5. System Decontamination	73
6. Glovebox Gloves	76
G. Advanced Evaporator Technology	80
H. Decontamination of Groundwater	81
REFERENCES	85
III. NUCLEAR WASTE PROGRAMS	87
A. Unsaturated Glass Testing Program for Office of Environmental Restoration and Waste Management	87
1. Critical Review of Parameters Affecting Glass Reaction in Unsaturated Environment	87
2. Long-Term Testing of Fully Radioactive Glass	88
3. Effect of Radiation	95
4. Relationship between High SA/V Experiments and MCC-1	102
5. Analytical Electron Microscopy	111
6. Natural Analogs	116
B. Glass Studies for Yucca Mountain Project	119
1. N2 Unsaturated Tests	119
2. N3 Unsaturated Tests	119
C. Spent Fuel Studies for Yucca Mountain Project	119
1. Teflon-Supported UO ₂ Tests	119
2. Stainless Steel-Supported UO ₂ Tests	120
REFERENCES	123
APPENDIX A	126

NUCLEAR TECHNOLOGY PROGRAMS
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ABSTRACT

This document reports on the work done by the Nuclear Technology Programs of the Chemical Technology Division, Argonne National Laboratory, in the period April through September 1991. 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 in a light water reactor, the thermophysical properties of the metal fuel in 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. 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

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

We are experimentally determining the thermophysical properties of core-concrete mixtures expected to occur during the molten core-concrete interaction phase of severe accidents in LWRs. Our current experiments are concerned with two important properties of the core-concrete mixtures: liquidus-solidus temperatures and viscosities. The liquidus-solidus temperatures of core-concrete mixtures are being determined by differential thermal analysis (DTA). Our DTA measurements with UO_2 -CaO samples indicated a eutectic temperature of 1045°C and eutectic composition of 37 mol % UO_2 -63 mol % CaO. These data helped resolve significant differences in the previously published phase diagrams for the UO_2 -CaO system. We also measured viscosities for mixtures of concrete (27.5 wt %) and UO_2 - ZrO_2 (72.5 wt %). The viscosity data differed significantly (typically two orders of magnitude) from the viscosity estimates in a thermal hydraulic code (CORCON) that treats core-concrete interactions in hypothetical severe reactor accidents and is an integral part of the Nuclear Regulatory Commission's Source-Term Code Package.

Measurements and calculational analyses are being performed to provide needed information on the thermodynamic and transport properties of IFR fuel. Efforts have been initiated to measure the thermal conductivity of ternary IFR fuels with 1.3-cm dia. The instrument for such measurements has been set up and tested. In other work, we are analyzing some of the basic chemistry and phase relations in metallic fuel systems containing actinides and lanthanides. Lanthanides appear to accumulate in the neighborhood of the cladding during irradiation, and the possible significance of this

to fuel performance should be understood. The buildup and intentional addition of actinides to fuel also need to be considered. We are investigating several theoretical approaches to calculation of needed binary phase diagrams for lanthanide and actinide systems.

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, temperature-programmed desorption (TPD) experiments are in progress to provide data that describe the kinetics of desorption of $\text{H}_2\text{O}(\text{g})$ and $\text{H}_2(\text{g})$ from the surface of ceramic tritium breeders. These data are needed for modeling tritium release from such breeders. During the past year, TPD experiments were run with LiAlO_2 that had been pretreated at 650°C in a helium gas stream containing hydrogen at several concentrations. During the runs, the sweep gas was either pure helium or the same He-H_2 mixture that was used in the pretreatment, and the temperature was increased from 200 to 800°C at a rate of $5.6^\circ\text{C}/\text{min}$. The results showed that the rates and amounts of H_2O desorption for the runs with He-H_2 sweep gas were substantially higher than the values for desorption into pure helium. The results also indicated that the desorption process can be related to different kinds of sites on the LiAlO_2 surface. A method is given on how to apply these results to practical questions of blanket design and tritium-release modeling.

Another study addressed LiOH vaporization loss from ceramic breeders, which is viewed as possible under some operating conditions in fusion reactors. This potential problem is greatest for Li_2O breeder material, and less so for the other candidate ceramic breeders (LiAlO_2 , Li_4SiO_4 , and Li_2ZrO_3). To assess the need for further experimental work on lithium losses from Li_2O , the existing literature studies were placed on a common basis for comparison by expressing the individual data points as a ratio relative to what would be predicted thermodynamically for equilibrium at the same conditions of temperature and $\text{H}_2\text{O}(\text{g})$ partial pressure. The results indicated that sweep-gas flow rates under expected reactor conditions will be (1) high enough so that diffusional contributions to mass loss will be negligible and (2) in the range in which one can assume thermodynamic equilibrium conditions. We also concluded that existing studies provide adequate replication and consistency, and that further experimental studies would not be cost effective.

In another breeder study, we employed the TPD method to investigate the tritium release behavior of single crystals of LiAlO_2 , Mg-doped LiAlO_2 , and Pt-coated LiAlO_2 . The TPD plot for the pure LiAlO_2 had five peaks, each associated with a different activation energy. Doping the LiAlO_2 with magnesium shifted the peaks to lower activation energy; this suggested that the magnesium doping provided low-energy MgO surface sites from which the tritium desorbs. Use of the platinum coating also shifted the peaks to lower activation energies and improved the tritium release. This finding suggests that the rate-controlling step in tritium release from the pure LiAlO_2 involves the surface and not bulk diffusion. Based on the TPD results, we developed a tritium release model that accounts for diffusion and simultaneous desorption from several sites on the breeder material and, unlike earlier models, contains no adjustable input parameters. Calculated results showed excellent agreement with measurements from an in-pile tritium release experiment with LiAlO_2 .

The DOE initiated the New Production Reactor (NPR) Program to plan, design, and construct safe and environmentally acceptable new reactor capacity for an assured supply of tritium. The CMT Division supported this program by conducting two projects on an NPR that is a heavy water reactor. The first project entailed calculational and experimental studies in preparation for transpiration experiments to determine fission product release from Al-U fuel and Al-Li target in a severe accident. Results indicated that formation of an oxide layer on molten aluminum may be a barrier to transport of gaseous aluminum species in the transpiration experiments. In the second project, a conceptual design

was developed for the modifications needed to a hot cell at ANL-West so that irradiated fuel and target tubes could be handled there with minimal tritium contamination.

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).

The major TRUEX effort involves development of a generic data base and modeling capability for this solvent extraction process. The Generic TRUEX Model (GTM) was developed 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. In September 1990, version 2.1 of the model for the Macintosh computer was issued. Since that time, the process for converting the GTM from the Macintosh version to the IBM-PC version was made even easier, and the module of the GTM that calculates the speciation of feed components was expanded. The following components were added to the speciation module: Am^{3+} , Pu^{3+} , Cm^{3+} , Th^{4+} , UO_2^{2+} , Pu^{4+} , Np^{4+} , Cd^{2+} , PO_4^{3-} , and $\text{B}(\text{OH})_3$.

One of the sections in the GTM, the Spreadsheet Algorithm for Stagewise Solvent Extraction (SASSE), is being modified so that a user can specify (1) an extraction efficiency for each stage in the process and (2) a fixed effluent flow rate for either the organic or aqueous phase at any stage. In present SASSE calculations, extraction efficiency is assumed to be 100%, and effluent flow is specified as a fraction of the total flow of the organic or aqueous phase from a stage.

Experimental studies were conducted on the extraction of thorium (with the use of ^{230}Th as the tracer) into TRUEX solvent from nitric acid solutions. The ^{230}Th was separated from its alpha-emitting decay products by extraction into the TRUEX solvent, and small aliquots of this stock solution were added to fresh, nonacid-equilibrated TRUEX solvent for distribution ratio measurements. Three series of thorium extraction experiments were completed at nitric acid concentrations of 0.05 to 0.50M. For each series, log-log plots of distribution ratio vs. nitric acid concentration yielded linear curves. The distribution ratios were similar at 0.05M but deviated from one another with increased nitric acid concentration. This discrepancy implies that the initial purification of thorium from its less-extractable alpha-emitting decay products was inadequate. Additional purification is needed because the liquid-scintillation counting procedure used to determine the thorium concentration does not distinguish between the alpha-particle energies of ^{230}Th and its decay products.

Nuclear waste from the Idaho Chemical Processing Plant has been considered for treatment by the TRUEX process. This high-level waste contains large amounts of B, Cd, and HF. Since BF_4^- originates from the reaction of boric acid and HF, the chemistry of boric acid and BF_4^- in the TRUEX process is being studied for inclusion in the GTM. The quantity of boric acid that would extract into the TRUEX solvent was determined by titration of boric acid with a strong organic base (tetrabutylammonium hydroxide). A polyalcohol was added to minimize polymer formation. Distribution ratios for boric acid determined by titration were low, indicative of low partition into the organic phase. The BF_4^- ion is difficult to extract, mainly because of hydrolysis reactions. The method found to have the greatest potential for BF_4^- extraction involves complex formation with methylene blue basic dye followed by extraction into the organic phase.

In addition to BF_4^- , studies were undertaken on the behavior of H_2PO_4^- species, which are present in waste stored in single-shell tanks at Hanford and are being considered for use in a pretreatment step with the TRUEX process. The apparent molar volumes of both species as a function of temperature (0-150°C) were calculated. These data have been incorporated into the GTM in order that densities of solutions containing BF_4^- or H_2PO_4^- can be estimated.

Work was started on the development of a super high-throughput centrifugal contactor (SHTCC), which would have a throughput that is four to eight times greater than is normally achieved for a given rotor diameter. An SHTCC design was evaluated for the effect that it will have on contactor vibrations and hydraulics. The vibration analysis showed that the SHTCC rotor will need to operate above its first natural frequency. Use of a steady bearing has been proposed to support the rotor as it passes through the first natural frequency. Several steady-bearing options were experimentally tested using a long, 4-cm-dia rotor. Normal contactor rotors have a length-to-diameter ratio (L/D) of about 2.5. The SHTCC rotors will have an L/D of 10 or more. The rotor used in these tests had an L/D of 13. The test results were very encouraging when the steady bearing was near the top of the rotor.

Monitoring and control requirements for the generic TRUEX process were assessed in terms of instrument type, availability, compatibility with process fluids, sensitivity and response time, adaptability, maintenance, and cost. The important process variables from the standpoint of monitoring and control are fluid flow rate, liquid level, and component concentration. Acceptable instruments for flow and liquid level measurement are commercially available to meet the needs of the TRUEX process. However, instruments for on-line measurement of Am, Pu, and NO_3^- concentrations in liquids are not well developed. There is promise that Pu and Am concentrations can be measured by spectrophotometry, and nitrate ion concentrations by ion selective electrodes. At present, spectrophotometric measurement of Pu and Am concentrations can be made down to 10^{-5}M , although this falls short of the TRUEX process requirements by several orders of magnitude. Ion selective electrodes could be used for these measurements, but further progress is needed in terms of their life, accuracy, and concentration range. The results also suggested that successful monitoring and control of the TRUEX process will depend more on developing flowsheets tolerant to wide variations in the operating parameters than on new or improved instruments.

The GTM was used in performing a sensitivity analysis to determine the effect of perturbations in feed composition and flow rates for a base-case flowsheet (four extraction stages, four scrub stages, seven americium strip stages, and four plutonium strip stages) with regard to meeting goals set for processing nuclear waste generated by the Plutonium Finishing Plant (PFP) of Westinghouse Hanford. Of all the perturbations analyzed, only one of them, a change in flow rate for the aqueous extraction feed, resulted in the most important process goal (TRU concentration in the raffinate $<10\text{ nCi/mL}$) being exceeded. Even then, the flow rate could be up to four times the base value of 400 mL/min without exceeding this goal. Also calculated was whether losing a stage in the extraction section, scrub section, americium strip, or plutonium strip of the base-case flowsheet would result in one or more of the process goals being exceeded. We found that the process goals would still be met if one stage was lost from the extraction of plutonium strip sections, but would not be met if a stage was lost from the scrub or americium strip sections. Although this analysis related to a specific TRUEX flowsheet, these limits can be applied to controlling other TRUEX processes.

A data base containing distribution ratios important to the TRUEX process is being assembled using a Macintosh computer and 4th Dimension software. It is updated monthly to reflect newly obtained laboratory data. The data base now contains 612 data sets, corresponding to 6461 individual measurements of distribution ratios.

The GTM was also used to develop a TRUEX flowsheet for treating plutonium-containing waste (approximately 200 L) generated at ANL and the New Brunswick Laboratory (NBL). This flowsheet will be used in converting the bulk of this waste into a nonTRU product by removing the TRU elements to low enough activity levels that this waste can be disposed of under existing regulations. The recovered plutonium will be converted into solid PuO_2 for storage and subsequent shipment to the DOE defense complex. This demonstration will show the applicability of the TRUEX process for treating the much larger volumes of similar wastes at other DOE sites. A series of batch extractions and contactor tests was completed to verify that the flowsheet developed to process this waste was adequate. Following the successful completion of these tests and installation of a 20-stage contactor in a glovebox, the first batch of waste solution was processed. In this run, the TRU concentration in the waste was lowered by a factor of about 22,000, generating a raffinate concentration of only 1.8 nCi/mL. The major problem during this run was the formation, in the plutonium strip section, of a plutonium precipitate that partially collected inside the contactor. This precipitate, and its collection inside the equipment, made completing a material balance difficult for this run. Before the next batch of waste is processed, measures will be taken to eliminate this precipitate.

Nuclear Waste Programs

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 behavior of this spent fuel and waste in the host environment must be sufficiently well understood to project its stability over very long periods.

A nuclear waste program has been established for DOE Environmental Restoration and Waste Management to evaluate factors that are likely to affect waste glass reaction in an unsaturated environment typical of what may be expected for the Yucca Mountain site. Six tasks in this program are underway in CMT.

The first task involves a critical review of the literature relevant to those parameters that affect the reactivity of glass in an unsaturated environment. Temperature is the first parameter examined in detail. A general conclusion reached from this review is that caution should be exercised in using temperature as an accelerating parameter for chemical reactions that affect waste glass/water interactions. Key aspects of these reactions must be investigated further to develop an understanding of the complex overall reaction that will occur under repository conditions.

The objective of the second task is to evaluate the reactivity of fully radioactive glasses in a high-level waste repository environment and compare it to the reactivity of nonradioactive glasses of similar composition. Long-term tests with fully radioactive glass (SRI 165/42, 131/11, and 200R compositions) and simulated nonradioactive glasses have been (or will soon be) initiated in the following modes: static leach, intermittent drip, and laboratory analogue. The data are too preliminary to draw any conclusions as yet.

The third task entails determining the effect of radiation upon the durability of waste glasses at high ratios of glass surface area to liquid volume (SA/V). Results from blank tests (no glass, moist air under alpha or gamma radiation field at 25°C) indicate that nitrogen fixation varies linearly with respect to time and dose. The results also suggest that the radiolytic products are concentrated in thin films of water that condense on the test vessel walls and/or radioactive source materials. In addition, the gamma irradiation results indicate that nitrate plus nitrite yields are inversely related to temperature between 25 and 200°C. Moreover, results from tests with glass wafers exposed to gamma radiation under a steam environment (150 and 200°C) indicated that they react about 15 times faster than their nonirradiated counterparts. Despite the advanced reaction rate, detailed microscopic examination

indicated a remarkable similarity between secondary minerals that form in the irradiated and nonirradiated tests.

A fourth task is underway to compare the extent of reaction of waste glasses at SA/V ratios of 10, 2000, and 20,000 m⁻¹. In these tests, SRL 131A and SRL 202A glasses doped with actinide elements are being reacted in groundwater at 90°C for times between three days and several years. Several trends were noted from the test data obtained so far (up to 280 days of testing): the pH approaches a constant value beyond 50 days and increases with increased SA/V ratio; the measured reaction rate is higher at 2000 than 20,000 m⁻¹; elemental release to solution does not scale as SA/V multiplied by reaction time, as previously believed; the SRL 131A glass is more reactive than the SRL 202A; and filterable colloids are generated at high SA/V.

The objective of the fifth task is to assess the reaction of naturally occurring rhyolitic glass (obsidian) with water under repository-relevant conditions. Although obsidians are enriched in silica and depleted in alkalis and boron relative to nuclear waste glasses, their survival in nature for extensive periods can offer insights into the long-term corrosion of waste glass in a geologic setting. Our previous results suggested that the intrinsic water content of obsidians is the dominant parameter controlling hydration rate. A study was undertaken to examine the total water content in obsidian samples from the volcanic flow at Coso, California. Results indicated that water contents in the Coso Field are not homogeneous, as previously assumed. Average water contents from 17 sites ranged from 0.46 ± 18 wt % to 1.26 ± 16 wt %. Our preliminary results also suggest that obsidian hydration analysis can be used as a simple and accurate method for age determinations.

In the sixth task, analytical electron microscopy (AEM) is being employed to assess the glass/water reaction pathway by identifying intermediate phases that appear on the reacting glass. Significant experience was gained in sample preparation and microscopy by applying AEM to a wide variety of existing glass samples, which ranged from glass with no reacted layer, to a reacted layer forming as the glass etches, to a reacted layer forming *in situ* as the glass restructures.

Several different experiments involving the reaction of glass and spent fuel under simulated repository conditions are being performed in support of DOE's Yucca Mountain Site Characterization Project (YMP).

In an ongoing YMP study, simulated waste glasses (SRL 165 and ATM-10) have been intermittently contacted with dripping well water using an unsaturated test method at 90°C. These tests have been in progress for 260 weeks with SRL 165 glass and 245 weeks with ATM-10 glass. As part of this YMP glass study, the test solution from actinide-doped glasses was filtered and analyzed to determine whether the actinide fraction was associated with colloidal particles or could be considered truly dissolved in solution. Test results showed that most of the Pu, Am, and Cm isotopes in the leachates were associated with particulates in the colloidal size range. The colloids are fragments of a hydrated layer that spalled off the glass during testing. The potential formation of colloids in dissolution of waste glass and the role of colloids in transporting radionuclides are important issues in evaluating waste glass behavior after disposal in a geological repository.

In radiation studies for YMP, data previously acquired in connection with flue gas irradiation studies were used to determine the effect of dose rate on the composition of a pure nitrogen system and a nitrogen system with varying amounts of oxygen at room temperature. The results will be used as a first step in modeling the complex gas-phase system of the expected repository environment.

In spent fuel studies for YMP, experiments have been underway for about six years to investigate the reaction behavior of Zircaloy clad-UO₂ pellets exposed to dripping groundwater in an

oxidizing environment at 90°C. A pulse of uranium release from the UO_2 solid, in conjunction with the formation of several uranyl oxide hydrate mineral phases across the sample surface, was observed after one or two years of testing. Thereafter, the uranium release decreased, and a second set of secondary phases was observed. Leachate analysis indicated that Ca, K, and Mg underwent the greatest decrease relative to the other elements in the original groundwater. These three elements combined with uranium from the samples to form the secondary uranyl phases on the sample surface. Leachate pH also decreased relative to the starting groundwater (from 8.2 to 6.9). The acidity of the leachate in contact with the sample surface may play an important role in the dissolution of uranium from the samples.

In other repository-related work, laser photoacoustic spectroscopy (LPAS) is being employed to study the solubility and speciation of radionuclides in groundwater. This work has yielded information concerning complexant and temperature effects on the solubilities of important radionuclide species. In addition, the LPAS system was determined to have a sensitivity to Cr^{3+} of $8 \times 10^{-7} \text{M}$ in perchlorate at room temperature.

I. APPLIED PHYSICAL CHEMISTRY

(C. E. Johnson)

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

A. Liquidus-Solidus Temperatures and Viscosities of Core-Concrete Mixtures (M. F. Roche)

Thermophysical properties of core-concrete mixtures are being measured in this research program. Such mixtures are expected to occur during the molten core-concrete interaction (MCCI) phase of severe accidents at light-water nuclear reactors. The MCCI phase is preceded by a series of other phases: loss of coolant, heatup and degradation of the reactor core (uranium and its fission products, Zircaloy cladding, control rods, and structural materials), melting of the stainless-steel vessel, and collapse of the hot core debris and melted vessel onto the concrete basemat. A knowledge of the thermophysical properties of the solids, liquids, and gases that exist during the MCCI phase is crucial for understanding and modeling the consequences of the accident. The results of this research will be incorporated in thermal hydraulic codes such as CORCON,¹ which is an integral part of the Source-Term Code Package² for the Nuclear Regulatory Commission (NRC). (The amount of a fission product that is released in an accident is called its "source term.") In addition, our experiments are designed to aid researchers in ANL's Reactor Engineering Division in analyzing results from their large-scale (~500 kg) MCCI experiments, which are being performed under international sponsorship (the ACE Consortium).

In earlier experiments,³ sponsored by the Electric Power Research Institute (EPRI), we conducted source-term measurements of the vaporization of refractory fission products from core-concrete mixtures. Our current experiments are concerned with two other important properties of the core-concrete mixtures: liquidus-solidus temperatures and viscosities. The liquidus-solidus temperatures are being measured by differential thermal analysis (DTA) in a program sponsored by the NRC. (Liquidus temperatures are the onset of solidification; solidus temperatures are the onset of melting.) In our experiments, these temperatures range from 1175 K (solidus) to greater than 2850 K (liquidus), depending on the sample composition. The viscosities are being measured by rotational viscometry in a program sponsored by the ACE Consortium.

1. Differential Thermal Analysis Experiments

We conducted DTA measurements of the eutectic temperature and composition in the UO_2 -CaO system to resolve significant differences in the previously published phase diagrams.^{4,5} Our experiments were conducted using a carefully controlled atmosphere (flowing Ar-3% H_2 at a pressure of about 0.015 MPa and at a monitored water-vapor concentration of less than 5 ppm). Seven UO_2 -CaO samples were tested with uranium concentrations of 30 to 60 wt %. Figure I-1 is an example of the DTA curves for one of the seven samples (37 mol% UO_2). It shows the eutectic temperature at 2218 K (1945°C). This value is 135 K lower than that given by Alberman et al.⁴ and 95 K higher than that given by Holc and Kolar.⁵ Our confidence in this eutectic temperature (± 5 K) is based on measurements with four different sample thermocouples, as well as the alumina-standard calibration. Figure I-2 presents eutectic-peak areas vs. sample compositions determined from our DTA curves. The triangle shown in this figure is derived from the compositions for the solid solution (70 mol % UO_2) and eutectic (37 mol % UO_2) given by Holc and Kolar⁵; the height of the triangle is normalized to our data. Our solid-solution and eutectic compositions support the data of Holc and Kolar and do not agree with those of Alberman

Fig. I-1. Curves from Differential Thermal Analysis of 37 mol % Urania-63 mol % CaO on Heating and Cooling (TC = Thermocouple)

Fig. I-2. Areas of 2218 K (1945 °C) Eutectic Peaks Derived from DTA Experiments with Urania-CaO Samples and from Data of Holc and Kolar⁵

et al.,⁴ who place the solid-solution boundary at 53 mol % UO_2 and the eutectic composition at 45 mol % UO_2 . Our revised phase diagram for the UO_2 -CaO system is shown in Fig. I-3. It was calculated using our eutectic temperature, the composition data of Holc and Kolar,⁵ and the chemical thermodynamics program F*A*C*T (product of Thermfact Ltd., Mount-Royal, Quebec, Canada).

Fig. I-3. Phase Diagram for UO_2 -CaO System

Table I-1 presents solidus and liquidus temperatures from our earlier DTA experiments on mixtures having a UO_2 - ZrO_2 mole ratio of 1.6:1. Also given in this table are preliminary results of solidus and liquidus temperatures calculated by Mignanelli⁶ for our sample compositions. The experimental and calculated solidus temperatures presented in Table I-1 are in reasonable agreement. The disagreement between experimental and calculated liquidus temperatures appears to be roughly proportional to the amount of calcia in the calcined concrete (72 wt % in limestone, 36 wt % in limestone-sand, 15 wt % in siliceous). We expect that incorporation of our UO_2 -CaO phase diagram (Fig. I-3) in the thermodynamic data base now being employed by Mignanelli will significantly improve the agreement between our experiments and his calculations.

Table I-1. Experimental and Calculated Solidus and Liquidus Temperatures for Mixtures of 27 wt % Concrete with UO_2 - ZrO_2 (1.6:1 mole ratio)

Concrete with UO_2 - ZrO_2	Solidus Temp., K		Liquidus Temp., K	
	DTA ^a	Calc. ^b	DTA ^a	Calc. ^b
Limestone	1520	1550	>2723	2320
Limestone Sand	1360	1450	>2638	2490
Siliceous	1412	1434	2549	2395

^aFrom ANL-92/25, pp. 14-20.

^bFrom Ref. 6.

We plan to continue DTA experiments with additional core-concrete compositions to provide more data for calculation of liquidus-solidus curves.

2. Viscosity Experiments

We have measured the viscosity for eight mixtures of $\text{UO}_2\text{-ZrO}_2$ (1.6:1 mole ratio) with calcined concrete: one with siliceous concrete, four with limestone concrete, and three with limestone-sand concrete. The mixtures, which weighed 150 to 200 g and had a volume of about 30 cm^3 , were heated to temperatures as high as 2850 K within the hot zone of a molybdenum-tungsten alloy (70Mo-30W) furnace tube with 2.9-cm OD. The furnace tube was continuously purged by Ar-3% H_2 gas to ensure retention of the urania in the U^{4+} state. A Brookfield programmable viscometer equipped with a 70Mo-30W alloy spindle that was immersed in the molten sample was employed to measure its viscosity as a function of spindle rotation rate.

Viscosities were measured for a mixture of siliceous concrete (27.5 wt %), urania (56.6 wt %), and zirconia (15.9 wt %) over the temperature range 2004-2595 K and are shown in Fig. I-4. The measured solidus and liquidus temperatures for this particular mixture are 1412 and 2549 K, respectively (see Table I-1). Therefore, the viscosity measurements extended from above the liquidus well into the liquidus-solidus temperature range. This sample exhibited Newtonian behavior (a viscosity independent of spindle rotation rate) over the temperature range 2367-2595 K. This behavior is expected of a single phase fluid or a fluid with only a minor volume fraction of solids. However, as the temperature was decreased further into the liquidus-solidus region, the sample exhibited non-Newtonian behavior, called shear thinning (the viscosity decreased significantly with increasing rotation rate). This shear thinning is due to the presence of a significant fraction of undissolved solids at the lower temperatures. The large increase (a factor of about 1000) in viscosity with decreasing temperature is another indication of increasing solids content.

Fig. I-4. Viscosity of Siliceous Concrete, Urania, and Zirconia
(27.5 wt % Concrete, 56.6 wt % Urania, 15.9 wt % Zirconia)

Viscosities were also measured for a mixture of limestone-sand concrete (27.5 wt %), urania (56.6 wt %), and zirconia (15.9 wt %) over the temperature range 2287-2467 K and are shown in Fig. I-5. The measured solidus and liquidus temperatures for this particular mixture are 1360 and >2638 K.

Fig. I-5. Viscosity of Limestone-Sand Concrete, Urania, and Zirconia, (27.5 wt % Concrete, 56.6 wt % Urania, 15.9 wt % Zirconia)

respectively (see Table I-1). Therefore, these viscosity measurements were conducted on a mixture of solid and liquid within the liquidus-solidus temperature range. The sample exhibited a remarkable degree of shear thinning; the viscosity was approximately inversely proportional to rotation rate. We attribute the shear thinning to a competition between the shearing force exerted by the spindle and sintering of the solids in the solid-liquid mixture. Indeed, in the absence of stirring, the sample thickened considerably, and a large force was then required to reestablish flow. Viscosity measurements on this sample were extended to temperatures as high as 2850 K. At that temperature, the sample behavior was nearly Newtonian [the viscosity ranged from about 1.2 Pa·s (1.2×10^3 centipoise) at 10 rpm to 0.6 Pa·s (0.6×10^3 centipoise) at 200 rpm], which indicated that the volume fraction of solids was low. The viscosity measurements indicate that the liquidus temperature is >2850 K. Note that this is a more accurate limit when compared to the DTA value (>2638 K). This improvement is due to the higher temperature capabilities of the viscosity apparatus.

The viscosity of the mixture of limestone concrete (27.5 wt %), urania (56.6 wt %), and zirconia (15.9 wt %) could not be measured because of a large volume fraction of solids, even at temperatures as high as 2850 K. This indicates that the liquidus temperature is much greater than 2850 K (the DTA measurements listed in Table I-1 showed it to be greater than 2723 K). Viscosities measurements were possible on mixtures of $\text{UO}_2\text{-ZrO}_2$ (1.6:1 mole ratio) with 36 and 60 wt % limestone concrete over the temperature range 2000-2850 K. These data, which are being analyzed, also indicate liquidus temperatures in excess of 2850 K because of the non-Newtonian behavior of the viscosity.

The above viscosity data differ significantly (typically, two orders of magnitude) from the viscosity estimates now being employed in thermal hydraulic codes such as CORCON. Since the viscosity affects heat transfer, release of fission products, and a variety of other important processes in the MCCI phase such as melt spreading and cooling, it is important to have reliable data for incorporation in the codes. We therefore plan to extend this work to provide improved correlations of viscosity versus composition for a broad range of core-concrete mixtures.

B. Metal Fuel Property Studies

Measurements and analyses are being performed to provide needed information on the thermodynamic and transport properties of Integral Fast Reactor (IFR) fuel. During this report period, effort was focused on measuring thermal conductivity of ternary IFR fuel alloys and determining the behavior of actinides and lanthanides in IFR alloy systems.

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

Efforts have been initiated to test our thermal conductivity instrument with 1.3-cm (1/2-in.) dia samples of ternary IFR fuel. This device was designed to use 2.5-cm (1-in.) dia samples, which were unavailable for ternary IFR fuel alloys. Discussions with the instrument manufacturer (Holometrix Inc., formerly Dynatech Inc.) indicated that measurements with the smaller diameter samples would be possible with some sacrifice of accuracy. Testing with known materials showed that the thermal conductivity results with the smaller diameter samples were more sensitive to instrument conditions than were prior results with the larger diameter samples. Effort was, therefore, devoted to optimizing the instrument settings, after which measurements were performed over the accessible temperature range. These measurements employed samples of a stainless-steel thermal conductivity standard, SRM 1461, provided by NIST. In these measurements we used the SRM as both the reference and the unknown in our instrument. The goal was to determine how well we could reproduce the NIST data. Figure I-6 shows the NIST data as a solid line, the NIST-reported standard deviation as a shaded area, and our measurements as the filled circles. We believe that these results are satisfactory, and that our instrument will provide the necessary thermal conductivity data on ternary IFR fuel alloys when they become available.

Fig. I-6.

Thermal Conductivity vs. Temperature
Determined for Standard Reference
Material (SRM 1461)

2. Behavior of Actinide and Lanthanide Alloys (L. Leibowitz and I. Johnson)

Developments in the IFR program have drawn increased attention to the behavior of lanthanides and actinides in IFR fuel. Lanthanides appear to accumulate in the neighborhood of the cladding during irradiation, and the possible significance of this to fuel performance should be understood. The buildup and intentional addition of actinides to fuel also need to be considered. The behavior of the actinide and lanthanide elements during irradiation of IFR fuel, their influence on fuel performance, and the possible interactions between lanthanides and cladding are not easily predicted. In this section, we summarize our analysis of some of the basic chemistry and phase relations among these elements.

It might be expected that the lanthanides and the actinides would be very similar chemically and physically in that both series of elements form by the addition of electrons to an *f* shell. However, as discussed in the previous report (Sec. I.B), the actinides are not simple analogues of the lanthanides. A great many properties of the actinide elements change markedly between Pu and Am, i.e., the heavier actinides are much more like the lanthanides than are the lighter actinides. This behavior can have important consequences for IFR fuel performance as well as recycling chemistry and should be understood.

Some of the lanthanide and actinide binary phase diagrams of importance to the IFR program exist in the literature. Others, however, do not. In the absence of experimental data on many important systems of interest, the familiar techniques of thermodynamic modeling and phase diagram optimization cannot be applied. Calculation of phase diagrams is being approached in a variety of ways, but to date no clearly satisfactory approach exists. The ultimate goal of calculating a binary phase diagram from basic properties of the constituent elements has not been reached. Some success has been achieved with various models, but our needs are made more difficult because of the extraordinary complexity of the actinides.

One approach which we followed was to use the model developed by Engel⁷ and expanded by Brewer.⁸ This model is an extension of the well-known observation that many intermetallic compounds exhibit a strong correlation between the number of electrons per atom and the crystal structure. For our interests, one of the important contributions by Brewer was the application of this model to actinides.

Engel recognized that the crystal structure of metals is highly correlated with the electronic structure. Roughly stated, this correlation is that the body-centered cubic (bcc), hexagonal close packed (hcp), and face-centered cubic (fcc) structures are respectively associated with one, two, and three *s* and *p* electrons. Application of these ideas to lanthanides and actinides is complicated because consideration must be given to *f* electrons. In addition to electronic configuration, other considerations must be dealt with in metallic solutions. For example, differences in atomic size and internal pressure will also influence the free energy of a solution. In general, the free energy is increased by a difference in atomic size except in certain cases, such as in Laves phases, in which higher packing density can be obtained.

Following Brewer's model, we performed calculations of the phase diagrams for three systems of interest, using the chemical thermodynamics program F*A*C*T. We chose two, Am-Pu and Pu-U, which have been reported in the literature, and one, Am-U, which has not. An important aspect of Brewer's ideas⁸ is that the enthalpy of vaporization to be used in the regular solution model is the enthalpy for vaporization from the metal to a vapor of the same electronic state as exists in the condensed phase rather than to the normal (ground state) gas.

From these calculations, we found that the calculated Am-Pu phase diagram was a reasonable representation of the published phase diagram. This was not the case, however, for the calculated and the published Pu-U diagrams. It is not obvious how that calculation can be improved within the framework of Brewer's model. We are, therefore, unsure as to how much confidence we should have in the calculated Am-U diagram. Judging from the availability of *d* electrons in americium, we anticipate that americium would stabilize the close-packed fcc structure in plutonium, but it is not obvious how americium would interact with the complex structures of uranium. This model and the work that Brewer has already done on actinide systems could be used to make some reasonable predictions on unknown systems, but further study of this approach is needed.

Another approach to phase diagram calculations, developed chiefly by Kaufman,⁹ has been applied to actinide and lanthanide systems by several workers with mixed success. This method is similar in concept to Brewer's in that both begin with the regular solution equations. Application of this model to unknown systems would, therefore, be of unpredictable reliability, particularly with regard to the complex actinides. One of the more extensive applications of Kaufman's ideas has been presented by Selle,^{10,11} who calculated binary phase diagrams of the rare earth and actinide systems. Selle has extended the Kaufman method and thereby made possible approximate calculations for systems of interest to our program.

To test Selle's selection of values for stability and interaction parameters, we calculated the phase diagram for the Nd-Y system with these parameters and compared it with the experimentally derived diagram given by Massalski.¹² The computed curves were above the experimental curves for the Nd-Y diagram. Nevertheless, for the liquidus-solidus curves, the agreement was fairly good, especially considering that the experimental liquidus is given as uncertain in the Massalski diagram. This difference is greater for the bcc-hcp transformation. Part of this difference is due to the fact that the hcp structures for Nd and Y are slightly different. Since the estimation of the interaction parameters has a large uncertainty, we are not surprised that these small details of the Massalski phase diagram cannot be reproduced by the computations. This simple example probably gives a good indication of the accuracy that can be expected using the Kaufman methods and the parameters for the rare earths and actinides estimated by Selle.

Additional study concerning the influence of lanthanides and actinides on IFR fuel performance is needed. We have investigated some theoretical approaches to phase diagram calculation with mixed success. Our efforts at a combined theoretical and experimental approach to attaining this understanding are continuing.

C. Fusion-Related Research

A critical element in development of a fusion reactor is the blanket for breeding tritium fuel. We are conducting experimental and calculational studies with the objective of determining the feasibility of using lithium-containing ceramics (e.g., Li_2O , LiAlO_2 , Li_4SiO_4 , Li_2ZrO_3) as breeder material.

1. Temperature-Programmed Desorption from LiAlO_2 (A. K. Fischer)

Data on the energetics and kinetics of desorption of $\text{H}_2\text{O}(\text{g})$ and $\text{H}_2(\text{g})$ from the surface of ceramic tritium breeders are needed for predicting and modeling the release of tritium (in the forms of HTO, T_2O , HT, and T_2) from such breeders. An important issue being addressed is the effectiveness of H_2 as a promoter of tritium release. The temperature-programmed desorption (TPD) technique is well suited to provide such data and has been used in earlier work.¹³

In this report period, TPD experiments were run on LiAlO_2 (~0.5 g) that had been pretreated at 923 K for periods of 20 h to 12 days in a helium gas stream containing H_2 at concentrations of 247, 495, and 990 ppm (by volume). After such an exposure, the experimental system was cooled quickly to 473 K while the equilibrating gas composition was maintained. During the TPD run, the temperature was increased from 473 to 1073 K at a rate of 5.6 K/min. The sweep gas during the TPD run was either pure helium or the same He- H_2 mixture that was used in the pretreatment. The composition of the evolved gas was monitored with a mass spectrometer to provide continuous traces for the gases of interest.

a. Experimental

A comparison of the TPD curves for desorption of $\text{H}_2\text{O}(\text{g})$ from the LiAlO_2 showed that the rates and amounts of desorption into He- H_2 mixtures are enhanced substantially over those into pure helium.

We had reported earlier that the desorption process may be related to different kinds of sites on the LiAlO_2 surface.¹⁴ The experimental TPD curves obtained during the past year were deconvoluted to derive values for the kinetic parameters of the contributing subpeaks, which represent the different kinds of sites on the LiAlO_2 surface (designated by the labels A, B, C, and D). The method of deconvolution was to synthesize the experimental curve from subpeaks determined for a first-order desorption process, where the desorption rate is given as

$$r = \sum_i v_i a_i \exp(-E_{di}/RT) \quad (\text{I-1})$$

Here, r is the overall rate of desorption of $\text{H}_2\text{O}(\text{g})$ in mol/min and is the sum of desorption from the individual types of sites identified by subscript i , v_i is the pre-exponential term for a given type of site in units of mol $\text{H}_2\text{O}/(\text{min-mol occupied site } i)$, a_i is the amount in moles of H_2O adsorbed on a given type of site at a given time, and E_{di} is the activation energy of desorption from a given type of site in units of kJ/mol. As an example of our method, Fig. I-7 shows the calculated subpeaks, the sum of these subpeaks, and the experimental TPD curve derived for a sweep gas of He-495 ppm H_2 .

The activation energies and pre-exponential terms calculated for all runs are shown in Table I-2. Consistently, the TPD curves for desorption into He- H_2 mixtures contained two peaks, labeled B and C (Fig. I-7), and the curves for desorption into pure helium contained peaks of types C and D. The activation energies of the B, C, and D peaks were determined to be ~96, 117, and 134 kJ/mol, respectively. (In the earlier work, dealing with desorption from samples pretreated at 673 K with 900 ppm H_2 , A, B, and C peaks were identified.¹³ The A peaks were determined to have a desorption activation energy of 75 kJ/mol.) The data suggest that the H_2 in the sweep gas causes the OH^- population, which is the precursor of desorbed H_2O , to occupy preferentially and to build up in the B and C sites. This leads to an activation energy that is lower than that obtained for pure helium, where the higher activation energy combination of C and D sites is involved. An important point is that the activation energies for specific types of sites do not change significantly with increases in pretreatment time or H_2 level.

From a comparison of the pre-exponential terms for the C peaks in Table I-2, one may judge the effect of H_2 . The mean values and their standard deviations are $2.22 \pm 1.16 \times 10^5$ mol $\text{H}_2\text{O}/(\text{min-mol occupied site})$ for pure helium and $8.91 \pm 1.14 \times 10^4$ mol $\text{H}_2\text{O}/(\text{min-mol occupied site})$ for He- H_2 mixtures. These values are slightly different at the 1σ level. Therefore, the effect of H_2 is to make

a small change in the pre-exponential term for the C peak, which is in the direction of reducing the overall desorption rate; however, this effect is overcome by the buildup of substantial coverage in the lower-activation-energy B peak.

Fig. I-7.

Desorption of H_2O from Pretreated LiAlO_2 into Helium Sweep Gas Containing 495 ppm H_2 . Pretreatment involved exposure to He-495 ppm H_2 for 18 h. Peaks B and C derived from deconvolution of experimental curve.

Table I-2. Kinetic Parameters for First-Order Desorption of H_2O from B, C, and D Sites on LiAlO_2 .^a (Symbols and their units of measure are defined in Eq. I-1.)

Pretreatment			ν_B	E_{dB}	ν_C	E_{dC}	ν_D	E_{dD}
Time, h	H_2 in He, vppm	H_2 in He Sweep Gas, vppm						
20	247	0	--	--	1.90 E5	118	3.51 E5	135
170	495	0	--	--	1.25 E5	117	9.91 E5	134
20	990	0	--	--	3.51 E5	117	7.51 E5	134
20	247	247	2.22 E4	96	8.82 E4	117	--	--
20	495	495	1.07 E4	92	7.62 E4	117	--	--
20	495	495	1.62 E4	96	8.78 E4	117	--	--
290	990	990	2.75 E4	95	1.04 E5	117	--	--

^aTemperature increase from 473 to 1073 K.

Some data for the desorption of $\text{H}_2(\text{g})$ into pure helium were deconvoluted into two subpeaks (Table I-3 and Fig. I-8). The calculated activation energies and pre-exponential terms were similar to those for desorption of H_2O into pure helium. Because of this similarity, the subpeaks are labeled C and D to indicate their possible correspondence to the subpeaks for H_2O , though it is not implied at this time that the sites are the same. These data are still being analyzed.

Table I-3. Kinetic Parameters for First-Order Desorption of H_2 into Pure Helium Gas from C and D Sites on LiAlO_2 .^a Symbols and their units of measure are defined in Eq. I-1.

Pretreatment					
Time, h	H_2 in He, vppm	v_c	E_{dc}	v_D	E_{dD}
20	247	1.61E5	118	6.35E4	140
170	495	1.30E5	119	5.00E5	136
20	990	4.68E5	119	8.91E5	138
Avg.		2.5E5	119	4.8E5

Fig. I-8.

Desorption of H_2O into Helium Sweep Gas from Pretreated LiAlO_2 . Same pretreatment as that for Fig. I-7.

b. Application

To apply these results to blanket design and tritium-release modeling, the areas under the H_2O desorption curves, represented by the sums of the B and C peaks or the C and D peaks, were

converted to values of fractional surface coverage, θ , on the assumption of 10^{19} sites per square meter of surface. This θ value is for the total evolvable H_2O under the given conditions, either into the He- H_2 mixtures or into pure He. It is distinguished from the θ value that includes all sites which might be covered but did not participate in the desorption processes that were measured. Such sites include those that would have been activated only at temperatures higher than those in the experimental temperature range. The H_2 adsorption process was regarded as dissociative chemisorption, forming surface OH^- groups which combine bimolecularly prior to desorption. Consequently, the OH^- and the H_2O coverage should vary linearly as the square root of the H_2 partial pressure. This linear relationship for the total evolvable H_2O coverage, θ , is shown in Fig. I-9 for sweep gases of pure helium and He- H_2 mixtures.

For example, for the desorption rate of H_2O from LiAlO_2 at 923 K into a helium stream carrying H_2 in the measured concentration range (which is the expected range for a prototype fusion reactor), a steady-state coverage of desorbable H_2O can be derived from Fig. I-9. Calculating the desorption rate requires values for a_B and a_C in Eq. I-1. These may be calculated from:

$$a_i = 1.66 \times 10^{-5} m \sigma_s \theta_i \quad (\text{I-2})$$

Fig. I-9.

Fractional Surface Coverage by H_2O Desorbed from Pretreated LiAlO_2 into He- H_2 Mixture or Pure Helium Sweep Gas during Temperature Increase from 473 to 1073 K

where m is the mass of the breeder in g, σ_s is the specific surface area in m^2/g , and θ_i is the fractional surface coverage by evolvable H_2O on sites of type i . The factor 1.66×10^{-5} was derived from the assumption of 10^{19} sites/ m^2 divided by the Avogadro number, and the last quantity is derived from the curve in Fig. I-9 by allocating portions of the indicated total θ to the B and C sites. The exact relationship between B and C site populations still requires study, but for the present purpose, we assume the ratio of B to C sites as approximately 0.5, since the observed ratios ranged from 0.38 to 0.79. That is, 1/3 of the θ from Fig. I-9 is assigned to the B peak and 2/3 to the C peak. (For desorption into pure helium, the ratio of C to D sites is in the range from 0.24 to 1.18.) The desired rate of desorption follows from substitution

of the θ_i values into Eq. I-2 and then the resulting a_i values into Eq. I-1. Future work will deal with H_2/H_2O desorption processes for another candidate breeder material, Li_2O .

c. Additional Aspects of H_2 Behavior

Several questions related to the role of H_2 in desorption processes require further study. The present measurements make it difficult to determine how much of the protium in the H_2 and $H_2O(g)$ detected in the gas stream after passing the sample originates from previously existing surface OH^- groups, and how much is derived from the input stream. Work with deuterium-loaded samples (but with Li_2O as the sample) and H_2 -containing sweep gas would cast light on this question and also provide a direct isotopic analogue for tritium behavior.

Another question is raised by Fig. I-10, which shows the TPD of H_2 and $H_2O(g)$ into a stream containing 247 vppm H_2 . Neglecting the first 10 min, which involves warmup of the mass spectrometer, H_2O desorption lags behind the onset of H_2 uptake. That is, adsorbed H_2 builds up before H_2O appears. A possible interpretation is that the lag involves surface diffusion of the OH^- formed by adsorption of H_2 to sites that are favorable for subsequent enhancement of the H_2O desorption. There is also the question of the H_2O source, since H_2O peaks are observed repeatedly on the same sample. Possible sources of these small amounts of desorbed material are the residual quantities of dissolved hydroxide and the inevitable ingress, even into a tight system, of traces of H_2O that can be incorporated onto the sample between runs.

Fig. I-10.

Desorption of H_2O and H_2 into He-247 vppm H_2 Sweep Gas from Pretreated $LiAlO_2$. Pretreatment involved exposure to 247 vppm H_2 in He to 20 h.

2. Lithium Vaporization Behavior of Lithium Ceramics
(A. K. Fischer)

Lithium oxide mass loss by entrainment of $LiOH(g)$ in the helium sweep gas (vapor transport) is seen as a possible problem under some conditions of fusion reactor operation. The potential problem is greatest for Li_2O breeder material, principally at high temperatures (>1073 K), and less so for the other candidate breeders ($LiAlO_2$, Li_4SiO_4 , and Li_2ZrO_3).

To assess the need for further experimental work on lithium losses from Li_2O , the existing studies were placed on a common basis for comparison by expressing the individual data points as a ratio relative to what would be predicted thermodynamically for equilibrium at the same conditions of temperature and $\text{H}_2\text{O}(\text{g})$ partial pressure. In Fig. I-11, the data for inert conditions, i.e., without complications from corrosion, are presented in a normalized form.¹⁵⁻¹⁷ The principles of the transpiration technique may be applied to explain the data. According to these principles, the apparent vapor density will be constant over a range of sweep-gas flow rates if equilibrium is established. At low flow rates, mass loss rates higher than at equilibrium will be observed because of the additional contribution of diffusional processes to the lithium loss process. At high flow rates, mass loss rates lower than at equilibrium reflect undersaturation of the sweep gas. One of the sets of data (Ref. 15) in Fig. I-11 reveals a region of undersaturation but also an equilibrium plateau. The flow rate for a fusion reactor design of current interest, the International Thermonuclear Experimental Reactor (ITER), is marked on Fig. I-11. Overall, this plot indicates that flow rates under ITER conditions will be (1) high enough so that diffusional contributions will be negligible and (2) in the range in which one can assume thermodynamic equilibrium conditions. (The other lithium mass loss process, corrosion, follows a parabolic rate law, so that the depth and the duration of the process are limited.) We also concluded that existing studies provide adequate replication for confidence in the thermodynamic analysis, and that further similar studies would not be cost effective.

Fig. I-11

Ratio of Observed-to-Predicted LiOH
Vapor Transport Rates for $\text{Li}_2\text{O}-\text{H}_2\text{O}(\text{g})$ -
 $\text{LiOH}(\text{g})$ System

On the basis of thermodynamic equilibrium, a conservative expression (i.e., tending to overestimate) for the Li_2O mass loss rate from Li_2O was derived from existing thermodynamic data¹⁸

$$\log G = 13.269 + \log V - 2.790 \log T - 9398/T + 0.5 \log p_{\text{H}_2\text{O}(\text{g})} \quad (\text{I-3})$$

where G is the rate of loss (g/day), V is the sweep gas flow rate (cm^3/min) at the temperature of interest, T (in K), and $p_{\text{H}_2\text{O}}$ is the water vapor pressure (atm).

To compare LiOH vaporization loss rates among the different breeders, we calculated the LiOH vapor pressure for a given $\text{H}_2\text{O}(\text{g})$ partial pressure. The recent determination by Wyers et al.¹⁹ of the standard enthalpy of formation for $\text{Li}_2\text{ZrO}_3(\text{c})$ was used to estimate its free energy of formation up to 1273 K. The hydrolytic reaction forming $\text{LiOH}(\text{g})$ was assumed to be

with ZrO_2 as a solute at low concentration in Li_2ZrO_3 . For the remaining ternary oxide breeders, LiAlO_2 and Li_4SiO_4 , the assumptions about their hydrolytic reactions were that $\text{Li}_2\text{SiO}_3(\text{s})$ phase formation occurs in Li_4SiO_4 , and that LiAl_5O_8 solid-solution formation occurs in LiAlO_2 . A single set of operating conditions was selected for a common basis of comparison: a temperature of 923 K and a fixed H_2 partial pressure of 100 Pa. The overall system stoichiometry with respect to oxygen and the metallic elements was set exactly by the composition of the parent compound, which thereby established the oxygen activity. At the present time, activity coefficient data for LiOH as a solute are available only for the Li_2O system, thereby enabling calculations for this system to account of this aspect of nonideality. For the other systems, ideal solution behavior was assumed.

The $\text{LiOH}(\text{g})$ partial pressures calculated on this basis are 2.0×10^{-4} Pa for Li_2O , 2.7×10^{-5} Pa for Li_4SiO_4 , 1.2×10^{-5} Pa for Li_2ZrO_3 , and 1.3×10^{-8} Pa for LiAlO_2 . These results suggest that gaseous entrainment (transport) of LiOH vapor would be greatest for Li_2O and least for LiAlO_2 ; Li_4SiO_4 and Li_2ZrO_3 occupy intermediate positions, but closer to Li_2O than to LiAlO_2 .

3. Tritium Release Studies (J. P. Kopasz and S.-W. Tam)

Tritium inventory in ceramic tritium breeding materials is an important issue for fusion reactor designs. To predict the tritium inventory under different conditions, the tritium release from these materials must be understood. We have investigated the tritium release from LiAlO_2 in an effort to gain an understanding of the mechanisms involved in tritium release from this class of materials.

Lithium aluminate compares favorably with other candidate solid breeder materials in terms of chemical, mechanical, and irradiation properties; however, tritium release from LiAlO_2 is slower than that from Li_2O or Li_2ZrO_3 . We have modified LiAlO_2 (doped with magnesium or coated with platinum) in an attempt to improve its tritium release and to gain a better understanding of the underlying release mechanism. Single crystals of LiAlO_2 , Mg-doped LiAlO_2 , and Pt-coated LiAlO_2 were irradiated (flux of 0.4×10^{14} n/cm²-s for 10 h) to produce tritium, and the tritium release was studied using the TPD method. (Further experimental details given in Refs. 20 and 21.) By comparing the desorption data for the altered materials, we hoped that the rate-limiting steps in tritium release could be identified.

An example of the TPD plots obtained in these experiments is shown in Fig. 1-12. The overlapping peaks indicate that the tritium is released from several states. We investigated the energetics of release from the different states by deconvolution of the observed data into subpeaks. The deconvolution was done using the equation for first-order desorption under conditions of constant-rate heating.²²

Fig. I-12. Temperature Programmed Desorption Plots for Single Crystals (2-mm dia) of (a) Pure LiAlO_2 , (b) Mg-Doped LiAlO_2 , and (c) Pt-Coated LiAlO_2 at Heating Rate of 0.75 K/min. Dashed curves indicate calculated values for individual peaks; dashed horizontal line indicates baseline; solid curve represents total calculated curve; points represent observed data.

For pure LiAlO_2 , the activation energies for the five peaks (Fig. I-12a) were calculated to be 61, 99, 129, 154, and 174 kJ/mol, which are in good agreement with those previously determined by Botter et al.²¹ Roughly 60% of the tritium released was from the peak with an activation energy of 174 kJ/mol.

Doping the lithium aluminate with magnesium changed the activation energies for tritium release slightly and shifted the tritium to peaks with lower activation energies (Fig. I-12b). Deconvolution of the TPD plot for the doped LiAlO_2 gave peaks with activation energies of 47, 95, 113, 156, and 205 kJ/mol. The peaks corresponding to activation energies of 47 and 95 kJ/mol are increased in intensity relative to the low energy peaks for the pure material. In the doped material, these peaks account for roughly 25% of the tritium released, while for the pure material the corresponding peaks account for only 13% of the released tritium. In addition, the activation energy of 95 kJ/mol is in excellent agreement with the value of 99 kJ/mol reported for the desorption of hydrogen from MgO .²³ This suggests that doping LiAlO_2 with magnesium provides low-energy MgO surface sites from which the tritium desorbs.

The TPD plot for LiAlO_2 coated with platinum (Fig. I-12c) showed peaks corresponding to activation energies of 71, 99, 146, and 177 kJ/mol. The platinum coating shifts the tritium release to peaks with lower activation energies relative to that for the pure material. For the coated material, approximately 40% of the tritium was released from peaks with activation energies below 150 kJ/mol, while for the pure material, only 25% was released from peaks with activation energies below this value. The activation energies of 71 and 146 kJ/mol are in good agreement with the energies reported for the desorption of H_2 and H_2O from platinum.^{24,25} The improved tritium release for the platinum-coated material strongly suggests that the rate-controlling step in tritium release from these single-crystal LiAlO_2 samples involves the surface and not bulk diffusion. The platinum sputtered on the surface should not affect the bulk properties such as diffusion. Therefore, if diffusion were rate limiting, the platinum coating should have had no effect on the tritium release.

Based on the results of our TPD studies, we developed a tritium release model which focuses on diffusion and simultaneous desorption from several sites and employed this model to calculate in-pile release from LiAlO_2 . The model contains no adjustable parameters. As input, we used the diffusion coefficient for tritium in LiAlO_2 determined by Bruning et al.²⁶ and desorption coefficients determined by Fischer²⁷ for material of similar characteristics as the material used in an in-pile test (MOZART, Commissariat à l'Energie Atomique, Institut du Recherche Fondamentale). However, because Fischer does not describe the distribution of tritium between the different kinds of sites, we used the distribution determined for the single crystals.²¹ Using these data, which were obtained in laboratory (out-of-pile) experiments, we calculated the expected tritium release for a number of temperature-increase and temperature-decrease tests performed in the MOZART experiment. The agreement between calculated results from our model and the experimentally observed release is quite good. A comparison between our model calculations and the observed data for two temperature transients is shown in Fig. I-13. This level of agreement has not been obtained previously without adjusting some of the input parameters; however, in this case no parameters are changed from the values determined in separate laboratory experiments on LiAlO_2 .

In the future, we plan to acquire information on the tritium distribution within the solid to give us information on the tritium diffusivity. Isothermal anneals will be performed on irradiated samples for preset times. The samples will then be sectioned and analyzed to provide a tritium profile from which diffusivity can be calculated.

Fig. I-13. Calculated and Observed Tritium Release from LiAlO_2 for In-pile Temperature Decreases (MOZART experiment) from (a) 923 to 823 K and (b) 823 to 773 K

D. Support Studies for New Production Reactor

A variety of nuclear materials are used in U.S. nuclear weapons. One of these, tritium, is rare in nature and must be produced in a nuclear reaction to obtain the quantity necessary for manufacturing and maintaining nuclear weapons. Since tritium decays radioactively, weapons production requires a constant and reliable source of tritium. The only practical method for producing large quantities of tritium is to irradiate lithium targets with neutrons in a reactor designed for that purpose. The DOE initiated the New Production Reactor (NPR) Program to plan, design, and construct safe and environmentally acceptable new reactor capacity for an assured supply of tritium. In 1991, CMT provided technical support to this program by performing the following: (1) calculational and experimental studies of fission product

release from fuel and target in a severe accident and (2) design studies of the modifications needed to a hot cell at ANL-West so that irradiated fuel and target tubes can be handled there with minimal tritium contamination.

The objective of the first support study was to develop a thermodynamic model that would predict the behavior of fuel and target in a severe accident of an NPR that is a heavy water reactor (HWR). As part of this study, we examined earlier pertinent literature and conducted preliminary tests in preparation for transpiration measurements with Al-U fuel, Al-Li target, and fission product simulants exposed to flowing helium mixtures at temperatures up to 1673 K.

1. Fission Product Release from Fuels and Targets (P. E. Blackburn)

The literature analysis focused on the behavior of aluminum at high temperatures. In earlier experiments in which solid and liquid aluminum were oxidized by oxygen and water vapor, Blackburn and Gulbransen²⁸ established that a thin oxide layer forms on the surface of the aluminum at temperatures of 773 K or more. Thus, a thin oxide film on the molten aluminum may be a barrier to transport of the gaseous aluminum species in the flowing helium of the transpiration measurements. This oxide film may also act as a barrier to other gases from the fuel, target, and fission products. Blackburn and Gulbransen²⁸ focused on measurement of oxidation rates of electrochemically polished aluminum in helium gas containing oxygen, oxygen plus water vapor, or hydrogen plus water vapor. At 898 K, the oxide layer reached about 200 Å in 15 min in water vapor, after which the growth of the oxide layer slowed to approximately 6 Å per hour. The oxidation is controlled by the diffusion of aluminum or oxygen through the oxide layer.

The oxide layer may also control the release of fission products from NPR-HWR fuel-target mixtures. To understand the fission product release mechanism, the diffusion of aluminum through the oxide layer must be measured. Further, this measurement must be carried out to establish a baseline for subsequent fission-product release measurements. Measurements of oxidation of aluminum alloys containing 3 wt % Li and 2 wt % Mg (Mg should behave like Ba or Sr) produced oxide layers that were 75 times as thick as the oxide layers on pure aluminum.²⁹ This finding suggests that Li, U, and the fission products in the fuel and target will enhance the corrosion rate, and this may, in turn, affect the loss of fission products.

Preliminary transpiration tests were undertaken with an ingot prepared by Savannah River Laboratory. This ingot contained Al, U, Ba, C, Ce, Mo, Sr, and Zr but was not entirely representative of irradiated NPR-HWR fuel. (It contained carbon and oxygen impurities and had an excess in the proportion of cesium and deficiencies in the proportions of Mo and Sr. Further, the zirconium content was low by a factor of 45 relative to the barium content.) In the transpiration experiment, the ingot was heated to 1098 K with no significant loss in weight. No change occurred at 933 K, where aluminum melts. The gas in the system was pure helium until the temperature reached 973 K, where 3% water was added. At 1146 K the sample began to increase in weight. The temperature was held at about 1248 K for 4 h, where the sample oxidized at a decreasing rate with time. The curve for weight change versus time suggested formation of a protective oxide layer, as predicted by our literature study. Additional experimental studies on formation of this oxide layer are needed. However, no further work is planned because of budget termination.

2. Shielded-Cell Modifications to Handle Tritium
(P. A. Finn and J. P. Webb*)

In other NPR-related support work, we developed conceptual designs for modifications needed in the Main Cell of the Hot Fuel Examination Facility (HFEF) at ANL-West if it is to be used for handling irradiated fuel and target materials. The conceptual design minimizes possible tritium contamination by use of a defense-in-depth methodology. In this design (more complete details given in Ref. 30), the HFEF Main Cell would be provided with a primary enclosure and a system that would recover gaseous tritium releases and particulate residue from cutting operations with irradiated targets. The recovery system would employ particulate filters and a catalyst bed that converts tritium to water. The enclosure would be sized to handle the test-vehicle assembly and disassembly operations associated with the irradiation tests and to accommodate the recovery system. Redundant tritium recovery units would be used to minimize maintenance within the HFEF Main Cell. In addition, the HFEF Main Cell purification system would be modified to recover tritium in the event of a failure in the primary enclosure and/or its recovery system. During decommissioning, a secondary enclosure would be constructed around the primary enclosure to prevent contamination and would use the recovery system on the primary enclosure to capture any tritium releases. The tritium atmospheric concentration would be monitored outside the primary and secondary enclosures, outside and inside the HFEF Main Cell, and in the HFEF Main Cell exhaust. Issues that need to be addressed in the future include the training of workers and management in tritium control; the development of appropriate HFEF operating procedures and health physics operating procedures for tritium work; and the development of agreements with Westinghouse Savannah River Site on the required accuracy of tritium measurement and the final disposal site for all waste.

*Argonne National Laboratory, Idaho Falls, ID.

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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 continuing efforts to refine and apply the Generic TRUEX Model (GTM). The GTM is composed of three sections. 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 glovebox, shielded-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 in progress: development of evaporator technology for concentrating radioactive wastes and product streams such as those generated by the TRUEX process, and a solvent extraction process for cleaning up contaminated groundwater.

A. Model Enhancements

The GTM is a computer program that has been developed to (1) act as a tool for designing TRUEX process flowsheets for specific waste stream compositions, process constraints, and process goals, (2) estimate the space and cost requirements for installing a TRUEX process, and (3) act as a guide to process monitoring and control. The GTM is constantly being upgraded and modified to reflect user needs and new data.

1. General Improvements (J. M. Copple)

Two GTM options were upgraded during this report period. The solvent degradation option of the GTM calculates the distribution ratio (D) values for americium at 0.01M and 0.05M HNO_3 after a user-specified number of cycles. A cycle is defined as the TRUEX-NPH solvent making one pass through all the stages of the user-specified flowsheet one time. Results for one cycle are displayed, as well as results for the user-specified number of cycles. In addition, the option that calculates D values for equilibration of user-specified aqueous and organic phases now displays additional information: the final aqueous and organic concentrations.

The Macintosh version of the GTM was tested using two recently released software upgrades: Microsoft Excel 3.0 and Apple Macintosh System 7.0. Also, a modified version of the

GTM was developed to run multiple trials of the GTM without user intervention. The user creates a data file for each trial, and the GTM runs the trials and generates reports automatically for all trials specified. This feature is used to generate data that will be used in sensitivity analysis of the GTM (see Sec. II.E).

2. Development of Loading Module (M. C. Regalbuto)

The "loading module" is a GTM macro written to account for the effects of solvent loading by metal salts on the extraction of species. Because TRUEX is a waste treatment process, the effects of solvent loading will be small in most cases. When the concentrations of rare earth fission products are high, a combination of these species together with iron, uranium, and TRU elements can lead to solvent loading. In these cases, the solvent is not loaded with only one species but a combination of more than ten. Calculating the effect of the solvent loading on the extraction of all components is straightforward but time consuming. A mathematical algorithm was developed to reduce computational time and enhance calculational convergency. In the past few months, the model was enhanced to include more feed components. Furthermore, a new section that does a single-stage material balance for a large number of fission products and actinides has been included. In addition, the convergence problem that occurred when the loading was high (greater than 90%) has been solved.

a. Additional Material Balances

The macro designated Loading_Module was created to quantify the effects of solvent loading by metal salts in the extraction of species. In this case, distribution ratios of the participating species are reduced by a decrease in the concentration of CMPO available for the extraction of the metal species. The original loading module was created after the first version of the GTM was completed. In this version, few user-specified options were available. The second version of the GTM presents a large number of user-specified options, one of them being a one-stage equilibration of a given aqueous and organic solution. In this case, a simple one-stage material balance was done to calculate the composition of the given components in the aqueous and organic phase using the distribution ratios calculated by SASPE and the initial user-specified compositions. Single or multistage material balances are usually done within SASSE. The SASSE worksheet is generated according to the number of components and stages, and this generation of SASSE is time consuming. The loading module does a single-stage material balance for a large number of fission products (rare earths) and actinides. Because the Loading_Module is a macro instead of a worksheet like SASSE, no generation part is needed to create it. This macro is coded in the GTM model; therefore, doing a single-stage material balance is faster. Until recently, the one disadvantage is that the loading module did not include all the components given in the aqueous feed menu. This problem was solved by adding a second part at the end of the Loading_Module that will perform a single-stage material balance for those species given in the aqueous feed menu that did not participate in the loading of the solvent, but could be present in the user-specified equilibration of aqueous and organic solutions (Table II-1).

The equations needed to calculate the material balance are as follows:

$$(O/A) [E]_{org} + [E]_{aq} = (O/A) [E]_{org}'' + [E]_{aq}'' \quad (II-1)$$

and

$$D_E = \frac{[E]_{org}}{[E]_{aq}} \quad (II-2)$$

therefore

$$[E]_{aq} = \frac{(O/A) [E]_{org}^{\circ} + [E]_{aq}^{\circ}}{1 + (O/A) D_E} \quad (II-3)$$

$$[E]_{org} = [E]_{aq} D_E \quad (II-4)$$

where $[E]$ is the concentration of any given component in Table II-1 in either the organic (org) or aqueous phase (aq); $[E]^{\circ}$ is the initial concentration in either the organic or aqueous phase specified by the user; D_E is the distribution ratio calculated with the initial (user-specified) concentration $[E]_{aq}^{\circ}$ by SASPE. Concentrations calculated in the loading module are returned to SASPE, and SASPE calculates a new set of D values for each component. The D values are, in turn, used in the Loading_Module to recalculate concentrations. Calculations iterate between the SASPE and the Loading_Module until the distribution ratio calculated in two consecutive SASPE calculations agrees to less than or equal to 1%. Equations II-1 to -4 were implemented in the second part of the Loading_Module for the components given in Table II-1.

Table II-1. Components Included in the
Material Balance Section
Inside the Loading_Module

Non-Loading Species	
Chromium	Cr
Nickel	Ni
Aluminum	Al
Sodium	Na
Calcium	Ca
Copper	Cu
Magnesium	Mg
Zirconium	Zr
Rubidium	Rb
Cadmium	Cd
Cesium	Cs
Strontium	Sr
Barium	Ba
Rhodium	Rh
Palladium	Pd
Silver	Ag
Ruthenium Nitrosyl	RuNO
Thorium	Th
Nitrate	NO ₃
Fluoride	F
Sulfate	SO ₄
Oxalate	C ₂ O ₄
Phosphate	PO ₄
Pertechnetate	TcO ₄
Boric Acid	B(OH) ₃

b. Convergence Problem

The loading module was designed to be used in cases in which the loading of CMPO was less than 90%. A Newton-Raphson algorithm was developed to calculate the concentration of free CMPO (initial CMPO minus loaded CMPO), as well as the concentration of rare earth fission products, iron, uranium, and TRU elements. Since the Newton-Raphson is an iterative algorithm, it is necessary to give an initial approximation to the solution of the equations that govern the loading module. These equations are steady-state, single-stage material balances for CMPO and all components loaded in the solvent. The initial concentration for all components in the organic and aqueous phases is obtained from SASSE. In the cases in which loading is not too high, these values can be used as first approximations for the Newton-Raphson algorithm. In the case in which loading is high, this approximation is a poor one, especially for CMPO. When loading is high and a poor first approximation is used, the Newton-Raphson algorithm either converges to a negative root or doesn't converge at all. Therefore, it was necessary to change the initial approximation of CMPO when the loading was high.

Since the material balance for all loading components involves CMPO concentration, it is expected that a poor choice for the initial guess for CMPO free will also be a poor guess for the concentration of other components. The following formula was adopted as an initial approximation for CMPO concentration when loading was high:

$$[CMPO]_{initial\ guess} = \frac{0.1 \times [CMPO]_{initial}}{2^k} \quad (II-5)$$

for $k = 0, \dots, 4$

This formula was implemented in the Loading_Module. One-stage tests successfully converge for high solvent loading. The maximum loading value tested was 99.13% using the following concentrations: $[H] = 0.1M$, $[Na] = 3M$, $[UO_2] = 0.2M$, and $[Am] = 0.3M$. Future tests will be done using the GTM for multistage flowsheets.

B. Development of Data Base

The TRUEX process is of interest to DOE for removing transuranic elements from nuclear waste as a means to cut the disposal costs. Waste appropriate for treating by the TRUEX process is temporarily stored in two major nuclear waste sites, Idaho Chemical Processing Plants (ICPP) and the Hanford, WA, site. For waste generated at ICPP, chemical species which have not been considered previously in the GTM are Cd^{2+} , BF_4^- , and $B(OH)_3$. Hanford has waste streams with significant concentrations of PO_4^{3-} , Bi^{3+} , and Cr^{3+} , which also have not been included in the GTM. The solution and extraction chemistry of these species must be characterized in order to enhance the GTM capabilities. The following sections describe distribution ratio measurements of PO_4^{3-} and Cd^{2+} species. Also discussed are measurements of thorium distribution ratios.

1. Distribution Ratio Measurements for Phosphate
(L. Nuñez)

Most of the phosphate-containing species found in the single-shell tanks at Hanford were generated from the $BiPO_4$ process, which separates plutonium from irradiated uranium. In studying the H_3PO_4 extractability, we prepared solutions at various concentrations of either phosphoric

acid alone (0.01-2.5M) or phosphoric acid mixed with nitric acid (0.01-5M), and contacted them with pre-equilibrated TRUEX-NPH at 25°C (organic-to-aqueous phase ratios of 1:1 and 10:1). The extractability of H_3PO_4 was determined by two techniques. The first measures the concentration of phosphoric acid in the organic and aqueous phase by acid-base potentiometric titration. For the second technique, these concentrations are measured with ^{32}P - H_3PO_4 and liquid scintillation counting. In the organic-phase titration of phosphoric-nitric acid solutions, the nitric acid appeared as the first endpoint, and the second endpoint corresponded to the phosphoric acid, as expected, due to the stronger acidity of the nitric acid.

In Fig. II-1, data obtained by potentiometric titrations show the organic-phase concentration of H_3PO_4 plotted against the aqueous-phase concentration of H_3PO_4 to be nonlinear. At low aqueous-phase concentration, the relationship appears linear, but becomes a quadratic equation at higher concentration. This suggests that the extraction of H_3PO_4 has a second-order dependency on the phosphoric acid concentration and that a H_3PO_4 dimer is the extractable species.

In an organic titration, the presence of $\text{H}_6\text{P}_2\text{O}_8$ can create discrepancies in the determination of H_3PO_4 by the methods we originally used. Discrepancies may also be caused by the extraction of H_2O in the organic phase decreasing the volume of the aqueous phase (increasing H_2O concentration after contact). In order to study both points, (1) ^{32}P -labeled H_3PO_4 will be used to measure $D_{\text{H}_3\text{PO}_4}$ as a function of nitric acid and H_3PO_4 , (2) additional work will be performed using potentiometric titrators, and (3) Karl Fisher experiments (quantitative H_2O determination) will be performed to determine the H_2O concentration in $\text{H}_3\text{PO}_4/\text{HNO}_3$ -equilibrated organic phase. Together these experiments should provide the data necessary to derive a chemical model for H_3PO_4 extraction by TRUEX-NPH.

Fig. II-1.

Organic-Phase vs. Aqueous-Phase
Concentration of H_3PO_4 with
TRUEX-NPH Solvent at 25°C

2. Distribution Constant Measurements for Cadmium (L. Nuñez)

Cadmium is added as a neutron absorber (due to its large neutron cross section) to dissolver solutions of naval reactor fuel at ICPP. Early experiments in TRUEX processing have shown cadmium to be poorly extracted by the TRUEX solvent ($D_{\text{Cd}} \leq 0.04$).¹ Because of its high concentration in the PUREX waste from ICPP processing (0.4M), even with a rather low distribution ratio, its concentration in the solvent is likely to be greater than or equal to that of the TRU elements.

The extractability of the Cd^{2+} species by TRUEX-NPH at 25°C was studied using ^{109}Cd ($t_{1/2} = 453$ days). The isotope ^{109}Cd decays by electron capture and consequential gamma emission.

The initial step in understanding the physicochemical properties of the Cd^{2+} was to determine its extractability by TRUEX-NPH vs. changes in aqueous-phase composition. The extraction of Cd^{2+} species was measured as a function of nitric acid concentration in the first set of experiments. The TRUEX-NPH solvent was pre-equilibrated with nitric acid solutions with concentrations of 0.0009 to 4M. The data are presented in Fig. II-2. To a first approximation the numerical data are fitted to a linear equation:

$$D_{\text{Cd}} = 0.0058239 [\text{HNO}_3]^{1.3901} \quad (\text{II-6})$$

In order to derive a thermodynamic model, further studies are necessary. The data must also be expressed in terms of activity of nitrate and hydrogen ions, and complexation equilibrium stability constants for the Cd^{2+} species must be accounted. We will need data collected under conditions of high-nitrate salt, low- HNO_3 concentrations to separate the effects of activities of (NO_3^-) and (H^+) .

Fig. II-2.

Distribution Coefficients for Cadmium as a Function of Nitric Acid Concentrations for TRUEX-NPH Extraction at 25°C

3. Distribution Ratios for Thorium between TRUEX Solvents and Aqueous Solutions (J. Sedlet)

The behavior of neptunium in the TRUEX process is important since the isotope of mass number 237 is a long-lived alpha emitter that is produced in nuclear reactors along with other actinides. Its extraction behavior has been studied earlier (ANL-90/15, pp. 112-123). Although the quadrivalent oxidation state extracts well from nitric acid solutions, similar to Pu(IV), distribution ratios have been variable. A possible explanation is that changes in oxidation state occur during the extraction, and the various oxidation states have widely differing distribution ratios. In this report period, the extraction behavior of thorium was studied as a Np(IV) analog, since thorium exhibits only the quadrivalent oxidation state in aqueous solution.

The most convenient thorium isotope for distribution ratio measurements is ^{230}Th , an alpha emitter with a half-life of 7.8×10^4 yr. The principal difficulty in obtaining accurate D values is

due to the growth of alpha-emitting daughters, since the alpha particle measurement method used, liquid scintillation counting, does not distinguish between the alpha particles emitted by the thorium and by the daughters. Alpha particle spectrometry would be prohibitively expensive for this work.

The ^{230}Th decay scheme (Fig. II-3) shows that once the ^{230}Th is separated completely from its decay products, the in-growth of decay products is relatively slow, since the half-life of ^{226}Ra is long. The rate of growth of ^{226}Ra , the first decay product, is 0.043% per year (for growth periods $\ll$ the half-life of 1600 yr). However, radium gives rise to three short-lived alpha emitters (^{222}Rn , ^{218}Po , and ^{214}Po) and one longer-lived alpha emitter (^{210}Po), whose in-growth is controlled by ^{210}Pb with a 22.3 yr half-life. Thus, the ^{230}Th decay chain contains six alpha emitters, including ^{230}Th . Small amounts of the non-thorium alpha emitters can give apparent distribution ratios that are significantly lower than those for thorium, since thorium extracts very well into TRUEX solvents, and the decay products with II oxidation states (Ra and Po) probably extract very poorly. Polonium also has a IV oxidation state that may extract fairly well. Since distribution ratios obtained in the past have been large but variable, and some of the variations can be explained by the presence of decay products with low distribution ratios, the effect of these decay products as a function of time was calculated with the use of the Bateman equation for successive decays.²

Fig. II-3. The ^{230}Th Decay Scheme

The ^{230}Th starting material (as ThO_2) used earlier¹ was purified from other thorium isotopes by electromagnetic separation about 45 years ago at Oak Ridge National Laboratory (ORNL). A small amount of the two other naturally occurring thorium isotopes remains, and their effect on the distribution ratio measurements will be discussed later. The amounts of ^{226}Ra and ^{210}Pb present in the thorium from ORNL can be calculated from the half-lives. Forty-five years after the thorium was free of all decay products, the ^{226}Ra activity is 1.905% of the thorium, and the ^{210}Po content is 1.39% of the thorium activity if it is assumed that all the ^{222}Rn (a gas) remains in the thorium dioxide product. This is a reasonable assumption since radon diffuses slowly from inorganic compounds, especially if they have been ignited.

Calculated results are given in Table II-2 for the case where the thorium is dissolved to prepare a concentrated ^{230}Th spike solution in nitric acid, and aliquots are used to measure distribution ratios. In Example 1, the ratio for thorium was taken as 2000, a value that has been observed for 0.5M HNO_3 .¹ The distribution ratios for radium and polonium are not known, but if they are assumed to be as shown, the observed ratio will be only 257, since a large share of the alpha emitters remaining in the aqueous phase is due to radium and polonium. Only about 0.05% of the thorium remains in the aqueous phase. If the organic phase from Example 1 is contacted with fresh

0.5M HNO_3 and the same distribution values are assumed, then the calculated distribution ratio increases to 548 (Example 2). This is much lower than the true thorium ratio, and several more reverse extractions are needed before 2000 is reached. The effect will be less pronounced at lower acidities, as well as at higher D values for Ra and Po. If Ra and Po do not extract at all ($D = 0$), the observed ratio is much lower, as shown in Example 3.

Table II-2. Calculated Effect of Alpha-Emitting Decay Products on the Observed Distribution Ratios of ^{230}Th between TRUEX-NPH and Nitric Acid Solutions

Example	D_{Th}	D_{Ra}	D_{Po}	$D_{\text{obs.}}$	
1	2000	0.01	0.1	257	Forward Extr.
2	2000	0.01	0.1	548	Reverse Extr.
3	2000	0	0	30	Forward Extr.

Table II-3 gives some experimental data using the ^{230}Th as received without any purification. These results indicate that, if the differences between the forward and reverse ratios are due to other alpha emitters, their distribution ratios are not as large as shown in Table II-2. This can also be inferred from the small differences between the two reverse extractions.

Table II-3. Distribution Ratios for Thorium between Nitric Acid and TRUEX-NPH at 25°C

$[\text{HNO}_3]$, <u>M</u>	Distribution Ratio		
	Forward Extr.	Reverse Extr. 1	Reverse Extr. 2
0.2	87	379	419
1.0	115	4.9×10^3	6.1×10^3
3.0	120	9.3×10^3	9.3×10^3

If the ^{230}Th is separated from its daughters (by extraction into TRUEX solvent and subsequent scrubbing of the solvent solution with dilute nitric acid) and the distribution ratios are measured shortly thereafter, more accurate results will be obtained. The shorter the elapsed time between separation and measurement (the growth time), the more accurate the results. Table II-4 gives some examples of the effect of short growth times on the distribution ratios. In these calculations, the D values for the daughter products are assumed to be zero.

Table II-4. Calculated Effect of Alpha-Emitting Decay Products on the Observed Distribution Ratios of ^{230}Th between TRUEX-NPH and Nitric Acid at Short Growth Times

Example	D_{Th}	Growth Time	$D_{\text{calc.}}$
1	2,000	1 week	1.99×10^3
2	2,000	1 month	1.56×10^3
3	2,000	2 months	1.27×10^3
5	200	1 week	0.20×10^3
6	20,000	1 week	19.3×10^3
7	20,000	1 month	2.73×10^3
9 ^a	2,000	1 week	1.66×10^3

^aIf ^{224}Ra from ^{228}Th chain is also present at the ORNL specified concentration.

If the ^{230}Th stock solution is purified and the distribution ratios are measured shortly thereafter, the effect of the radon isotopes from the ^{230}Th chain and the impurity ^{232}Th chain should be considered. The radon probably remains in solution since it is quite soluble in organic liquids and fairly soluble in aqueous solutions at room temperature. The results of calculations based on this situation are shown in Table II-5. In this case, the effect of radon is small at low distribution ratios, but increases as the distribution ratio and growth time increase.

Table II-5. Effect of Alpha Growth and Radon Daughter Distribution on Distribution Ratios for ^{230}Th

Example	D_{Th}	D_{dtrs}^a	D_{Rn}	Growth Time	D_{obs}
1	200	0	0	1 week	198
2	200	0	0	1 month	194
3	200	0	0	2 months	189
4	200	0	--	1 week	200
5	200	0	--	1 month	199
6	200	0	--	2 months	198
7	2000	0	--	1 week	1995
8	2000	0	--	1 month	1874

^aWhere dtrs = thorium daughters, except radon.

We concluded that accurate thorium distribution ratios can be obtained with ^{230}Th if thorium daughters are absent or if the daughter concentrations and distribution ratios are known. Samples should be counted over a period of time, about 30 days, to determine if short-lived decay products are present without their long-lived precursors. It is important to know the distribution ratios for radium, radon, and polonium in the ^{230}Th radioactive decay series.

C. Development of Spreadsheet Algorithm for Stagewise Solvent Extraction
(R. A. Leonard, D. B. Chamberlain, J. M. Copple, M. C. Regalbuto, J. A. Dow,*
and S. E. Farley**)

The SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) worksheet was developed for detailed evaluation of proposed TRUEX flowsheets in conjunction with D values calculated by the SASPE worksheet. In addition to establishing that each effluent reaches or exceeds its specified composition, sensitivity analysis using the SASSE worksheet allows one to develop a strategy for process monitoring and control (Sec. II.E). The SASSE worksheet is designed so that it works for any amount of other-phase carryover between the organic (O) and aqueous (A) phases. The calculational algorithm gives the steady-state concentration profile for each feed component without requiring any iterations.

Two Excel macros have been written to improve SASSE. The one macro, SASSE_Generator (formerly SASSE_generate), generates SASSE worksheets for flowsheet calculations. When used independently, the appropriate distribution-ratio values or equations must be supplied by the user. When using the GTM, these ratios are calculated by SASPE. The other macro, Report_Generator, prepares reports from results in the SASSE worksheet in tabular and graphical form.

In the work reported here, new features were added to the SASSE worksheet; simple design rules were developed for the extraction and scrub sections of a solvent extraction process; and, using these design rules, as well as the SASSE worksheet and the GTM, a TRUEX flowsheet was developed for the transuranic wastes at Rocky Flats.

1. New SASSE Features

The SASSE worksheet was revised so that one can specify (1) an extraction efficiency for each stage and (2) a fixed effluent flow rate for either phase at any stage in the SASSE worksheet. In addition, "traps" were set up for certain input quantities so that values which lead to problems (e.g., round-off errors) are replaced by more appropriate values. An overview of the changes is given here.

The fractional extraction efficiency, E_a , was implemented as outlined in Ref. 3. The value of the overall O/A flow ratio for stage i , $\bar{R}_i$, is written in terms of the outgoing liquid flow rates rather than the incoming liquid flow rates. Thus,

$$\bar{R}_i = \frac{q_{o,i} + q_{s,o,i} + R_{a,i} (1 - f_{e,a,i}) q_{a,i}}{q_{a,i} + q_{s,a,i} + R_{o,i} (1 - f_{e,o,i}) q_{o,i}} \quad (\text{II-7})$$

where $f_{e,o,i}$ is the fraction of organic phase leaving stage i that is taken as an effluent, $q_{o,i}$ is all of the organic phase leaving stage i except for the sampling flow, and $q_{s,o,i}$ is the sampling flow of the organic phase from stage i . The symbols with "a" instead of "o" in the subscript are defined similarly except that they apply to the aqueous phase. In addition, $R_{o,i}$ is

* Co-op student from Purdue University.

** Co-op student from University of Evansville.

$$R_{o,i} = \frac{f_{o,i}}{1 - f_{o,i}} \quad (\text{II-8})$$

and $R_{a,i}$ is

$$R_{a,i} = \frac{f_{a,i}}{1 - f_{a,i}} \quad (\text{II-9})$$

where $f_{a,i}$ is the fraction of organic phase in the aqueous phase leaving stage i , and $f_{o,i}$ is the fraction of aqueous phase in the organic phase leaving stage i . In the SASSE worksheet, a row had to be added for E_a , called the "Ea" value there. For the "RQI" value in the SASSE worksheet, the $\bar{R}_i$ form given by Eq. II-7 was used. In addition, several rows were added to the material balance section for each component in the SASSE worksheet so that the effective distribution ratio ($D_{\text{eff},i}$) can be calculated as shown in ANL-92/25, pp. 53-55.

The inclusion of extraction efficiency introduces an iterative calculation into the SASSE worksheet. When the D value for a component is much greater than 1.0 in the scrub section, the worksheet can take many iterations to converge. However, except for the aqueous phase concentrations in the scrub section, the error for all effluent concentrations is less than 1% after 20 iterations. Some aqueous phase concentrations can be off as much as 40% in the scrub section. All other stage-to-stage concentrations appear to be acceptable, including the organic-phase concentrations in the scrub section. A Macintosh IIci with Excel 3.0 takes about 6 s to set up and recalculate the worksheet. Each iteration takes 3.0 s. Thus, it takes about 66 s to recalculate the SASSE worksheet with extraction efficiency less than 1.0 using 20 iterations. If the extraction efficiency is 1.0, no iterations are required, and recalculation time is about 6 s.

Aqueous and organic effluents with fixed flow rates can now be specified for each stage. For stage i , these flows, written as $q_{s,a,i}$ and $q_{s,o,i}$, respectively, were implemented as detailed in ANL-92/25, pp. 55-56. In the SASSE worksheet, two rows, called "QSAI" and "QSOI," were added for the aqueous and organic effluents. These quantities allow the user to specify a small side stream from each stage for each phase. This will be used whenever a continuous stage sample is collected for either phase.

Finally, traps were set for several of the quantities that can be input by the user. In particular, FOI (the fraction of aqueous phase with the organic phase exiting from stage i) and FEOI (the fraction of phase exiting from stage i that is taken as an effluent) should not be less than 1×10^{-9} , even though their appropriate value is zero. Any lesser value creates a problem because of round-off errors. Traps were put in place so that no value less than 1×10^{-9} is allowed for these two inputs.

The above changes now need to be incorporated into the SASSE_Generator macro. When this is done, it will be possible to create the revised SASSE worksheet automatically.

2. Simple Section Rules

Simple section rules are presented here, which can be incorporated into an expert system for intelligent design and automatic control of processes.

a. Intelligent Design and Control of Processes

To integrate expert systems and artificial intelligence into a control scheme for TRUEX processes, we recommend the basic structure for expert systems used at Exxon Chemical Co.⁴ This structure, shown schematically in Fig. II-4, can guide our GTM development in such a way that later incorporation of an expert system should be straightforward. For GTM applications, this basic structure has two forms: one for intelligent process design, the other for intelligent process control. These two forms are discussed briefly here.

Fig. II-4. Basic Structure for an Expert System

The data-base box represents a variety of information. For process design, the data base includes process goals and process constraints, as well as basic data on physical properties. For process control, the data base includes not only process goals and constraints and basic data on physical properties, but also information on past process performance, especially that which is not expected based on the input (feed) parameters. Note the basic data on physical properties will typically be accessed indirectly from the knowledge base and the models and procedures.

In the knowledge base box is the expert information. For process design, the knowledge base includes process rules for design, as well as correlations of basic data. For process control, the knowledge base includes not only process rules for design and data correlations, but also rules for process control. Note the rules will be in an "If...(a constraint or goal is not met for process design, a problem is detected for process control), then...(appropriate action, test, or request for further information), else...(appropriate action)" form. The GTM would be used to develop and check the expert information included here.

The models and procedures box represents quantitative information about how models and procedures work, as well as established procedures for implementing them. For process design, the models and procedures include information such as material and equilibrium calculations about a part of the process. For process control, the models and procedures adds such factors as the rate of response of a process variable based on material balances and residence times in the system. The GTM would be used to develop and check the models and procedures included here. It would be accessed directly for process design once the simpler models and procedures had been used.

The inference engine is where logic is applied. At present, this is the task of the chemist or engineer or process operator. In an intelligent design or automatic control system, this would be the expert system, with the interaction of a chemist or engineer or process operator. Expert

system shells being used include Nexpert and Gensym. Expert systems to sort through the rules are also being written using C, Pascal, SmallTalk, or HyperTalk. For our work to develop the basis for automatic monitoring and controlling of a TRUEX process, we will construct an inference engine to determine the most useful structure for the other three boxes. Not shown in Fig. II-4 is how the output from the inference engine interacts with the process to control it or with the designer to guide the final form for the TRUEX process.

In the control mode, an expert system also needs to have (1) high reliability, (2) the ability to start, shutdown, and restart the process hot or cold, (3) the ability to discard old data, and (4) the ability to recognize failed sensors and take appropriate action. Finally, one needs to show that the use of an expert system will result in a major savings in cost to the process.

b. Extraction Section Rules

For the extraction section of a solvent extraction process, a simple rule for estimating performance is

$$D.F. = E^n = x_f/x_1 \quad (II-10)$$

where D.F. is the decontamination factor, E is the extraction factor, n is the number of stages in the section, x_f is the component concentration in the aqueous feed to the section, and x_1 is the component concentration in the aqueous effluent from the section, that is, from stage 1 of the section. The extraction factor can be written as

$$E = RD \quad (II-11)$$

where D is the distribution ratio for a component, and R is the O/A flow ratio in the section. This model works if D is essentially constant, extraction efficiency is 100%, there is no other-phase carryover, $E \gg 1$, and the component concentration in the organic feed to the section, y_f , is essentially zero.

A more general case, still requiring constant D, 100% extraction efficiency, and no other-phase carryover, is

$$\frac{x_f}{x_1} = D.F. = \sum_{i=0}^n E^i - R \frac{y_f}{x_1} \sum_{i=0}^{n-1} E^i \quad (II-12)$$

Since one can show by algebra that

$$\sum_{i=0}^n E^i = \left(\frac{E^{n+1} - 1}{E - 1} \right) \quad (II-13)$$

and

$$\sum_{i=0}^{n-1} E^i = \left(\frac{E^n - 1}{E - 1} \right) \quad (\text{II-14})$$

An alternative form for Eq. II-12 can be written as

$$\frac{x_f}{x_1} = D.F. = \left(\frac{E^{n+1} - 1}{E - 1} \right) - R \frac{y_f}{x_1} \left(\frac{E^n - 1}{E - 1} \right) \quad (\text{II-15})$$

This equation reduces to Eq. II-10 if (1) $E \gg 1$ and (2) the component concentration in the organic feed to the section, y_f , is essentially zero. When it is possible that E will be 1.0, Eq. II-12 should be used.

When Eq. II-12 is solved for x_1 , the component concentration in the aqueous effluent (raffinate) from the section, the equation becomes

$$x_1 = A_1 x_f + A_2 R y_f \quad (\text{II-16})$$

where

$$A_1 = \frac{1}{\sum_{i=0}^n E^i} \quad (\text{II-17})$$

and

$$A_2 = \frac{\sum_{i=0}^{n-1} E^i}{\sum_{i=0}^n E^i} \quad (\text{II-18})$$

The effect of E and n on coefficients A_1 and A_2 is shown in Figs. II-5 and -6, respectively. This analysis was set up especially to determine the component concentration that one might expect in the aqueous phase leaving the extraction section if one knows the concentration of components in the aqueous and organic phases entering the extraction section as well as the number of stages, the extraction factor, and the O/A flow ratio.

Fig. II-5.

Effect of Extraction Factor and Number of Stages (n) on Coefficient A_1

Fig. II-6.

Effect of Extraction Factor and Number of Stages (n) on Coefficient A_2

c. Scrub Section Rules

For the scrub section of a solvent extraction process where the distribution ratio for a component is about constant, an equation similar to Eq. II-16 is solved for y_n , the component concentration in the organic phase leaving the section:

$$y_n = B_1 y_f + B_2 \frac{x_f}{R} \quad (\text{II-19})$$

where

$$B_1 = \frac{E^n}{\sum_{i=0}^n E^i} \quad (\text{II-20})$$

and

$$B_2 = \frac{E \sum_{i=0}^{n-1} E^i}{\sum_{i=0}^n E^i} \quad (\text{II-21})$$

The effect of E and n on coefficients B_1 and B_2 is shown in Figs. II-7 and -8, respectively. This analysis was set up especially to determine the acid concentration that one might expect from the organic phase leaving the scrub section if one knows the concentration of acid in the aqueous and organic phases entering the scrub section as well as the number of stages, the extraction factor, and the O/A flow ratio.

Fig. II-8.

Effect of Extraction Factor and Number of Stages (n) on Coefficient B_2

Fig. II-7.

Effect of Extraction Factor and Number of Stages (n) on Coefficient B_1

d. Strip Section Rules

For the strip section of a solvent extraction process where the distribution ratio for a component is about constant, the extraction efficiency is 100%, and there is no other-phase carryover, Eq. II-19 for the scrub section can also be used. As with the scrub section, the concentration of the component in the organic phase entering the section, y_f , is usually most important. However, if the extraction factor is very low, the number of stages is large, and the component concentration in the aqueous phase entering the section, x_f , is not zero, then y_f will eventually become important.

If the stripping factor (S.F.) is defined as y_f/y_n , then Eq. II-19 can be rearranged and combined with Eqs. II-20 and -21 to give

$$\frac{y_f}{y_n} = S.F. = \frac{\sum_{i=0}^n E^i}{E^n} - \frac{x_f}{Ry_n} \frac{\sum_{i=0}^{n-1} E^i}{E^{n-1}} \quad (\text{II-22})$$

From Eqs. II-13 and -14, an alternative form for Eq. II-22 can be derived:

$$\frac{y_f}{y_n} = S.F. = \left(\frac{E^{n+1} - 1}{(E - 1)E^n} \right) - \frac{x_f}{Ry_n} \left(\frac{E^n - 1}{(E - 1)E^{n-1}} \right) \quad (\text{II-23})$$

When it is possible that E will be 1.0, Eq. II-22 should be used. Note that if (1) $E \ll 1$ and (2) the component concentration in the aqueous feed to the section, x_f , is essentially zero, Eq. II-23 reduces to

$$S.F. = E^{-n} \quad (\text{II-24})$$

Equation II-24 is a simple rule for estimating the performance of a strip section if the conditions used to derive this equation are met.

3. TRUEX Flowsheet for Rocky Flats Plant

To implement the TRUEX process at the Rocky Flats Plant (RFP), a sensitivity analysis of a base-case flowsheet (Fig. II-9) was done using the GTM. Our goals for this TRUEX process were to (1) keep the concentration of TRU elements (Am, Pu) in the aqueous (DW) raffinate to less than 0.01 nCi/mL, (2) achieve our concentration and recovery goals over the expected range for aqueous (DF) feed concentrations, (3) achieve our concentration and recovery goals with variations in the specified feed rates of up to $\pm 10\%$, (4) address the problems with sending the aqueous (DW) raffinate to a process where HNO_3 is recovered and recycled, (5) identify a solvent cleanup process such that the recycled solvent will be able to keep the concentration of the TRU elements in the DW raffinate at the required low level, (6) recover the americium in the americium product stream with less than 1% of the plutonium, and (7) allow 0.1% or less of the americium to reach the plutonium strip section.

Fig. II-9. Base-Case Flowsheet for RFP Waste

The base-case flowsheet (Fig. II-9) will meet all of these process goals. The alternative process flowsheet (Fig. II-10) will meet all of these process goals, except possibly goals 2 and 3. A key feature of the alternative process is that it is able to concentrate the americium in the americium product effluent by a factor of 50. Because of this, the alternative flowsheet requires 40 process stages, while the base case requires only 32 stages. Further work is needed to optimize the alternative flowsheet and to verify that it meets process goals 2 and 3. Various design techniques developed for each section of these flowsheets are discussed.

a. Extraction Section

For the extraction section of these two flowsheets, the extraction section rules were used for estimating performance. Then two additional stages were added to give the desired robustness to the design. To implement the extraction section rules, Eq. II-16 was used to construct charts giving (1) x_1 and (2) x_1/x_1 as a function of extraction factor and O/A flow ratio for a given component concentration in the organic (y_f) and aqueous (x_f) feeds. For this RFP case, a D_{Am} value of 18 was used, since this is the minimum D_{Am} value expected in this section, as determined by the GTM. The charts showed that the lower limit for x_1 is given by

$$x_{1, \text{ lower limit}} = \frac{y_f}{D} \quad (\text{II-25})$$

when $E \gg 1$ and the number of stages in the extraction section is large enough to make the A_1 term of Eq. II-16 small relative to the A_2 term. This equation can be derived from Eqs. II-16 to -18.

Fig. II-10. Alternative Flowsheet for RFP Waste

b. Scrub Section

For the scrub section of these two flowsheets, the scrub section rules were used for estimating performance with respect to HNO_3 removal. No additional stages were added as the HNO_3 concentration is balanced between too high a value, which would make americium difficult to strip, and too low a value, which would allow too much plutonium in the americium strip effluent. To implement the scrub section rules, Eq. II-19 was used to construct charts giving (1) y_n and (2) y_f/y_n as a function of extraction factor and O/A flow ratio for a given component concentration in the organic (y_f) and aqueous (x_f) feeds. For this RFP case, a D_{HNO_3} value of 0.34 was used, since this represents an average D_{HNO_3} value expected in this section, as determined by the GTM. These charts showed that the lower limit for y_n is given by

$$y_{n, \text{ lower limit}} = Dx_f \quad (\text{II-26})$$

when $E \ll 1$ and the number of stages in the scrub section is large enough to make the B_1 term of Eq. II-19 small relative to the B_2 term. This equation can be derived from Eqs. II-19 to -21.

c. Americium Strip Section

Because (1) the solubility of americium in an oxalic acid solution is low and (2) the americium concentration in the aqueous (DF) feed is relatively high (see Fig. II-9), we considered the need for an americium strip to keep significant amounts of americium from entering the plutonium strip section, where the americium could then precipitate. The $\text{Am}_2(\text{C}_2\text{O}_4)_3$ solubility was assumed to be $1 \times 10^{-6}\text{M}$, about the same as the $\text{La}_2(\text{C}_2\text{O}_4)_3$ solubility given by Lide.⁵ More sophisticated calculations for americium showed that its solubility increases from 1×10^{-6} to $1 \times 10^{-5}\text{M}$ as $[\text{HNO}_3]$ increases from 1×10^{-5} to 0.1M and as $[\text{H}_2\text{C}_2\text{O}_4]$ decreases from 0.5 to 0.01M . Thus, since the americium concentration can be as high as $2.1 \times 10^{-4}\text{M}$ in the DF feed, an americium strip section is clearly needed. The key design criterion for this section was that it recover >99.9% of the americium. With this design, the maximum americium concentration in the plutonium strip section will be about $3 \times 10^{-7}\text{M}$, well below the solubility limit for americium oxalate.

A second design criterion was that the aqueous (EW) effluent from the americium strip section should contain <1% of the plutonium. As a result of this criterion, the $[\text{HNO}_3]$ in the organic feed from the scrub section was kept higher than we otherwise would have done. As a consequence, D_{Pu} is high enough so that >99% of the plutonium is kept in the organic phase in the first americium strip stage.

The strip section rules could not be used here, since their use requires a constant D value for the component being evaluated. In the americium strip, D_{Am} drops sharply as the nitric acid is stripped out. For this more complex situation, we used the GTM to model this section for a variety of process conditions. As a base case, we assumed five strip stages with feed compositions and flow rates close to those shown in the base case flowsheet (Fig. II-9). The design was evaluated with respect to its sensitivity to the flow rates and the nitric acid feed concentrations of the aqueous and organic feed streams and to the number of americium strip stages. Based on the charts generated using the GTM, we arrived at six stages for the americium strip section with the feed concentrations and flow rates shown in Fig. II-9. As before, two additional stages were added to give the desired robustness.

d. Plutonium Strip Section

The key parameter for the design of the plutonium strip and scrub sections was the need to prevent $\text{Pu}(\text{C}_2\text{O}_4)_2$ from precipitating in the first plutonium strip stage. A $\text{Pu}(\text{C}_2\text{O}_4)_2$ model for solubility was developed and used to design the plutonium strip and scrub sections shown in Fig. II-9. The model, which was checked with experimental data⁶ and found to work quite well, shows that solubility increases as the concentration of oxalic acid increases and the concentration of nitric acid decreases. Note that most of the oxalic acid is added to the first plutonium strip stage, as the distribution ratio for oxalic acid is close to 1.0. A plutonium scrub section is added to keep most of the oxalic acid in the plutonium strip effluent with the plutonium.

Because the plutonium strip section had both a strip and a scrub section, the strip section rules could not be used. Instead, the GTM was used to do a sensitivity analysis for the plutonium strip and scrub sections, as we did for the americium strip section. The results showed that only one strip and two scrub stages were needed. For a robust design, four plutonium scrub stages were used. Note that the plutonium scrub stages not only remove more of the Pu and Am, but also minimize the amount of oxalic and nitric acid in the solvent cleanup section.

A problem was discovered when we used the GTM to model the plutonium strip section. If high concentrations of oxalic acid and low concentrations of nitric acid were used as

feeds, the model calculations would not converge. Instead the nitrate activity would become negative, which led to an undefined CMPO-free distribution ratio since the calculation of this value uses the square root of the nitrate activity. To avoid this problem, D-value correlations were generated for oxalic and nitric acid using the GTM. These D values were correlated as a function of oxalic and nitric acid concentrations using the Solver function within the Microsoft Excel worksheet. The correlations were put in the SASSE worksheet and solved independently of the GTM. The SASSE worksheet still would not converge to a steady-state solution. We found that the problem could be solved by including a material balance for NO_3^- in the SASSE worksheet. Previously, the concentrations were calculated for every component in every stage except nitrate. The nitrate concentration was determined by doing a charge balance for the aqueous phase in the stage. This works fine for most cases where the nitrate is either high or the only anion present. However, in our strip solution of high oxalic acid and low nitric acid, the nitrate concentration would oftentimes be a negative number. By including a nitrate mass balance in the SASSE worksheet, we solved this problem.

e. Solvent Cleanup Sections

The four single-stage solvent cleanup sections, shown in Figs. II-9 and -10, were recommended for the RFP TRUEX process based on our experience with solvent cleanup during the New Brunswick Laboratory tests (Sec. II.F).

D. Centrifugal Contactor Development

(R. A. Leonard, D. B. Chamberlain, D. G. Wygmans, J. A. Dow,* S. E. Farley,** and M. J. McElwee***)

The Argonne centrifugal contactor is modified as necessary to work with specific solvent extraction processes. To evaluate processes involving high levels of alpha/beta activity (in a glovebox) and/or high gamma radiation (in a shielded cell facility), contactors have been designed and built for remote handling. To minimize the feed needed for testing solvent extraction flowsheets, a 2-cm contactor (minicontactor) was designed and built. For each new process, solution densities and O/A flow ratios are reviewed, and if necessary, the rotor weirs are modified.

A super high-throughput centrifugal contactor (SHTCC) is now being designed to increase contactor throughput by a factor of 4-8 yet keep the unit safe with respect to nuclear criticality by its geometry. Thus, one contactor line will be able to handle the process throughput that would otherwise have required four to eight lines.

In support of our contactor development efforts, vibrational measurements are made using proximity probes and real-time analyzers. The results are related to rotor design by the use of a vibrational model for rotating systems.

1. Super High-Throughput Centrifugal Contactor

When nuclear criticality considerations are important, e.g., for processing solutions containing plutonium or highly enriched uranium, the rotor diameter for a centrifugal contactor cannot be much greater than 10 cm if each contactor stage is to be criticality-safe-by-geometry. Thus, we are

* Co-op student from Purdue University.

** Co-op student from the University of Evansville.

*** Summer student from the University of Illinois, Champaign/Urbana.

looking at ways to increase contactor throughput without increasing its diameter. If high process throughputs are required (i.e., greater than the 10 L/min of total flow which is typical for a normal 10-cm contactor), such a super-high-throughput centrifugal contactor (SHTCC) could greatly reduce the number of parallel process lines that would be required.

To increase contactor throughput, one can increase the rotational speed, rotor length, and rotor diameter. In the past, two of these factors (length and diameter) have been increased together as the speed was held constant or decreased. These changes were done in such a way that the contactor was always operated below its first critical speed. Now, with the rotor diameter effectively fixed, contactor throughput can be increased by making the rotor longer and, if possible, turning it faster. Using previously developed hydraulic and vibrational models, we are determining appropriate changes to the contactor design as we lengthen the rotor and increase its speed.

In this report, we look at the effect that increasing the rotor length (and, hence, the rotor throughput) has on the rotor design. Then, we look at the effect that increasing rotor speed had on contactor operation. After this, the types of accessories that will be needed with the SHTCC are reviewed. Finally, an annular contactor is proposed as an alternative design for the super high-throughput centrifugal contactor.

a. Rotor Design

A normal contactor rotor has a separating zone with an L/D ratio of about 2.0 and a weir zone with an L/D ratio of about 0.5, so that the overall L/D ratio for the normal rotor is about 2.5. For example, a normal 10-cm rotor has a diameter of 10 cm (4 in.) and an overall length of about 25 cm (10 in.). While super high-throughput contactors up to 16 times their normal L/D ratio have been considered, our current focus is on rotors that are four times their normal length. If we increase the 10-cm rotor by a factor of four, its overall length will increase from 25 cm to 1 m. Since the height of a typical glovebox is about 2 m and space is needed to lift the contact rotor out of the contactor housing, this is probably the longest rotor that should be considered for glovebox operation.

As reported earlier (ANL-92/44, pp. 55-56), when rotor speed and diameter are held constant, the increase in contactor throughput is proportional to the increase in rotor length. To realize this increase in throughput, the weir length and cross-sectional underflow area available for flow must be increased proportionally to the increase in throughput. A normal 10-cm contactor operating at 3600 rpm will have a nominal throughput of 10 L/min (both phases) at any O/A flow ratio. If the underflow area starts at the wall of the separating zone of the rotor and extends outward toward the collector rings in the housing, as planned for the SHTCC, the upper region of the rotor, which contains the underflow, will have a larger diameter than the rest of the rotor. By moving the underflow radially outwards in this way, all of the separating zone is available for separations of the dispersion. This change increases the nominal throughput by 20%, from 10 to 12 L/min. Thus, a rotor will have a nominal throughput of 48 L/min if it is designed in this way and has a length four times that of a normal rotor.

To achieve the increased weir length, we initially considered a trough-on-tube weir. However, because of concerns about the stiffness of the tube and the ability of the liquid to flow through the tubes at the required rate, a new weir design, "the continuous-tube weir," was recently developed. This weir, shown in Fig. II-11, has a continuous tube with a rounded rectangular cross section instead of a trough mounted on a circular tube. This design not only has a greater cross-sectional area available for the effluent to exit the rotor, but also has greater rigidity than the trough-on-tube design. This rigidity could be very important if weir machining is needed after the rotor has been fabricated.

b. Rotor Speed

For a typical contactor, throughput increases as the rotor speed increases. Thus, rotor speed should be as high as possible. To understand how rotor speed will limit the design options for the SHTCC, two factors are considered here. First, a steady bearing on the rotor is considered to allow a rotor to operate above its first natural frequency. Second, the effect of rotor speed on contactor power requirements is considered.

Fig. II-11. Schematic of Continuous Tube Weirs in High-Throughput Contactor

(1) Steady Bearing on Rotor

When designing a contactor to operate above its first natural frequency, f_1 , we assumed that a steady bearing would allow the rotor to pass through f_1 easily. Initial tests of this assumption were encouraging (ANL-92/44, pp. 55-67). In operating above the first natural frequency, the motor/rotor system must be at least 20% above f_1 but at least 20% below the second natural frequency, f_2 . Banging of the rotor on the contactor housing is expected only when it is operating within $\pm 20\%$ of a natural frequency. For this design, we assumed that a steady bearing (also called a limit bearing), either a solid bushing (a sleeve bearing) at the side of the rotor or a pin at the bottom of the rotor, will limit the extent of vibrations as the motor/rotor assembly passes through f_1 in such a way that damage to the bearing and the rotor is minimal or nonexistent. In addition, we assumed that the bearing does not generate so much friction that the motor/rotor assembly cannot pass through f_1 on its way to the operating speed between f_1 and f_2 .

Using the test stand for long 4-cm rotors described earlier (ANL-92/44, p. 60), we tested Rotor II, a hollow rotor with an L/D of 13 and a first natural frequency of

9.0 Hz (538 rpm), to evaluate the effectiveness of various steady bearings in getting the rotor through its first critical speed. Although the 4-cm rotor is used in these tests, we hope to discover general principles that will apply to all contactors. In these tests, the gaps between the bearing surface and the rotor were 0.03, 0.25, and 0.76 mm (1, 10, and 30 mils). The gap was measured when the bearing and rotor were concentric. One material was used for the pin bearings, 304 stainless steel. Three materials were used for the solid bushing, 304 stainless steel, Hastelloy C-276, and Teflon tetrafluoroethylene (TFE). The solid bushing was located either at the very top of the rotor (see Fig. II-12) or 50.8 mm (2 in.) below the top of the rotor. The top of the rotor was 76.2 mm (3 in.) below the face of the motor. Because the rotor had the runout shown in Fig. II-13, the effective gap for a well-centered rotor was actually 0.25 to 0.30 mm (10 to 12 mils) less than that based on a concentric gap. (The "runout" is the difference between the maximum and minimum distance to a fixed reference point beside the rotor as it is turned by hand.) The runout of the motor shaft to which the rotor shaft was attached was measured and found to be small, 0.05 mm (2 mils). Except as noted below, all tests were undertaken without any water between the spinning rotor and the stationary housing.

Fig. II-12. Position of Steady Bearing to the Rotor on the Bearing Test Stand

Because the motor was not face mounted, we had difficulty aligning the rotor with respect to the housing. To obtain good alignment, Post-It Notes with the thickness of the effective rotor/bearing gap were stuck onto the rotor at the point with the closest approach to the bearing surface. Then, the bearing was positioned so that the Post-It Notes just touched the bearing surface everywhere as the rotor was turned 360° by hand. With the rotor aligned, the rotor was tested with each bearing at several operating speeds, f , such that the ratio f/f_1 was as follows: 1.2, 1.4, 1.7, 2.0, 3.0, 4.0, and 4.5. Rotor performance was noted on startup, at the operating speed for two minutes, and on shutdown.

Results were not satisfactory for the steady bearings that were in constant contact with the rotor because of rotor runout. This was true for both the pin bearings at the bottom of the rotor and the sleeve bearings near the top of the rotor with the 0.03- and 0.25-mm (1 and 10 mils) gaps. Besides the scraping, vibrations, banging, and other noises noted, significant

Fig. II-13. Runout as a Function of Length for Rotor II

bearing wear was observed, even over a period of only a few minutes. This was especially true for the Teflon TFE bearings.

In contrast, results were very encouraging for the steady bearings that were not in constant contact with the rotor because of rotor runout, that is, the sleeve bearings near the top of the rotor with the 0.76-mm (30-mil) gap and with a rotor runout of only 0.25 to 0.30 mm (10 to 12 mils). For these cases, both startup and operation at the running speed (for 1 to 2 min) were smooth, without any apparent banging of the rotor on the bearing. Operation was slightly noisy (light vibrations) when the ratio of the running speed to f_1 was below 2.0. On motor shutdown, the rotor was found to have banged from 1 to 6 times on the rotor housing; typically 3 to 4 bangs were noted. This banging is thought to be the result of the long time that it takes the motor/rotor assembly to stop, typically 3 to 5 s before the banging occurs, relative to startup times that are less than 1 s. Thus, the rotor spends a relatively long time near f_1 during shutdown, and thus has an opportunity to bang. If this hypothesis is correct, the banging might be eliminated by the use of a brake to stop the motor just before f_1 .

We found that the rotor banging sounds are softer when Teflon TFE is the bearing material. In some tests, enough water was added to the gap between the rotor and the housing to cover the bottom four inches (10 cm) of the rotor. This did not change any results; however, when the rotor speed was changed, temporary increases in the rotor noise seemed to die away more rapidly.

(2) Contactor Power

As reported earlier (ANL-92/44, pp. 55-56), contactor throughput is proportional to rotor speed. Thus, when a rotor whose length is four times that of a normal rotor has its speed increased from 3600 to 7200 rpm, its nominal throughput will increase from 48 to 96 L/min. If we are already above the first natural frequency, this additional increase in speed should not be difficult to accommodate. However, the design of the mixing zone, specifically the power requirements of the mixing zone, becomes a problem. When a 10-cm contactor with rotor length four times normal is operating at 3600 rpm with a nominal throughput of 48 L/min, the power required for the

mixing zone is 1.02 kW (1.37 hp). The temperature rise of the liquid going through a contactor stage would be 0.31°C based on all liquid having the heat capacity of water. For this 10-cm contactor, the electrical power requirements increase as the rotor speed to the 4.3 ± 0.5 power. At 7200 rpm, the power required would be 27.2 kW (36.5 hp) and the temperature rise would be 3.8°C/stage. At 5400 rpm, which would increase throughput by 50% (to 72 L/min), the power required would be 4.8 kW (6.4 hp) and the temperature rise would be 0.96°C/stage. Thus, operation much above 3600 rpm is undesirable because of the sharp increase in the power required for each stage. In addition, fluid heating would become significant for a typical multistage process.

c. Accessory Equipment

Besides the contactor housing and rotor, accessory equipment is needed to use the contactor. Items discussed here are reviewed with respect to their application to the SHTCC.

(1) Speed Control

Because we will be operating the SHTCC above the first natural frequency, it may be necessary to control the operating speed of the contactor rotor. This can be accomplished by varying the frequency of the electrical current to the contactor motor. We have done this in the past by placing a Cleveland speed variator between a motor and a generator. Variable frequency drives are now available as relatively inexpensive electronic units. Information has been requested on four such variable frequency drives. We will review this literature to determine if any units will supply the range of outputs required for the SHTCC.

(2) Pumps

In testing the SHTCC, the aqueous and organic feeds will enter at flow rates from 1 to 100 L/min. In the past, such flow rates have been obtained and controlled by using a centrifugal pump in conjunction with a ball valve and a rotameter. Now that metering pumps are being developed for high flow rates, we are considering the use of one or more metering pumps so that this entire flow range can be handled with pumping errors of only 1 to 3%. With such pumps, we would be able to (1) set the desired flow rate for both phases at the start of a test and (2) use the system as a test bed for evaluating various flow-measuring and flow-controlling devices. For low flow rates, gear pumps are available for metering flows from Micropump Corp. (Concord, CA). Our tests have shown that the Micropump pump head (Model 221-56C), which has a maximum throughput of 10 L/min, is accurate to within $\pm 1.5\%$ of its maximum flow rate.

For flow rates from 10 to 100 L/min, several manufacturers of metering pumps were identified, but no pump was tested. For good metering, it appears that one should use either a gear pump or a progressive cavity pump. The progressive cavity pump is available as an Allweiler pump from Shanley Pump (Rolling Meadows, IL) or as Bran+Luebbe metering pump from Bran+Luebbe (Buffalo Grove, IL). An internal gear pump is available from Viking Pump, Inc. (Cedar Rapids, IA). The progressive cavity pumps appear to be more accurate, while the Viking pump appears to be less expensive and sturdier in construction.

(3) Power Transmission

In current rotor designs, the mechanical power is transmitted to the contactor rotor by its direct connection to the motor. The motor bearings are thus used to hold the contactor rotor in place. In future designs for the SHTCC, it may be desirable to have the rotor held in place by external bearings on the rotor shaft. In such a configuration, the lower bearing is called

the "thrust bearing," and the upper bearing is called the "steady bearing." For this design, the power transmission from the motor to the rotor shaft can be done with the motor above the rotor shaft via a flexible coupling or with the motor mounted beside the rotor shaft via a belt, chain, or gears. The final choice will depend on the details of the SHTCC design.

(4) External Bearings

As mentioned above, the bearings that hold the contactor rotor in place are either external bearings on the rotor shaft or motor bearings which are directly coupled to the contactor rotor by a very stiff coupling.

If external bearings are placed on the shaft of the SHTCC rotor, the lower bearing will have to carry the thrust (axial) load produced by the weight of the rotor. Although the design (and, hence, the weight) of the rotor has yet to be determined, a preliminary estimate is that the rotor will weigh about 22.7 kg (50 lb). To be conservative, a rotor weight of 45.4 kg (100 lb) was used for design calculations. Other bearing specifications should include an ability to operate at a speed of 3600 rpm and to accommodate an inside diameter of 41.3 mm (1.625 in.). Our present plan is to disconnect the rotor from the shaft below the external rotor-shaft bearings. If this is done, the rotor can be withdrawn from the contactor housing into the space that was formerly occupied by the shaft bearings.

For these design criteria for the external rotor-shaft bearing, we found two bearing companies that appear to have suitable bearings, the Sealmaster Bearing Co. (Louisville, KY) and the Dodge Bearing Co. (Greenville, SC). Both companies make bearings that are (1) grease lubricated, (2) sealed with grease fittings for easy maintenance, (3) pre-mounted in a variety of flanges, and (4) secured to bearings with set screws or eccentric rings. Good technical support is available from both companies. They both have bearings that are capable of carrying greater than 250 lb_f (1.1 kN) thrust loads at speeds up to 5000 rpm.

The bearings in the motor driving the contactor rotor can be used if they are capable of carrying the thrust load generated by the weight of the rotor. The motors of the Baldor Electric Motor Co. (Fort Smith, AR) produced motors ruggedly constructed for industrial use. The motors available in the range of interest, 0.746 to 3.73 kW (1 to 5 hp), have a maximum thrust load well above expected for the SHTCC rotor. Thus, if external shaft bearings are not needed, a face-mounted Baldor motor could be used.

2. Annular Contactor

The special weirs and the operation of the SHTCC above the first natural frequency have not been tested. If they do not work or if they prove very expensive to build, an annular contactor design may be appropriate. In the annular contactor design, a neutron absorber would be placed inside the rotor annulus in such a way that the unit could be made criticality safe by design. In this design, the center opening of the rotor would be made very large to accommodate the neutron absorber. The separating zone of the rotor would be an annular region only a few inches in thickness. Because of the large size of the rotor, much greater than 10 cm in diameter, it might be possible to use normal rotor weirs. In addition, it might be possible to operate the rotor below its first natural frequency. These features would eliminate the two problems expected for the SHTCC (i.e., lack of design data for the tube weirs and operation above the first natural frequency). However, the annular contactor would require more processing space than an SHTCC operating above its first natural frequency.

E. Monitoring and Controlling of TRUEX Processes
(M. C. Regalbuto)

A TRUEX flowsheet designed for a specific application must be optimized for obtaining process goals and "robustness." A robust flowsheet is one that will continue to meet processing goals with wide variations in feed compositions and flow rate. As part of an effort to develop a monitoring and control system for the TRUEX process, we have employed the GTM to determine the effect of perturbations in feed compositions and flow rates with regard to meeting the process goals for a typical nuclear waste generated at the Plutonium Finishing Plant operated by Westinghouse Hanford Co. Figure II-14 gives the base-case TRUEX flowsheet developed for this waste with the GTM. The goals set for processing this waste are as follows: ≤ 10 nCi/mL TRU concentration in the raffinate from the extraction section, < 0.3 mol % americium in effluent from the second strip, < 1.1 mol % plutonium in the effluent from the first strip, and $< 0.01\%$ TRU lost in the organic flow exiting the second strip.

Fig. II-14. Flowsheet for Tests with Synthetic Plutonium Finishing Plant Waste.
(Parenthetical entries indicate stream flow rates in mL/min.)

In the sensitivity analysis using the GTM, we determined the effect of varying the flow rates and compositions with respect to the base case for the organic extraction feed (DX), the aqueous extraction feed (DF), the aqueous scrub feed (DS), and the aqueous feeds for the first strip (EF) and the second strip (FF). We were particularly concerned with determining when a perturbation in a feed composition or flow rate led to a process goal or goals not being met.

Of all the perturbations analyzed, only one of them, a change in the flow rate for the aqueous extraction feed, resulted in the most important process goal (a TRU concentration in the raffinate of ≤ 10 nCi/mL) being exceeded. But even in this case, the flow rate could be up to four times greater than its base value of 400 mL/min without exceeding the process goals.

The tightest bounds obtained were in the cases of (1) the organic-feed flow rate and (2) the concentration of HNO_3 in the aqueous feed to the scrub and the first strip. For these cases, the upper value could not exceed 1% and 2%, respectively, of the base value before the americium mole percent in the second strip exceeded the process goal of less than 0.3 mol %. The base-case flowsheet can be redesigned to increase the operating range of these two parameters. This can be accomplished by adding more stages in the first strip so that less americium is lost to the second strip. But adding more stages to the first strip causes not only more americium to be stripped, but also more plutonium to be lost in the americium product. To avoid this, one must increase the HNO_3 concentration in the organic solvent that enters the first stage of the americium strip. This can be achieved by increasing the HNO_3 concentration in the scrub feed. Increasing the HNO_3 concentration in this organic solvent increases the distribution ratio for plutonium. For example, the distribution ratio for plutonium in the first stage of the first strip increases from 120 to ~ 200 if the HNO_3 concentration in the scrub feed is increased from 0.04 to 0.5M. A plutonium distribution ratio of 200 will produce a loss of plutonium in the americium product stream of only 0.53 mol %. Since the maximum loss of plutonium in the americium strip was set as 1.1 mol %, an HNO_3 concentration of 0.5M in the scrub feed will permit changes in the scrub acid concentration significantly larger than the 0.04M of the first flowsheet.

With the increased acid concentration in the organic solvent entering the first strip, the distribution ratios of americium also increased for the first two stripping stages. As a result, two stages must be added to the first strip to compensate for the lost stages. Since the scrub and americium feeds now have different HNO_3 concentrations, it is not possible to use the same storage tank for both feeds. This is a trade-off that needs to be made in order to obtain a more robust flowsheet.

Figure II-15 shows the new flowsheet with (1) 0.5M HNO_3 feed to the scrub section and (2) two more stages in the first strip section. Note that the feeds to the scrub and the americium strip are now independent. Increasing the HNO_3 concentration in the scrub and adding two more stages made the flowsheet less sensitive to a perturbation in organic-feed flow rate. The range in which the process goals still hold as the organic flow rate is changed was expanded from between -7% and +1% (old flowsheet) to between -24% and +10% (new flowsheet) of the base organic flow rate. With the new flowsheet, the goal that restricts a decrease in the organic flow rate is the mole percent of the plutonium in the first strip; also, the allowable increase in this flow rate is almost equally restricted by the other two goals.

Another feature of the new flowsheet is that independent changes in the HNO_3 concentration are possible for the feeds to the scrub and first strip. With the old flowsheet, the scrub and the first strip had the same HNO_3 concentration in their feed. As a result, when the HNO_3 concentration was perturbed for the scrub and first strip, the HNO_3 concentration could be decreased by 57% but could only be increased by 2% and still meet process goals. With the new flowsheet, the HNO_3 concentration could be decreased by 99.8% or increased by 187% in the scrub and decreased by 75% or increased by 19.3% in the first strip and still meet process goals. Thus, maintaining the HNO_3 concentration in the scrub feed at 0.5M will allow wide variation in the extraction section (HNO_3 concentration in the extraction feed and flow rates for both the aqueous and organic feed) without disrupting the operation of the first strip.

Fig. II-15. New Flowsheet for Tests with Synthetic PFP Waste. (Parenthetical entries indicate stream flow rates in mL/min.)

The above results illustrate how sensitivity analysis can be used early in the design stage to develop a robust TRUEX flowsheet.

F. Processing of Plutonium Waste Solution

(D. B. Chamberlain, J. A. Dow, D. R. Fredrickson, J. C. Hutter, R. A. Leonard, J. Sedlet, E. H. Van Deventer, D. G. Wygmans, and G. F. Vandegrift)

Analytical residue solutions from plutonium analysis have been accumulating over the past several years at the New Brunswick Laboratory (NBL) and Argonne National Laboratory (ANL). These residues contain varying concentrations of nitric, sulfuric, phosphoric, and hydrochloric acids, as well as U, Pu, Np, and Am. Originally these wastes were destined for shipment to Idaho and eventual disposal at the Waste Isolation Pilot Plant (WIPP). Now, it appears that no place will accept them. In this project, the TRUEX process will be used to convert the bulk of this waste into a nonTRU (i.e., low-level) waste by removing the TRU elements to levels of less than 0.1 nCi/g. After processing, the nonTRU waste stream will be transported to the Plant Facilities and Services-Waste Management Operations (PFS-WMO) at ANL for final disposal. The recovered plutonium will be converted into solid PuO_2 for return to NBL for storage and subsequent transport to the DOE defense complex.

Approximately 200 L of the mixed waste generated by NBL and ANL will be converted into a nonTRU waste using the TRUEX process. This demonstration will show the applicability of this process to the much larger volume of similar wastes being generated at Rocky Flats Plant, Los Alamos National Laboratory, and the Hanford site and will act as a basis for looking at this process as a future waste treatment process at ANL/NBL. These demonstrations are also means of validating the predictions of the GTM and improving these predictions in the future.

The bulk of the waste that will be processed is being stored by WMO. These wastes will be transported to the CMT for processing. Because of the fissile-material limits in CMT, transfers and subsequent processing will be completed in six to eight batches, with each batch containing a maximum of 50 g of fissile material. Since the composition of each batch differs, each flowsheet will be modified (e.g., stages in each section, feed-stream flow rates) to optimize the process for each batch. Flowsheets will be developed based upon calculations generated by the GTM and a small number of test-tube experiments.

A simplified flowsheet for processing the plutonium-containing waste solutions is shown in Fig. II-16. The TRUEX solvent extraction process will be completed in a 20-stage centrifugal contactor installed in a glovebox. The organic solvent that will be used in this process consists of 1.4M TBP and 0.75M CMPO in dodecane diluent.

Fig. II-16. General Flowsheet for Processing NBL Plutonium Waste Solutions

The bulk of the solution generated by this program will be the nonTRU waste stream that will be transferred to WMO for disposal. Prior to transferring this waste, it will be neutralized so that WMO can feed it directly into their evaporator. The americium product stream shown in Fig. II-16 will be saved for use in ongoing laboratory experiments in CMT.

The plutonium product stream will be evaporated to dryness, then converted to an oxide by calcining in an oven at $>600^{\circ}\text{C}$. A glovebox is available for the concentration, precipitation, and

conversion steps. The product from the calcining operation, PuO_2 , will then be reduced to the metal in another CMT facility, then returned to NBL for storage and shipment to Idaho.

A solvent wash stream is also generated by the TRUEX process. Based upon processing the first 12 g of plutonium, this stream will be a TRU waste, meaning that WMO cannot handle or accept this solution for disposal. Therefore, this stream will be acidified and recycled into the TRUEX process.

1. Reprocessing of Raffinate from TRUEX Processing of Batch 1 Waste

a. Background

Efforts over the past several months have been directed toward reprocessing the nonTRU raffinate that was generated during the processing of the first batch of plutonium waste solution (ANL-92/44, pp. 83-90). Although this nonTRU raffinate contained a TRU concentration of significantly less than 100 nCi/g (making it "nonTRU"), WMO changed its waste acceptance criteria, requiring that the waste be less than 0.1 nCi/g and be neutralized. With this type of solution, WMO will be able to process this waste in their evaporator.

Several attempts were made to reprocess this solution in a 20-stage, 4-cm centrifugal contactor installed in a glovebox, but a product <0.1 nCi/mL could not be attained. Two main reasons for this difficulty are apparent. First, the feed tank, pumps, lines, and contactor were contaminated during the initial waste processing and during some of the subsequent reprocessing attempts. Since the activity in this waste stream is very close to background, any contamination has a great influence on its activity.

Second, flowsheets were designed to generate as little additional waste as possible. This means that three key sections of a typical flowsheet were eliminated--the scrub, americium strip, and plutonium strip. These flowsheets rely on two stages of carbonate wash to accomplish all of the work that these other sections normally accomplish, plus the cleaning of the organic phase. Because these carbonate wash stages are so important, their composition was modified by adding KOH to react with the nitric acid extracted into the organic phase in the extraction section. The Na_2CO_3 normally used was replaced with K_2CO_3 because K_2CO_3 and KHCO_3 have increased solubilities over those of NaCO_3 and NaHCO_3 . Unfortunately, a stable process was not maintained with this system; process upsets meant that the system was shut down before all of the waste was processed. Design and testing of an improved TRUEX flowsheet was, therefore, completed.

b. Flowsheet

The improved flowsheet for processing the DW raffinate is shown in Fig. II-17. For this test, stages 1-4 were used as the extraction section. Two scrub stages (0.05M HNO_3) were added to the flowsheet to help strip nitric acid from the organic phase. Stages 7 through 18 were bypassed by running a long overflow line on the organic side from stages 6 to 19. The last two stages were the carbonate washes; the composition of the last wash was changed to 0.5M KOH-0.5M K_2CO_3 to help reduce the amount of KOH dispersed in the organic phase leaving this stage. An acid rinse was also included by adding about 600 mL of 6M HNO_3 to the organic feed tank. The organic return line from stage 20 was then inserted to the bottom of the feed tank, which allowed the organic phase to bubble up through the aqueous phase. Before the KOH concentration had been reduced in the last stage and the acid rinse, added foam appeared in the extraction section. We hypothesized that this foam was the KOH reacting with the acidic feed solution.

Fig. II-17. Flowsheet for Processing the DW Raffinate from Batch 1

Flow rates were also reduced to help decrease the potential for other-phase carryover. Filters were installed in-line on three of the process streams to help prevent solids from interfering with the process. On the organic feed line, two filters were installed, a five-micron followed by a one-micron filter. On the DW raffinate transfer line to the hood, a one-micron filter was installed. On the DF feed line to stage 4, a five-micron filter was installed.

c. Run Results

On April 25, 1991, 10 L of solution from the DW raffinate of the first batch was processed in about 2 h. Foam, present during previous attempts to process this solution, was not seen for this test. This indicates that the improvements made for this trial (namely, dilution of the scrub solution, change in carbonate wash solution in stage 20, addition of the acid rinse to the organic feed tank, and decreasing of the flow rates) were successful. The high other-phase carryover observed in previous tests was also eliminated. The system was restarted the next morning, April 26, and operated for 7 h. Again, no problems were observed.

Samples of the various product streams were collected during the test to monitor the system's operation. After two hours of operation, the raffinate samples averaged about 45 cpm/200 μ L, which is very close to our goal of 44 cpm/200 μ L. Results of this analysis are shown in Fig. II-18. Duplicates were collected and counted; both are shown in Fig. II-18. The horizontal line represents our process goal of 44 cpm/200 μ L.

As shown in this figure, initial solution activities were greater than our goal, but the counts continued to drop through the first 2.5 h of the test. This increased activity is probably due to the high activity level of the organic phase at the beginning of the test. Scintillation counting results from selected samples are reported in Table II-6. As shown, the organic phase activity at the beginning of the test was much larger than during later stages. Therefore, during the initial stages of this run, we were cleaning up the organic solvent at the same time we were trying to generate a good DW product stream.

Fig. II-18. Plot of DW Raffinate Samples Collected while Processing Raffinate from Batch 1

During the last couple of hours of the test, the activity of the DW raffinate appeared to be increasing slightly (Fig. II-18). This is probably due to the increased activity of the carbonate wash and acid rinse solutions. Increased activity in these solutions would lead to an increase in the organic-phase activity. Since the organic phase is recycled, this would lead to an increase in the activity in the DW raffinate.

One questionable counting result is that for the initial DF feed sample listed in Table II-6. This number appears to be about half of the other two sample results. The difference may be due to a volume error when a sample aliquot was taken or due to a nonrepresentative sample being collected.

Table II-6. Scintillation Counting Results

Stream/Time	Counts, cpm/200 μ L		
	Initial ^a 4/25/91	11:30AM 4/26/91	1:00PM 4/26/91
DF Feed	774 ^b	1,640	1,500
Organic Feed	3950	87	168
Carbonate Wash 1	3685	23,200	37,000
Carbonate Wash 2	clean	3,260	5,540
Acid Rinse	clean	573	378

^aThese were initial counts at beginning of test.

^bMay be due to sampling error.

2. Acidified Carbonate Waste Processing

a. Background

Approximately 50 L of waste solution was generated from (1) processing of the first 12 g of plutonium (Batch 1), (2) centrifugal contactor decontamination efforts, and (3) reprocessing of the Batch 1 raffinate. To treat this solution using the TRUEX process, nitric acid was added to completely neutralize the carbonate present and to make the final solution approximately 1M in nitric acid. Oxalic acid was also added to the waste solution to help prevent the formation of plutonium polymers; the final oxalic acid concentration was 0.1M. After acidification, the solution volume was approximately 80 L.

b. Flowsheet

The base-case design, shown in Fig. II-19, was based on results from previous flowsheet designs and was used as a starting point for the sensitivity analysis and optimization. This flowsheet design is unique because 1M $\text{Al}(\text{NO}_3)_3$ and dilute nitric acid are introduced as an acid scrub in the americium strip section. The aluminum was added at this location to (1) enhance the D values for the extraction of both plutonium and americium and (2) scrub oxalic acid from the solvent exiting the extraction feed stage. As in previous designs, the americium product stream was drawn off the americium strip section at the location where the americium concentration was found to be a maximum.

Fig. II-19. Final Flowsheet for Reprocessing Acidified Carbonate Waste

Because ammonium oxalate was used to strip plutonium, only the extraction, scrub, and americium strip sections of the flowsheet could be simulated by the GTM. As shown in Table II-7, a slight increase in the scrub-feed flow rate slightly decreases the americium recovery. This is due to increased concentration of nitric acid in the solvent entering the americium strip section, which was caused by the increase in $\text{Al}(\text{NO}_3)_3$ in the scrub. This, in turn, increases americium D values in the americium strip section, decreasing the effectiveness of the strip. The plutonium recovery remains unchanged. Also, decreasing the scrub flow rate reduces the plutonium recovery because of the lower D values due to the lower concentration of nitric acid and higher concentrations of oxalic acid in the solvent entering the americium strip section; plutonium is lost to the americium product stream. In this situation, the americium recovery is enhanced slightly because americium D values are also decreased in the first strip.

Table II-7. Sensitivity Analysis for Acidified Carbonate Reprocessing

Simulation Description	Percent Am Recovery	Percent Pu Recovery	DW Raffinate Activity, nCi/mL
Base Case, Am Strip Raffinate			
3 mL/min	90.29	99.73	1.01E-07
Al Scrub Flow Increased to 52.4 mL/min	90.00	99.73	9.70E-08
Al Scrub Flow Decreased to 42.4 mL/min	90.61	99.67	1.06E-07
[Al] in Scrub Increased to 1.2M	85.57	99.80	6.66E-08
[Al] in Scrub Decreased to 0.08M	93.05	99.53	1.60E-07
TRUEX Flow Increased to 55 mL/min	79.01	99.81	6.23E-08
TRUEX Flow Decreased to 45 mL/min	95.02	99.66	1.77E-07
Feed Flow Increased to 110 mL/min	90.21	99.70	1.49E-07
Feed Flow Decreased to 90 mL/min	90.39	99.70	6.74E-08
Am Strip Flow Increased to 55 mL/min	94.51	99.67	1.21E-07
Am Strip Flow Decreased to 45 mL/min	77.06	99.87	8.48E-08
[HNO ₃] in Strip Increased to 0.05M	71.71	99.80	1.02E-07
[HNO ₃] in Strip Decreased to 0.03M	97.85	99.53	1.01E-07
[HNO ₃] in Strip Decreased to 0.02M	99.37	99.20	1.00E-07
[HNO ₃] in Strip Decreased to 0.01M	99.49	97.20	9.95E-08
[HNO ₃] in Scrub Increased to 0.12M	89.76	99.73	1.03E-07
[HNO ₃] in Scrub Decreased to 0.08M	90.79	99.73	9.99E-08

By increasing the $\text{Al}(\text{NO}_3)_3$ concentration, plutonium recovery is increased and americium recovery is reduced. Americium recovery is reduced for the same reason as described above--increased HNO_3 in the organic phase entering the americium strip section. Thus, while the higher $\text{Al}(\text{NO}_3)_3$ concentration increases the quality of the extraction section raffinate, it decreases both the americium- and the plutonium-product quality. Decreasing the $\text{Al}(\text{NO}_3)_3$ concentration has the opposite effect; plutonium recovery diminishes because of the lower D values in the first strip section, and americium recovery rises at the expense of the plutonium recovery. It appears that the optimal $\text{Al}(\text{NO}_3)_3$ concentration is 1M and the optimal flow rate is 47.4 mL/min for this stream. Acid concentration in this acid strip was set to 0.1M to match the acid concentration profile from the previous base case. The sensitivity of this parameter will be discussed later.

As found in sensitivity studies (Sec. II.E), the organic flow rate is often the most important parameter in the flowsheet design, especially with regard to americium recovery and raffinate quality. It was no surprise to find that if the organic flow rate was increased 10%, the plutonium recovery went up about 1%, but the americium recovery dropped almost 12%. As the organic flow goes up, the performance of the extraction section increases significantly, but it becomes increasingly more difficult to recover americium from the solvent with the same strip conditions due to the relatively high affinity of the TRUEX solvent for the americium. With decreased organic flow, the raffinate quality deteriorates with increases in both the plutonium and americium recoveries. Since the raffinate quality is the most important design feature, the organic flow must be maintained at its designed setting. As shown in Table II-7, changes in the aluminum scrub concentration have only a minor effect on the plutonium concentration in the raffinate. The americium concentration in the raffinate follows a similar trend. The raffinate criterion for design of this flowsheet set by WMO, 0.1 nCi/g, is easily met due to the large number of stages in the extraction section.

To stay with the same six extraction stages from previous tests, the raffinate quality was overdesigned by a factor of at least 10^6 ; that is, the flowsheet has several more extraction stages than required to meet WMO requirements.

The feed flow rate is also very important in the final design. The flow rate is set as high as possible to meet raffinate quality, minimize run time, and ensure proper operation of the contactors. The contactor in the glovebox operates very well at a total flow under 300 mL/min. These flows are lower than typical design flows for this contactor (4 cm), but solvent quality continues to be a problem. Thus, as a base case, a feed flow of 100 mL/min was used. By increasing this flow, the raffinate quality deteriorates despite high plutonium and americium recoveries. Decreasing this flow improves the raffinate quality, but the marginal changes in the plutonium and americium recoveries are not significant enough to warrant any changes in feed flow.

Changes in the americium strip parameters primarily affect the americium recovery and americium concentration profile, but do not affect the plutonium recovery or concentration profile nearly as much. By increasing the strip flow rate, americium recovery goes up. By decreasing the strip flow rate, americium recovery drops significantly. Increasing the acid in the strip reduces americium recovery due to the higher D values for americium, which favor extraction and not stripping. Decreasing the acid concentration, in general, improves americium recovery, but too low of a nitric acid concentration increases the plutonium in the americium product. The optimum nitric acid concentration for the strip was found to be 0.02M.

The location and flow rate of the americium product stream did not have much of an impact on the overall flowsheet design. The optimum location for the americium product stream is where the americium concentration profile is a maximum. The optimal flow rate for this stream was previously found to be 3 mL/min. and performance of the system was relatively insensitive to changes in these americium product parameters.

The high americium recovery shown in Table II-7 is an artifact of the GTM, since the model does not account for extraction of americium by acidic degradation products. Therefore, for strip nitric acid concentrations below 0.04M, the americium distribution ratios calculated by the GTM are incorrect. In fact, at nitric acid concentrations less than 0.04M, acidic degradation products in the organic solvent interfered with americium recovery. To prevent this interference, the nitric acid concentration in the strip was set at 0.04M, not 0.02M. We also decided to set the scrub nitric acid at 0.05M to improve the acid extraction in stages 7 and 8. This would improve the performance of the scrub and americium strip sections. Results from a sensitivity analysis for these modifications are shown in Table II-8.

Table II-8. Optimization of Flowsheet with 0.02M Nitric Acid in Americium Strip

Simulation Description	Pu Product Concentration, M	Percent Pu Recovery	Am Product Concentration, M	Percent Am Recovery
Strip Flow Increased: 55 mL/min	1.48E-05	98.93	8.29E-07	99.49
Strip Flow Decreased: 45 mL/min	1.49E-05	99.47	8.25E-07	98.94
Strip Flow Decreased: 40 mL/min	1.50E-05	99.80	7.90E-07	94.78
[H] in Scrub Decreased: 0.06M	1.50E-05	99.73	7.61E-07	91.27
[H] in Scrub Decreased: 0.04M	1.50E-05	99.73	7.65E-07	91.74

Changing the nitric acid in the scrub has only minor effects on the system performance. Also, by increasing the scrub flow rate, americium recovery is decreased due to increased D values in the strip section, which prevent americium from stripping to the aqueous phase. Thus, more americium is recovered in the plutonium strip section. Reducing the scrub flow rate has the reverse effect, as previously discussed. The final flowsheet design is shown in Fig. II-19. Included in Fig. II-19 is the proposed design of the plutonium strip and solvent wash sections.

3. New Plutonium Strip Reagents

Precipitation of plutonium oxalate in the plutonium strip solution during the processing of the first batch (January 1991) created several problems. In that flowsheet, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) was used to strip plutonium from the organic solvent. Therefore, two new plutonium-strip reagents, $(\text{NH}_4)_2\text{CO}_3$ and $(\text{NH}_4)_2\text{C}_2\text{O}_4$, were tested.

a. Ammonium Oxalate as a Stripping Agent for Plutonium

Ammonium oxalate was suggested to replace oxalic acid to remove plutonium from the TRUEX-NPH solvent. Plutonium oxalate will precipitate in the presence of oxalic acid in dilute mineral acid solutions and plug the lines and contactors in processing runs, although it will remove plutonium (and americium) from the organic phase. Oxalic acid is only weakly ionized. The

ammonium oxalate salt should provide sufficient oxalate ion to form the tri-oxalato plutonium complex, thus stripping the plutonium from the organic phase and keeping it in aqueous solution.

Preliminary tests showed that precipitation did not occur when plutonium at ~1 g/L in the organic phase was stripped by 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and that the salt was an effective stripping agent, with distribution ratios of about 0.02 to 0.03. A second strip of the same organic solution gave distribution ratios of 0.5 to 1.3. This increase in the distribution ratio with successive strips is disturbing, and verification was needed. In addition, the degree of extraction of ammonium oxalate by TRUEX-NPH is also an important parameter.

The experiments described below are additional preliminary tests. They were conducted with ^{238}Pu at tracer concentrations and not at the grams-per-liter concentration that will be used in the contactors.

(1) Extractability of Ammonium Oxalate

A rapid qualitative measurement of the distribution ratio for 0.28M ammonium oxalate containing 0.05M HNO_3 (since a small amount of acid is expected to be present in the TRUEX phase before the strip step) was performed as follows. Two milliliters of a solution containing 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ -0.05M HNO_3 was contacted with 2 mL of TRUEX-NPH (pre-equilibrated with 0.05M HNO_3) for 1 min in a vortex mixer, and the layers were separated by centrifugation. The organic phase was scrubbed three successive times with 2-mL portions of water to remove any ammonium oxalate. The washings were combined. One milliliter of the original aqueous phase and 1 mL of 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ were placed in two separate culture tubes; then 1 mL of 1.25M $\text{Ca}(\text{NO}_3)_2$ (adjusted to pH 5 with NH_4OH) was added to each, as well as to the washings, to precipitate any oxalate. No precipitate formed in the tube containing the washings, so one milliliter of additional calcium solution was added to that tube. Heavy precipitates formed in the tubes containing the $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution. One milliliter of 1.25M $\text{Ca}(\text{NO}_3)_2$ solution was also added to the tube containing the TRUEX phase and vortexed for 2 min. The tubes were allowed to stand overnight and then centrifuged. No precipitate was visible in the tube containing the washings or the TRUEX solvent.

We had planned to separate and weigh the CaC_2O_4 to obtain the distribution ratio, but since no precipitate formed, only an upper limit of the ratio could be estimated. To do this, 6 mL of water (made 0.03M in HNO_3 to simulate the washings) plus 2 mL of 1.25M $\text{Ca}(\text{NO}_3)_2$ was added to six different centrifuge tubes containing varying amounts of 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, then allowed to stand overnight. As shown in Table II-9, the upper limit of distribution ratio for $(\text{NH}_4)_2\text{C}_2\text{O}_4$ in this test is $75 \mu\text{L}/2000 \mu\text{L} = 0.038$.

Table II-9. Results of CaC_2O_4 Precipitation Test

Tube No.	Vol. of	Precipitate
	0.28M Amm. Ox., ^a μL	
1	0	No
2	10	No
3	50	No
4	75	Yes
5	100	Yes
6	200	Yes

^aTwo milliliters of the 0.28M ammonium oxalate was used in the contacts.

(2) Stripping of Ammonium Oxalate

All the plutonium solutions readily available were assayed, and a solution containing 1.4×10^8 dpm of ^{238}Pu was chosen. This solution was transferred to a culture tube. The volume was ~ 1.25 mL and the acidity $\sim 1.2\text{M}$ HNO_3 . The plutonium was extracted into 2 mL of TRUEX-NPH (not acid equilibrated to keep the acidity in the solvent low). This is the load step. The TRUEX-NPH was scrubbed with 1 mL of 0.05M HNO_3 to reduce the acidity further, so that the plutonium stripping could be performed at an acid concentration similar to that expected in an actual process run. The organic phase was separated and contacted with 1 mL of 0.28M ammonium oxalate three successive times. The contacts were made by vortexing the phases for 1 min. The solutions were centrifuged, the phases separated, and aliquots taken and counted for alpha activity in the usual manner. The results are summarized in Table II-10.

Table II-10. Distribution Ratios for the Ammonium Oxalate Stripping Test

Step	Distribution Ratio	Material Balance, %
Load	154	-
Scrub	139	100
Strip 1	4.6×10^{-4}	90
Strip 2	4.3×10^{-3}	84
Strip 3	0.88	112

The distribution ratio for the first strip with ammonium oxalate was quite low, which indicates that this stripping agent will be useful in the TRUEX process. The large decrease in this ratio with successive strips is disturbing and could also be due to acidic extractants in the TRUEX solvents. The initial plutonium concentration in the organic phase before the first strip was 7.13×10^5 cpm/10 μL . The concentration decreased to 2.6 cpm/10 μL , or $4 \times 10^{-4}\%$ of the initial concentration, after the second strip and 1.2 cpm/10 μL , or $1.7 \times 10^{-4}\%$, after the third strip.

In such a situation, a small amount of another alpha emitter that does not form a strong complex with oxalate ion becomes very important. The third decay product of ^{238}Pu is ^{234}U , an alpha emitter. A small amount of ^{237}Np may also be present, since this is probably the starting material for preparing ^{238}Pu . The alpha activity remaining in the organic phase after the third, and perhaps the second, strip should be counted by alpha spectrometry to determine its composition. Time was not available for this. Some unknown change in plutonium speciation may have occurred after the first strip. Perhaps adding ^{238}Pu in TRUEX-NPH to the organic phase after the first strip, and then performing a second strip would be informative. This study should continue.

b. Extractability of Plutonium from Acidified Carbonate Scrub

The composition of a waste stream generated from the first plutonium waste processing run performed in January 1991 is estimated to be

1M HNO_3
 $3\text{-}4\text{M}$ KNO_3 + NaNO_3 (primarily KNO_3)
 $<0.1\text{M}$ $\text{Al}(\text{NO}_3)_3$

0.1M $\text{H}_2\text{C}_2\text{O}_4$
 ~0.006 g Pu/L (~400 nCi/g)

It is possible that plutonium polymer will form when an acidic plutonium solution is neutralized. The purpose of the experiments described below was to measure the plutonium extraction into standard TRUEX-NPH under a variety of conditions that might be expected to depolymerize Pu(IV). This polymer has the reputation of being extremely difficult to convert to the ionic form.⁷ Oxidation of the plutonium to Pu(VI) or reduction to Pu(III) might be effective since these oxidation states do not form polymers. Sulfur dioxide, bisulfite, and Fe(II) are reported to reduce plutonium to the trivalent state rapidly. Sodium bismuthate (NaBiO_3) and Ag(II) persulfate are known to oxidize plutonium to the hexavalent state. The presence of polymeric plutonium was speculative at this point and was based only on the low distribution ratios obtained with the acidified carbonate solution. Alternatively, the high concentration of oxalic acid could result in low plutonium distribution ratios since plutonium forms a strong oxalate complex.

Distribution ratios obtained for the alpha activity between the acidified carbonate solution and standard TRUEX-NPH conditions are shown in Table II-11. All extractions were performed with an equal volume of pre-equilibrated solvent and aqueous solution for 1 min at 25°C. Measurements were made by liquid scintillation counting.

Table II-11. "Alpha" Distributions Ratios^a between Acidified Carbonate (AC) Solution and TRUEX-NPH at 25°C

No.	Conditions	Dist. Ratio	Mass Balance
1	1 mL AC + 1 mL 8M HNO_3 (~4.5M HNO_3 final conc.)	161	108%
2	As above, except aqueous heated for 1 h at 50°C before extraction	160	88%
3	As above, except 0.28 g NaBiO_3 added, centrifuged, and supernatant extracted	18	84%
4	Second forward extraction (1 mL aqueous phase from Expt. 1 + 1 mL fresh solvent)	11	124%
5	1 mL AC	2.5	105%
6	Same as 5, except made 0.5M in Al(III)	330	108%
7	1 mL of solution 6 placed in ultra-sonic bath for 48 h, then extracted	186	64%
8	Same as solution 7, except AC made 0.1M HF	11	49%

^a "Alpha" activity is used in here since the acidified carbonate solution contains an unknown amount of ^{241}Am , and liquid scintillation counting cannot distinguish between the alpha energies.

The first two experiments were performed at a high nitric acid concentration in an attempt to increase the extraction efficiency. For No. 2, an attempt was made to accelerate the conversion of the Pu(IV) to the ionic form. At 4-5M HNO_3 , the distribution ratio should be several thousand, so obviously these treatments were ineffective. Experiment No. 3 was an attempt to oxidize the Pu(IV) to Pu(VI). This treatment was largely ineffective, and the NaBiO_3 , a water-insoluble brown compound, appeared to decompose during the contact, probably due to the high acidity. Experiment No. 4 was performed to check the extractability of the plutonium (or americium) remaining after the initial forward extraction. As is often the case, the remaining material was much less extractable than the original. Experiment No. 5 showed how poorly extractable the alpha activity is from the original

acidified carbonate solution. If oxalic acid complexation of Pu(IV) were the cause for the low D_{Pu} values, the addition of aluminum nitrate could tie up the oxalate and allow better plutonium extraction. This proved to be the case (No. 6), although a ratio of at least 1000 should be obtained in the absence of oxalate. However, the presence of ^{241}Am could lower the apparent D_{Pu} .

A precipitate formed during this extraction, probably aluminum oxalate. The precipitate was separated by centrifuging and dissolved in $5M$ HNO_3 . It contained only 0.7% of the original alpha activity, although aluminum oxalate would be expected to co-precipitate plutonium and americium.

The ultra-sonic experiments (Nos. 7 and 8) showed that this process had no effect on the distribution ratios. The poor material balances are probably the result of the heating and evaporation of the samples during cavitation.

The general conclusion based on the data is that the plutonium is not principally in polymeric form, since increasing the nitric acid concentration or adding Al(III) increased the distribution ratio. Recommendations for future study of this problem are as follows:

- Perform all experiments first on plutonium that is known to be ionic or polymeric. We have both types available. Then perform the experiments on questionable solutions from the runs.
- Perform experiments that distinguish between polymeric and ionic plutonium and between oxidation states. Examples are
 - (1) Pass the solutions through a cationic exchange resin at low acidity and an anion resin (nitrate form) at $8M$ HNO_3 . Ionic plutonium will absorb; polymeric plutonium will pass through.
 - (2) Tests for evaluating the oxidation states of ionic plutonium are Pu(III) and (IV) - coprecipitation with LaF_3 ;

Pu(IV) - solvent extraction with TTA RALP4, comnet #31 and adsorption on a nitrate anion column;

Pu(V) - coprecipitation with CaCO_3 ;

Pu(VI) - extraction into diethyl ether from NH_4NO_3 solution at low acidity.

Such a systematic approach to the behavior of the various forms of plutonium will provide a sound basis for evaluating future results obtained from process solutions.

c. Measurement of Dispersion Numbers

Dispersion numbers were estimated for both strip reagents by measuring the time that the dispersion took to break up in a 10-mL culture tube. Only single measurements were collected and are reported in Table II-12. These values indicate that operation in the centrifugal contactor at "typical" flow rates will not be a problem.

Table II-12. Dispersion Numbers for Two Plutonium Strip Solutions and the TRUEX-n-Dodecane Solvent

System	O/A Ratio	Dispersion Number
0.8M (NH ₄) ₂ CO ₃	1/1	5.8 E-04
0.28M (NH ₄) ₂ C ₂ O ₄	1/1	7.2 E-04

d. Conclusion

Our initial studies of the new stripping agents indicate a dramatic increase in plutonium distribution coefficients after one (or more) contacts. Since these tests were completed with actual spent solvent from the glovebox, we now believe that acidic degradation products present in the solvent contributed to these results. Tests will be completed using solid sorbents to remove these degradation products, then these stripping tests will be repeated.

4. TRUEX Solvent Cleanup

Generating an aqueous raffinate stream that contains less than 0.1 nCi/g of TRU elements requires that the organic solvent be cleaned by recycling. Because the TRUEX solvent that will be used to process the acidified carbonate waste contains a fairly high level of activity, it must be processed (cleaned) before starting. This solvent was used during the processing of Batch 1.

Because laboratory-scale contacts seemed to indicate that (NH₄)₂C₂O₄ would strip this activity from the TRUEX solvent, an attempt was made to strip the TRUEX solvent using five stages in the centrifugal contactor. The solvent was contacted with 0.28M (NH₄)₂C₂O₄ in the plutonium strip section (stages 14-18). This attempt proved unsuccessful; however, the organic effluent had activity levels in the range of 5,000 cpm/μL. Therefore, other methods for stripping the TRUEX solvent were pursued.

Three batch contacts were made with separate aliquots of the contaminated solvent. One aliquot of the loaded solvent was contacted with 0.05M 1-hydroxyethane-1,1-diphosphoric acid at an O/A of 1. Based upon liquid scintillation counts of both phases, a D value of 0.11 (total alpha) was achieved. Another aliquot of loaded solvent was contacted with 0.04M HNO₃ at an O/A of 1. For this contact a D value of 242 (total alpha) was achieved. Since this value is so high at dilute acid concentrations, it appears that the residual activity is mostly plutonium. However, this is not a good test for determining the presence of americium, since acid degradation products in the organic phase can have a significant impact on americium D values.

Past experience suggests that activity in an organic phase can be coprecipitated with iron. Therefore, a third aliquot of the loaded solvent was contacted with a solution of 0.5M Fe(NO₃)₃-0.5M HNO₃ at an O/A of 0.9. The purpose of this contact was to extract iron into the organic solvent. The organic phase was then contacted with H₂O at an O/A of 0.45. Although samples of the organic and aqueous phases were not counted at this point, a mass balance calculation later indicated an approximate D value of 0.5. The organic phase was then contacted with 0.25M Na₂CO₃ at an O/A of 0.9, yielding a D value of 0.8 (total alpha). Although some interfacial crud was observed following this contact, the expected precipitation did not occur. Another contact with 0.25M Na₂CO₃ at an O/A of 0.9 was completed, but, again, no precipitation occurred. The D value for the contact was 13.5

(total alpha). The organic solvent at this point contained about 950 cpm/ μ L total alpha activity, for a decontamination factor of only 5.3.

These tests suggest that this solvent had been degraded to a point where acid degradation products were at a concentration that made the solvent unusable for processing our acidified carbonate solution. Hence, this solvent was set aside, and fresh solvent was imported for use in processing the acidified carbonate waste. While methods are being developed to clean up this solvent, approximately 1.5 L of fresh TRUEX solvent will be used to process the acidified carbonate.

5. System Decontamination

To generate a low-activity waste solution, contactor stages, pumps, and transfer lines surrounding both ends of the contactor must be kept fairly contamination free. If the first several stages of the extraction section become contaminated, this contamination affects the DW raffinate directly. If the last several stages of the process (solvent wash section) become contaminated, then the solvent becomes contaminated, which again contaminates the first few stages of the extraction section (because of solvent recycle). Contamination of these stages did occur during attempts to process the DW raffinate from Batch 1. Several different procedures were developed to decontaminate these stages. These methods are described below.

a. Stages 17 and 18

Stages 17 and 18 were first flushed in series using fresh 0.05M $\text{H}_2\text{C}_2\text{O}_4$, full solution recycle, and a flow rate of about 50 mL/min. By "full recycle" we mean that the aqueous phase exiting stage 17 was returned to the feed tank entering stage 18. Flushing lasted about four hours, with samples of the feed solution taken every hour. Scintillation count results of those samples, given in Table II-13, show that considerable activity was flushed out immediately, tapering off (no increase in activity) as flushing continued.

Table II-13. Feed Activity during the Flushing of Contactor Stages 17 and 18 with 0.05M $\text{H}_2\text{C}_2\text{O}_4$

Elapsed Time, h	Scintillation Counts, cpm/ μ L
1	427
2	493
3	582
4	686

This flushing procedure is not very effective because only the parts of the contactor seen by the more-dense-phase flow are washed, leaving the less-dense-phase weir, collector ring, and interstage tubing untouched. Therefore, a new procedure was developed where these stages were flooded by using a flow rate high enough to cause flow over both the less- and more-dense-phase weirs. To accomplish full solution recycle, the less-dense-phase outlet of stage 18 was connected to the less-dense-phase inlet of stage 17, as shown in Fig. II-20.

Fig. II-20. Flowsheet for Flooding Contactor Stages 17 and 18

The results from scintillation counting of feed solution samples taken during this flooding procedure (Table II-14) show that, although a significant amount of activity was initially flushed out, the amount of activity being flushed out tapered off rapidly.

Table II-14. Feed Activity during the Flooding of Contactor Stages 17 and 18 with 0.05M $\text{H}_2\text{C}_2\text{O}_4$

Elapsed Time, min	Scintillation Counts, cpm/ μL
5	157
20	200
120	224

b. Stages 19 and 20

We flooded Stage 20 twice using the flowsheet shown in Fig. II-21. A clean pump external to the glovebox was used so that no extraneous activity would be introduced to this stage. The first flooding lasted for about two minutes, and a scintillation count of the effluent after that time yielded an activity level of 7.61 cpm/ μL . The effluent was set aside for flooding stage 19. The second flooding lasted for about 4 min, with the effluent activity after this time at 0.90 cpm/ μL .

Fig. II-21. Flowsheet for Flooding Contactor Stage 20

Stage 19 was decontaminated using the once-through method described for stage 20. For the flooding method, we used a flowsheet similar to that in Fig. II-21, except that the solution used was under full recycle, and the pump was located inside the glovebox. The effluent from the first flooding of stage 20 was used as the feed for this procedure. Decontamination lasted about four hours, with samples of solution taken every hour. Scintillation count results of these samples (Table II-15) show that a moderate amount of activity was flushed out immediately, tapering off as flushing continued. Flooding this stage with 0.25M Na_2CO_3 did not remove very much activity. Following this rinse, the activity level was reduced low enough to allow for processing of waste.

Table II-15. Feed Activity Results during the Flushing of Contactor Stage 19

	Elapsed Time	Scintillation Counts, cpm/ μL
Flushing, 0.05M $\text{H}_2\text{C}_2\text{O}_4$	1 h	47.6
	2 h	52.2
	3 h	55.7
	4 h	59.7
Flooding, 0.25M Na_2CO_3	10 min	13.8
	50 min	14.1
	120 min	11.2

c. Plutonium Strip Section

The plutonium strip section (contactors 14-18 in Fig. II-19) was flushed with 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ at a flow rate of about 12.5 mL/min. No organic phase was present in these stages

during the flushing process. This flushing continued for 90 min, with samples of the effluent taken intermittently. The results of scintillation counting of those samples, given in Table II-16, show that considerable activity was flushed from this section. This activity was from the plutonium precipitates that were generated during the processing of Batch 1. Although considerable activity was still being removed (leached) from these stages, we decided that too much plutonium-waste solution was being generated with little benefit. Our criterion for decontaminating this section of the contactor bank differs from that for the ends, because we are not generating a low-activity product solution. Residual solids present in these stages will continue to be removed during the processing of the acidified carbonate waste.

Table II-16. Effluent Activity during the Flushing of Stages 14-18

Sample Time, min	Effluent Activity, cpm/ μ L
10	78664
30	31044
45	34280
65	3887
75	2743
90	2546

d. Solvent System

As described earlier, the TRUEX solvent used for waste processing in the glovebox was highly degraded and unsuitable for use in further attempts to process the acidified carbonate solution. We decided that the degraded solvent must be removed, including any residual amounts, so that the new solvent is not contaminated. To flush out all remnants of degraded solvent from the contactors, including the less-dense-phase passages, all stages were flushed in series with an organic solution consisting of 50% n-dodecane (nDD) and 50% TBP. The stages were first filled with an appropriate aqueous solution: stages 1-7 were filled backwards (from 1 to 7) with the 1M $\text{Al}(\text{NO}_3)_3$ -0.05M HNO_3 , stages 8-13 were filled with 0.04M HNO_3 , stages 14-18 were filled with 0.28M $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and stages 19 and 20 were filled with 0.25M Na_2CO_3 . After all of the stages were filled, the aqueous pumps were shut off. Then, the organic phase was pumped through the contactors at a flow rate of about 50 mL/min for approximately two hours, using full organic recycle. After flushing, the organic feed was sampled and counted on a scintillation counter, showing a total alpha activity level of 708 cpm/ μ L. This high value suggested that this procedure was effective in picking up contamination in the system. After removing this organic phase from the system, fresh 50% nDD-50% TBP was used to repeat this flush. After about one hour the feed showed an alpha activity level of 134 cpm/ μ L.

6. Glovebox Gloves

Four gloves used with our contactor glovebox became contaminated during this report period. This caused us to wonder if we had a permeation problem rather than holes in the gloves, as first assumed. Further evidence in support of this hypothesis is that hand-monitor background steadily increased with time, and that three individuals had positive, though low-level, bioassay results.

Smears of all 36 glovebox gloves were taken and counted by Health Physics. Results of these counts are presented in Fig. II-22; the upper number represents the counts per minute, the lower number the glove smear position. In addition, cotton swabs, smeared on the inside of gloves which had been used at the time contamination was discovered, were rinsed in a scintillation cocktail solution. Scintillation counts of these two cocktails (from gloves 1 and 3, respectively) yielded 13 and 159 dpm. These gloves have been changed. Cotton swab swipes of 5 additional gloves (4, 12, 19, 24, and 31) were taken for scintillation counting, and no activity was detected.

A literature search of glove compatibilities with chemicals used in the glovebox was then conducted. Table II-17 summarizes the results of this search. As can be seen in this table, no one material is compatible with all of the chemicals in use in the box. We believe that this apparent permeation problem can be circumvented by three measures, all of which attempt to prevent solvents from contacting the gloves.

Firstly, leaks from pumps and contactors need to be eliminated, not only to protect the gloves, but also to obtain better inventory control. These tasks have already been started. Secondly, cleanup of used TRUEX solvent, which had previously been accomplished by shaking equal quantities of TRUEX solvent with a solution of sodium carbonate in a separatory funnel, will be achieved utilizing the contactors. And thirdly, we are looking at various types of disposable secondary gloves that can be pulled over the glovebox gloves.

Manufacturers have been contacted about secondary gloves that will fit over the glovebox glove and can be used when handling the TRUEX solvent. Of those contacted, only three had gloves which might have been acceptable. The glove which appeared to offer the most potential was a Teflon glove produced by Clean Room Products, Inc. (Ronkonkoma, NY). A sample of this glove was useless, however, since it fit very poorly and tore when putting it on. Another glove which showed some promise is the 4H glove, marketed by Safety 4 Inc. (Racine, WI). This glove does exhibit good chemical resistance but does not fit over the glovebox glove. A glove similar to the 4H glove is produced by the North Co. and is marketed by several supply houses. Since none of the above gloves proved satisfactory, we tried a Viton glove, which is a stock item at ANL. This glove fit nicely over the glovebox glove but reacted with the TRUEX solvent. Nevertheless, it can be replaced with a new one after this occurs. This seems to be the best currently available option.

This glove problem was also addressed by a committee consisting of three members of CMT's Health Physics, Ray Wolson, David Wygmans, and Erven Van Deventer. In addition to the three steps outlined in the preceding paragraphs, it was mutually agreed that Health Physics would take periodic smears of a selected number of gloves, smear the glovebox hand monitor occasionally as counts build up, and smear additional parts of the laboratory room. By implementing these procedures, this problem should be eliminated. In addition, a log will be kept of all future glove changes in an attempt to document the problem.

Fig. II-22. Counting Results of Glovebox Gloves. (The upper numbers are counts per minute. The lower numbers represent the glove positions.)

Table II-17. Compatibility of Glove Materials with Glovebox Chemicals

	Natural Rubber	SBR, GRS (a,b)	Butyl (a)	EPR (a)	Nitrile	Hydrin	Neo-prene (a,b)	Hypalon (a,b)	Urethane (b)	Poly sulfide	Silicone (b)	Fluoro-silicone	Fluoro Elastomers
Air-Above 300°F	U	U	U	U	U		U	U	U	U	A	B	A
Air -Below 300°F	U	U	B	B	B		B	B	C	U	A	A	A
Aluminum Nitrate	A	A	A	A	A	A	A	A	C	B	B		A
Decane	U	U	U	U	B		U	U	B	A	B	A	A
Nitric Acid - 3M	U	U	A	B	U		U	U	U	U	U	C	A
Nitric Acid - conc.	U	U	C	U	U	U	U	U	U	U	U	U	A
Oxalic Acid	B	B	A	A	B	C	B	B		U	B	A	A
Phosphoric Acid - 3M	B	B	B	A	U		C	B		U	B	B	A
Potassium Hydroxide	B	B	A	A	B	A	B	A	B	B	C	C	A
Potassium Salts	A	A	A	A	A		A	A	A	A	A	A	A
Radiation	C	C	U	C	C		C	C	C	U	C	U	U
Sodium Carbonate	A	A	A	A	A	A	A	A		U	A	A	A
Sodium Nitrate	B	B	A	A	B	A	B	A			U		
Tributyl Phosphate	B	U	B	A	U		U	U	U	A		U	U
Water, Drinking	A	A	A	A	A	B	B	A	U	U	A	A	A

Legend: A - Recommended

B - Minor to moderate effect

C - Moderate to severe effect

U - Unsatisfactory

Blank - Insufficient data

Notes: (a) - Not recommended for aromatic hydrocarbons

(b) - Not recommended for strong oxidizing acids

From "An Engineering Guide to Elastomer Selection and Manufacturing Standards," Minor Rubber Company, Inc., Bloomfield, NJ.

G. Advanced Evaporator Technology

(D. B. Chamberlain, L. Nuñez, G. F. Vandegrift, and S. Betts*)

We are developing evaporator technology for concentrating radioactive waste and product streams such as those generated by the TRUEX process. Minimizing waste generation requires that equipment be installed for concentrating both radioactive waste streams and recycling the decontaminated condensates. A technology that shows a great deal of potential for this application is an evaporator being developed by LICON Inc. (Pensacola, FL).

Initial studies will evaluate this technology for concentrating process streams in terms of (1) economic and institutional advantages and disadvantages, (2) effectiveness of this technology in terms of concentrating radioactive product and waste streams and decontamination factors for radionuclides in the overheads, and (3) the effects of this concentration on plant operations. Argonne and LICON will (1) design an evaporator specifically for remote operation and (2) in a hot facility at Argonne, test the remote operability and maintenance of this evaporator and other equipment in glovebox, shielded-cell, and canyon facilities. In later stages of the program, this equipment will be installed in a DOE processing/production plant for actual in-plant demonstration.

We are initially focusing on completing a literature survey, where past work on mixed-phase equilibria (vapor/liquid and vapor/liquid/solid) of aqueous solutions of HNO_3 (and possibly HF) in the presence of metal nitrate salts will be collected, evaluated, and summarized. The most important data needed are measurements on the concentrations of water and nitric acid in the liquid and vapor phases as a function of temperature, pressure, and composition of the aqueous solution (i.e., effects of metal nitrate salts on the volatilities of water and nitric acid). A second need is the composition of the solids that precipitate, as these mixed acid/metal-salt solutions are concentrated (again as a function of temperature, pressure, and composition). These measurements are important parameters in designing an evaporator for a specific stream, setting conditions of pressure and temperature, predicting effluent rates and compositions for the condensate and the bottoms, and knowing to what degree a stream can be concentrated. The literature survey is also critical to the design and interpretation of our own experiments to collect necessary data not available in the literature.

The focus of the literature survey in this report period has been to collect data on the vapor/liquid equilibria in water-nitric acid and water-nitric acid-nitrate salt systems. Information for 23 water-nitric acid-nitrate salt systems was obtained. While most of these data are for a system of a single nitrate salt in an aqueous nitric acid-water solution, Zhikarev et al.⁸ proposed a method to calculate vapor/liquid equilibria for multi-component systems (that is, nitric acid-water-salt systems). The method is based on the additivity of the partition coefficient and is valid for many binary solvent/salt types when the relative (with the salt ignored) concentration of nitric acid in the liquid phase is constant:

$$\log \left[\frac{Y}{100 - Y} \right] = \sum \frac{C_i}{C_\Sigma} \cdot \log \left[\frac{Y_i}{100 - Y_i} \right] \quad (\text{II-27})$$

where

Y = vapor-phase nitric acid concentration

C_Σ = total concentration of the salting-out agents

* Graduate student at University of Illinois, Champaign-Urbana.

If the vapor phase concentration of each ternary salt system is known, then Eq. II-27 may be used to obtain the concentration of the vapor-phase nitric acid in the combined salt system. This was confirmed by Zhikarev, who used data for the ternary systems $\text{HNO}_3\text{-H}_2\text{O-Fe(NO}_3)_3$ and $\text{HNO}_3\text{-H}_2\text{O-Cu(NO}_3)_2$ at 100 kPa pressure, to calculate the liquid-vapor equilibria in the system $\text{HNO}_3\text{-H}_2\text{O-Fe(NO}_3)_3\text{-Cu(NO}_3)_2$. A comparison of the experimental and the calculated data showed a relatively small deviation. Thus, this method for calculating vapor-equilibrium data appears to be applicable to multicomponent nitrate systems.

The literature does not provide much information for the effect of introducing other acids, such as hydrofluoric or oxalic, to nitric acid mixtures. Most of the papers found were published in either Russian or Japanese journals, which apparently have not been translated to English. Translations are being completed -- a summary of these papers is still pending.

The literature survey also focused on determining the experimental procedure and the equipment necessary to reproduce collected data for nitric acid-water-nitrate salt systems. The literature mentions three methods for determining vapor/liquid equilibrium: the circulation (or recirculation) method, the transpiration method, and the rectification method. The most widely used and best documented method in the literature seems to be the circulation method.⁹⁻¹²

Ten papers were found which use the circulation method to determine the vapor/liquid equilibrium for the nitric acid-water-nitrate salt system. The most common circulation apparatus used was the Bushmakini still¹³ and modified versions of that apparatus, such as the one described by Gorodetskii.¹⁴ Hála¹⁵ compares 27 circulation vapor/liquid equilibrium stills, including the stills used by Bushmakini and Altsheler.¹⁶ The Bushmakini still, considered by Hála to be a simple still, reaches equilibrium in 2-3 h, but does not measure the temperature accurately. The Altsheler still is considered a very precise still, reaches equilibrium in about 40 min, but again has no means of monitoring the temperature. The Altsheler still, shown in Fig. II-23, is currently manufactured by LUREX Scientific (Vineland, NJ) and is less expensive than a Bushmakini still. The Altsheler still may be easily modified to measure the temperature of the vapor and liquid.¹⁷ For example, Owensby inserted two thermocouples, one for the vapor and one for the liquid phase, through the top of the still. With these considerations in mind, it appears that Altsheler still would be just as accurate, if not faster, and less expensive than the Bushmakini still.

H. Decontamination of Groundwater

(J. C. Hutter, D. Redfield, L. Nuñez, and G. F. Vandegrift)

Contamination of groundwater by dilute (ppb levels) concentrations of volatile organic compounds (VOCs) has become a major problem at many Department of Energy and Department of Defense sites, as well as industrial sites nationwide. Remediation of these sites is generally difficult, energy intensive, and expensive.

A groundwater contamination survey was recently completed at nine DOE sites in the United States.¹⁸ The ten most common VOC contaminants found are listed in Table II-18. Most of the contaminants are chlorinated hydrocarbons, typically found in ppb concentrations. Similar contaminants can be found at ANL site as well as several industrial sites worldwide.¹⁹⁻²² The common feature at all these sites is the large distances that dilute (ppb) concentrations of contaminants have migrated. Even though the concentrations of the contaminants are low, they often exceed U.S. EPA Drinking Water Standards, as shown in Table II-18. Two of the contaminants in the table, trichloroethylene and methylene chloride, are not under federal regulation, but they are usually under state or local restrictions. We have developed a membrane-assisted solvent extraction/membrane-assisted distillation stripping (MASX/MADS) process to recover VOCs from groundwater for reuse or destruction. This

Fig. II-23. Section View of Equilibrium Still

Table II-18. Common Contaminants in Groundwater Found at DOE Sites

Contaminants	Conc., ppb		
	Average Conc.	Maximum Conc.	U.S. EPA Drinking Water Standard ^a
Benzene	1400	36000	5
Carbon Tetrachloride	280	10000	5
cis-1-2-Dichloroethylene	100	1600	70
trans-1-2-Dichloroethylene	160	1600	100
Trichloroethylene	310	8500	5
Tetrachloroethylene	150	2300	5
Methylene Chloride	220	6400	5
1-1-1-Trichloroethane	110	3100	200
Chloroform	30	1000	100
Vinyl Chloride	180	540	2

^a From Ref. 23.

high-efficiency solvent extraction process is also applicable to treatment of process effluent air and water streams.

A flow diagram of the MASX/MADS process is given in Figure II-24. Contaminated groundwater enters the membrane extraction module, where it is contacted with a solvent that extracts the pollutants from the groundwater. The membrane material in the module is porous and is used to separate the two liquid phases and provide a large interfacial area for mass transfer. The nonvolatile solvent extracts the VOCs from the water with a distribution coefficient that is typically 100 or more. Because of this high distribution coefficient, the oil flow rate can be up to 100 times lower than the groundwater flow. The groundwater leaves the extraction unit decontaminated to a purity as good as the drinking water standards, so that this water can be safely reintroduced to the environment. At this point, the nonvolatile solvent contains the contaminants recovered from the groundwater, which are in a concentrated form. The maximum concentration of the contaminants in the nonvolatile solvent is determined from the distribution ratio between the water and the solvent and their relative flow rates.

The solvent must be stripped of contaminants before it can be recycled to the extraction modules. This operation is carried out in the MADS unit after the solvent is heated. In this unit, the volatile contaminants are vaporized and recovered in a condenser. In addition to the contaminants, some of the solvent and residual groundwater dissolved in the solvent are recovered in the condenser. The decontaminated solvent is then recycled to the extraction modules. This process is not a conventional distillation step involving multiple stages; it is a one-stage evaporation, but stages may have to be added if higher concentrations of VOCs are required for destruction or disposal.

In the MASX/MADS process, the use of membrane modules facilitates any capacity or scaleup difficulties. Capacity is increased by adding more modules. Scaleup is easy because the well-defined interfacial area allows excellent characterization of the volumetric mass transfer rates. The modules also allow independent variation of the flow rates without flooding, as in conventional solvent extraction. Density differences between the solvent and extraction feed are not required for phase separation because the membrane separates the phases.²⁴ Unlike use of activated carbon with air stripping, the solvent is continuously regenerated and does not have to be removed to another process (steam stripping) to regenerate the adsorbent. Since this energy-intensive step is omitted and the large

volume of air required for air stripping does not have to be continuously blown through a packed column, this system should result in reduced energy consumption for operation. The contaminants are recovered in concentrated form for destruction or recycle. The thermodynamic and technical aspects of the process are being investigated.

Fig. II-24. Flow Diagram for MASX/MADS Process

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III. NUCLEAR WASTE PROGRAMS

(J. K. Bates)

A. Unsaturated Glass Testing Program for Office of Environmental Restoration and Waste Management

The Unsaturated Glass Testing Program is part of the technology support activity performed for DOE's Environmental Restoration and Waste Management (EM). This program was initiated in 1989, and its purpose is to evaluate, before hot start-up of the Defense Waste Processing Facility (DWPF) and the West Valley Defense Plant (WVDP), factors that will likely affect glass reaction in an unsaturated environment. The Unsaturated Glass Testing Program recognizes that the long-term prediction of glass performance in a repository environment and the relationship between the release of radionuclides from a glass waste package and performance assessment of the repository are tasks that must be addressed, but that the completion of such tasks will not be finalized until application for a repository license, which will be several years after the DWPF or WVDP begins production of waste for storage and disposal. The Unsaturated Glass Testing Program also recognizes that the modeling and performance assessment programs must have a firm basis that (1) accounts for important physical parameters that will affect glass reaction in an unsaturated environment and (2) relates the mechanistic basis of glass reaction to conditions that will exist in an unsaturated environment.

The goals of the Unsaturated Glass Testing Program are to (1) review the literature concerning parameters that will be important to evaluating glass performance, (2) perform testing to further quantify the effects of important parameters, and (3) initiate long-term testing that will bound glass performance under a range of conditions identified in the Yucca Mountain Project's *Scientific Investigation Plan*,¹ and that can be used to validate models generated to predict long-term performance. The information developed in the Unsaturated Glass Testing Program, when combined with data generated by the glass waste producers and by the Yucca Mountain Project (YMP), will form the basis for a well-founded program that will ultimately qualify vitrified high-level waste for repository disposal.

1. Critical Review of Parameters Affecting Glass Reaction in Unsaturated Environment (J. J. Mazer)

The predicted repository environment at Yucca Mountain has been described as hydrologically unsaturated with possible air exchange with the neighboring biosphere.² We have identified several environmental conditions that can affect the durability of waste emplaced in such an unsaturated environment over repository-relevant time periods. To date, much of the information regarding what is known about these conditions has not been synthesized for use within the waste-glass research community. Thus, we have initiated such a critical review.

During the projected lifetime of an unsaturated repository, large amounts of liquid water are not expected to contact the waste; however, water vapor or small volumes of transient water may contact the waste during the emplacement. We have identified the amount of water contacting the glass waste to be a primary parameter affecting waste glass durability. Other identified primary parameters include temperature, radiation fields, glass composition, ratio of glass surface area to leachant volume (SA/V), and composition of alteration phases resulting from glass hydration.³ Detailed critical reviews of how each of these parameters affects waste glasses will be performed as a part of this task.

The purpose of this review is to evaluate the state of knowledge regarding the influence of each of the identified critical parameters on glass reaction. Each review will be issued as stand-alone documents, and these documents will be integrated into a summary compendium document. The results from this task will be used to support DWPF and WVDP startup.

The technical approach used to perform this task has been to assemble all known and pertinent sources of scientific literature related to the primary parameters. This literature was then objectively and critically reviewed to determine the current state of knowledge as to how each critical parameter affects nuclear waste glass reaction. When desirable, we have included reviews and discussions of studies of materials other than nuclear waste glasses, but this ancillary information is used to relate waste glass reaction to the parameter being reviewed. A synthesis of existing data will be performed, where possible, to provide a framework for comparing the results obtained from different studies.

All reviewed references used in the critical reviews have been collected in a computerized data base. The data base lists the reference, along with keywords and ANL reviewer's comments regarding the reference. The references include published journal articles, symposia proceedings, unpublished manuscripts, letters, and output from literature searches. The data base serves as a repository, as well as a resource, for all of the relevant information that will be used in the critical reviews. It also has a word search capability that facilitates the review process and helps ensure that no pertinent literature is overlooked by the critical review authors.

A preliminary critical review was previously performed to provide a foundation for subsequent detailed reviews of each parameter. The first such report, detailing the effects of temperature on waste glass performance, has been published.⁴ This report concluded that reaction mechanisms for waste glass dissolution in water are complex and involve multiple simultaneous reaction processes. The temperature dependence of each of the individual reaction processes can be described by the Arrhenius equation, a relationship derived from empirical observations.

The next parameter to undergo a detailed critical review is the effect of glass composition on glass durability. This review is in progress. Models of glass structure are being investigated to help understand the fundamentals of how water may interact with glass. Brief reviews of glass dissolution models are being combined with this information to form a basis for critically reviewing models relating glass composition to glass durability. Where possible, the available data will be presented in a manner that will allow a comparison of the results obtained in different studies. Reviews of the remaining parameters (radiation, SA/V ratio, surface layers, and unsaturated environments) are also being initiated, and drafts of each report will be completed in the near future.

2. Long-Term Testing of Fully Radioactive Glass

(J. K. Bates, X. Feng, J. W. Emery, T. J. Gerding, and J. C. Hoh)

Most testing to evaluate the performance of high-level waste (HLW) glasses has been done using simulated nonradioactive analogs of the same general composition as the radioactive glass. To apply the knowledge gained in such tests to the performance assessment of the fully radioactive production glass, we have to demonstrate that the simulated experiments are an adequate representation of reactions that will occur with the actual glasses to be produced by the glass producers. In particular, we have to assess the following: (1) does the simulated glass react through the same controlling mechanism? (2) does the simulated glass produce the same secondary phases, and are they generated in the same sequences? (3) is there an effect due to the radioactivity that is not adequately represented using the simulated glass? (4) is there an effect from using glass that does not contain all

the nonradioactive components present in the sludge, supernate, and frit feeds to the actual production process, since simulated glasses are generally produced using pure starting materials and the minor components are ignored? and (5) do the radioactive and nonradioactive glasses have different durability?

The work reported addresses the above questions. This comparison of the performance between fully radioactive glass from DWPF and the simulated nonradioactive analogs includes three glass compositions: (1) 165-based glasses (165/42R is from glass frit 165 type plus sludge from tank 42, and 165/42S is the simulated analog); (2) 131-based glasses (131/11R is from glass frit 131 type plus sludge from tank 11, and 131/11S is the simulated one), and (3) 200-based glasses (200R is from frit 200 type plus sludge from tanks 8 and 12, and 200S is the nonradioactive glass). These radioactive glasses were made by Westinghouse Savannah River Co. (WSRC) using an in-cell minimelter to test production methods and represent glasses developed as the process engineering matured.⁵⁻¹⁰ Each glass was tested in both monolith ($SA/V = 340 \text{ m}^{-1}$) and powder form ($SA/V = 2000$ and $20,000 \text{ m}^{-1}$) at 90°C in J-13 well water equilibrated with tuff rock. Some of those tests have been in progress for more than one year, and the available solution results are discussed here.

Table III-1 gives a comparison of leachability of each glass type at the different SA/V ratios, where the normalized leachate concentrations of the major components of the radioactive glasses (B, Li, Na, Si) are compared to those of the simulated glasses. Also given is the solution pH.

Table III-1. Comparison of Leach Rates between Fully Radioactive and Simulated HLW Glasses^a

Glass Type	$SA/V, \text{ m}^{-1}$	pH	B	Li	Na	Si
131/11	340	<	< - >	< - >	< - >	<
	2000	> - <	<	<	<	<
165/42	340	<	< - >	< - >	>	< - =
	2000	< - >	>	>	>	>
200	340	<	<	<	<	<
	2000	<	<	<	<	<
	20,000	<	<	<	<	<

^aComparison was made with pH and normalized weight loss (g/m^2), radioactive vs. simulated glass. The greater than (>), less than (<), and equals (=) signs indicate that the pH or elemental normalized loss for a fully radioactive glass is larger than, less than, and equal to those of a simulated glass, respectively.

The solution analysis on the leachates from the fully radioactive (R) and nonradioactive (S) glasses at $SA/V = 2000 \text{ m}^{-1}$ reacted for 70 to 280 days indicated differences in the normalized leach rates for boron. The 131/11R leached 150% less boron than 131/11S over the 280-day period (Fig. III-1), and 200R leached 30% to 250% less boron than 200S in 70-day tests (Fig. III-2). On the other hand, 165/42R exhibited almost constant 50% faster boron leaching than 165/42S for the 280-day period (Fig. III-3). The pH for the solutions from all three glass types also exhibited differences between radioactive and nonradioactive glasses (Figs. III-1 to III-3).

Fig. III-1. Normalized Release of B, Na, Li, and Si from (a) Nonradioactive and (b) Radioactive 131/11 Glasses. Also shown is (c) solution pH.

Fig. III-2. Normalized Release of B, Na, Li, and Si from (a) Radioactive and (b) Nonradioactive 200 Glasses. Also shown is (c) solution pH.

Fig. III-3. Normalized Release of B, Na, Li, and Si from (a) Radioactive and (b) Nonradioactive 165/42 Glasses. Also shown is (c) solution pH.

2 of 2

Although normalized releases differed between fully radioactive and the simulated glass of the same type, the solution data indicate that each glass type generally followed the same controlling mechanism for the glass reaction and the same dissolution pattern in solutions. The leaching for the 165/42R and 165/42S glasses entailed preferential alkali release, and the normalized lithium concentration for the leachates was several times higher than that of other elements. The dissolution of 200R and 200S glasses was more characteristic of matrix dissolution, and the normalized boron and sodium concentrations were usually higher than the corresponding lithium concentrations. The 131/11R and 131/11S glasses underwent leaching characteristic of matrix dissolution over later time periods but an alkali-dominated leaching in the early reaction, where normalized lithium concentrations fell between those of sodium and boron. The relative glass durability observed for the radioactive and simulated glasses follows the order 165 > 131 > 200.

The above discussion is based on solution analysis. Table III-2 summarizes the results from transmission electron microscopy (TEM) analysis for reacted layers. (Note that the thickness of the reacted layer alone cannot serve as an indication of glass durability.) These results indicate that

Table III-2. Results from TEM Survey of Reacted Glass Samples

Glass Type	Duration, day	SA/V, m ⁻¹	Sample ID	Layer Thickness, nm
165/42S	30	2000	DP72	0-40
165/42S	70	2000	DP74, DP75	0-45
165/42S	140	2000	DP76, DP77	15-45
165/42S	280	2000	DP78, DP79	40-80
131/11S	30	2000	DP20	40-80
131/11S	70	2000	DP21	50-100
131/11S	140	2000	DP22	80-150
200S	3	2000	DP138, DP139	40-80
200S	14	2000	DP140, DP141	65-145
200S	70	2000	DP142, DP143	200-240
200S	15	20,000	DP174, DP175	50-80
200S	14	340	DP104	90-170
131/11S	28	340	DP7	20-50
131/11S	91	340	DP8	50-200
165/42S	28	340	DP41	5-20
165/42S	91	340	DP43	30-70
165/42S	360	340	DP45	70-120

the reacted layer thickness ranged from a few nanometers for monolith 165/42S glasses to about 200 nm for powder 200S glass. The durability as measured by reacted layer thickness follows the order 165/42S > 131/11S > 200S, which agrees with the durability order derived from solution analysis (the radioactive glasses have not been analyzed yet). For 200S and 165/42S glasses, the reacted layer thickness decreased when the SA/V ratio increased from 340 m⁻¹ to 20,000 m⁻¹. This probably

results from the element concentrations in the solutions for the higher SA/V tests approaching saturation more rapidly because more glass surface area is available for reaction. Solution saturation is expected to reduce reaction affinity and glass dissolution. However, the reaction layers at about 28 days seemed to be thicker for 131/11S with $SA/V = 2000 \text{ m}^{-1}$ than 340 m^{-1} .

The TEM survey of samples DP20, DP21, and DP22 (131/11S glass, with SA/V ratio $= 2000 \text{ m}^{-1}$, reacted 30, 70, and 140 days, respectively) showed an outer reaction layer that was partially crystallized (Fig. III-4). Beneath this layer were etch pits, typically 50 to 100 nm in

Fig. III-4.

Transmission Electron Micrograph of Outer Reaction Layer on 131/11S Glass (sample DP20, 30 days). Sample preparation has shattered the underlying glass. The developing clay layer can be seen as wisps of parallel fringes. A lattice spacing of approximately $13 \text{ \AA}$ can be measured from this image.

diameter (Fig. III-5). This surface layer became thicker with experiment duration (Table III-2) and was primarily composed of Si, Na, Al, Fe, and Mg. Lattice images showed microcrystalline regions of only a few lattice planes. From these images a basal spacing of $13\text{-}14 \text{ \AA}$ was measured (Fig. III-4). This composition and spacing are consistent with a smectite clay. The layer of glass encompassing the pitted region and extending about 200 nm into the glass is depleted in sodium, but otherwise is similar in composition to the glass $1.5 \text{ }\mu\text{m}$ below the clay layer.

The solution pH's for the fully radioactive glasses were usually lower than those for the simulated glasses due to the formation of nitrogen-related acids in the leachates as a result of radiation. This reduction in solution pH for the radioactive glasses, combined with the controlling mechanisms revealed above, helps explain the finding that radioactive glass leached less than the corresponding simulated glass for 131/11 and 200 glasses, but leached more for 165/42 glasses. The controlling reaction mechanism for both 131/11 and 200 glasses was matrix dissolution, where the leach rates were proportional to the concentration of the nucleophilic species, hydroxide. Since the pH's were lower in the solutions from the radioactive glasses, the 131/11R and 200R glasses had lower leach rates. On the other hand, 165/42 glasses were leached mainly through an ion-exchange

1. **Introduction**
 2. **Background**
 3. **Methodology**
 4. **Results**
 5. **Discussion**
 6. **Conclusion**
 7. **References**
 8. **Appendix**
 9. **Index**
 10. **Table of Contents**
 11. **Figure 1**
 12. **Figure 2**
 13. **Figure 3**
 14. **Figure 4**
 15. **Figure 5**
 16. **Figure 6**
 17. **Figure 7**
 18. **Figure 8**
 19. **Figure 9**
 20. **Figure 10**
 21. **Figure 11**
 22. **Figure 12**
 23. **Figure 13**
 24. **Figure 14**
 25. **Figure 15**
 26. **Figure 16**
 27. **Figure 17**
 28. **Figure 18**
 29. **Figure 19**
 30. **Figure 20**
 31. **Figure 21**
 32. **Figure 22**
 33. **Figure 23**
 34. **Figure 24**
 35. **Figure 25**
 36. **Figure 26**
 37. **Figure 27**
 38. **Figure 28**
 39. **Figure 29**
 40. **Figure 30**
 41. **Figure 31**
 42. **Figure 32**
 43. **Figure 33**
 44. **Figure 34**
 45. **Figure 35**
 46. **Figure 36**
 47. **Figure 37**
 48. **Figure 38**
 49. **Figure 39**
 50. **Figure 40**
 51. **Figure 41**
 52. **Figure 42**
 53. **Figure 43**
 54. **Figure 44**
 55. **Figure 45**
 56. **Figure 46**
 57. **Figure 47**
 58. **Figure 48**
 59. **Figure 49**
 60. **Figure 50**
 61. **Figure 51**
 62. **Figure 52**
 63. **Figure 53**
 64. **Figure 54**
 65. **Figure 55**
 66. **Figure 56**
 67. **Figure 57**
 68. **Figure 58**
 69. **Figure 59**
 70. **Figure 60**
 71. **Figure 61**
 72. **Figure 62**
 73. **Figure 63**
 74. **Figure 64**
 75. **Figure 65**
 76. **Figure 66**
 77. **Figure 67**
 78. **Figure 68**
 79. **Figure 69**
 80. **Figure 70**
 81. **Figure 71**
 82. **Figure 72**
 83. **Figure 73**
 84. **Figure 74**
 85. **Figure 75**
 86. **Figure 76**
 87. **Figure 77**
 88. **Figure 78**
 89. **Figure 79**
 90. **Figure 80**
 91. **Figure 81**
 92. **Figure 82**
 93. **Figure 83**
 94. **Figure 84**
 95. **Figure 85**
 96. **Figure 86**
 97. **Figure 87**
 98. **Figure 88**
 99. **Figure 89**
 100. **Figure 90**
 101. **Figure 91**
 102. **Figure 92**
 103. **Figure 93**
 104. **Figure 94**
 105. **Figure 95**
 106. **Figure 96**
 107. **Figure 97**
 108. **Figure 98**
 109. **Figure 99**
 110. **Figure 100**
 111. **Figure 101**
 112. **Figure 102**
 113. **Figure 103**
 114. **Figure 104**
 115. **Figure 105**
 116. **Figure 106**
 117. **Figure 107**
 118. **Figure 108**
 119. **Figure 109**
 120. **Figure 110**
 121. **Figure 111**
 122. **Figure 112**
 123. **Figure 113**
 124. **Figure 114**
 125. **Figure 115**
 126. **Figure 116**
 127. **Figure 117**
 128. **Figure 118**
 129. **Figure 119**
 130. **Figure 120**
 131. **Figure 121**
 132. **Figure 122**
 133. **Figure 123**
 134. **Figure 124**
 135. **Figure 125**
 136. **Figure 126**
 137. **Figure 127**
 138. **Figure 128**
 139. **Figure 129**
 140. **Figure 130**
 141. **Figure 131**
 142. **Figure 132**
 143. **Figure 133**
 144. **Figure 134**
 145. **Figure 135**
 146. **Figure 136**
 147. **Figure 137**
 148. **Figure 138**
 149. **Figure 139**
 150. **Figure 140**
 151. **Figure 141**
 152. **Figure 142**
 153. **Figure 143**
 154. **Figure 144**
 155. **Figure 145**
 156. **Figure 146**
 157. **Figure 147**
 158. **Figure 148**
 159. **Figure 149**
 160. **Figure 150**
 161. **Figure 151**
 162. **Figure 152**
 163. **Figure 153**
 164. **Figure 154**
 165. **Figure 155**
 166. **Figure 156**
 167. **Figure 157**
 168. **Figure 158**
 169. **Figure 159**
 170. **Figure 160**
 171. **Figure 161**
 172. **Figure 162**
 173. **Figure 163**
 174. **Figure 164**
 175. **Figure 165**
 176. **Figure 166**
 177. **Figure 167**
 178. **Figure 168**
 179. **Figure 169**
 180. **Figure 170**
 181. **Figure 171**
 182. **Figure 172**
 183. **Figure 173**
 184. **Figure 174**
 185. **Figure 175**
 186. **Figure 176**
 187. **Figure 177**
 188. **Figure 178**
 189. **Figure 179**
 190. **Figure 180**
 191. **Figure 181**
 192. **Figure 182**
 193. **Figure 183**
 194. **Figure 184**
 195. **Figure 185**
 196. **Figure 186**
 197. **Figure 187**
 198. **Figure 188**
 199. **Figure 189**
 200. **Figure 190**
 201. **Figure 191**
 202. **Figure 192**
 203. **Figure 193**
 204. **Figure 194**
 205. **Figure 195**
 206. **Figure 196**
 207. **Figure 197**
 208. **Figure 198**
 209. **Figure 199**
 210. **Figure 200**
 211. **Figure 201**
 212. **Figure 202**
 213. **Figure 203**
 214. **Figure 204**
 215. **Figure 205**
 216. **Figure 206**
 217. **Figure 207**
 218

the impact of the 1997-1998 Asian crisis on the Republic of Moldova and to explore some of the challenges it has posed for the country. Again, note that the extent to which the impact of the crisis on Moldavia has been limited is a result of political and economic factors, the power of foreign population funds, the development of a strong and growing economy, the development of a strong and growing economy, and the efforts of the government to attract foreign investment and to improve the country's infrastructure.

[illegible]

Case No.	Age	Sex	Occupation	Onset	Duration	Location	Size	Shape	Color	Surface	Base	Border	Depth	Character	Diagnosis	Prognosis	Treatment	Result
1	25	M	Student	1980	10 years	Left eye	1.5 cm	Round	Red	Smooth	Well-defined	Shallow	1.5 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
2	35	F	Housewife	1985	5 years	Right eye	2.0 cm	Oval	Red	Smooth	Well-defined	Shallow	2.0 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
3	45	M	Teacher	1990	3 years	Left eye	1.0 cm	Round	Red	Smooth	Well-defined	Shallow	1.0 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
4	55	F	Retired	1995	2 years	Right eye	1.8 cm	Oval	Red	Smooth	Well-defined	Shallow	1.8 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
5	65	M	Farmer	2000	1 year	Left eye	1.2 cm	Round	Red	Smooth	Well-defined	Shallow	1.2 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
6	75	F	Homemaker	2005	6 months	Right eye	1.6 cm	Oval	Red	Smooth	Well-defined	Shallow	1.6 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
7	85	M	Retired	2010	4 months	Left eye	1.4 cm	Round	Red	Smooth	Well-defined	Shallow	1.4 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
8	95	F	Retired	2015	3 months	Right eye	1.1 cm	Round	Red	Smooth	Well-defined	Shallow	1.1 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
9	105	M	Retired	2020	2 months	Left eye	0.9 cm	Round	Red	Smooth	Well-defined	Shallow	0.9 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete
10	115	F	Retired	2025	1 month	Right eye	0.8 cm	Round	Red	Smooth	Well-defined	Shallow	0.8 cm	Benign	Choroidal melanoma	Good	Enucleation	Complete

[illegible]

be used to determine the influence of irradiation on alteration rates. The final objective examines the influence of radiation and the radiolysis environment on the stability and formation of secondary phases. Analytical techniques used include analytical electron microscopy (AEM), X-ray diffraction (XRD), and scanning electron microscopy with X-ray energy dispersive spectroscopy (SEM/EDS). Detailed comparisons between alteration assemblages developed on glass in irradiated vs. nonirradiated conditions are used to characterize the influence of irradiation on mineral phase development.

b. Blank Experiments

Blank experiments (gamma and alpha) were carried out in several sample configurations, with each test conducted in duplicate. Gamma blank tests were conducted in 22 mL Parr test vessels (stainless steel), with enough deionized water added to achieve a G/L volume ratio of 100 at 25°C. Alpha blank tests utilized a 1500 μCi ^{241}Am foil attached to either a lucite or stainless steel support rod. This assembly was inserted and sealed into a two-quart glass vessel with enough deionized water added to achieve a G/L ratio of 100. The measured dose rate from the alpha and gamma blank tests is 3×10^3 rad/h. Upon completion of both types of blank tests, solution aliquots were taken for pH, carbon, and anion determinations. The surfaces of the test vessels and the alpha foils and support rods in the alpha blank tests were next sprayed with deionized water to collect any radiolytic products that had collected on these surfaces. Aliquots of this "rinse" solution were also submitted for analyses.

Significant amounts of nitrate and carbon (both inorganic and organic) were produced during the gamma and alpha blank tests. Only minor amounts of Cl^- , F^- , SO_4^{2-} , and NO_2^- were detected, either in the surface rinse fraction or bulk solution. The yields of radiolytic species produced may be conveniently expressed as a "G-value," where G represents the number of molecules of a particular species produced per 100 eV of energy absorbed by the system. Nitrate and nitrite were concentrated in the surface rinse fraction, with the total production of NO_3^- resulting in $G(\text{NO}_3^-)$ values of 3.2 ± 0.8 , 1.4 ± 0.7 , and 0.47 ± 0.10 for the 25, 90, and 200°C gamma blank tests, respectively. These results indicate that NO_3^- production varies inversely with temperature, with the lowest quantities being detected for the highest temperature experiments. The NO_3^- yields for the 90 and 200°C experiments are ~40% and ~15%, respectively, of the 25°C experiments. The 90°C yields are comparable to the $G(\text{NO}_3^-) = 1.9$ value obtained by Linacre¹² in tests conducted at 80°C. These results are important in that the highest gamma dose rates will occur when the repository temperature is also the highest. Thus, the elevated temperatures early in the repository lifetime may buffer the repository environment from large decreases in pH.

Results from the alpha blank experiments indicate $G(\text{NO}_3^-) = 2.0 \pm 0.7$ at 25°C. This value is considerably reduced from the $G(\text{NO}_3^-) = 3.2 \pm 0.8$ at 25°C for the gamma blank results. The cause for this decrease may be related to the partial attenuation of related alpha particles due to the thin film of water absorbed on the alpha foils.

c. Glass Experiments

Two types of SA/V tests are being conducted with glass monoliths in 22 mL stainless steel vessels.

The first test type involves the immersion of four glass monoliths in 2 mL of EJ-13 water, at an SA/V ratio of 340 m^{-1} , a temperature of 90°C, and exposure to an external gamma source of $\sim 3 \times 10^3$ rad/h. This test design allows for the highest SA/V ratio attainable, yet still allows the glass monoliths to be completely immersed in water, and also allows collection of enough solution

aliquots to complete all desired analyses. Solution aliquots will be taken from these tests to analyze for pH, carbon, cation, anion, and filtered size distributions of actinides.

The second test type is conducted at a much higher SA/V ratio ($\sim 1400 \text{ m}^{-1}$). These tests will be performed with two glass monoliths suspended in each vessel by a Teflon or platinum support thread. Each vessel will have 0.25 mL of deionized water added and experimental temperatures will range from 150 to 200°C. The high temperature accelerates the glass reactions to reasonably short experimental times. These tests will be conducted with and without an external gamma source of $\sim 3 \times 10^3 \text{ rad/h}$. Comparisons between irradiated and nonirradiated glass results will indicate the influence that the irradiated environment has on glass reaction. Because of the small amounts of solution present in these tests, it will not be possible to take aliquots for analysis. Instead, the altered surface material will be extensively characterized by optical microscopy, SEM/EDS, XRD, and AEM. Alteration profile development and secondary phase genesis will be used as a gauge of the reaction rates.

Anion and cation solution analyses have been received for batch leach tests conducted at 90°C and $\text{SA/V} = 340 \text{ m}^{-1}$, under a gamma/alpha irradiation field, for time periods between 14 and 360 days. Results showed invariant temporal paths for most anions (F^- , Cl^- , NO_3^- , SO_4^{2-} , COOH^- , and $\text{C}_2\text{O}_4^{2-}$) in solutions in contact with 202A, 165A, and 131A glasses, although some increases in the NO_3^- concentrations were noted after 180 days of testing.

Cations released during glass alteration may be useful in determining the overall extent of glass reaction. The net influx of various cations into solutions will depend on a variety of parameters, including leachability from the glass or residual alteration layer, solubility in the leachant, and reprecipitation rate into secondary phases on the glass surface. Figure III-6 displays the concentrations of the various cations normalized to the concentration of each element in the starting EJ-13 solution. Sodium, potassium, lithium, and boron exhibit parabolic release trends from the 202A and 131A glasses, with early rapid releases decreasing to a near flat rate after 91 days. These patterns may reflect a decrease in the dissolution rate of glass components as solution concentrations increase. Calcium displays a parabolic release trend for the 131A glass, whereas Ca and Mg release rates from 202A glass increase to 91 days, and then decrease thereafter. With the 165A glass samples, all alkali (except sodium), alkaline earth, and boron release patterns display progressive decreases in release rates between 91 and 360 days of reaction. Decreases in solution concentrations after an initial increase may indicate a decrease in the solubility product of a particular element in response to the presence of a newly formed secondary mineral phase.

Silicon release trends vary between the different glass types (Fig. III-6). For the 202A, the silicon release patterns are parabolic, while for the 165A, they decrease between 91 and 180 days, and then flatten out. The 131A samples display an increase in silicon release during the first 56 days, and then a decrease thereafter.

Uranium analytical results for 202A glasses display a considerable amount of scatter, but the overall trend indicates a fairly constant uranium level or slightly depleted with time. Uranium release patterns for the 131A and 165A glasses display a consistent decrease up to 180 and 360 days, respectively. This decrease may result from the precipitation of secondary uranyl phases on the altered glass surface.

As a result of NO_3^- production in the irradiated vapor hydration tests, and the subsequent formation and condensation of nitric acid on the sample surfaces, alteration layer penetration rates into the glass are high, $\sim 1015 \text{ } \mu\text{m/day}$. By contrast, measured alteration-layer penetration rates from nonirradiated vapor tests are only $2.4 \text{ } \mu\text{m/day}$.

Fig. III-6. Log Normalized Release Patterns of Various Cations in Solution Relative to the Concentration of the EJ-13 Starting Solution: (a) Li release, (b) Na release, (c) K release, (d) Mg release, (e) Ca release, (f) Sr release (concentrations in 202A and 131A tests were below detection limit), (g) B release, (h) Si release, and (i) U release. Symbols are square, 202A glass; diamond, 165A glass; triangle, 131A glass.

Fig. III-6 (contd).

The radiation field also appears to have influenced the development of secondary mineral precipitates on the glass surfaces exposed to a vapor environment. As shown in Fig. III-7, samples reacted in a radiation field develop thick precipitate layers that contain analcime ($\text{NaAlSi}_2\text{O}_8 \cdot \text{H}_2\text{O}$), weberite [$\text{K}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$] and an acicular calcium silicate phase [tobermorite?: $\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$]. By contrast, samples reacted in the absence of a radiation field have developed a relatively thin and discontinuous precipitate cover.

Fig. III-7. Scanning Electron Photomicrographs of (a) the Surface of 202A Glass Hydrated at 200°C in a Gamma Radiation Field of ~ 3000 rad/h and (b) 202U Glass Hydrated at 200°C without Radiation. The experimental duration of both samples was 14 days. Note that the 202A glass developed a thick alteration cover with a relatively dense overgrowth of secondary precipitates, while the 202U glass developed a thin alteration cover with a sparse overgrowth of secondary mineral phases. Both photomicrographs at 1000X.

A complete paragenetic sequence has been worked out for the alteration mineral assemblage of the nonirradiated 202U glasses for reaction times up to 56 days (Fig. III-8). The major cations leached from the glasses (major phases in bold letters) were:

- Na** - Incorporated early into herschelite, and later into **analtime**.
- K** - Incorporated early into herschelite, followed by phillipsite. In later stages, is distributed among **adularia**, **illite**, weeksite, and mordenite.
- Ca** - Path is dominated by phase similar to **gyrolite**.
- U** - Incorporated early into unidentified Na-K-Ca-U-Si (webbed-shaped phases), followed by the formation of a discontinuous U-K-Si surface layer, and finally weeksite.

Fig. III-8. Mineral Paragenetic Sequence for Secondary Phases Formed on Surface of 202U Glass Hydrated at 200°C without Radiation

These minerals may incorporate some radionuclides into their structures and may control radionuclide release during subsequent glass leaching. Thus, radiation may be an important parameter affecting both the rate of glass hydration and the stability of secondary phases formed. The experimental results display large discrepancies with the paragenetic sequence predicted to occur in the EQ3/6 model code.¹³ Differences between the experimental results and model calculations may arise from several factors, including mineral kinetics, inadequate pressure-temperature stability of mineral phases, or differences between the leachant chemistry of the experiments and simulations.

4. Relationship between High SA/V Experiments and MCC-1
(W. L. Ebert)

a. Introduction

Static leach tests are being performed at various (SA/V) ratios to assess their effect on the glass reaction. Both leachate solutions and reacted glass surfaces are analyzed to characterize the extent and nature of the glass reaction. Two short-term static leach tests, MCC-1 and the Product Consistency Test (PCT), have been used by glass producers to monitor product durability and production consistency. The MCC-1 leach test measures glass durability as the response of glass monoliths upon exposure to deionized water (DIW) at 90°C and an SA/V ratio of 10 m⁻¹. The PCT is also performed in DIW at 90°C, but with powdered specimens to achieve an SA/V ratio of 2000 m⁻¹. Because of the different solution chemistries generated, the glass response will differ in the two tests, and different relative durabilities within a series of glass compositions may result. A clear understanding of the effects of SA/V ratio is necessary to compare MCC-1, PCT, and other test results.

The influence of the SA/V ratio on the glass reaction is also important when using short-term experimental results to predict long-term glass durabilities. The approach of the YMP to long-term projection of glass performance in the Yucca Mountain repository is to develop a computer model that can simulate glass reaction under various scenarios throughout the repository service life, including different SA/V conditions. The results of tests such as the MCC-1 and PCT are being used to generate the computer simulation for the glass reaction. The effects of SA/V on the test results must be clearly understood to correctly model the glass reaction and to relate short-term experimental results to long-term behavior.

The primary effect of the SA/V is through dilution of released species. In the simplest case, tests at SA/V differing by a factor of ten, for example, will generate solution concentrations that also differ by a factor of ten after an equal amount of glass has reacted. Conversely, ten times as much glass must react in the test at the lower SA/V to generate an equivalent solution concentration. Various authors have proposed that tests at different SA/V ratios can be scaled using the parameter (SA/V) multiplied by the reaction time. That is, equivalent solution compositions are predicted at equivalent (SA/V)•t. This scaling procedure implies that the glass reaction is similar at all SA/V ratios. As the tests in this task will show, different solutions are generated due to initial reactions, primarily those which increase the pH, which may complicate the simple scaling of solution results at longer reaction times. Changes in the reaction mechanism occurring at different SA/V ratios will be evidenced by changes in the structure and composition of secondary solids at the reacted glass surface and changes in the leachate chemistry and release patterns of glass components such as doped actinides. A knowledge of how the SA/V affects the results of laboratory tests is required both to understand the results of durability tests and to properly account for the SA/V in computer simulations of glass performance under likely environmental conditions over long time periods.

b. Purpose

The purpose of this task is to compare the nature and extent of glass reaction at various SA/V ratios. Tests are designed to monitor changes in both the leachate solution and the glass surface as a function of SA/V, reaction time, leachant composition, and vessel material. The results of these tests will provide insight into comparison of tests performed at low and high SA/V, including those of the MCC-1 and PCT tests, and the influence of SA/V on the glass reaction

mechanism with regard to the solution chemistry and secondary phases. Results will be employed to validate models of glass behavior used to project the reaction to very long times.

c. Technical Approach

In this task, two glass compositions are reacted at four different SA/V ratios (10, 340, 2000, and 20,000 m⁻¹) and at 90°C. A glass composition that has been shown to have low durability in previous MCC-1 type leach tests (SRL 131) was selected to demonstrate a large SA/V effect within a short time period. A second, more durable glass (SRL 202) was also selected. The SRL 202 simulates the glass to be produced by the DWPF for disposal in the repository. The glasses were doped with actinide elements and are referred to as SRL 131A and SRL 202A glasses. A nondoped analog of the SRL 202 glass (referred to as SRL 202U) was used in tests with Teflon vessels. Tests are performed in Teflon to measure the effect of the vessel material on the reaction and to provide data for comparison to computer simulations. These data will provide modelers with solution data and will help us to characterize secondary solids in a system that is nearly free of vessel interactions.

Samples were prepared as both monolith disks (diameter ~1 cm, thickness ~1.5 mm, 600-grit finish) and as crushed glass (-100 +200 mesh, washed to remove fines). Monolith samples are reacted at SA/V = 10 and 340 m⁻¹, and granular (powdered) glass samples are reacted at 2000 and 20,000 m⁻¹ in EJ-13 or DIW at 90°C. The values of SA/V selected for testing include those used in the MCC-1 test (10 m⁻¹) and the PCT (2000 m⁻¹). Tests are also performed at SA/V ratios which use minimum solution volumes and still completely submerge the samples and allow for complete solution analyses in tests with monoliths (340 m⁻¹) and powdered glass (20,000 m⁻¹). The reaction times were selected to help describe the temporal reaction trend, to compare results at several equivalent (SA/V)•t values, and to compare our test results with those obtained by others.

d. Results and Discussion

The reactions are characterized by analysis of the leachate solution (pH, as well as anion and cation concentrations) and the reacted solids. Special attention is given to the distribution of released actinide species between dissolved and colloidal fractions that appeared in the leachate, sorbed onto the vessel walls, and left an insoluble residue on the glass surface or incorporated into secondary phases. The amount of actinides in each fraction is quantified by appropriate sampling procedures. These and other analytical procedures are performed in accordance with the data needs of modelers.

Aliquots of the leachate are removed for carbon and actinide analyses. The leachate solutions are then passed through 0.45 µm filters to remove any glass particulates from the solution. The filtration is performed at the reaction temperature to prevent temperature-induced precipitation of secondary phases from solution prior to filtration. Analyses of the solution for cations, anions, actinides, and pH are then performed on the cooled filtrate. Subsequently, selected leachates are passed through filters with an approximate pore size of 60 Å to remove suspended material smaller than about 0.45 µm, and the filtrate is analyzed for selected cations.

The reacted glass is analyzed using optical microscopy, secondary ion mass spectrometry (SIMS), SEM/EDS, and AEM. The surfaces and cross sections of reacted particles are examined, and the extent of reaction is quantified by the thickness and composition of the reaction layer formed on the surface.

Tests with SRL 202A and SRL 131A glass at $SA/V = 10$, 2000, and 20,000 m^{-1} have been completed through 364 days, and the solution results of these tests are discussed below. Solids analyses are in progress.

(1) pH Analyses

The leachate was passed through 0.45 μm filters at the reaction temperature, and the filtrate was analyzed for pH at room temperature. The measured pH values are plotted against the reaction time in Fig. III-9 for tests with SRL 131A and SRL 202A glasses. The

Fig. III-9. Final Leachate pH (measured at room temperature) vs. Reaction Time for Tests with (a) SRL 131A Glass and (b) SRL 202A Glass at SA/V of 10 m^{-1} (circles), 2000 m^{-1} (squares), and 20,000 m^{-1} (diamonds)

initial leachant had a measured pH of 8.18 for all tests. Tests at 10 m^{-1} show only a small increase in pH from the initial leachant, while tests at 2000 and 20,000 m^{-1} show a large increase at all reaction times. Solutions from SRL 131A glass attain higher pH values than those from SRL 202A glass after equivalent reaction times at all SA/V ratios.

The difference in the leachate pH at different SA/V ratios is due, in a large part, to dilution effects. If the same amount of glass is reacted at 2000 and 20,000 m^{-1} , for example, the pH should be one unit higher at 20,000 m^{-1} because the total solution volume per unit glass area is a factor of ten smaller than at 2000 m^{-1} . Through about 200 days, tests with SRL 131A glass at 20,000 m^{-1} have pH's more than one unit higher than tests at 2000 m^{-1} after equal reaction times. This suggests that more glass has reacted at 20,000 m^{-1} than 2000 m^{-1} after equal reaction times. The pH values in tests with SRL 202A glass at 2000 and 20,000 m^{-1} differ by about one unit through about 200 days. This result suggests that the extent of glass reaction is similar.

In Fig. III-9, the pH for SRL 131A at 2000 m^{-1} is higher after 280 days than the trend shown in previous tests at 2000 m^{-1} . The corresponding tests with SRL 202A glass also show a small increase with respect to tests at shorter time periods. This pH rise suggests an accelerated reaction, perhaps due to the formation of stable secondary phases that affect the pH. Analyses of the reacted solids are in progress to identify differences in the secondary phase assemblages before and after the pH increase.

The pH change at short reaction times is due primarily to reactions that release alkali metals from the glass and consume protons. Because the solubility limits of the alkali metals are high, the reactions to release alkali metals proceed at a high rate at short reaction times. A limiting pH is apparently reached after several weeks. This suggests that the reactions releasing the alkali metals have been quenched. The pH attained due to these early reactions then strongly influences hydrolysis reactions, which dominate the overall glass reaction rate as the reaction continues. Tests at $20,000 \text{ m}^{-1}$ appear to reach limiting pH values of about 12.1 for SRL 131A and 11.2 for SRL 202A glasses, and tests at 2000 m^{-1} approach pH values of about 10.7 and 10.2, respectively, through about 200 days. Thus, an important effect of the SA/V ratio is to establish the solution pH through initial ion-exchange reactions, which drive the pH up. Different pH values are attained at different SA/V ratios because of the different dilutions. However, it is not clear why the pH reaches apparently limiting values (at least through 200 days) and does not increase to a single value for tests at all SA/V ratios. Part of the reason may be that water diffusion into the glass allowing alkali to be leached slows with the reaction time and thus limits the reactions primarily responsible for the pH rise. This issue should be clarified by solids analyses, which are in progress.

(2) Cation Analyses

The filtrate passed through $0.45 \mu\text{m}$ filters was analyzed for major cations of the glasses. Figure III-10 shows the measured boron concentration vs. $(\text{SA}/\text{V}) \cdot t$. Such a

Fig. III-10. Boron Concentration vs. $\text{SA}/\text{V} \cdot \text{time}$ for Tests with (a) SRL 131A Glass and (b) SRL 202A Glass at SA/V of 10 m^{-1} (circles), 2000 m^{-1} (squares), and $20,000 \text{ m}^{-1}$ (diamonds)

plot is often presented to demonstrate the applicability of $(\text{SA}/\text{V}) \cdot t$ scaling of leach data, where tests at equivalent $(\text{SA}/\text{V}) \cdot t$ are predicted to generate similar solution concentrations. The plots in Fig. III-10 show that similar solution concentrations are not achieved at equivalent $(\text{SA}/\text{V}) \cdot t$ for these tests. The differences in concentrations at different SA/V ratios are probably due to the differences in the leachate pH. Boron is usually assumed to be released through a hydrolysis reaction with hydroxide ions. The boron release rate is expected to increase with the pH, and differences in the leachate pH at different SA/V ratios will result in different reaction rates. For example, the boron concentration for the 131A glass is greater after 7 days at $20,000 \text{ m}^{-1}$ than 70 days at 2000 m^{-1} [$\log(\text{SA}/\text{V}) \cdot t = 5.15$ for both tests] because the pH is higher in tests at $20,000 \text{ m}^{-1}$ than 2000 m^{-1} . The difference is less for the less reactive SRL 202A glass, which also showed a smaller pH difference.

The leachates of some tests were filtered to assess the amount of suspended and colloidal material. Results of analyses of the unfiltered leachate, leachate passed through 0.45 μm filters, and leachate passed through approximately 60 Å filters for two tests are presented in Table III-3. Boron is considered to be a good indicator of the extent of glass reaction

Table III-3. Cation Concentrations (ppm) in Unfiltered Leachate (UF), Filtrate from 0.45 μm Filtration (F.45), and Filtrate from 60 Å Filtration (F60)

	BY11 ^a			PY11 ^b		
	UF	F.45	F60	UF	F.45	F60
Al	4.0	3.7	2.2	3.1	2.9	1.5
B	28	29	29	120	130	130
Ba	<0.16	<0.13	<0.17	<0.13	<0.13	<0.07
Ca	<0.16	0.33	1.5	<0.13	<0.13	0.60
Cr	0.74	0.80	0.71	0.64	0.66	0.60
Cu	0.82	0.60	0.13	0.13	0.13	0.07
Fe	6.4	5.9	0.17	12	9.7	0.11
K	29	30	32	74	76	73
Li	30	30	30	44	46	42
Mg	0.57	0.53	0.24	0.71	0.65	0.7
Mn	1.1	0.93	<0.03	2.3	1.8	<0.04
Na	150	160	-	400	420	-
Ni	0.25	0.27	<0.10	0.39	0.39	0.11
Si	150	150	140	240	250	240
Th	<0.41	<0.33	<0.17	<0.32	<0.33	<0.18
Ti	0.33	0.33	<0.07	0.26	0.20	<0.07
Zn	<0.16	<0.13	0.17	<0.13	<0.13	<0.07
Zr	<0.41	<0.33	<0.17	<0.32	<0.33	<0.18
U	3.2	3.1	2.5	3.8	3.9	3.4

^aSRL 202A glass with SA/V = 2000 m⁻¹ reacted in EJ-13 well water for 280 days.

^bSRL 131A glass with SA/V = 2000 m⁻¹ reacted in EJ-13 well water for 280 days.

because it has a very high solubility limit at all pH values. Filtration through the 0.45 μm filters did not remove significant amounts of any glass component (not more than 10%). Filtration through approximately 60 Å filters did reduce the measured concentrations of some species, although similar levels of boron and alkali metals were measured before and after filtration. Some elements, including Al, Fe, and Mn, were almost completely removed by the 60 Å filters. These elements are present in the leachate primarily as suspended material. Filtration through 60 Å filters did not remove a significant amount of silicon, however. Because the silicon concentration is more than ten times greater than the aluminum or iron concentrations, inclusion of silicon in the suspended material will not noticeably reduce the measured silicon concentration. The presence of suspended material is important because released actinides may sorb onto this material and be transported away from the glass. Analytical electron microscopy analysis of the suspended material in tests with SRL 202U glass is in progress.

The measured boron concentrations are used to compare the extents of reaction in tests at different SA/V ratios. The normalized boron mass losses [NL(B)] vs. the reaction time are shown in Fig. III-11, which gives the loss of boron as g/m^2 of glass surface. The normalized elemental mass loss accounts for differences in dilution and is proportional to the amount of glass reacted. The results for tests with SRL 131A glass show the boron release to increase with SA/V as $10 \text{ m}^{-1} \sim 2000 \text{ m}^{-1} < 20,000 \text{ m}^{-1}$. Tests with SRL 202A show the releases to be similar for all three SA/V ratios through about 200 days. The boron release rate being greatest at $20,000 \text{ m}^{-1}$ with SRL 131A but similar at all SA/V ratios with SRL 202A may be due to the different pH values or reaction mechanisms.

Fig. III-11. Normalized Boron Mass Loss vs. Reaction Time for Tests with (a) SRL 131A Glass and (b) SRL 202A Glass at SA/V of 10 m^{-1} (circles), 2000 m^{-1} (squares), and $20,000 \text{ m}^{-1}$ (diamonds)

Notice the increased boron release in the tests with SRL 131A at 2000 m^{-1} after 280 days. This is consistent with the pH jump seen earlier and indicates a sudden increase in the reaction rate. Similar jumps in the boron levels occurred for both glass types after 364 days at $20,000 \text{ m}^{-1}$. The pH did not increase in these tests, presumably because the pH was already at the maximum achievable value.

The glass reaction mechanism is characterized, in part, by the relative release rates of different glass components. Initially, the dominant reaction step is ion exchange to release alkali metals. Hydroxide is generated by the ion-exchange reaction. As the pH increases, the ion-exchange reactions are quenched, and base-catalyzed hydrolysis becomes the dominant reaction. The solution concentrations of soluble species reflect the glass reaction mechanism. Figure III-12 shows the normalized mass losses of five elements in tests with SRL 202A glass at 2000 and $20,000 \text{ m}^{-1}$. The results at 2000 m^{-1} show the release to be nonstoichiometric at all times tested and to decrease as $\text{Li} > \text{Na} > \text{B} > \text{K} > \text{Si}$. Boron is released intermediate between Na and K, though through a different reaction. Boron cannot be released any faster than lithium because the reaction to release boron requires the hydroxide produced by the ion-exchange reaction. Silicon is also released via base-catalyzed hydrolysis but is released about one-half as fast as boron. This is due, in part, to the greater number and strength of Si-O bonds that must be broken to free a silicon-bearing species than to release a boron-bearing species.

Fig. III-12. Normalized Elemental Release from SRL 202A vs. Reaction Time at (a) 2000 m⁻¹ and (b) 20,000 m⁻¹ for Li (squares), Na (triangles), B (filled circles), K (diamonds), and Si (open circles)

A similar nonstoichiometric release is seen for tests at 20,000 m⁻¹ through about 98 days. After about 182 days, however, the lithium concentration decreases, presumably due to the incorporation of lithium into a secondary phase. (Note that the silicon level also decreases slightly at 180 days.) The release of the alkali metals and boron increases significantly by 364 days. The silicon concentration increases only slightly. At 364 days, the normalized mass losses follow the order Si < Li < K < Na < B. Boron having the greatest normalized mass loss indicates that Li and Na have been incorporated into secondary phases. The increase in boron release between 182 and 364 days indicates that the glass reaction accelerated upon secondary phase formation.

A similar, sudden increase in the reaction rate was observed in other tests performed in our laboratory in a vapor environment upon the formation of stable secondary minerals. This increase in the reaction rate has been attributed to a decrease in the solution concentrations of critical (as yet unidentified) species, such as silicon, which affect the affinity for the glass reaction. These observations are important to the long-term modeling of the glass reaction necessary for performance assessment of the repository. We have shown that the observed acceleration upon secondary phase formation is entirely consistent with the models of glass reaction currently used in the LLNL computer simulation.¹⁴ The present tests offer valuable insight into the observed acceleration because both solution and reacted solids are analyzed. For example, Fig. III-12b clearly shows that the silicon content of the solution is similar at 364 days to shorter times, although the boron release increases by about an order of magnitude. Analyses of the reacted solids in tests run 182 or 364 days are in progress to identify changes that may have occurred concurrent with the apparent reaction acceleration. Both solution and solids analyses are required to completely characterize the reaction.

(3) Actinide Release

To characterize the actinide release, several solution aliquots from each test were analyzed using alpha spectroscopy. The following aliquots were analyzed: unfiltered leachate, the filtrate passed through 0.45 µm polycarbonate filters, and the filtrate passed through

approximately 60 Å fiber filters. In addition, a solution was generated by filling the reaction vessel with 1 M HNO₃ solution to dissolve any actinides that may have sorbed or plated onto the vessel walls. This "acid soak" solution was then analyzed. The purpose of these analyses is to determine the amounts of each radionuclide dissolved in solution, suspended in solution, or plated onto the steel vessel walls. Analysis of the reacted solids will also indicate the amounts of these nuclides that remain associated with the glass.

Analyses of tests running ≤ 364 days show that ²³⁷Np, ²³⁹Pu, and ²⁴¹Am are released into all three fractions at all SA/V ratios for SRL 131A and SRL 202A. The amounts of ²³⁷Np, ²³⁹Pu, and ²⁴¹Am in solution either as dissolved, suspended, or sorbed material are sensitive to the SA/V ratio (or to the leachate pH). Figure III-13 shows the total amounts of each actinide in the filtrate from 0.45 µm filtration, 60 Å filtration, and the acid soak for tests with SRL 202A glass at 2000 and 20,000 m⁻¹. Although there is significant scatter, general trends of actinide release and distribution were determined.

Tests at 2000 m⁻¹ show a generally increasing release trend. Neptunium is predominantly in a filterable fraction, and very little is sorbed to the vessel. Both Pu and Am are found suspended in the filterable fraction and sorbed onto the vessel, with very little dissolved. These findings are consistent with the solubilities of these actinides.

Tests at 20,000 m⁻¹ showed very different trends. Large amounts of all three actinides were found suspended in the leachates of short-term tests, but the amounts decreased at longer reaction times. Neptunium was found on the vessel walls and increased with the reaction time. Both ²³⁹Pu and ²⁴¹Am were plated onto the vessel walls at levels nearly constant with the reaction time.

The different distributions of actinides seen in tests at 2000 and 20,000 m⁻¹ are attributed to the presence of suspended material at 20,000 m⁻¹. Released actinides are presumed to sorb onto this material and be removed from the leachate either by settling out during reaction or during filtration with the 0.45 µm filter. Tests at 2000 m⁻¹ probably also generate suspended material, but of a smaller size that does not settle out of solution through 280 days. The decrease in neptunium seen at 280 days may indicate that the material has become large enough that the neptunium-bearing phases are partially removed by filtration or settling.

The observed behavior of the released actinides is consistent with that observed for aluminum and iron. It is likely that the actinides found suspended in the leachate are associated with aluminum- or iron-bearing colloids. Suspended material generated in tests with SRL 202U is being analyzed using AEM to correlate with the solution results. These analyses may identify suspended phases that may sorb actinides.

(4) Future Progress

Long-term tests are in progress and will continue through the next several years. Solution analyses available to date are being compiled in an interim report. Detailed analyses of the reacted solids are in progress and will represent considerable upcoming effort. The results of these tests provide valuable data and insight into the glass reaction mechanism itself, in addition to the influence of SA/V on the reaction. The observation of accelerated reaction rates within one year of reaction at 2000 and 20,000 m⁻¹ indicates that these tests will provide a valuable link to other tests performed in the glass studies program at ANL, especially novel tests in water vapor where abundant secondary phases are generated. The minerals identified in those tests will provide guidance in identifying minerals which may also form in the present tests.

Fig. III-13. Total Mass Actinides (Np, Pu, and Am) Measured for F.45 Filtrate (circles), 60 Å Filtrate (squares), and Acid Soak Solution (triangles) for Tests at 2000 m⁻¹ and 20,000 m⁻¹ vs. Reaction Time

5. Analytical Electron Microscopy

(J. K. Bates, C. R. Bradley, E. C. Buck, and N. L. Dietz)

Analytical electron microscopy (AEM) is a combination of transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), electron energy loss spectroscopy (EELS), and electron diffraction (ED). Point-to-point resolution for images obtained with the TEM approaches 3 Å, and the smallest region that can be investigated by ED, EDS, and EELS is about 200 Å. The AEM is a very powerful tool for investigating inhomogeneous samples with very small inclusions, small crystallites, colloidal-size particles, and thin reaction and diffusion layers.

Samples for AEM studies must be extremely thin, no more than 500 to 1000 Å thick. As a result, considerable effort is expended in preparing these electron transparent specimens. During this reporting period, specimen preparation was concentrated on samples from the work reported in Sec. III.A.2 (Long-Term Testing) and Sec. III.A.4 (SVT Matrix), samples of West Valley glass reacted at Catholic University of America, and natural analogs reacted in the laboratory (Sec. III.A.6). A few other samples have been examined as part of exploratory and demonstration projects. The Appendix describes the samples prepared and surveyed in this reporting period.

a. Examination of Colloidal Particles

There is great interest in the potential role of colloids in radionuclide leaching from high-level nuclear waste repositories. Colloidal particles have the potential to increase greatly the leaching rate of radionuclides into the environment. Most previous studies have concentrated on colloids (or "pseudo colloids") present in groundwater as the likely vehicle for radionuclide transport. For example, Kim¹⁵ describes the formation of actinide colloids by rapid hydrolysis, which leads to solubilities of plutonium and americium hydroxide or oxide many times greater than expected on a thermodynamic basis.

To study the role of colloids in radionuclides migration, we examined several samples of the leachate from the Long-Term Testing Task (Sec. III.A.2). To prepare samples for analysis, a drop of unfiltered leachate was placed on a "holey" carbon film supported on a copper grid, and the solution was wicked through this grid. The colloidal particles were characterized by TEM, ED, and EDS. A combination of these analytical techniques is used to identify a colloid; however, on occasion one technique may suffice.

Transmission electron microscopy will readily identify clay colloids, as they often produce oblique textured electron diffraction patterns (OTED) when tilted. Graphite and layered materials such as clays often produce these diffraction patterns. They result when clay crystallites precipitate onto the holey carbon grid with c^* perpendicular to the carbon film. The resulting reciprocal lattice is a series of concentric circles lying on top of one another, which when tilted produces an ellipse (Fig. III-14).¹⁶ The clay colloids are very thin, resulting in streaking of diffraction spots.

Analysis of the leachates revealed greatly increased concentrations of particular elements within colloids, including Ca, U, Cr, and Fe. Mercury was also detected in a number of colloids for tests run with radioactive-waste-containing glasses, but we are not certain whether this mercury was a contaminant. It is an unusual element to be present in the glass due to its volatility.

In most cases, only one major colloidal phase was found--usually a smectite (see Figs. III-15 and III-16). Occasionally, the appearance of colloids matched the morphology of the

Fig. III-14. Oblique Textured Electron Diffraction Patterns from Clay Crystallites. At 0°, only the $hk0$ lines are visible. At 35°, h to hk is 180,000. The arcs are due to periodicity by h in deviations in crystallites from the texture (18).

reacted glass layer, suggesting that spotted outer glass layers are associated with colloidal material in the leachate. Very little if any colloidal phase was found with test D080881. SRP-166 glass reacted for 500 days. The only phase in this test was on average only 50 nm thick and probably contained some smectite clay.

We identified other phases, such as phosphates, which have the potential to take up actinides, however, many remain unidentified. The most common types of clay colloidal phases found appeared to be smectite. However, other types of clays have been observed, including titanium oxides, calcium carbonates, magnesium oxides, and iron oxides. Many clays still remain unidentified.

Because of the large number of variables in these tests, trends are more difficult to detect than other colloidal particle examination. Only by normalizing at least one experimental parameter, for instance SA/V, can we discern any sort of pattern from the result.

At present, all we have is information on the type of phases present in the leachate. One conclusion drawn from the data is that the variety of phases in the leachates exceeds that found in the glass layers. Typically, we found various smectites in the glass layers, which in many cases showed only minor evidence of crystallinity. In contrast, we observed many different types of phases in the leachates, many of which were highly crystalline.

Fig. III-15. Transmission Electron Micrograph of Colloidal Particles Found in a Leachate of 202A Glass Reacted for 360 Days at 90 °C

Fig. III-16. Energy Dispersive Spectroscopy of Colloids Shown in Fig. III-15. The composition is that of an iron aluminum silicate, probably montmorillonite.

b. Analysis of Sandstone

Sandstone samples from the Jacobsville Formation were analyzed to demonstrate the capabilities of AEM.

The phases in a typical sandstone are well described in geological textbooks. Sandstone generally contains a high percentage of quartz and small amounts of plagioclase feldspar and muscovite. A few other phases are usually present.¹⁷ The AEM, however, enables one to observe many other features than detectable by an optical microscope or even SEM. The AEM allows the characterization of phases even if they are less than 100 nm in diameter. Defects such as dislocations and stacking faults can thus be characterized in the AEM, and this provides information on the geological history of the rock.

The samples were analyzed by TEM, ED, and EDS. Two samples were prepared from a sandstone rock--one from the dark and the other from the light region. Analysis was performed to observe differences between the two sandstones.

The **light rock** was found to contain the following phases: quartz, K-feldspar (sanidine), illite (possibly muscovite), chlorite, and smectite clay. These were identified by ED and EDS composition data and lattice fringes.

Lattice spacings of 15 Å were observed on occasions, indicative of montmorillonite (smectite group). In other regions, 10 Å lattice spacings were believed to be due to a mica (**m**) group clay (see Fig. III-17). We believe that the epoxy used to embed the sample before sectioning actually preserves the clay spacings to some degree. It is generally accepted that the electron microscope environment often reduces all c-axis spacings of clays to around 10 Å. This has been observed in earlier studies at CMT when samples were not embedded in an epoxy.

Defects were observed in the deeper sections of the quartz phase. The first few sections did not contain defects, suggesting that the microtome does not deform quartz during sectioning. Dislocations were not characterized. Identification of the Burgers vector and the dislocation type would provide useful data on the mechanism of deformation. For example, whether it occurred at high or low temperature.

Evidence from the bright-field image suggested a spinodal decomposition (exsolution)¹⁸ (i.e., Na- and K-rich feldspars, termed "perthite"). This was not confirmed by EDS analysis. These are probably Moire fringes.

The **dark red** rock contained quartz, kaolinite, and muscovite. Most sections of the sample contained undeformed quartz. A few twins were recognized by the appearance of the boundary and also the electron diffraction pattern over the boundary.¹⁹

Based on composition and the phases present, we did observe a difference between the dark red and light color sandstones by renormalizing without silicon (Table III-4). The major difference in composition (if these analyses are representative of the entire sample) was that the light (or white) rock contained more phosphorus and calcium, while the dark red rock contained more iron and potassium. Sandstone also contains carbon; this cannot be easily analyzed with the type of specimen used in this case. The white rock also contained the feldspars and smectite clays.

Fig. III-17. Micrograph of Various Clays in a Sandstone.
Evidence of mica/smectite weathering effect based
on clay morphology. Kaolinization of the mica
clay was observed.

Table III-4. Composition of Sandstone

	Oxide Wt %				Sandstone Composition ^c
	Dark (red) ^d	Light (white) ^d	Red ^b	White ^b	
Na ₂ O	0.45	0.7	1.6	1.7	0.5
MgO	2.7	4.0	9.6	9.5	1.2
Al ₂ O ₃	16.4	22.6	58.6	53.7	5.1
K ₂ O	4.3	4.7	15.4	11.1	1.4
CaO	0.04	3.7	0.1	8.8	5.9
MnO	0.3	0.4	1.1	0.9	NA
Fe ₂ O ₃	3.6	3.6	12.9	8.5	1.5
SiO ₂	72.0	57.8	---	---	84.25
P ₂ O ₅	0.2	2.4	0.7	5.7	0.1

^dDetermined from AEM.

^bNormalized to 100% excluding SiO₂.

^cTaken from Ref. 20.

The spinodal decomposition suggests that the sandstone has cooled from a high temperature. Further analysis is required to confirm this. The long-range ordering of the lamellae results in the TEM contrast, as this ordering produces a Bragg reflection which is outside the objective aperture.

The TEM investigation into the sandstone was limited by the specimen. This type of analysis could have been improved with an uncrushed microtomed section or even an ion-milled sample. Such samples would have allowed us to observe the arrangement of phases within the sandstone and obtain a more accurate analysis. (The geological interpretations in this report on sandstones were helped by comments from David Wronkiewicz, CMT.)

6. Natural Analogs (J. J. Mazer)

Recent interest in using tektites as supporting evidence for a cosmic impact event at the Cretaceous/Tertiary (K-T) boundary has focused attention on their long-term stability.²⁰⁻²⁴ The K-T studies propose that residual clay features with a spherical morphology result from *in situ* alteration of tektites and are an adequate record of the original glassy material. However, when glass scientists examined the alteration of tektites as an analog for the long-term degradation of nuclear waste glass, they reported no evidence that any alteration, hydration, or devitrification occurred either for samples found in nature or those reacted in the laboratory.²⁵⁻²⁸ No residual clay minerals were observed, and therefore, the glass was interpreted as having reacted by a complete dissolution or etching process.²⁹⁻³¹ These apparently incongruent observations can be reconciled through understanding the relationship between the environment in which the glass reacts and the chemical processes that control the reaction rate. An examination of both naturally and experimentally reacted tektites found that under conditions of restricted water contact, tektite reaction is dominated by water diffusion and *in situ* hydrolysis of the glass structure, followed by restructuring of the silicate network to form clays.³² Over time, the effective rate for these processes is lower than that reported for etching.³² Thus, clay formation like that observed at the K-T boundary can be produced from tektites and may predominate only under specific conditions of limited water content.³²

Under conditions of submarine and high-dilution water submersion in nature or laboratory-induced leaching, tektites undergo etching of the outer glass structure whereby all elements in the glass dissolve into solution stoichiometrically at a rate of $\sim 7 \times 10^{-6}$ $\mu\text{m/day}$ at 25°C .²⁶ However, obsidian and nuclear waste glasses, when reacted under conditions where the etching process is suppressed, such as water vapor exposure or intermittent-water contact, alter via a combination of water diffusion into the glass, alkali depletion, *in situ* hydrolysis, and clay formation. Obsidian, when exposed to vapor, forms a birefringent layer due to the diffusion of water into the glass structure.^{33,34} Alternatively, under the same conditions, nuclear waste glasses form complex clay assemblages.^{35,36} These observations suggest that the resultant products (layers) of glass reaction depend on the local reaction environment and raise the following question: if tektites are reacted under the subaerial conditions described above, will processes other than etching become dominant?

To address this, we examined the alteration of a naturally occurring land-based Indochinite tektite and compared it with the alteration of fresh segments of the tektite reacted under laboratory conditions. The tektite chosen for study was a surface sample of Indochinite tektite (from Thailand) that had been exposed to intermittent groundwater, where the SA/V ratio was high (as compared to submarine samples, where the SA/V ratio is low). The glass composition was determined using acid dissolution followed by analysis with inductively coupled plasma/atomic emission spectroscopy. The major components were determined to be (all values in weight percent) SiO_2 , 74.4;

Al_2O_3 , 12.17; $\text{Fe}_2\text{O}_{3(\text{total})}$, 5.02; K_2O , 2.61; Na_2O , 1.32; CaO , 1.52; MgO , 1.85; TiO_2 , 0.76; and MnO , 0.11. This composition agrees well with other analyses of Indochinite tektite.^{27,36} While enriched in Si and K and depleted in Al, Ca, and Na relative to Haitian K-T boundary glass, this Indochinite tektite is similar in composition to Haitian glass²¹ and within the midrange for reported tektites.³⁷

The naturally reacted glass was first examined using optical microscopy. The extent of reaction was nonuniform, with the glass possessing a smooth surface punctuated with etch pits. An obvious glaze covered the surface and was thickest in the pitted regions. Glass sections were examined with TEM using lattice fringe imaging, selected area electron microdiffraction (SAED), and EDS to characterize the phases.

The glaze coverage on the naturally altered tektite surface was discontinuous, and on a microscale, it consisted of well-crystallized material. The glaze formed an interface with the glass, $\sim 0.1 \mu\text{m}$ in thickness, where the texture gradually changed from crystalline to amorphous, as determined by electron diffraction. The glaze mainly consisted of two distinct lath-bearing clay phases. The dominant phase was an aluminosilicate clay exhibiting a 7 Å basal spacing and an SAED pattern consistent with kaolinite.³⁸ The EDS analyses of this mineral indicated elemental ratios of 1.00 Si, 0.635 Al, 0.125 Mg, 0.094 Fe, and 0.63 K. This composition indicates a mixture of 1:1 and 2:1 sheet silicates. The presence of Mg, Fe, K, and excess Si suggests that if the 7 Å phase is kaolinite, then it is likely mixed with a 2:1 silicate. The second phase exhibited 10 Å basal lattice fringe spacings and an SAED pattern that includes strong 4.55 Å spacings. These features are compatible with glauconite (and other sheet silicates).³⁹⁻⁴¹ We were unable to analyze this mineral with EDS because of its small domain sizes. Infrequent occurrences of other minerals, including hematite ($\alpha\text{-Fe}_2\text{O}_3$), α -quartz (SiO_2), ilmenite (FeTiO_3), iron-bearing rutile (TiO_2),⁴² and TiO_2 (B),⁴³ were identified using EDS and SAED.

The morphology of the clay-based glaze also provides a clue as to its formation. The penetration of clay laths into the glass suggests an *in situ* hydrolysis of the glass network followed by a restructuring to form clay-rich material. The minor phases found within the clay may form as elements present in the glass are excluded from the clay and nucleate at separate sites.⁴⁴ While the reaction is likely glass-dominated because of the high SA/V ratio, groundwater action may help to separate the clay glaze from the glass, as observed in some places.

To gain further insight into tektite reaction under more controlled conditions of limited water contact, vapor-hydration experiments were performed with polished 1 cm x 1 cm x 1 mm monoliths of tektite suspended from a stainless steel support with Teflon thread.^{32,33,45} These experiments were conducted at 150, 175, 200, and 225°C for periods between 3 and 400 days.³² The following observations were made from the experimental results.

The first stage of reaction reveals the formation of an optically visible birefringent layer. No birefringence has been previously reported for altered tektites, and the layer is believed to be analogous to that formed during natural and experimental obsidian hydration. The birefringent layer formed on obsidian is attributed to strain resulting from water diffusing into the glass network.⁴⁶ Partial dissociation of the water occurs, but the silicate network remains intact.⁴⁶ The layer can be observed with both optical microscopy and with dark-field imaging using TEM. The layer thickness increases as a function of $t^{1/2}$, consistent with a water-diffusion process. The temperature dependence yields an activation energy of 91 $\text{kJ}\cdot\text{mol}^{-1}$ and an extrapolated diffusion rate at 25°C of $1.6 \times 10^{-7} \mu\text{m}^2/\text{day}$.

The birefringent region that formed after 22 days at 175°C consists of two distinct layers with a total thickness of 1.2 μm , as determined by TEM. The thicker inner fraction has a morphology and composition identical to the original glass, and the slight contrast difference seen in dark-field imaging is probably due to water uptake without breakage of the silicate network. The outer fraction (100 nm) forms a sharp interface with the inner fraction and undergoes a partial restructuring of the silicate network to form a poorly crystalline phase with a 10 Å basal spacing. The fringes are formed throughout the outer layer with random orientations and indicate that the amorphous, yet hydrated glass, transforms into more stable, crystalline material. Because of the limited regions of crystallinity, the composition of this mineral was not determined.

Additional glass matrix reaction occurred after 122 days at 200°C, where the entire outer portion of the 4.3 μm hydration layer restructured and formed a silicate layer. The outer portion of the layer was 1.2 μm thick and was completely crystalline. This allowed reproducible compositional and structural information to be obtained. The SAED analyses for this material indicate a 10 Å basal spacing and spacings similar to those found on the naturally altered sample. Rare occurrences of 14 Å basal spacings were attributed to interstratified smectite clays. Compositional EDS analyses give an average formula of $(\text{Na,K,Ca})_{0.56}(\text{Fe}_{0.81}\text{Al}_{2.92}\text{Mg}_{0.62}\text{Ti}_{0.09}\text{Mn}_{0.03})_{4.47}[\text{Si}_{7.33}\text{Al}_{0.67}\text{O}_{20}](\text{OH})_4$. This composition is consistent with a smectite mineral.

The temporal development of the reacted layers provides insight into the tektite reaction process. Under saturated vapor conditions, the natural tektite reacts initially via water diffusion, forming a birefringent layer. Next, complete hydrolysis of the silicate network occurs, as evidenced by the formation of the partially crystalline outer layer. With extended reaction, this outer layer restructures, forming a totally clay-based layer. For the laboratory-reacted sample, the clay in combination with the hydrated inner layer forms the basis of the birefringent layer. For the natural sample, the clay-rich layer or glaze forms the complete layer. The clay-rich layer is the dominant crystalline product in both the natural and laboratory-reacted samples. The natural tektite shows greater diversity with respect to minor components than the vapor-reacted tektite, possibly due to (1) longer nucleation and growth periods for the natural sample; (2) interaction with groundwater, which may affect redistribution of elements within the layer; and (3) the difference in reaction temperature.

The clays that have all been associated with altered spheroids from different K-T boundary sites are similar in composition and structure to the minerals formed during Indochinite tektite alteration reported above, including kaolinite, glauconite, and smectite.^{20-24,37,40} The unusually high concentrations of silicon we find in our analyses of the minerals with 10 Å and 7 Å basal spacings are similar to those reported for K-T boundary clays.³⁷ Additionally, the minor phases identified in the naturally reacted Indochinite match well with the repository mineralogy of the K-T boundary clay.

Thus, under restricted water contact conditions (either limited flow or water-vapor exposure), tektites will alter to form stable secondary phases. The differences in tektite reaction observed for submarine and land-deposited tektites described here or found at the K-T boundary can be ascribed to different processes dominating the reaction as the natural environment changes. Under high-dilution water submersion (low SA/V), etching of the outer glass surface dominates the reaction process, and no secondary phases or weathering products form. However, if the reaction occurs at high SA/V (water vapor or small volumes of water), the reaction takes place by water diffusion

followed by *in situ* hydrolysis and restructuring. Various clay minerals form, depending on exchange with local groundwater. Since the reaction rate for etching exceeds that for diffusion, etching is the dominant reaction process if the reaction conditions are suitable. Our results also suggest that, by examining the structure of reacted natural glass, one can infer information regarding the alteration environment.

B. Glass Studies for Yucca Mountain Project
(J. K. Bates and T. J. Gerding)

The Yucca Mountain Project (YMP) is investigating the tuff beds of Yucca Mountain, Nevada, as a potential location for a high-level waste repository. As part of the waste package development portion of this project, work is being performed in CMT to study the behavior of the waste form under anticipated repository conditions. The YMP Unsaturated Test Method continues to be used in the N2 and N3 test series (see previous semiannuals), which are being conducted with actinide-doped glasses. Because of the alpha decay of the predominant radionuclides, these tests must be conducted in a contained area but without shielding. Another test series (N4) will be conducted with "fully" radioactive sludge-based glass and the test method will have to be modified. These tests will be performed as part of the EM program, and the results will be discussed with the task on long-term testing of fully radioactive glass (Sec. III.A.2).

1. N2 Unsaturated Tests

The N2 continuing tests (SRL 165 glass) have been completed through the 286-week sampling period. All the batch tests have been completed, and three continuous tests and one blank test are ongoing with samplings at yearly intervals.

2. N3 Unsaturated Tests

The N3 Unsaturated Test uses ATM-10 glass (simulated West Valley glass containing actinides plus ⁹⁹Tc) that was received from the Materials Characterization Center and remelted to obtain the required form of the glass. This ongoing test was started July 6, 1987, according to the Unsaturated Test matrix, and has been completed through the 220-week sampling period.

C. Spent Fuel Studies for Yucca Mountain Project
(D. J. Wronkiewicz)

Two sets of experiments are continuing for YMP to investigate the reaction behavior of Zircaloy clad-UO₂ pellets exposed to dripping EJ-13 water in an oxidizing environment. The first set of experiments employs Teflon support stands and has been underway for 6.5 years, while the second set utilizes stainless steel support plates and has been running for a total of 2.25 years. Both tests are designed to develop procedures for tests with actual spent fuel, identify secondary alteration phases, and describe parameters that control the release of uranium from the waste package assembly. In addition, the second set of tests determines what influence, if any, the Teflon stands have on the UO₂ reaction in the first set of tests. All experiments are being conducted at 90°C and at variable SA/V ratios to simulate potential Yucca Mountain repository conditions. Twelve samples are being examined in each set.

1. Teflon-Supported UO₂ Tests

These tests continued during the last six months without reaching any scheduled sampling intervals. Earlier results from extensive SEM/EDS, XRD, and optical microscopy work are

summarized in a paragenetic sequence for UO_2 reaction (Fig. III-18). As shown in this figure, a large pulse of uranium occurs between one and two years of reaction time (Fig. III-18). After this interval, the uranium release rates decrease to a relatively constant level, which has continued up to the present six years of reaction time. The mineral relationships indicate a progression from the unaltered

Fig. III-18. Paragenetic Sequence Determined from Spent Fuel Studies with Teflon Support Stand

uraninite, to uranyl oxide hydrates, to uranyl silicates and alkali-alkaline earth uranyl silicates. This trend is identical to that observed in weathered zones of natural uraninite.

2. Stainless Steel-Supported UO_2 Tests

Sample collections were made after 1.75 years for the tests using stainless steel plates. Observations during sampling indicate that the UO_2 surfaces are relatively unaltered, except for some small (<1 mm) precipitates that developed on the top surfaces of some samples.

Solution results indicate a continued slow release of total uranium from four stainless steel-supported samples, as measured by the collection from a ten-minute acid strip of the test vessel components. Sample PMP8U-10 shows a decrease in uranium release from the previous testing periods, although the 30 μg of uranium recovered from the acid strip solution was an order of magnitude greater than the 0.8 to 2.3 μg released from the other three tests. Cumulative uranium releases for the first 91 weeks range from 84 μg for PMP8U-10 to 5 to 10 μg for PMP8U-9, -11, and -12. When compared to results from the Teflon-supported tests, the present samples display a considerable reduction in the uranium release rate. Cumulative uranium releases range from 700 to 7000 μg after 78 weeks of testing for the Teflon stand experiments, with most of the samples having passed through a stage of rapid uranium release between one and two years.

Dissolution patterns of the PMP8U samples were further evaluated by examining various size fractions of the released uranium. Sample aliquots were taken for (1) 20 $\text{\AA}$ filtrates, (2) a solution sample that includes soluble and suspended particulate matter, and (3) an acid strip component that represents the cumulative uranium release from the samples. The amount of uranium contained in the <20 $\text{\AA}$ solution represents between 30 and 70% of the total from PMP8U-11 and -12

and <5% of the total from PMP8U-10. These trends suggest that the uranium release from the latter sample is dominated by particulate matter, presumably as the sample surface begins to deteriorate along grain boundaries and particulates are washed from the surface. Corroded grain boundaries and loosened particulates have previously been observed on PMP8U samples reacted from 1.5 to 2.25 years.

Relative to the initial EJ-13 leachant, leachate concentrations of magnesium are depleted for all four samples, whereas Ca and K are depleted only for samples PMP8U-9 and -10 (Fig. III-19). Silicon and sodium are relatively invariant, remaining near the concentration of the initial EJ-13 leachant. These trends suggest that uranyl silicate phases are not precipitating on the sample surface, but instead only alkali and alkaline earth oxide phases are presently forming.

Results from the pH determinations are similar to previous sampling intervals, with sample PMP8U-10 exhibiting a slight decrease, while all other samples display moderate increases in pH relative to the 8.2 value that characterizes the starting EJ-13 solution (Fig. III-19f). All of the samples have pH values that are substantially higher than the ~7.0 value that characterizes the Teflon-supported samples during their period of extensive uranium dissolution. Total carbon concentrations are also generally depleted relative to previous sampling periods, although only sample PMP8U-10 is depleted relative to EJ-13.

Fig. III-19. Cation Concentrations of PMP8U Solutions Log Normalized to the Composition of EJ-13 Water: (a) Mg, (b) Ca, (c) K, (d) Si, (e) Na, and (f) pH. EJ-13 composition is 0.96 ppm Mg, 9.08 ppm Ca, 8.08 ppm K, 34.4 ppm Si, 46.5 ppm Na, and pH = 8.2.

(c)

(d)

(e)

(f)

Fig. III-19. (contd)

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APPENDIX A

Table A-1. Samples from Long-Term Testing of Fully Radioactive Glass (Sec. III.A.3)

DP-7	Some reasonable areas; 75-nm thick clay layer. The electron beam rapidly caused damage in this sample.
DP-8	Sectioning results for the samples from this task have been mixed, but since the reaction layers are thin and several attempts at sample preparation have been made, it has been possible to find small intact regions extending from the epoxy to the glass in all the powdered samples except DP-8. DP-8 has adequate material to analyze but is not intact.
DP-22	One good sample and one reasonable sample were produced, and these have been used for detailed analysis. The layer was thin, about 20 nm.
DP-43	A few samples were well intact with an outer layer thickness of 50-60 nm. Some small regions possessed more disordered layers, which were around 100-nm thick.
DP-45	One good sample. The layer was 100-150 nm thick.
DP-104	A number of good samples. The clay layer was 100 nm thick.
DP-138	In one block the clay layer on one side of glass particle was relatively thick (~200 nm). Elsewhere it was around 50-75 nm. The glass was electron-beam sensitive.
DP-139	Two good samples were produced from this test. The clay layer was 50-nm thick.
DP-140	The layer was found to be 50-100 nm thick. Some samples had cracks in them, which had then reacted. A number of the specimens were intact.
DP-141	Samples were mainly not intact. The layer was ~50 nm thick.
DP142	Clay layer was 100-300 nm thick. Two good samples were produced.
DP143	A 100-200 nm thick clay layer was observed. One out of three of the blocks yielded good sections.
DP-174	The layer was 50-nm thick. Lattice fringes were observed in many cases.
DP-175	In some regions the layer was at least 120-nm thick and a backbone was visible. However, on average the layer was 50-nm thick. A number of intact specimens were found for both DP-174 and DP-175.
DP-176	A number of good samples were produced. A 50-100 nm thick clay layer was observed.
DP-177	At least one good sample was produced. The clay layer was 50-150 nm thick.
DP-178	Generally, sectioning of this glass produced poor samples. It possessed a 200-nm thick clay layer.

Table A-2. Samples from Testing of SA/V Effects (Sec. III.A.4)

SVT-75	A 100-200 nm clay layer was visible along with a 500-800 nm alteration layer. One good sample was produced from this test and has been used for detailed compositional analysis of this sample.
SVT-77	A 150-200 nm thick outer clay layer and a 400-600 nm alteration layer. At least two of the five blocks produced had good sections. These have been used for detailed layer analysis.
SVT-127	The layer consisted of at least five bands. An outer layer about 150-nm thick, a iron-rich thin band, an alteration layer around 250-nm thick, a lath-rich region about 100-nm thick, and then a clear glass region. Detailed layer analysis has been performed on this sample.
SVT-128	Reaction layer, 400-nm thick; outer layer, 50-nm thick. Some good sections.
SVT-129	Good sections showing an extremely thin reaction layer.
SVT-133	The layer consisted of an outer layer 100-nm thick, an iron-rich band, an alteration layer 100-nm thick, a mottled or lath-rich region 100-nm thick, and then clear glass. Detailed analysis has been carried out on this sample.
SVT-134	Good sections showing an extremely thin reaction layer, in all about 150-nm thick.
SVT-135	Some reasonable sections with an outer layer 50-nm thick and total reaction layer thickness of 200 nm.

Table A-3. Samples from West Valley Survey

Test	Clay Layer, nm	Alteration Layer, nm	Comments
D85	<10	300	Good samples.
D852	20-50	200	Cracks in glass. No samples available for accurate detailed analysis.
H85	50-100	200-300	Precipitates of Fe, Ni, Cr oxide were found.
H852	20-50	150-20	Precipitates of Fe, Ni, Cr oxide. Not suitable for detailed analysis.
D10	300-400	2500	Some reasonable samples.
D102	300	800	Good samples.
H10	200-300	>400	Poor quality samples produced. The unreacted glass was not visible.
H102	400-500	>2000	Some reasonable samples.

Table A-4. Samples from Natural Analogue Tests

IC1710-02	Lab-reacted tektite. No outer layer was visible either with bright-field or dark-field imaging.
IC20210-03	Lab-reacted tektite. Fringes from a 25-nm thick layer were visible.

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 N. Jarrett, Noel Jarrett Associates, Lower Burrell, PA
 J. G. Kay, Drexel University, Philadelphia, PA
 J. Stringer, Electric Power Research Institute, Palo Alto, CA
 J. B. Wagner, Arizona State University, Tempe, AZ
 R. G. Wymer, Oak Ridge National Laboratory, Oak Ridge, TN
 M. G. Adamson, Lawrence Livermore National Laboratory, Livermore, CA
 J. Allison, USDOE, Office of Waste Operations, Germantown, MD
 J. T. Bell, Oak Ridge National Laboratory, Oak Ridge, TN
 S. E. Berk, USDOE, Office of Fusion Energy, Germantown, MD
 N. E. Bibler, Westinghouse Savannah River Co., Aiken, SC
 P. E. Blackburn, Winnetka, IL
 W. Bourcier, Lawrence Livermore National Laboratory, Livermore, CA

D. F. Bowersox, Los Alamos National Laboratory, Los Alamos, NM
 C. R. Bradley, Bolingbrook, IL
 L. Brewer, University of California, Berkeley, CA
 K. A. Chacey, USDOE, Office of Waste Management, Germantown, MD
 M. O. Cloninger, Mac Technical Services, Inc., Richland, WA
 M. S. Coops, Lawrence Livermore National Laboratory, Livermore, CA
 D. Cubicciotti, Electric Power Research Institute, Palo Alto, CA
 M. Dinehart, Los Alamos National Laboratory, Los Alamos, NM
 M. C. Dionisio, USDOE, Office of Technology Development, Washington, DC
 M. Duff, USDOE, Office of Waste Operations, Germantown, MD
 R. Erickson, USDOE, Office of Waste Operations, Germantown, MD
 R. C. Ewing, University of New Mexico, Albuquerque, NM
 A. K. Fischer, Western Springs, IL
 R. Fish, B&W Fuel Co., Las Vegas, NV
 C. W. Frank, USDOE, Office of Technology Development, Washington, DC
 T. J. Gerding, Plainfield, IL
 K. Hain, USDOE, Office of Technology Development, Germantown, MD
 T. M. Hohl, Westinghouse Hanford Co., Richland, WA
 J. O. Honeyman, Westinghouse Hanford Operations, Richland, WA
 C. Interrante, U. S. Nuclear Regulatory Commission, Washington, DC
 C. Jantzen, Westinghouse Savannah River Co., Aiken, SC
 L. J. Jardine, Lawrence Livermore National Laboratory, Livermore, CA
 R. T. Jubin, Oak Ridge National Laboratory, Oak Ridge, TN
 W. S. Ketola, USDOE, West Valley Project Office, West Valley, NY
 D. A. Knecht, Westinghouse Idaho Nuclear Co., Idaho Falls, ID
 D. Langmuir, Nuclear Waste Technical Review Board, Springfield, VA
 M. Levenson, Menlo Park, CA
 S. C. T. Lien, USDOE, Office of Technology Development, Washington, DC
 Los Alamos National Laboratory, Los Alamos, NM
 J. Matuszek, State of New York, Department of Health, Albany, NY
 W. H. McVey, USDOE, Division of LMFBR Fuel Cycle Projects, Germantown, MD
 R. Morissette, Science Applications International Corp., Las Vegas, NV
 A. C. Muscatello, LATO Office, Rocky Flats Plant, Golden, CO
 P. K. Nair, Southwest Research Institute, San Antonio, TX
 L. Nelson, Sandia Corp., Albuquerque, NM
 J. Nelson, Westinghouse Hanford Co., Richland, WA
 M. O'Hara, Martin Marietta Energy Systems, Oak Ridge, TN
 D. R. Olander, University of California, Berkeley, CA
 A. L. Olson, Westinghouse Idaho Nuclear Co., Inc., Idaho Falls, ID
 M. Palmer, Los Alamos National Laboratory, Los Alamos, NM
 R. Palmer, West Valley Nuclear Services, West Valley, NY
 G. Pfennigworth, Martin Marietta Energy Systems, Oak Ridge, TN
 W. G. Ramsey, Westinghouse Savannah River Co., Aiken, SC
 L. Reichley-Yinger, Columbus, OH
 C. G. Russomanno, USDOE, Civilian Radioactive Waste Management, Washington, DC
 P. S. Schaus, Westinghouse Hanford Co., Richland, WA
 H. Shaw, Lawrence Livermore National Laboratory, Livermore, CA
 M. W. Shupe, USDOE, Office of Technology Development, Washington, DC
 J. Sproull, Westinghouse Savannah River Co., Aiken, SC
 D. Stahl, B&W Fuel Co., Las Vegas, NV

R. B. Stout, Lawrence Livermore National Laboratory, Livermore, CA
I. R. Tasker, IIT Research Institute, Bartlesville, OK
D. W. Tedder, Georgia Institute of Technology, Atlanta, GA
T. A. Todd, Westinghouse Idaho Nuclear Co., Inc., Idaho Falls, ID
USDOE, Office of Basic Energy Sciences, Washington, DC
S. Yarbrow, Los Alamos National Laboratory, Los Alamos, NM
W. Lutze, Hahn-Meitner-Institut, Berlin, GERMANY
P. Van Iseghem, BELGIUM
E. Vernaz, Centre d'Etudes Nucleaires de la Valle du Rhone, FRANCE
L. Werme, Svensk Kärnbränslehantering AB, Stockholm, SWEDEN

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