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NUCLEAR TECHNOLOGY PROGRAMS
SEMIANNUAL PROGRESS REPORT

October 1990 - March 1991

Chemical Technology Division

J. E. Battles, Director

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Previous Reports in this Series

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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 October 1990-March 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, thermophysical, and transport behavior of selected materials in environments simulating those of fission and fusion energy systems.

Solidus-liquidus temperatures are being determined by differential thermal analysis (DTA) measurements on three calcined concretes (limestone, limestone-sand, and siliceous) and mixtures of each of these concretes with $\text{UO}_2\text{-ZrO}_2$ at temperatures as high as 2673 K. Such mixtures are expected to occur during the molten core-concrete interaction phase of severe reactor accidents in light water reactors. The results are to be incorporated into 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. During this report period, measured solidus and liquidus temperatures for three core-concrete mixtures (27 wt % concrete plus 73 wt % $\text{UO}_2\text{-ZrO}_2$) were found to agree reasonably well with temperatures calculated at the Atomic Energy Authority, Harwell. Also, our DTA apparatus was modified so as to improve its sensitivity.

Measurements and calculational analyses are being performed to provide needed thermophysical property data for Integral Fast Reactor (IFR) fuels. Our efforts are focused on gaining a more thorough understanding of the phase relations involved in the U-Fe-Zr system as part of fuel-cladding compatibility studies. The DTA curves derived from several U-Fe-Zr samples were found to be similar to those previously determined for the U-Fe system and showed a eutectic at about 1000 K. In another study, the literature was reviewed concerning ignition temperatures for U, Pu, and Zr. The results from this study will be used in planned activities by others to demonstrate IFR fuel reprocessing. In a third study, 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.

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 has supported this program by conducting several studies on an NPR that is a heavy water reactor (HWR). One such study concerns the release of fission products and tritium from U-Al fuel and Li-Al targets in a hypothetical severe accident with the HWR-NPR. Two approaches were pursued in this study: experimental measurements using transpiration and high-temperature mass spectrometry and thermodynamic analyses using the SOLGASMIX computer code. Results are given from analysis of relevant literature and preliminary experimental work. It was concluded that formation of an oxide layer on molten aluminum may be a barrier to transport of gaseous aluminum species in the transpiration experiments. Preliminary results are also reported for SOLGASMIX calculations for U-Al, Li-Al, and selected fission products at 1000 and 1700 K. Conclusions reached from these calculations are that LiI is important as a gaseous species and in the condensed phases, tellurium is bound by uranium as UTe and is retained in the condensed phases, iodine is essentially not bound as UI_3 or AlI_3 in the gas or condensed phases, and AlTe is significant in the gas phase.

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) measurements are in progress to provide data that describe the kinetics of desorption of $H_2(g)$ and $H_2O(g)$ from one of the candidate ceramic breeders, $LiAlO_2(s)$, under a helium pure gas at high temperature. Some of the $LiAlO_2$ samples were pretreated at 923 K in a helium purge gas containing 247, 495, or 990 ppm H_2 . During the TPD 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 473 to 1073 K at a rate of 5.6 K/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. Some data were also obtained for the desorption of $H_2(g)$ into pure helium. These data were still being analyzed.

In another blanket study, we analyzed the problem of tritium percolation through a porous lithium ceramic material. For this analysis, we developed a random network percolation model in which local transport in individual pore channels is described by convection-diffusion-reaction equations, the heterogeneous structure of the blanket is accounted for by Monte Carlo methods, and long-range transport is described by a matrix technique. This model was then applied to a residence time analysis for tritium release. The results indicated that the analysis of experimental tritium release rates with average residence times needs to be done with caution.

We are providing support to the Dynamic Helium Charge Experiment (DHCE), the objective of which is to provide baseline irradiation data on the effects of concurrent helium production and neutron irradiation on the physical and mechanical properties of vanadium alloys. The DHCE is designed to simulate the simultaneous $He(g)$ production and irradiation damage anticipated in a fusion device and will be conducted in the Fast Flux Test Facility at Westinghouse Hanford. During this report period, we obtained needed experimental data in preparation for DHCE.

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 or 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 (SRL 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- UO_2 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 thermochemical, thermophysical, and transport behavior of selected materials in environments simulating those of fission and fusion energy systems.

A. Behavior of Core-Concrete Mixtures under Accident Conditions (M. F. Roche and L. Leibowitz)

The objective of this research program is to provide experimental data on the onset of melting (solidus temperature) and the onset of solidification (liquidus temperature) for mixtures of urania and zirconia with four types of concrete: limestone, limestone-sand, basalt, and siliceous. Such mixtures are expected to occur during the molten core-concrete interaction (MCCI) phase of severe reactor accidents in light-water reactors (LWRs) and pressurized-water reactors (PWRs). 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 each of these phases is crucial for understanding and modeling the consequences of the accident.

In the previous report in this series (ANL-92/25, pp. 12-14), we described the development of a differential thermal analysis (DTA) apparatus capable of operating at temperatures as high as 2400°C. In addition, we presented measurements of solidus and liquidus temperatures for three types of concrete (limestone, limestone-sand, and siliceous) and for their mixtures at 27.5 wt % concrete with 72.5 wt % $\text{UO}_2\text{-ZrO}_2$ (1.625:1 mole ratio of UO_2 to ZrO_2). During this report period, DTA measurements were continued on other core-concrete mixtures, and the DTA apparatus was further modified to improve its sensitivity.

Two experiments were completed with basalt concrete. One of these employed basalt concrete alone, and the other employed a mixture of basalt concrete (27.5 wt %) with $\text{UO}_2\text{-ZrO}_2$ (1.6:1 mole ratio). In these experiments, the samples, which weighed up to 20 g, were held in covered molybdenum crucibles (9 cm³) that rested on a sample thermocouple within a high-temperature furnace cavity. A gas of Ar-3% H_2 (at a pressure of about 0.03 MPa) was added to the furnace cavity to minimize vaporization losses to less than 2% of the sample mass. The output from the sample thermocouple was compared with that from a control thermocouple which drives a furnace, via a programmable power supply, between two temperature limits at a prescribed rate (e.g., 900 to 2400°C at a rate of 30°C/min). The peaks in the resulting DTA curves on heating and cooling are related to the liquidus and solidus temperatures.

The DTA experiment with basalt concrete indicated a glass transition over the temperature range 900 to 1100°C; X-ray diffraction on a portion of the sample after the DTA measurements showed it to be amorphous. Figure I-1 shows DTA curves for a mixture of basalt concrete (5.0 g), urania (10.2 g), and zirconia (2.9 g). These curves indicate a glass transition over the temperature range 900 to 1200°C. In addition, there are complex peaks in the range 2100 to 2400°C (probably caused by the melting of a $\text{UO}_2\text{-ZrO}_2$ phase). At present, we are unable to determine a liquidus temperature from these DTA curves, because the sample corroded through the wall of the molybdenum crucible at some point during three cycles of the type shown in Fig. I-1. Only 3 g of the 18-g sample remained in the crucible at the end of the experiment; 15 g of the sample had drained through a large crack in the crucible wall onto the lower thermocouple and baffles in the DTA apparatus (these components were destroyed and later replaced). The crucible, which was obviously corroded, had evidently reacted with some components of the sample

under the reducing atmosphere (Ar-3% H₂ at a pressure of about 40 kPa) present in the high-temperature furnace. We suspect that the reaction consisted of alloy formation between the molybdenum crucible and the iron and aluminum from the iron oxide and aluminum oxide components of the basalt concrete. These components have a significant concentration (about 6 and 11 wt %, respectively) only in the basalt concrete, and we have only experienced this corrosion problem with the basalt concrete.

Fig. I-1. Differential Thermal Analysis of 72.5 wt % UO₂-ZrO₂ (1.6:1 mole ratio) and 27.5 wt % Basalt Concrete

Two experiments were conducted on samples of 60 wt % limestone concrete with 40 wt % UO₂-ZrO₂. In the first experiment, the sample thermocouple was in contact with the base of the molybdenum crucible holding the sample (our usual procedure); there was very little structure in the DTA curves from this experiment. In the second experiment, the sample thermocouple passed through the molybdenum-crucible lid and was directly immersed in the concrete-UO₂-ZrO₂ mixture in the hope of obtaining maximum sensitivity to thermal events. Even with this condition, however, there was very little structure in the DTA curves. Figure I-2 shows DTA curves at the highest scan rate (30°C/min) employed in this experiment. In the earlier DTA experiments on limestone concrete and on mixtures containing 27 wt % limestone concrete with UO₂-ZrO₂ (1.6:1 mole ratio), prominent peaks were seen at the solidus temperatures (1222°C for limestone concrete and 1247°C for concrete-UO₂-ZrO₂) and at higher temperatures. The present sample (60 wt % concrete) probably has a solidus temperature in the same range (~1250°C), but the absence of any peaks in Fig. I-2 prevents determining the exact value.

Because of the problems in obtaining satisfactory DTA curves, new crucibles and lids for use in our DTA experiments were machined from molybdenum rod stock. The base of the crucibles (1.9-cm OD x 3.8-cm height) contains a specially designed thermocouple well (0.5-cm OD x 1-cm height) that provides a high sensitivity to thermal events occurring in the sample. Figure I-3 shows DTA curves obtained for about 6.6 g of an alumina standard (NBS Standard Reference Material 742, melting point: 2053±5°C) in one of the new crucibles. The curves, which were computed directly from the sample and

Fig. I-2. Differential Thermal Analysis of 40 wt % $\text{UO}_2\text{-ZrO}_2$ (1.6:1 mole ratio) and 60 wt % Limestone Concrete

control thermocouple signals without any electronic amplification, show that the new crucibles provide a high level of sensitivity to thermal events; the peaks are easily distinguished from background.

In Fig. I-3, solidification of the molten alumina on cooling is seen to occur when the sample temperature is $\sim 1920^\circ\text{C}$; this represents a significant degree of undercooling since the actual melting point of the alumina is 2053°C . The heating peaks shown in Fig. I-3 begin at a temperature of $\sim 2030^\circ\text{C}$, and our detailed analysis of these curves indicated a melting point for the standard of $2030 \pm 5^\circ\text{C}$. This is about 25°C lower than the true melting point; the difference may be due to an error in the sample thermocouple or to a difference between the calibration experiments (tungsten crucibles in vacuum) and our experiment (molybdenum crucibles in $\text{Ar-3\% H}_2$ at 40 kPa).

Figure I-4 shows the results of a DTA experiment employing limestone-sand concrete (43 wt %) plus $\text{UO}_2\text{-ZrO}_2$ (5:1 mole ratio) in the new crucible. The solidus temperature is approximately 1200°C ; the liquidus temperature is above 2400°C . Experiments with other concretes (at 43 wt % concrete) are planned.

Table I-1 presents solidus and liquidus temperatures from our earlier DTA experiments (ANL-92/5, pp. 9-20) on mixtures having a $\text{UO}_2\text{-ZrO}_2$ mole ratio of 1.6:1. Also given in this table are preliminary results of solidus and liquidus temperature calculated by Mignanelli.¹ 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 concrete (72 wt % in limestone, 36 wt % in limestone-sand, 15 wt % in siliceous). Our current experiments are directed toward a resolution of this discrepancy. In particular, we are now measuring eutectic temperatures and compositions in the $\text{UO}_2\text{-CaO}$ system. This system appears to be the key for establishing better agreement between our measurements and the thermodynamic calculations. The next report will review the data previously available for this system and our measurements.

Fig. I-3. Differential Thermal Analysis of NBS Alumina Standard

Fig. I-4. Differential Thermal Analysis of 57 wt % $\text{UO}_2\text{-ZrO}_2$ (mole ratio = 5:1) and 43 wt % Limestone-Sand Concrete

Table I-1. Experimental and Calculated Solidus and Liquidus Temperatures for Mixtures of 27 wt % Concrete with 73 wt % $\text{UO}_2\text{-ZrO}_2$ (1.6:1 mole ratio)

Concrete with $\text{UO}_2\text{-ZrO}_2$	Solidus Temp., °C		Liquidus Temp., °C	
	DTA ^a	Calc. ^b	DTA ^a	Calc. ^b
Limestone	1247	1247	>2450	2047
Limestone-Sand	1037	1177	>2365	2217
Siliceous	1139	1161	2276	2122

^aFrom previous semiannual (ANL-92/25, pp. 9-20).

^bFrom Ref. 1.

B. Thermophysical Property Studies

Measurements and analyses are being performed to provide information on the thermophysical properties of the fuel for the Integral Fast Reactor (IFR), an advanced reactor concept under development at ANL.

1. Phase Studies of U-Fe-Zr Systems (L. Leibowitz and R. A. Blomquist)

An important area in the development of advanced reactors with metal fuel is chemical interactions between the U-Pu-Zr fuel and steel claddings (HT9, D9, or Type 316). We have been attempting to examine simpler systems than actual fuel-cladding mixtures to clarify phase relations in those systems. We have previously presented our results on the U-Zr² and U-Fe³ systems and have recently performed some DTA studies of the U-Fe-Zr system. Results of scanning electron microscopy (SEM) examinations of these residues and revised phase diagram calculations are not yet available. These findings should thus be considered preliminary.

A sample containing 43.8 at.% U, 43.5 at.% Fe, and 12.7 at.% Zr was heated in an yttria crucible at 10°C/min to about 1580°C, after which several heating/cooling curves were initiated at various rates. The resulting DTA curves were very similar to those obtained for the simple Fe-U system.³ We also compared the U-Fe results with those of (U, Zr)-Fe and (U, Zr)-HT9, where U-10 wt % Zr fuel was used for the (U, Zr). (These alloys had roughly the same U/Fe ratio.) The major peak in the DTA curves for U-Fe was due to a eutectic at 725°C in that binary system. The major peak in the other systems occurred at close to the same temperature; other peaks in the DTA curves were very small. Preliminary phase diagram calculations for the U-Fe-Zr system indicated that the composition of the ternary eutectic is very close to the U-Fe binary edge. This is independent of whether or not corresponding binary intermetallics (Fe_2U and Fe_2Zr) are considered miscible. It is not surprising, therefore, that the peak temperatures were fairly close. Further study and modification of the calculations are in progress, and the results will be reported when complete. We are proceeding with SEM examination of the ternary test residues and are planning a similar test with a plutonium-containing alloy.

As part of our standard practice, the DTA system was recalibrated during this reporting period. We measured melting points of five high-purity metals, including two Standard Reference Materials (SRM) obtained from the National Institute of Standards and Technology (NIST). These were SRM 44e (Al) and SRM 45d (Cu). The other metals used and their reported purities were Ni (99.9975%), Pb (99.9999%), and Sn (99.999+%). Standard samples of SRM 43h (Zn) and SRM 49e (Pb) have been

ordered. Several heating and cooling cycles were obtained on each material at about 10 °C/min. Previous experience revealed no differences between melting points obtained at 1 and 10 °C/min. Repeat melting point determinations showed a difference of, at most, 5 °C. Results of this calibration are presented in Table I-2.

Table I-2. Measured and Literature Metal Melting Points for Five Metals

Metal	Melting Points, °C		Temp. Difference, °C
	Measured	Literature ^a	
Sn	230	232	-2
Pb	326.5	327.5	-1
Al	662	660	2
Cu	1090	1085	5
Ni	1458	1453	5

^aBased on the 1968 International Practical Temperature Scale (IPTS-68).

A calibration curve based on these results has been prepared and will be applied to reported values, as done in the past. As an additional improvement to the DTA system, we have acquired a differential scanning calorimetry (DSC) head for the instrument, which will allow enthalpy measurements to be performed. This device also requires extensive calibration.

2. Ignition Studies (L. Leibowitz and R. A. Blomquist)

In attempting to estimate ignition temperatures relevant to planned activities in demonstrating IFR fuel reprocessing at EBR-II, we have reviewed the available relevant literature on metal ignition. A summary of this information is presented below.

a. Ignition of Uranium

An extensive review of chemical reactions in nuclear reactor materials summarizing information available through about 1967 has been published.⁴ Much of the basic information available on uranium ignition is contained in two papers^{5,6} published by ANL workers. An earlier study of uranium powder ignition has also been published.⁷

Heating of uranium in air has often been observed to lead, not to well-defined ignition, but to thermal cycling, unless high surface area material is used.⁴ Studies of uranium ignition have been performed⁵ by the so-called burning curve method under various conditions. In this method, samples are heated at a constant rate in a flowing oxidizing gas, while the sample temperature is measured. The ignition temperature, as indicated by rapid self-heating, is defined as the intersection of the pre-ignition and post-ignition heating curves, ignoring subsequent thermal cycling. It is important to remember that an abrupt change in ignition temperature occurs between 400 and 500 °C, which corresponds to a change in the mechanism of uranium oxidation at 450 °C.⁸

It is not only the specific area, however, that determines the ignition temperature. The state of aggregation, which can significantly influence heat transfer, is also important.^{5,7} In studies of

uranium powder ignition,⁷ Tetenbaum et al. found that the ignition temperature fell as the depth of the powder bed increased until a limiting ignition temperature occurred. These so-called critical heights varied from about 1.5 to 9 mm, depending on sample particle size and heating rate. The powder ignition temperatures are substantially lower than the single-particle ignition temperatures for the same specific area.

The influence of alloying additions on the ignition of uranium was also studied.^{6,9-10} Schnizlein et al.⁶ examined 70 binary alloys containing 24 different elements. Many of these elements were studied at concentrations of 0.5, 1, and 2 at.%, with a few studied at higher concentrations. The results were interpreted in terms of the effect of the alloying element on the oxidation rate of uranium. Some elements lowered the ignition temperature, some raised it, still others showed a reversal as the concentration varied.

Baker et al.⁵ presented a thermal model of burning curve ignition, which was successful in describing the course of events. The basic equation is:

$$C_p \frac{dT}{dt} = \frac{QM_U S}{10^3 M_{O_2}} \frac{dw}{dt} - hS(T - T_a) - \sigma \epsilon S(T^4 - T_a^4) \quad (I-1)$$

where C_p is the specific heat of uranium, T is the metal temperature, T_a is the furnace temperature, t is time, Q is the heat of reaction, M_U is the atomic weight of U, M_{O_2} is the molecular weight of oxygen, S is the sample specific area, w is the quantity of oxygen reacted, h is the heat transfer coefficient, σ is the Stefan-Boltzmann constant, and ϵ is the total emissivity of the surface. The primary difficulty in applying this equation to new alloys lies in determining the oxidation rate. For uranium, measurements had been made on the oxidation rate as a function of temperature,⁸ and that information was used in calculating ignition temperatures.⁵ Without measurements on the alloy of interest, prediction of ignition temperatures would be speculative at best.

b. Ignition of Plutonium

Ignition of plutonium and some of its alloys, which has been studied in some detail,¹¹⁻¹⁴ shows complex behavior similar to that shown by uranium. As was observed with uranium, the ignition temperature changed markedly between about 350 and 450 °C, which is consistent with the oxidation behavior of plutonium. Shielded ignition temperatures were also measured.¹⁴ For these measurements, the sample was heated in an inert atmosphere before being exposed to the oxidizing atmosphere. In the low-temperature regime, burning curve and shielded ignition temperatures were about the same, but in the high temperature region shielded ignition temperatures were lower. Measurements in air and oxygen were generally in reasonable agreement. These results can be understood as indicating that the rate of heat generation is controlled by chemical kinetics.

Burning curve studies of plutonium powders¹⁵ showed very low ignition temperatures for a 1 wt % gallium alloy (δ -stabilized). For example, an ignition temperature of about 190 °C was reported for a 60-mesh powder sample. This is considerably lower than the ignition temperature of about 285 °C for a comparable uranium powder.

c. Ignition of Zirconium

The information available on zirconium ignition has been well summarized in Ref. 4. Pure zirconium is very difficult to ignite in air because of the highly protective oxide which forms. Single

pieces of zirconium heated at about 10 °C/min in air would not ignite even when heated to 1300 °C. Shielded ignition temperatures were measured for pure zirconium in air and oxygen. About the same temperatures were found in air as in oxygen. Dilute alloys of Ni, Cu, U, V, Sn, and Al had about the same ignition temperature as pure zirconium. However, a major reduction in ignition temperature was found for titanium alloys. The ignition temperature of pure zirconium, 786 °C, was lowered to about 373 °C for a 14.9 at.% alloy with Ti. This greatly reduced ignition temperature, consistent with oxidation rate data, further illustrates the difficulty of predicting ignition temperatures without experimental information.

3. Minor Actinide Studies (L. Leibowitz and I. Johnson)

In several IFR fuel cycle concepts under consideration, the recycled fuel could contain concentrations of the so-called minor actinides, which would have an effect on the fuel properties and behavior. We are therefore exploring theoretical approaches to the estimation of solubilities and phase relations for fuel systems containing minor actinides. One of the more attractive approaches appears to be a model developed by Engel¹⁶ and expanded by Brewer.¹⁷ This model was 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.¹⁸

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 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. For actinides, moreover, an important change in the behavior of the *f* electrons occurs beginning with americium.¹⁹ This change must be taken into consideration.

Other considerations must be dealt with in considering metallic solutions, in addition to electronic configuration. 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 size except in certain cases, such as Laves phases, in which higher packing density can be obtained. Differences in internal pressure for solution A-B increase the enthalpy by an amount given by²⁰

$$\Delta H = 0.5(V_A + V_B) (\delta_A - \delta_B)^2 \quad (\text{I-2})$$

where δ is the Hildebrand and Scott solubility parameter, and V is the molar volume. The internal pressure is given by

$$\delta^2 = \Delta H_v/V$$

where ΔH_v is the enthalpy of vaporization.

Although the basic models were generated some time ago, development of these ideas has been continuing (e.g. Refs. 21, 23). Some of the data needed for application of these ideas to the actinide alloys of our present interest are available (for example, Refs. 19, 20, 22), and we are attempting to apply these ideas to estimation of needed information on actinide alloys. Calculation alone will not suffice for

these estimates but should provide guidance for minimizing the experimentation needed. It appears that application of the Engel-Brewer model would be a fruitful approach to this problem. The necessary data are available, and the model has been applied by Brewer to lanthanides and transition metals. Application of this model to the complex actinide systems of interest, however, will be difficult. Further study of this area is needed.

C. Severe Accident Fission Product Release from HWR-NPR Fuel and Targets
(P. E. Blackburn, A. K. Fischer, and S. W. Tam)

The objective of DOE's New Production Reactor (NPR) Program is to provide safe and environmentally acceptable new reactor capacity for an assured supply of tritium. We have provided technical support to this program by conducting the following for an NPR that is a heavy water reactor (HWR): (1) the development of thermodynamic models that will predict the behavior of the HWR-NPR fuel and target during a severe accident and (2) experimental measurements on U-Al fuel, Li-Al target, and fission product simulants (I, Cs, Te, Sr, Ba, La, Ru, and Mo) using the transpiration technique. The planned experimental effort included (1) fission product release from fuel during melting, (2) tritium release from targets during melting, (3) longer term release from melts as a function of temperature, and (4) release from molten aluminum during high-temperature oxidation or burning. The thermodynamic estimates (using the SOLGASMIX computer code)²⁴ were intended to characterize the vapor and the condensed phases for relevant species for (1) fuel only, (2) target only, and (3) fuel/target mixtures. However, because of funding cutbacks, no further work is planned. The results below document work done in FY 1991.

1. Apparatus Assembly and Operation

Prediction of the release of fission products from NPR-HWR core-melt accidents requires information on kinetic, transport, and thermodynamic factors. The transpiration experimental technique is well suited for this work because all aspects of the release and transport process can be investigated. The transpiration technique involves passing a gas at a known flow rate over the material to be studied and measuring the amount of material that is volatilized. Experimental studies are performed as functions of flow rate, temperature, and condensed-phase composition, and the results provide information on pressure and speciation of the vapor phase.

The transpiration apparatus consists of a closed-end tube into which a crucible containing the material of interest is placed at high temperatures. Gas is passed down the tube, and an inner collector tube is positioned so that the gas flows over the sample and up through the collector tube. As the gas flows up the collector tube, a thermal gradient causes volatilized material to condense. At the end of a run, the collector tube is removed, and the condensed material is analyzed. The apparatus includes a gas handling system, a laboratory furnace for service to 1923 K, a programmable temperature controller, and a Cahn recording vacuum microbalance. The Cahn balance can measure the weight of the sample continuously to $\pm 10 \mu\text{g}$ while the weight change is recorded over time.

In our experiments, the sample is held in an alumina crucible, which is suspended from the vacuum balance so that the vaporization rate can be measured during the experiment. The furnace tube is fixed in a vertical position, with the crucible located in the hottest part of the furnace. This arrangement enables measurement of the most volatile species. Partial pressures of less volatile species are determined from analysis of the condensed material. Very volatile species are trapped with liquid nitrogen cooled traps. The helium carrier gas is discharged into exhaust lines running from the vacuum frame hood.

To test our experimental system, an alumina crucible containing aluminum (99.999% purity) was heated in a stream of helium gas (99.995% purity). The weight change was recorded with respect to time, temperature, and gas flow rate. In the first set of measurements, the temperature was raised slowly to 1534 K, where the weight loss was equivalent to an aluminum pressure of 8×10^{-6} atm (0.8 Pa). This pressure may be compared with the pressure calculated from JANAF²⁵ of 2.9×10^{-5} atm (2.9 Pa). A second set of measurements at 1534 K produced pressures of 2.95×10^{-5} , 1.42×10^{-5} , and 1.74×10^{-5} atm (2.9, 1.4, and 1.7 Pa), about 2/3 the JANAF pressure.²⁵ Both of these sets of measurements were at helium flow rates of 700 cm³/min. A third set, at 1534 K and a reduced flow rate of 70 cm³/min, produced pressures of 1.8×10^{-6} and 3.2×10^{-6} atm (0.18 and 0.32 Pa), about 1/16 to 1/9 the JANAF value.²⁵ Continuation of the third set at 1534 K gave a negative pressure; the sample gained weight instead of losing weight as previously observed. The temperature was increased to 1670 K, where the sample weight was almost constant. A fourth set of measurements failed to produce weight loss in 700 cm³/min helium at temperatures up to 1451 K. The fifth set of measurements lost weight at 1461 K, corresponding to a pressure of 5.9×10^{-7} atm (0.059 Pa), about 1/15 the JANAF value,²⁵ but gained weight at 1455 K and 1561 K.

We assumed that the aluminum liquid was slowly oxidizing at the low oxygen partial pressure in the helium gas. The helium gas purity was not tested in the first three sets of measurements. An oxygen monitor was added to the exhaust line for the fourth and fifth sets. Oxygen pressures varied from 0.0015% to 0.0068% for the fourth set and from 0.00023% to 0.00095% for the fifth set.

2. Analysis Preliminary to Experimental Work

In earlier oxidation measurements of solid and liquid aluminum by oxygen and water vapor, Blackburn and Gulbransen established that a thin oxide layer forms on the surface of the aluminum at temperatures of 773 K or more.²⁶ A thin oxide film on the molten aluminum may be a barrier to transport of the gaseous aluminum species in the flowing helium. This oxide film may also act as a barrier to other gases from the fuel, target, and fission products. Blackburn and Gulbransen²⁶ measured oxidation rates of electrochemically polished aluminum in oxygen, oxygen plus water vapor, and 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. Since the oxide layer is important in the oxidation process, it is expected that this layer may also control the release of fission products. 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 measurements of fission product release. Field et al.²⁷ measured oxidation of aluminum alloys containing 3 wt % Li and 2 wt % Mg (Mg should behave like Ba or Sr) and found that oxide layers 75 times as thick as the oxide layers on pure aluminum. This suggests that U, Li, and the fission products in the fuel and target will enhance the corrosion rate, which could affect the loss of fission products. The effect of fuel and target corrosion on fission product loss needs to be investigated.

3. Transpiration Studies on Ingot

In preparation to initiating studies on an ingot (No. 32) prepared by Savannah River Laboratory, a run was completed with a cesium chloride sample in an alumina crucible for temperature calibration. The partial pressure of CsCl(g) and Cs₂Cl₂(g) was measured at 1000 K. The results of these measurements compare favorably to JANAF results, as shown in Table I-3. Another calibration will be completed later when higher temperatures (~1700 K) are required.

Ingot 32 contained Al, U, Ba, C, Ce, Mo, Sr, and Zr (Table I-4) but was not truly representative of irradiated NPR-HWR fuel. (It contained carbon and oxygen impurities and had an excess of cesium and deficiencies in the quantities of Mo and Sr. Further, the zirconium content was low by a factor of 45 relative to the barium content.

Table I-3. Experimental and JANAF Data for CsCl(g) and Cs₂Cl₂(g) Pressures at 1000 K

Source	Pressure, atm	
	CsCl	Cs ₂ Cl ₂
JANAF ²⁶	3.14E-4	3.56E-4
Experiment	2.52E-4	3.09E-4

Table I-4. Results of Chemical Analysis of Ingot 32 (by Savannah River Laboratory)

Element ^a	Weight Percent
Aluminum	79.1
Uranium (0.2 wt % enriched)	18.4
Barium	0.30
Carbon	0.25
Cerium	1.03
Molybdenum	0.46
Oxygen	0.12
Strontium	0.30
Zirconium	0.03

^aCr, Ca, Mn, and Ni are < 0.01 wt %.

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 vs. time suggested formation of a protective oxide layer, as predicted by our analysis in Sec.I.C.2. Additional experimental studies on formation of the oxide layer are needed.

In our next experiments, we planned Cs, I, and Te release measurements at 933 K (the aluminum melting point) from Ingot 32. To prevent loss of Cs, I, and Te at lower temperatures, we calculated pressures over I₂, Cs, and Te as elements and compounds: I as CsI, Te as Al₂Te₃, and the rest of the Cs as CsAlO₂. The compounds are those that might be formed in an accident. The equilibrium CsI pressure was estimated as 1.5×10^{-4} atm at the alloy melting point, 933 K. If the CsAlO₂ remains intact and the water pressure is above 0.03 atm, the cesium hydroxide pressure over CsAlO₂ is 2.6×10^{-3} atm at

the alloy melting point. The tellurium pressure over Al_2Te_3 is less than 10^{-9} atm below 1100 K, but rises to 2×10^{-5} atm at 1500 K.

4. Calculations on Fuel-Target-Fission Product System

Thermodynamic calculations (using the SOLGASMIX code) were carried out to identify the most probable vapor species above the fuel and target mixtures at 1000 and 1700 K. The temperature of 1000 K was selected because it is slightly above the melting point of the intermetallic compound LiAl , and the 1700 K temperature is a little higher than the upper temperature for which interest was expressed by the NPR Program. The initial calculations were performed for a system consisting of the fuel (U-Al), the target (Li-Al), and selected fission products (Cs, I, Te, and Ba). The thermodynamic properties for this system were taken from JANAF data²⁵ and from Barin and Knacke.²⁸ Data for CsI were taken from an earlier CMT survey.²⁹

The fuel, target, and fission product system was defined as a single fuel assembly, which is physically some 15-cm dia and 3-m long and consists of several concentric tubes of U-Al fuel and Li-Al target. Each fuel or target tube is clad in aluminum. The composition of the fuel, target, and fission product system was taken from information provided by J. E. Matos (Reactor Analysis Division, ANL). The initial system was assumed to be extremely aluminum-rich: 19.7 g-atoms uranium, 30.0 g-atoms lithium, and 1841 g-atoms aluminum. For this assembly composition, the SOLGASMIX code had difficulty simulating the equilibrium condition at 1000 K but was able to do so when the amount of aluminum was reduced by a factor of 10, still a very aluminum-rich system. This change in the aluminum content is not expected to have any effect on the fission product calculation, as the ratio of aluminum to fission product is still extremely large and the quantity of fission product is small. The SOLGASMIX code had no difficulty in the calculations at 1700 K with the full amount of aluminum.

For the SOLGASMIX calculations, the condensed phases were assumed to be an Al-U phase and a Li-Al phase. For the Al-U phase, the parent element species are Al and UAl_4 at 1400 K and Al and UAl_2 at 1700 K. Although the phase diagrams suggest that these Al-rich systems are far removed from the indicated intermetallic compounds, they were included to make some allowance for attractive interactions between Al and U, rather than just to treat the U as a simple solute in Al. For the Li-Al phase, data for the intermetallic compound, LiAl , were found only up to the melting point (966 K), and these data were extrapolated to 1000 K. For the 1700 K calculation, the Al-rich system was treated as an ideal solution of Li in Al.

No inquiry was made into the ternary system, U-Al-Li. It will be important to determine how immiscible the U-Al and U-Li systems are, so that the most realistic calculations of fission product distribution can be made. Experimental exploration of the overall features of the U-Al-Li phase diagram could be pursued by thermal analysis or quench-and-analyze techniques. A further question to be examined is whether it is more realistic to group the salt-like species (e.g., LiI , CsI , BaI_2 , Li_2Te) as a separate phase rather than as solutes in the metallic phases.

The outcome of the SOLGASMIX calculations is summarized in Table I-5. Several salient conclusions emerged from the SOLGASMIX calculations. One is that the LiI species at 1700 K is prominent both in the gaseous and condensed phases. Also, tellurium is bound by uranium as UTe and is retained in the condensed phase, especially at the lower temperature; AlTe is also significant in the gas phase. While UTe was included as a species in the condensed phases, no data for it were in the consulted literature. Instead, data for USE were used. The importance of UTe that emerged (certainly at 1000 K, though less so at the higher temperature) suggests that more emphasis be placed on this species.

Table I-5. Calculated Results for Concentrations of Fission Product Species

	Calculated Results	
	1000 K	1700 K
Cesium		
Vapor	Cs(g) dominant, 4E-4 atm.	Cs(g) dominant, 8E-4 atm.
Condensed	94% as element, 50% as CsI.	100% as CsI.
Iodine		
Vapor	CsI(g) dominant, 2E-8 atm.	LiI(g) dominant, 4E-6 atm; CsI, AlI(g) lower by 1E-2.
Condensed	92% CsI, 8% LiI.	99% LiI, 1% CsI.
Tellurium		
Vapor	Te(g) at 2E-26 atm.	Te(g) at 2E-11 atm.
Condensed	100% as UTe.	5% as UTe, 95% as Li ₂ Te.
Barium		
Vapor	Ba(g) at 7E-9 atm.	Ba(g) at 1E-6 atm.
Condensed	39% in U-Al, 61% in LiAl.	39% in U-Al, 61% in LiAl.

The following observations were made based on a thermodynamic analysis of our experimental system. When the U-Al fuel is heated, the aluminum matrix will melt first, then as the temperature is increased, UAl₄ will gradually dissolve in the liquid aluminum. At about 1003 K, the UAl₄ intermetallic will peritectically decompose to UAl₃, which will then continue to dissolve in the liquid aluminum. For 33.6 wt % U fuel, all of the uranium will be in solution at about 1373 K. Thus, at temperatures of about 1273 K, the system will consist of a liquid Al-U solution containing about 5 at. % U. If the fuel sample is co-melted with the Li-Al target, the liquid phase will contain lithium in solution. This will increase the activity coefficient of uranium in the solution and could result in the precipitation of a U-Al intermetallic. The chemical form of the fission products in this system will determine their release rates. In two cases (Kr and Xe) where the fission product does not react with any of the other elements present, the release rate will be controlled by physical processes, such as the rate of bubble formation and their migration to the sample surface. Whether or not the fuel sample is co-melted with the Li-Al target will have only a minor effect on the release of the rare gases, unless the added lithium in the liquid metal solution drastically affects the bubble formation and migration (large effects on surface tension and viscosity would be required).

The two alkali metals, Rb and Cs, do not appear to be chemically reactive or significantly soluble in U, Al, or Li. Unless these elements react with other fission products present, their release would be expected to be controlled by physical processes. There may be a small solubility of Cs in Al, which would help explain its low release rate from low-burnup samples. The addition of lithium to the system would not be expected to affect the release rate of the alkali metal fission products.

Bromine and iodine form bromides or iodides with U, Al, and Li. If formed, the U and Al halides may volatilize as MX₃ species, and so their release rate will be controlled by the transport of these species to the fuel surface. However, CsI is much more stable than the U and Al halide. As a result, even though there is more U and Al present in the system, it seems reasonable to predict that CsI will form.

The addition of lithium to the system would not be expected to increase the volatility of the halogen fission products.

Selenium and tellurium, two fission products that have relatively high volatility, form quite stable selenides and tellurides with U, Al, and Li. Their stability needs to be investigated by a review of the literature and thermodynamic computations. There may be a potential problem here, especially under oxidizing conditions, where the formation of TeO_2 gas might occur. The addition of lithium to the system is expected to affect the tellurium activity.

The refractory metals all form intermetallic compounds with aluminum, which will reduce even further their already low vapor pressures. Since these metals appear to be very insoluble in lithium, adding lithium to the liquid metal solution is expected to increase the activity coefficient and, therefore, decrease the solubility of the aluminum-containing intermetallic compounds. The activities of these metals in the liquid aluminum solution would be expected to be very low due to negative deviations from ideality and low concentrations. Some of these metals form volatile oxides (such as Mo and Ru) under oxidizing conditions (air or steam gaseous atmospheres), but it is expected that their activities are low enough that their formation will be insignificant.

The rare earth metals, which are immiscible with uranium in the liquid state and have very low solid solubilities, form stable intermetallic compounds with aluminum. Their reactivity with lithium is not known. If, as suspected, the rare earth metals are immiscible with lithium, then the addition of U and Li to the liquid aluminum solution would decrease the solubilities of the LnAl_4 intermetallic compounds. Since the addition of lithium is expected to cause the precipitation of UAl_4 , the rare earths are almost certain to co-precipitate. The release of rare-earth fission products is not expected to be significant.

This analysis suggests that three classes of release mechanism might be significant. First is the release of the rare gases that are not significantly soluble or chemically reactive with the liquid metal system. Their release will depend on nucleation, growth, and migration of bubbles in the liquid metal. This is an area where there has been extensive study, and hence, no further study is needed. Previous studies have shown that large releases of these gases take place. Second is substances, such as cesium, which do not react chemically with the liquid aluminum solution but may have very low solubilities. This class needs additional study to determine the factors that control the release. The third class is those fission products, such as the halogens or the chalcogenides, that form relatively stable compounds with U, Al, or Li, but are probably not significantly soluble in the liquid metal solution. Additional study on these release mechanisms, including experiments, is needed.

D. Desorption Characteristics of $\text{LiAlO}_2\text{-H}_2\text{-H}_2\text{O(g)}$ System (A. K. Fischer)

1. Introduction

The objective of this effort is to describe the energetics and kinetics of desorption of $\text{H}_2\text{O(g)}$ and H_2 from the surface of ceramic tritium breeders (LiAlO_2 in the present case) and thereby facilitate predictions of tritium release from fusion reactors. Earlier reports in this series discussed the use of the temperature programmed desorption (TPD) technique for measuring the activation energy and pre-exponential terms for the desorption rate equation and also presented results for TPD runs on LiAlO_2 that had been pretreated with He-H_2 gas at 673 K. It was not clear whether H_2 in the gas stream facilitated desorption under that pretreatment condition; a higher pretreatment temperature was seen as possibly

necessary to reveal the enhanced release that was observed with irradiated samples in a He-H₂ sweep gas.³⁰ Results are presented here for TPD runs on LiAlO₂ that was pretreated with He-H₂ at 923 K.

2. Experimental

The TPD experiments were run on LiAlO₂ that had been pretreated at 923 K overnight or, in a few cases, for 7-12 days in a gas stream containing H₂ at concentrations of 990, 495, and 247 ppm by volume (vppm). After pretreatment, the system was cooled quickly to 473 K while the equilibrating gas composition was maintained. The temperature was then increased from 473 to 1073 K at a ramp rate of 5.6 K/min. The sweep gas during the TPD run was either pure helium or the same He-H₂ mixture that was used in the pretreatment. When pure helium was the sweep gas, the gas composition was switched from the He-H₂ mixture to pure helium just before the temperature ramp began. Differences in the desorption peaks allowed us to determine the effect of H₂ in the sweep gas on the desorption processes.

The gas composition was monitored with a mass spectrometer to provide continuous traces for H₂, H₂O, N₂, and O₂. The N₂ and O₂ data provided ongoing evidence for the absence of leaks in the TPD apparatus. At the end of the temperature ramp, there was a soaking period of 10 min at 1073 K followed by cool down to 923 K. This was the temperature during the succeeding equilibration with the desired He-H₂ mixture for the next run.

The TPD peaks for the evolution of both H₂O and H₂ were obtained during desorption into pure helium. During runs of desorption into He-H₂ mixtures, peaks due to desorption of H₂ would be obscured against the strong background of H₂ in the sweep gas mixture. Nevertheless, some significant hydrogen effects were observed and are discussed below.

3. Results and Discussion on Desorption of H₂O

Figures I-5 to I-7 show TPD curves from different runs for desorption of H₂O into pure helium and into a He-H₂ mixture; in a given figure, the pretreatment gas composition was the same whether the following desorption was into helium or into the same mixture. The y-axis gives the rate of evolution from the particular sample in units of mol/min-m². The areas under the curves reflect the amounts of evolved material. It is evident in each case that the rates and amounts of H₂O desorption into the mixture are enhanced substantially over the values for desorption into pure helium. Earlier we had found that the desorption process involves multiple processes reflecting desorption from different kinds of sites (designated A, B, C, and D) on the surface of the LiAlO₂.³¹ The desorption peaks were analyzed to derive values for the kinetic parameters of the contributing subpeaks.

The method of analyzing the peaks was to synthesize them from subpeaks of the correct functional form for a first-order desorption process:

$$r = \sum v_i a_i \exp(-E_{di}/RT) \quad (\text{I-3})$$

where r is the overall rate of desorption of H₂O(g) expressed by the measured curves 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 H₂O/(min-mol occupied site i), a_i is the moles of H₂O adsorbed on a given type of site at a given time, and E_{di} is the activation energy of desorption (units of kcal/mol) for a given site i .

Lotus 1-2-3 was used for deconvolution calculations and to display the subpeaks, their sum, and the match between the sum and the observed desorption curve. With this spreadsheet, the iterations were quickly made manually, allowing visual judgments of closeness of fit. The "best" values of activation energies, temperatures of peak maxima, and amounts of coverage could be defined narrowly since closeness of fit was visibly affected by small changes in values of the parameters in Eq. I-3.

Fig. I-5.

Plot for TPD of H_2O from LiAlO_2 Treated with He-247 vppm H_2 into Helium or Same Gas Mixture

Fig. I-6.

Plot for TPD of H_2O from LiAlO_2 Treated with He-495 vppm H_2 into Helium or Same Gas Mixture

Fig. I-7.

Plot for TPD of H_2O from LiAlO_2 Treated with He-990 vppm H_2 into Helium or Same Gas Mixture

Figures I-8 and I-9 show deconvoluted TPD spectra for an example of desorption into He and into He-495 vppm H_2 , respectively. Consistently, the curves for desorption into He- H_2 mixtures contained two types of peaks, labeled B and C, and the curves for desorption into pure helium contained C and D peaks. Results for all runs are shown in Table I-6, which also gives the data for the pre-exponential terms. The activation energies of the B, C, and D peaks are ~23, 28, and 32 kcal/mol. (In earlier work dealing with desorption from samples pretreated at 673 K, we identified A, B, and C peaks.³² The A peaks have a desorption activation energy of 18 kcal/mol.) The data indicate that the H_2 in the sweep gas causes the precursors of desorbed H_2O , namely, OH^- population, to shift 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, when the higher activation energy combination of C and D sites is involved. An important point is that the activation energies of the sites do not change significantly with increases in pretreatment time or H_2 level.

Fig. I-8.

Plot for TPD of H_2O into He-495 vppm from LiAlO_2 Treated with Same Mixture (deconvoluted into B and C subpeaks)

Fig. I-9.

Plot for TPD of H₂O into Pure Helium
from LiAlO₂ Treated with He-495 vppm
H₂ (deconvoluted into C and D subpeaks)

The pre-exponential terms are not as constant as the activation energies. Standard deviations for the sets of ν_i range from 13 to 52% of the respective mean values. Table I-7 gives the averaged kinetic parameters determined from the data in Table I-6. Where the ν values may be compared to determine the effect of H₂ in pre-exponentials (namely, for the C peaks), the values of $(2.22 \pm 1.16) \times 10^5$ vs. $(8.91 \pm 1.14) \times 10^4$ for pure He and for the mixture, respectively, are slightly different at the 1σ level. Therefore, the effect of H₂ is to make a small change in the pre-exponential term for the C sites, 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 sites when H₂ is in the sweep gas.

Table I-6. Kinetic Parameters for First-Order Desorption of H₂O from B, C, and D Sites on LiAlO₂.^a
(Symbols and their units of measure are defined in Eq. I-3.)

Soak Gas Pretreatment		H ₂ in Sweep Gas, ppm						
Time, h	H ₂ in He, vppm		ν_B	E_{dB}	ν_C	E_{dC}	ν_D	E_{dD}
20	247	0	-	-	1.90E5	28.2	3.51E5	32.2
170	495	0	-	-	1.25E5	28.0	9.91E5	32.0
20	990	0	-	-	3.51E5	28.0	7.51E5	32.0
20	247	247	2.22E4	23.0	8.82E4	28.0	-	-
20	495	495	1.07E4	22.0	7.62E4	28.0	-	-
20	495	495	1.62E4	23.0	8.78E4	28.0	-	-
290	990	990	2.75E4	22.8	1.04E5	28.0	-	-

^aTemperature increase from 473 to 1073 K.

Table I-7. Averaged Kinetic Parameters for B, C, and D Peaks for H₂O Desorption from LiAlO₂ into He-H₂ Mixtures and into He

	ν_B	E_{dB}	ν_C	E_{dC}	ν_D	E_{dD}
He	-	-	2.22E5	28.1	6.9E5	32.1
Mixture	1.91E4	22.7	8.91E4	28.0	-	-

4. Application

To apply these results to blanket design and tritium-release modeling, the areas under the H₂O 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 H₂O under the given conditions, either into the respective He-H₂ 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 are those that would have been activated only at temperatures higher than those in the experimental temperature range. The H₂ adsorption process was regarded as dissociative chemisorption, forming surface OH⁻ groups which combine bimolecularly prior to desorption. Consequently, the OH⁻ and the H₂O coverage should vary as the square root of the H₂ partial pressure. This linear relationship for the total evolvable H₂O coverage, θ , is shown in Fig. I-10 for sweep gases of pure He and He-H₂ mixtures.

Fig. I-10.

Fractional Surface Coverage by H₂O Desorbed into He-H₂ Mixture or Pure Helium for Temperature Ramp of 473-1073 K

As an example, the rate of desorption of H₂O at steady state from a breeder at 923 K into a helium stream carrying H₂ in the measured concentration range (which is a prototypic range for a fusion reactor) can be derived from Fig. I-10. To calculate the desorption rate requires knowledge of the values of a_B and a_C in Eq. I-3. These may be calculated from:

$$a_i = 1.66 \times 10^{-5} m \sigma_s \theta_i \quad (\text{I-4})$$

where the factor $1.66 \times 10^{-5} = (10^{19} \text{ sites/m}^2)/6.02 \times 10^{23}$, m is the mass of the breeder in g, σ_i 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 last quantity is derived from the curve in Fig. I-10 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; the observed ratios ranged from 0.38 to 0.79. That is, $1/3$ of the θ from Fig. I-10 is assigned to the B peak and $2/3$ to the C peak. (For desorptions into pure helium, the observed ratio of C to D sites is in the range from 0.24 to 1.18.) The rate of desorption follows from substitution of these values into Eq. I-4 and then the resulting a_i values into Eq. I-3.

5. Results and Discussion for Desorption of H_2

Some H_2 data were also obtained for the TPD of H_2 into pure helium. Desorptions into pure helium provided desorption peaks, which were deconvoluted. The results from this analysis are presented in Table I-8. It is striking that the kinetic parameters are very similar to those for H_2O desorption. The subpeaks are labeled C and D to indicate their similarity to the ones for H_2O , though it is not implied at this time that the sites are the same. Figure I-11 shows the deconvolution for the most prominent H_2 peak observed.

Table I-8. Kinetic Parameters for First-Order Desorption of H_2 into He from C and D Sites on LiAlO_2

Pretreatment					
Time, h	H_2 in He, vppm	ν_C	E_{dC}	ν_D	E_{dD}
20	247	1.61E5	28.2	6.35E4	33.5
170	495	1.30E5	28.5	5.00E5	32.5
20	990	4.68E5	28.5	8.91E5	33.0
Average		2.5E5	28.4	4.8E5	33.0

Fig. I-11.

Plot for TPD of H_2 into Pure Helium from LiAlO_2 Treated with He-247 vppm H_2 (deconvoluted into C and D subpeaks)

The fit is the best of all that were done (Figs. I-11 to I-13). However, there are still puzzling aspects for which further study is planned. For example, Fig. I-12 compares the evolution of H_2 into a pure helium stream and the changes in H_2 level in a helium sweep gas with an initial concentration of 247 vppm H_2 . Ignoring the first 10 minutes or so, which is a warmup period for the mass spectrometer, the droop in the upper curve indicates that H_2 is being taken up by the system until a temperature of approximately 1080 K (710°C) is reached, whereupon H_2 evolution commences. This behavior roughly parallels the lower curve for desorption into pure He. One question is how much of the H_2 in the gas stream, after passing the sample, originates from the sample and how much from the input stream. Planned work with deuterium-loaded samples (but with Li_2O as the sample) and H_2 -containing sweep gas should cast light on this. It would provide a direct isotopic analog for questions of tritium behavior.

Fig. I-12.

Plot for TPD of H_2 into Pure Helium or into He-247 vppm H_2 Mixture from $LiAlO_2$ Treated with He-247 vppm H_2

Fig. I-13.

Plot for TPD of H_2O and H_2 into Pure Helium or into He-247 vppm H_2 from $LiAlO_2$ Treated with He-247 vppm H_2

Figure I-13 shows H_2 and H_2O peaks for a single desorption run into a stream of He-247 ppm H_2 . (The H_2 -into-He curve in Fig. I-12 has been replaced by the H_2O -into-mixture curve.) Here, it appears that H_2O desorption lags behind the onset of H_2 uptake. Adsorbed H_2 builds up before H_2O appears. A question is whether to regard the process as reduction by H_2 to form H_2O or as displacement of H_2O from the surface. Along with this is the question of the oxygen and/or water source, since H_2O peaks are observed repeatedly on the same sample. An experimental approach to identify the oxygen source is to perform the TPD measurements on a sample labeled with ^{18}O . However, the practicality of this in terms of expense and sensitivity has not been explored yet.

6. Future Work

Further numerical analyses of the data are still possible. However, the program plan calls for measurements with Li_2O , because of the interest in that breeder for the International Thermonuclear Experimental Reactor (ITER). The issues raised here indicate the need, in the forthcoming work with Li_2O , not only for innovations in experimental technique (use of deuterium and possible use of ^{18}O) but also for extension of the basic experimental variables that form the core of a comprehensive TPD study (ramp rate and the temperature limit of the ramp).

E. Tritium Percolation through Porous Ceramic Breeders (S. W. Tam and V. Ambrose*)

1. Introduction

The problem of describing tritium transport and release from lithium ceramic breeder materials in a realistic and comprehensive manner is an important issue for fusion reactor design. A model for tritium transport with predictive capability is necessary to provide a coherent basis for estimating tritium inventory and other related factors. Many mechanisms act in concert in driving the transport of tritium. They have been treated with different emphasis by the ceramic breeder modeling community. In general, one can divide the various mechanisms into two broad groups, depending on the length scales through which they act.

The first group of processes is active through a length scale of angstroms up to the size of an individual grain, which typically ranges from a fraction of a micrometer to about $10\ \mu m$ for ceramic breeder materials. Such processes take place either within the grain (i.e., bulk) or on grain surfaces. The bulk processes include intergranular diffusion, interaction with impurities and defects within the grain, and precipitation. Grain surface processes include adsorption/desorption and re-dissolution.

The second group of processes involves a mechanism that acts in a length scale of magnitude at least comparable to a single grain up to the size of the whole breeder system. This latter scale, for the purpose of understanding tritium release, is represented by the average distance between purge channels (typically on the order of a centimeter).³³ Purge channels are pathways introduced into the ceramic breeder materials by design to facilitate the extraction of tritium-bearing species from the interior of these breeder materials by use of an inert gas (usually helium) purge flow.

The most important process in this latter class is the gas transport through the interconnected porosity from pores inside the breeder to the purge channel. Compared to bulk diffusion and surface processes, gas transport through porous breeder ceramics has been subjected to much less thorough

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analysis. The difficulties in a realistic treatment of tritium-bearing gas percolation differ from those of (for example) analysis of bulk diffusion.

Firstly, there is a statistical element to the process arising from the heterogeneous nature of the pore structure and channels that needs to be taken into account. Traditionally, this has been subsumed into a so-called tortuosity factor, which is essentially a "fudge factor." A more satisfactory approach should be based upon experimentally determined pore-size distribution as input. Detailed data on pore-size distributions are beginning to become available for lithium ceramic breeders.³⁴ Utilization of such statistical structural information would render the Monte Carlo method³⁵ a natural approach to describe tritium percolation through the porous ceramic medium.

Secondly, the length scales through which the percolation process works can range over several orders of magnitude. Consequently, in many cases, gradients of operating parameters such as pressure and temperature cannot be neglected. Furthermore, such gradients are often anisotropic due to the ceramic breeder configuration (e.g., thin slabs, cylindrical pellets). These constraints imply that a one-dimensional analysis of tritium pore percolation may be inadequate. In the following, a formalism is described that addresses the statistical nature of the pore microstructure and the multi-dimensional character of the transport process. This formalism is adapted from the theory of random transport modified to treat the problem of gas percolation, including factors such as generation source and desorption processes, which are central to tritium transport processes.³⁶ Recent analysis of an annealing experiment performed on irradiated ceramic breeder indicates that bulk diffusion is not the rate-limiting process (see ANL-92/25, pp. 32--37). Consequently, in the present treatment, intragranular diffusion is not included. In the following discussion, the physical basis of the approach and its implementation are presented. The formalism is then applied to residence time, which has become an increasingly popular parameter in analyzing experimental data on tritium release.³⁷

2. Theory

The interconnected (i.e., open) porosity in the ceramic is likely to be intragranular. The pores lie on grain boundaries and grain edges. In the present analysis, the intragranular porosity is modeled as a network of interconnected pores. A simple cubic network structure is assumed. Only two-dimensional calculations will be presented in this work, with the square network being the corresponding structure. However, the formalism is completely general and is not limited in principle to any particular spatial configuration. The bonds (i.e., links) between nodes of the network represent the pore channels. If a fraction p of these channels is open, and if P represents the fraction of open channels that are interconnected all the way to the breeder exterior, then the average radius r_c of the pore channel is given by:

$$r_c = \frac{2\phi}{S_g \rho} \frac{P}{p} \quad (\text{I-5})$$

Here, ϕ is the porosity, ρ is the theoretical density of the breeder, and S_g is the specific surface area. The relationship between P and p is governed by percolation theory.³⁸ In the limiting case of all the channels being open ($p = 1$), P will be one and Eq. I-5 reduces to the traditional formula for average radius. For the present work, we will concentrate on this case.

A distribution of pore sizes could be supplied from empirical microstructural information on the particular ceramic breeder that is of interest. However, a uniform pore-size distribution with r_c given

by Eq. I-5 had been adopted as an illustrative representation in the present analysis. Nevertheless, the formalism can treat as input a wide class of pore size distributions, including mono- and bimodal ones. Physically, structural disorder (in the form of variation of pore sizes) would lead to complicated flow processes. Acceleration or deceleration of this flow would occur as the tritium-bearing species (such as HTO or HT) migrate along pore channels of differing sizes and along different directions in our two-dimensional simulations. The migration process is governed by convective transport and diffusion. The tritium-bearing species is introduced into the channels by generation from the grain interiors and desorption from the grain surfaces. The tritium-bearing species can also be removed from the vapor phase in the pores by readsorption onto the pore surfaces. For a particular tritium species, such as HT, these mechanisms are represented by the following equations:

$$\frac{\partial C_g}{\partial t} = \frac{u}{\partial x} \frac{\partial C_g}{\partial x} = \frac{D_g}{\partial x^2} \frac{\partial^2 C_g}{\partial x^2} + k_d C_s - k_a C_g \quad (I-6)$$

$$\frac{\partial C_s}{\partial t} = g - k_d C_s + k_a \langle C_g \rangle \quad (I-7)$$

where C_g = gas phase concentration
 C_s = concentration on grain surfaces
 u = velocity of tritium species in the pore channel
 D_g = gas phase diffusion coefficient
 k_d = desorption rate constant
 k_a = adsorption rate constant
 g = tritium generation rate
 $\langle C_g \rangle$ = average gas phase concentration
 t = time
 x = distance

Equations I-6 and I-7 apply to HT and HTO, but with different transport coefficients (e.g., diffusion coefficients). For simplicity, HT is the representative species chosen for this work. Note that these equations are assumed to be valid within one individual pore (i.e., over a length scale of the order of microns). No assumption has been made on the applicability of the equations (particularly Eq. I-6) over macroscopic lengths (i.e., over many pores). Thus, D_g in Eq. I-6 is the molecular diffusion coefficient with no unknown fudge factors such as tortuosity included. For D_g the Bosanquet representation³⁹ has been used:

$$\frac{1}{D_g} = \frac{1}{D_k} + \frac{1}{D_{AB}} \quad (I-8)$$

where D_k is the Knudsen diffusion coefficient, which is valid when the mean free path of the gas becomes the same order or larger than r_c , the radius of the pore channel. The symbol D_{AB} is the molecular diffusion coefficient of a gas mixture A and B.³⁸ Here A is HT, and B is helium, the principal component of the purge gas mixture. When the mean free path of the gas is much smaller than r_c , D_{AB} is the correct transport coefficient to use. Equation I-8 is a good description of D_g over the entire range of the ratio (mean free path)/ r_c that is of interest to the present analysis. There are some corrections to Eq. I-8, but they are unimportant due to the dilute nature of HT (or HTO) in the helium purge gas ($\leq 10^{-4}$).⁴⁰

Equations I-6 and I-7 are solved by Laplace transform and direct quadrature. The resulting C_g can be expressed in terms of $C_g(0)$ and $C_g(l)$, the concentrations at the two ends (i.e., nodes) of the pore channel (where l is the length of the pore channel). The current $I(x)$ along each channel can then be evaluated using the expression³⁶

$$I(x) = (uC_g - D\partial C_g/\partial x) A \quad (I-9)$$

where A is the channel area.

If one assumes that at each node there is no net accumulation by the species represented by C_g , then the following holds true for the i^{th} node of the random pore network:

$$\sum_j I_{ij} = 0 \quad (I-10)$$

where I_{ij} is the current in the channel with the i^{th} and j^{th} nodes as its two end points. The summation is over all the nearest neighbor pore channels to the i^{th} node.

Equation I-10 is equivalent to a matrix equation:

$$\tilde{A} C = G \quad (I-11)$$

where C is a vector representing the node concentrations for all the nodes in the network, G is a vector incorporating the initial and boundary conditions, and $\tilde{A}$ is a matrix that incorporates the dynamical parameters (such as diffusion, convection, etc.) of the network. Direct solution of Eq. I-11 enables the concentration and, hence, the output flux to be evaluated.

To test this approach, we have applied it to a two-dimensional square network of pore channels whose cross-section radius is distributed in a random manner over a range such that the mean radius is given by Eq. I-5. The analysis in the next section employs materials data (such as S_g and ϕ) on Li_2O taken from the MOZART experiment.³⁷ The square network is considered to be a cross-sectional slice of a three-dimensional section of solid breeder. Because of the two-dimensional nature of the calculation and the limited size of the network (11×11 , representing approximately 10^2 grains), the results of the analysis cannot yet be compared directly with experiment. Calculations using a much larger network size, together with scaling analysis, would be part of the next stage of our work.

3. Application of Model to Residence Time Analysis

In recent years the concept of residence time τ has been increasingly employed to analyze and interpret in-pile measurements on tritium release rate. The concept has been quantified (somewhat arbitrarily) as the time necessary to attain a certain fraction of the steady-state tritium release rate. Typically that fraction is around $2/3$. Other applications involve estimating τ in terms of the ratio of the steady-state inventory to the steady-state release rate. For this kind of approach to be useful in analyzing release data, it is necessary to understand the physical basis of this concept and the benefits and

limitations in using a single number (i.e., τ) to characterize the data. The random network model presented here offers an excellent tool with which to address this issue. In the following analysis all calculations have been carried out in dimensionless units. For example, time has been expressed relative to the typical transit time across one single channel.

If one injects a sharp pulse at the center node of the system, then the present model can calculate the output flux $P(t)$ at the outlet node through the four corners. In fact, $P(t)$ represents the probability distribution of the "first passage time." That is, the first time at which the tritium-bearing species arrives at the outlet node after it has been injected in a sharp pulse at the central node. Figure I-14 shows the result of the simulation for output flux $P(t)$ versus transient times for a single pulse. Note the broad structure and the long tail of distribution. This broad and highly skewed curve arises from several sources. First, there are many different pathways through which the gas molecule can reach the outlet from the source. Because of the distribution in pore sizes, the transit time for each pathway can differ significantly. This is so even for two pathways which may have nominally the "same" geometrical path lengths. This then results in the broad distribution of transit time. The long tail is characteristic of the complex structure of the pathways and the diminished concentration gradient with increased time.

Fig. I-14.

Output Flux versus Time for One Pulse (in dimensionless units of time it takes to move across one single pore of length r_c)

An important consequence of these findings is that the most probable transit time, $\tau_{\max}$ (as represented by the peak in the distribution curve), can significantly differ from the average transit time τ_{avg} [as computed from the probability distribution $P(t)$]. In the case of the results in Fig. I-14, τ_{avg} can be as much as a factor of two above $\tau_{\max}$. If τ is to be interpreted as the residence time, then a single value for it may lead to a misleading interpretation of the experimental data. In fact, τ_{avg} is simply the first moment $\langle t \rangle$ of $P(t)$. What the present results indicate is that the higher order moments, $\langle t^k \rangle$ ($k = 2, 3, \dots$), may be necessary to characterize $P(t)$ and the experimental release data.

Figures I-15 to I-17 illustrate the concentration profile at early, intermediate, and late transient times. Figure I-15 represents the profile at the time at which very little HT has exited from the outlet. Figure I-16 gives the profile at $\tau_{\max}$. Here, the profile is much more spread out than for the early time. In addition, there is a rapid fall off in the profile near the four corners connected to the outlet node. This is consistent with the maximal behavior of the output flux at that time. Figure I-17 represents the

concentration profile at very late time (~ 400 in Fig. I-14), which represents a temporal regime where most of the initial pulse has exited from our network. This physical visualization of the dynamics agrees with the long tail region of Fig. I-14.

Fig. I-15.

Concentration Profile at Early Time for One Pulse (in dimensionless units of time it takes to move across one single pore of length r_c)

Fig. I-16. Concentration Profile at Intermediate Time for One Pulse (in dimensionless units of time it takes to move across one single pore of length r_c)

Fig. I-17. Concentration Profile at Late Time for One Pulse
(in dimensionless units of time it takes to move
across one single pore of length r_c)

This skewness in the distribution of residence times is expected to be further enhanced if there is a spatial distribution of tritium generation sources. To illustrate this point, simulations have been performed for a two-pulse case, in which one pulse is introduced at the center (as before), and the second pulse is added next to one of the corners. Another simulation has been performed in which one pulse is introduced at $t \geq 0$ for every node ($> 10^2$ pulses). The resulting output fluxes as a function of time are shown in Fig. I-18. The increasing skewness of the distribution with enhanced distribution of sources is evident. In the many-pulse case, the rise occurs in an extremely short time. Table I-9 indicates the increasing deviation of the mean residence time ($\langle t \rangle$) from the most probable ($\tau_{\max}$) as the number of pulses increases from one to two to about 120. The location of the pulse sources relative to the outlet nodes is also of crucial importance.

4. Conclusion

We have analyzed the problem of tritium percolation through a porous lithium ceramic material. The technique that we have employed is a random network percolation model. Local transport in each individual pore channel is described by a set of convection-diffusion-reaction equations. Long-range transport is described by a matrix technique. The heterogeneous structure of the medium is accounted for by Monte Carlo methods. The approach has been applied to an analysis of the concept of tritium residence time, which is associated with the first passage time, a direct output of our analysis. It was shown that the distribution of first passage time has a significantly skewed structure with a long time tail. An adequate description of such a distribution requires higher order moments, such as $\langle t^2 \rangle$, than the average residence time. Therefore, analysis of experimental tritium release rates with average residence time needs to be treated with caution.

Fig. I-18.

Output Fluxes versus Time for One, Two, and Many Pulses (in dimensionless units of time it takes to move across one single pore of length r_c)

Table I-9. Comparison of Mean Residence Time to Most Probable*

No. of Pulses	$\langle t \rangle$	τ_{max}	% Deviation
1	85	40	53
2	55	20	64
>100	30	<3	>90

*See text for definition of symbols.

F. Sample Preparation for Dynamic Helium Charge Experiment

(J. P. Kopasz, C. E. Johnson, D. L. Smith,* B. A. Loomis,** M. L. Hamilton,*** R. G. Clemmer,*** L. R. Greenwood,*** H. Matsui,**** and K. L. Pearce*****)

The objective of the Dynamic Helium Charge Experiment (DHCE) is to provide baseline irradiation data on the effects of concurrent helium production and neutron irradiation on the physical and mechanical properties of vanadium alloys. The DHCE⁴¹ is designed to enhance helium production in specimens of vanadium alloys during irradiation in the MOTA experiment performed in the Fast Fusion Test Facility (FFTF). The objective is to simulate the simultaneous gas production and irradiation damage (dpa) anticipated in a fusion device. In the FFTF reactor, helium is normally produced in

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vanadium at a very low rate, about 0.02 appm/dpa, solely by fast neutron (n, α) reactions. The ratio of helium production to dpa level in fusion reactors, however, will be about 5-to-1 due to the presence of 14 MeV neutrons. Since helium will cause swelling and may influence the evolution of the vanadium microstructure, fusion simulations of helium production are needed to determine the importance of these effects. In this experiment helium will be produced by the decay of tritium, which will be dissolved uniformly in vanadium specimens during the irradiation. (A detailed description of the technique is presented in Ref. 41.)

In preparation for DHCE, tritium was loaded into vanadium foils to provide the initial tritium in the test capsules. The foils were nominally 2.5 x 3.8 x 0.025 cm. These foils were pretreated to allow easier absorption of the tritium. The pretreatment consisted of exposing the samples to dynamic vacuum at room temperature followed by heating to 900 °C under vacuum and several hydrogen-soak/dynamic-vacuum cycles. The hydrogen soaks were performed at 400-500 °C, while the dynamic vacuum cycles were performed at 800 °C. Hydrogen absorption increased with repeated soakings due to the reduction of surface oxides and removal of impurities trapped in the alloy during the high-temperature evacuations.

The tritium obtained from the supplier was found to be contaminated with high levels of helium, as well as lower levels of various carbon and oxygen-containing compounds and protium impurities. The helium in the gas would drastically slow the kinetics of the tritium uptake, since the helium effectively blankets the sample in a static gas system. The gas handling apparatus was modified to include a uranium bed to remove the impurities other than protium and helium. The as-supplied tritium gas was adsorbed on the uranium bed. The helium impurity, which does not absorb, was pumped away. The uranium bed was then heated to recover the tritium, while impurities other than protium were retained by the bed. While this method removed most of the impurities in the tritium gas, it did not eliminate H₂.

The purified tritium was loaded into the vanadium foils as follows. The vanadium foil was placed in a quartz sample tube and heated to 900 °C under vacuum to remove the hydrogen adsorbed during the pretreatment. The foil was then exposed to vacuum for a minimum of 12 h at 900 °C, then quenched to room temperature. Tritium was desorbed from the uranium bed into a calibrated volume to produce the desired tritium pressure and then expanded into the quartz sample tube. The foil was then heated to 500 °C, and the pressure dropped as the tritium was adsorbed. The sample was cooled slowly to 300 °C, where the solubility of tritium in vanadium is higher, and the pressure was allowed to drop until the desired amount of tritium was absorbed. The valve to the quartz tube was then closed, and the vanadium foil cooled to room temperature. After the foil reached room temperature, the valve to the quartz tube was opened, and the final pressure was recorded so that the actual amount of tritium absorbed could be calculated. The residual gas was expanded into a vial for analysis to determine the hydrogen-to-tritium ratio. After the vial was closed, any residual tritium was absorbed onto the uranium bed.

The vanadium foils doped with tritium were then placed in test capsules. Also added were vanadium disks to be analyzed by transmission electron microscopy after irradiation, other specimens of vanadium alloys to be used in mechanical tests, and lithium enriched in ⁶Li. The latter was added so that sufficient tritium would be generated to compensate for losses due to decay and permeation through the capsule. The lithium also serves as a heat conductor and oxygen getter.

This loading of the vanadium and lithium was performed in an argon-filled glovebox. The tests capsules were then electron-beam welded shut. The capsules were leak checked to verify that there would be no unintentional tritium release, and the required nondestructive testing was performed (visual inspection, dye penetrant inspection, helium leak check, and X-ray radiography) to verify that the welds were satisfactory. These vanadium samples will be irradiated at 425-600 °C during MOTA 2B. The

capsules will be disassembled after MOTA 2B is discharged, and the microscopy and mechanical test specimens will be examined.

G. Sealing Systems for Heavy Water Reactor
(P. A. Finn)

The technology of seal systems (flanges, elastomers, valves, and pumps) was reviewed to develop a data base for the design of the coolant components for an HWR. The seal systems important for the HWR are the flange seal on the reactor head; the dynamic elastomer seals for fuel tubes, control rods, and safety rods; the isolation valves; and the reactor pumps. The data base was derived from operating experience and seal development work for reactors in the United States, Canada, and Europe. The results from this review are presented in an ANL report.⁴²

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II. SEPARATION SCIENCE AND TECHNOLOGY

(G. F. Vandegrift)

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

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

A. Enhancements to Generic TRUEX Model (J. M. Copple and R. J. Jaskot)

The Generic TRUEX Model (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. Last September, GTM Version 2.1 for the Macintosh computer was given to the National Energy Software Center (NESC) for distribution. Since that time improvements have been made to existing code.

The process for converting the GTM from the Macintosh to the IBM-PC version has been finalized. The conversion is required since the new model versions are developed on a Macintosh and, after testing, moved to an IBM-PC. Most of the files can be transferred to an IBM-PC without any changes. As a result, less time needs to be spent on testing and debugging the PC version. It was found that the IBM-PC contained insufficient conventional memory for running the GTM, but this problem was solved by using Windows 3.0, a commercial software application from Microsoft.

Modifications have been made to the SASPE macro because of the expansion of its "speciation module," which calculates the speciation of certain feed components in the TRUEX process. Originally, this module only calculated the speciation of the cations Fe^{3+} , Al^{3+} , Zr^{4+} ; the anions $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , and F^- ;

and elements that were summed together and referred to as "rare earths": La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Pm^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , and Y^{3+} . The expanded speciation module now adds the components Am^{3+} , Pu^{3+} , and Cm^{3+} to the rare earth sum. This module will also calculate the speciation of Th^{4+} , UO_2^{2+} , Pu^{4+} , Np^{4+} , Cd^{2+} , and PO_4^{3-} , along with the neutral species $\text{B}(\text{OH})_3$. Two of the components that were added to the speciation module, PO_4^{3-} and $\text{B}(\text{OH})_3$, also had to be added to the allowed feed components.

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

The SASSE worksheet was developed for detailed evaluation of proposed flowsheets in conjunction with distribution ratios obtained from the generic TRUEX data base (Sec. II.G). In addition to establishing that each effluent reaches or exceeds its specified composition, sensitivity analysis using SASSE allows one to develop a strategy for process monitoring and control (Sec. II.F.4). The SASSE worksheet is designed so that it works for any amount of other-phase carryover. The calculational algorithm rapidly gives the steady-state concentration profile for each component without requiring any iterations.

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

The structure of the SASSE worksheet is now being revised so that one can specify (1) an extraction efficiency for each stage and (2) a fixed effluent flow rate for either phase (organic or aqueous) at any stage. The incorporation of extraction efficiency into the SASSE worksheet facilitates TRUEX calculations for mixer settlers. It also allows one to model the drop in extraction efficiency in a centrifugal contactor when it is used at very high or very low organic-to-aqueous (O/A) flow ratios. The fixed effluent flow rate allows one to model sampling streams taken from various process stages. The SASSE_Generator macro will be modified so that it generates this revised SASSE worksheet for use within the GTM.

C. Extraction of Thorium by TRUEX-NPH
(I. R. Tasker, J. Sedlet, and D. R. Fredrickson)

1. Introduction

The behavior of thorium in the TRUEX process is being studied with the ^{230}Th isotope, an alpha emitter with a half-life of 7.54×10^4 years and a specific activity of 4.6×10^7 dpm/mg. This is the only thorium isotope useful for tracer studies other than ^{224}Th , a 24-day beta-gamma emitter that must be separated from a large quantity of ^{238}U .

Distribution-ratio measurements are needed for modeling the extraction behavior of thorium; satisfying this need has two prerequisites. First, the data obtained must be reliable and reproducible. Second, the experiments must be conducted over a range of distribution ratios suitable for observing the effect of complexants. To address these needs, we measured the distribution ratios of ^{230}Th for nitric acid solutions with initial concentrations varying from 0.05 to 0.5M.

2. Experimental

A detailed description of the preparation of the ^{230}Th stock solution used in the distribution-ratio measurements appears in the previous semiannual report (ANL-92/25, pp. 65-66). The distribution ratios were measured by the usual procedure. Equal volumes of the two phases were placed in a culture tube, equilibrated at 25 °C in a thermostated beaker, and mixed with a Vortex stirrer for 1 min. The tubes were centrifuged, the phases separated, and aliquots counted for alpha particle activity in a liquid scintillation counter. Because the ^{230}Th was dissolved in TRUEX-NPH, the tracer was added to the organic phase in these experiments. Also, because the solvent was not pre-equilibrated with nitric acid, equilibrium aqueous nitric acid concentrations were calculated using the GTM.

3. Results and Discussion

Three series of experiments were performed, and the results are given in Tables II-1 to -3. In Table II-1, the distribution ratios are the average of triplicate measurements, and the standard deviations for these are given in parentheses. In Tables II-2 and -3, each series consisted of an initial extraction followed by a second extraction using the organic phase from the first extraction.

Table II-1. Distribution Ratios for ^{230}Th between Nitric Acid and TRUEX-NPH^a for First Series

<u>[HNO₃], M</u>		Dist. Ratio
Initial ^b	Equil. ^c	
0.05	0.0469	24.1 (±0.7)
0.10	0.0899	71.0 (±2.0)
0.20	0.169	165 (±3)
0.50	0.384	593 (±36)

^aStandard TRUEX, 1.4M TBP, 0.2M CMPO (100% purity assumed) in C₁₂-C₁₄ Conoco NPH.

^bInitial nitric acid concentration.

^cEquilibrium nitric acid concentration calculated using GTM.

Table II-2. Distribution Ratios for ^{230}Th between Nitric Acid and TRUEX-NPH^a for Second Series

Extraction 1			Extraction 2		
<u>[HNO₃], M</u>	Dist. Ratio	Mass Bal.%	<u>[HNO₃], M</u>	Dist. Ratio	Mass Bal.%
0.0469	23.7	74	0.0497	24.8	96
0.0899	54.0	73	0.0983	79.4	107
0.169	111	74	0.192	241	108
0.384	388	74	0.463	1388	108

^aStandard TRUEX, 1.4M TBP, 0.2M CMPO (100% purity assumed) in C₁₂-C₁₄ Conoco NPH.

Table II-3. Distribution Ratios for ^{230}Th between Nitric Acid and TRUEX-NPH^a for Third Series

Extraction 1			Extraction 2		
$[\text{HNO}_3]$, <u>M</u>	Dist. Ratio	Mass Bal.%	$[\text{HNO}_3]$, <u>M</u>	Dist. Ratio	Mass Bal.%
0.0469	26.0	80	0.0497	22.8	94
0.0899	62.8	82	0.0983	76	94
0.169	118	78	0.192	221	97
0.384	444	84	0.463	1275	95

^aStandard TRUEX, 1.4M TBP, 0.2M CMPO (100% purity assumed) in $\text{C}_{12}\text{-C}_{14}$ Conoco NPH.

The results in Tables II-1 to II-3 are shown in Fig. II-1 as a log-log plot. All three data sets form a nearly linear curve, but each has a different slope. The data for the second extraction (Table II-2 and II-3) show a second-order dependence on nitric acid concentration, which is also the case for Pu(IV). This can be explained by $\text{Th}(\text{NO}_3)_2^{2+}$ being the major aqueous species in this nitric acid concentration range or by the extraction of HNO_3 by CMPO diminishing Th^{4+} extractability. We will test these hypotheses by measuring the extraction of thorium under conditions of high nitrate salt and low nitric acid concentrations.

Fig. II-1. Measured Distribution Ratios for ^{230}Th between Nitric Acid Solutions and TRUEX-NPH as a Function of Equilibrium Acid Concentration. Average of extraction 1 from Series 2 and 3, and average of extraction 2 from Series 2 and 3.

All three data sets were expected to fall on the same straight line when plotted against the equilibrium acid concentration. However, this is not the case, as illustrated in Fig. II-2. Treating the data as a whole (Fig. II-3) suggests that the highest concentration data point (0.463M) for extraction 2 could be an outlier. Figure II-4 shows the same data plotted as Fig. II-3, except without the potential outlier.

The distribution ratio (D) data may be expressed as $\log_{10} D = A + B \log [\text{HNO}_3]$. The coefficients of the fits for the data are given in Table II-4. Inspection of Figs. II-3 and II-4 and Table II-4 shows that the best-fit curve is quite similar for these two combined data sets. It is possible that the data possess considerable scatter, and that one datum point is an outlier. This would imply that we are unable to obtain D values in this system to an accuracy of 10% or better.

Possible explanations for the nonreproducibility of the data are: (1) the ^{230}Th stock solution contains some poorly extractable non-thorium alpha emitters (since the samples were counted by liquid scintillation, which does not resolve the alpha energies of these nuclides), and (2) since a small fraction of the thorium is present as a poorly extractable species in the first extraction, subsequent extractions of the same organic phase should give reproducible distribution ratios. Note that the data in Table II-2 and II-3 support this possibility. Experiments to clarify the problem are planned.

Fig. II-2. Best-Fit Curves Obtained from Distribution Ratios Measured for ^{230}Th between Nitric Acid Solutions and TRUEX-NPH as Function of Equilibrium Acid Concentration

Fig. II-3. Best-Fit Curves Obtained for All Distribution Ratios Measured for ^{230}Th between Nitric Acid Solutions and TRUEX-NPH as Function of Equilibrium Acid Concentration

Fig. II-4. Best-Fit Curves Obtained for All But One Distribution Ratio Measured for ^{230}Th between Nitric Acid Solutions and TRUEX-NPH as Function of Equilibrium Acid Concentration

Table II-4. Coefficients of $\log D = A + B \log [\text{HNO}_3]$ for Data in Tables II-1 to II-3

Data Set	A	B	R^2 *
Series 1	2490	1.495	0.996
Series 2	1369	1.320	0.994
Series 3	4963	1.793	0.998
Series 1 + Series 2	1846	1.408	0.979
Series 1 + Series 2 + Series 3	2697	1.556	0.968
Series 1 + Series 2 + Series 3 ^b	2029	1.443	0.978

*Correlation coefficient of fit (from Cricketgraph 1.2).

^bSeries 3, extraction 2 data point at $\text{HNO}_3 = 0.463\text{M}$ omitted.

A second discrepancy in the results is the mass balance, which is about 75% for the first extraction and 95-100% for the second. The low mass balance in the first extraction may be due to an inaccurate assay of the tracer solution, or a loss of thorium at the interface or on the walls of the culture tube. Treatment of the walls with HF did not recover any significant amount of thorium. Interfacial losses will be explored later.

D. Solution Chemistry of BF_4^- and Related Species (L. Nunez, I. R. Tasker, and M. A. Tranovich*)

1. Introduction

Nuclear waste from the Idaho Chemical Processing Plant (ICPP) has been considered for treatment using the TRUEX process. The ICPP high-level waste, originating from reprocessing of naval nuclear reactor fuel, has large amounts of B, Cd, and HF. Boron and cadmium, which have large neutron

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cross sections, are added to the wastes as neutron absorbers to avoid criticality. The solution chemistry involved in using TRUEX on the wastes has not previously been modeled.

Boron(III) in the presence of excess acid and HF forms the BF_4^- ion. The production of tetrafluoroborate ion from boric acid proceeds through a series of equilibria, giving rise to a number of intermediate hydroxyfluoride species which have not been considered for the GTM in previous waste treatment. The chemistry of BF_4^- must be understood in order to treat the ICPP high-level waste by the GTM. A preliminary literature search suggested that four areas should be focused upon to help determine the extraction chemistry of BF_4^- and related species: (1) thermodynamic stability and hydrolysis in water, (2) determination of BF_4^- species by potentiometric titration, (3) separation and detection of the BF_4^- species by means of ion exchange chromatography, and (4) extraction of BF_4^- from waste solutions. In addition to this, two other areas must be investigated prior to incorporation of a new species into the GTM: (1) thermodynamic activity data must be available (or some estimate made), and (2) volumetric data or estimates of volumetric measurements are needed. To address these needs, we have conducted a literature review and experimental work.

2. Literature Survey

Important findings from the literature review are summarized below.

a. Thermodynamic Stability

It is well known that BF_4^- originates from the reaction of boric acid with a high concentration of HF. The BF_4^- forms after a series of intermediate reactions involving hydroxyfluoride species. These reactions, along with the equilibrium constants for each reaction, are as follows¹:

Overall, we have

That shows that the hydrolysis of HBF_4 to B(OH)_3 under acid conditions is slow.

b. Potentiometric Titrations

Since BF_4^- is quite stable, potentiometric determination of boron concentration has been used for materials such as steel,¹ silicon glass,¹ soil,² etc. Some of the most common titrations are the BF_4^- titration with cetyltrimethylammonium bromide with a pH range of 4 to 8,³ or with triphenylmethane dyes or benzyldimethyltetradecylammonium chloride using Crystal Violet as an indicator.⁴ An indirect method to determine BF_4^- is determination of F^- by total decomposition of the BF_4^- (by heating in glycerol in the presence of Fe^{3+}).⁵ Other methods are based on ionometric determination.

The primary disadvantages of the potentiometric method are that it's highly pH dependent; usually shows broad transitions; and NO_3^- , SO_4^{2-} , and other ions interfere. The latter creates difficulties because the BF_4^- species will be in a matrix containing high concentration of these ions.

c. Chromatography

Extensive research has been done on the separation of BF_4^- from other anions by using ion chromatography. Two methods have been successfully applied: (1) multidimensional chromatography⁶ and (2) ion exchange chromatography.⁷ Multidimensional chromatography, which combines two columns in a sequential process, efficiently separates BF_4^- from PO_4^{3-} . The ion exchange method separates BF_4^- under a wide variety of conditions. The anion exchange resin is composed of acid salts of partially cross-linked polyamine polymer. A common example is Amberlite XE-230 resin, which is composed of an N-methyl glucamine functional group. Experimentation⁷ with these columns shows that the BF_4^- strongly interacts with the resin (see Table II-5). These experiments used 0.01M Na_2CO_3 /0.003M NaHCO_3 as eluant and flow rates of 115 mL/h, giving a retention time for BF_4^- of 6 min. The difference in retention time between BF_4^- and other species permits the recovery of boron by ion exchange chromatography.

Table II-5. Effect of Diverse Ions on BF_4^- Recovery by Ion Exchange Chromatography

Ion	Added As	Mole Ratio to Boron	Recovery, %
CrO_4^{2-}	K_2CrO_4	100 to 1	101.4
NO_3^-	NaNO_3	100 to 1	
SO_4^{2-}	NaSO_4	100 to 1	99.1
HPO_4^{2-}	$\text{NaHPO}_4 \cdot 9\text{H}_2\text{O}$	100 to 1	

d. Other Methods

Since BF_4^- is highly stable, several methods have been developed for BF_4^- extraction based on the following:

1. Coprecipitation with $\text{Al}(\text{OH})_3$.⁸
2. Reverse osmosis at pH = 4 and autoclave with $\text{Ca}(\text{OH})_2$ and CaCl_2 .⁹
3. Precipitation as $\text{K}(\text{BF}_4)$ from concentrated eluant solution.¹⁰

4. Absorption by activated charcoal or surfactant complexation. (Arman C, Armac T).¹¹
5. Use of acid salts of partially cross-linked polyamine polymers as ion exchange to remove BF_4^- .¹
6. Complex formation with methylene blue (MB) basic dye and extraction into organic phase.¹²

The method with the most potential for success in quantitative determination of BF_4^- species¹² for the TRUEX process is MB (Fig. II-5) extraction.

Fig. II-5. Structure of Methylene Blue

The extraction of the BF_4^- as the complex of methylene blue (or other thionin derivatives) is brought about in 1,2-dichloroethane. This process has been studied extensively with dyes of this type, and all dyes were found to extract BF_4^- .⁴ In addition, it has been proven that various solvents can extract the BF_4^- .⁴

3. Extraction of Boric Acid by TRUEX-NPH

Since BF_4^- originates from the reaction of boric acid with hydrofluoric acid, and in general, acids can be extracted by the TRUEX components, initial experiments were conducted to determine to what degree boric acid and tetrafluoroboric acid would extract into the TRUEX solvent. The procedure to determine the quantity of boric acid transferred into the organic phase involved an organic titration of boric acid (a weak acid) with a strong organic base [0.101M tetrabutylammonium hydroxide (TBAOH)].

A problem arises in observing the titration transition of the boric acid in the organic phase. A closer examination of the chemistry revealed that boric acid polymer forms at boric acid concentrations greater than 0.025M. The polymerization is described by the following¹³:

The polymerization can be reduced by the addition of polyalcohols such as glycerol and polyethyleneglycols.¹⁴ In particular, the reaction with $B(OH)_3$ and H_2L (where L is mannitol or glucose) in water yields $H[B(L)_2]$ with an increase in the acidity of the acid: $pH = 5.14$ with mannitol and $pH = 2.27$ with glucose.

The mannitol is more efficient than the glucose in forming a complex.¹⁵ The mechanism by which the polyalcohol increases the acidity is

In forming this complex, the polymerization equilibrium is shifted toward the monomer. (Other methods of determining the concentration of boric acid include indirect titration,¹⁶ gravimetric titration,¹⁷ and spectrophotometric techniques.¹⁸) The simplest and fastest alternative method involves the complexation of boric acid with an indicator (brilliant green) and monitoring of the spectrum at 637 nm.¹⁸

Our solvent extraction experiments were performed in the usual manner, and the boric acid concentration was analyzed by titration. The average concentration in each phase and the corresponding distribution ratios of boric acid are given in Table II-6. The plot of organic $B(OH)_3$ against aqueous $B(OH)_3$ in Fig. II-6 shows that a linear curve will fit the data reasonably well. While the data show some scatter, a linear relationship can be mathematically represented as

$$D_{B(OH)_3} = [B(OH)_3]_{org} / [B(OH)_3]_{aq} \quad (II-9)$$

The slope (0.039) of the line in Fig. II-6 is equal to the distribution ratio of boric acid. The data in Fig. II-6 indicate that the behavior cannot be attributed to CMPO loading effects. Studies of the distribution ratios of boric acid as a function of boric acid and nitric acid concentrations are underway.

Table II-6. Distribution-Ratio Calculations for Boric Acid from Organic Titration Data

Solution Number	H_3BO_3 Conc., <u>M</u>			Dist. Ratio
	Initial	Org.	Aqu.	
1	0.030	0.00197	0.0280	0.070
2	0.049	0.00285	0.04610	0.062
3	0.097	0.00613	0.0897	0.068
4	0.154	0.00470	0.1490	0.032
5	0.197	0.00610	0.1906	0.032
6	0.261	0.00670	0.2540	0.027
7	0.302	0.00856	0.2935	0.030
8	0.357	0.01595	0.3410	0.046

Fig. II-6. Organic $B(OH)_3$ Concentration as a Function of Aqueous $B(OH)_3$ Concentration

4. Apparent Molar Volumes of BF_4^- and $H_2PO_4^-$

In addition to BF_4^- , it has recently become desirable to incorporate into GTM the behavior of $H_2PO_4^-$ species, because they are present in the single-shell tank (SST) waste at Hanford and are being considered for use in a pretreatment step with the TRUEX process. To this end, the apparent molar volumes, $V_{\phi,2}$, of these species as a function of temperature are being determined in order that solution densities can be estimated.

The literature¹⁹⁻²¹ gives the following values for apparent molar volumes ($V_{\phi,2}$) at 25 °C: BF_4^- , 44.18 cm³/mol; $H_2PO_4^-$, 29.1 cm³/mol. Since no other data are available on these ions, comparison with similar ions and estimation methods were investigated. The method finally adopted is given below.

Many investigators have used semiempirical equations of the type:

$$V_{\phi,2}^{\circ} = A r^3 - \frac{B Z^2}{r} \quad (II-10)$$

$$V_{\phi,2}^{\circ} = \alpha r^3 + A' \frac{Z^2}{r} - \frac{B' Z^2}{r} \quad (II-11)$$

$$V_{\phi,2}^{\circ} = \alpha' (r + A'^3) - \frac{B' Z^2}{r} \quad (II-12)$$

where Z is the ionic charge; r is the ionic radius; and A , A' , A'^3 , B , B' , B'^3 , α , and α' are constants from fitting experimental values of density as a function of temperature. Such equations can be used to calculate $V_{\phi,2}^{\circ}$ if values of the constants are available. Millero²² has published values of the constants A , A' , A'^3 , B , B' , and B'^3 (α and α' were set to 2.52) over the temperature range 0-200 °C for anions

and cations. Millero used three alternative measures of ionic radius. For our purposes, rather than choose one of these three alternatives, the ionic radius r was adjusted so that the value of $V_{\phi,2}^{\circ}$ obtained using Eq. II-10 was the same as the experimental value (44.18 cm³/mol at 25 °C). Equation II-10 was chosen arbitrarily for its simplicity. Substituting $V_{\phi,2}^{\circ} = 44.18$ mL/mol, $A = 4.58$, and $B = 8.65$ (A and B from Millero's tabulation) into Eq. II-10 for BF_4^- gives

$$4.58r^4 - 44.18r - 8.65 = 0 \quad (\text{II-13})$$

The real, positive root of this equation was determined using Mathematica software (Wolfram Research): $r = 2.19035$ Å for BF_4^- and $r = 1.94219$ Å for H_2PO_4^- . At 25 °C intervals from 0 to 150 °C, these r values, together with values of A and B appropriate for the temperature, were substituted into Eq. II-10. The results of the calculations are given in Table II-7 and in Figs. II-7 and II-8. Included in the table and figures are $V_{\phi,2}^{\circ}$ values for ClO_4^- (as a comparison for BF_4^-) and NO_3^- (as a comparison for H_2PO_4^-). The results of fitting the data are:

$$V_{\phi}^{\circ} = 41.304 + (0.11359 \cdot T) - (0.00042305 \cdot T^2) \text{ for } \text{BF}_4^- \quad (\text{II-14})$$

$$V_{\phi}^{\circ} = 27.186 + (0.081043 \cdot T) - (0.00039752 \cdot T^2) \text{ for } \text{H}_2\text{PO}_4^- \quad (\text{II-15})$$

These results have been incorporated into GTM.

Table II-7. Calculated Values of V_{ϕ}° as Function of Temperature

Temp., °C	Constants ^a		$V_{\phi}^{\circ, b}$ mL/mol			
	A	B	BF_4^-	ClO_4^-	H_2PO_4^-	NO_3^-
0	4.26	7.88	41.17	40.70	27.15	25.60
25	4.58	8.65	44.12	44.12	29.10	29.00
50	4.78	9.09	46.08	45.10	30.34	30.30
75	4.90	10.54	46.68	46.90	30.47	30.70
100	5.18	12.35	48.60	47.90	31.59	31.90
125	5.31	14.61	49.13	48.60	31.38	31.60
150	5.45	18.87	48.66	48.20	30.21	30.00

^aFrom Ref. 21.

^bValues for ClO_4^- and NO_3^- from Ref. 21 and included for comparison.

Fig. II-7. Apparent Molar Volume vs. Temperature for BF_4^- and ClO_4^-

Fig. II-8. Apparent Molar Volume vs. Temperature for H_2PO_4^- and NO_3^-

E. Centrifugal Contactor Development

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1. Introduction

The Argonne centrifugal contactor is modified as necessary to work with specific solvent extraction processes. For each new process, solution densities and organic-to-aqueous (O/A) flow ratios

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are reviewed, and if necessary, the rotor weirs are modified. In support of contactor development, vibrational measurements are made using proximity probes and real-time analyzers. The results are related to the design of the spinning rotor and the stationary support frame by using vibrational models.

2. High-Throughput Contactor

When nuclear criticality considerations are important, 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. With this constraint in mind, we are investigating ways to increase contactor throughput without increasing its diameter. If high process throughputs are required (that is, greater than 10 L/min of total flow, which is typical for a normal 10-cm contactor), such a high-throughput contactor could greatly reduce the number of parallel process lines that are required.

To increase contactor throughput, one can increase the rotational speed, the rotor length, and the 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, that is, the first natural frequency (f_1) of the spinning rotor. Now, with the rotor diameter effectively fixed, we are increasing throughput by making the rotor longer and, possibly, turning it faster. To develop this design, we have been analyzing the vibrational and hydraulic limits that will occur as we lengthen the rotor and increase its speed. The results of these mechanical and hydraulic considerations are presented here, along with some initial experimental work aimed at developing a steady bearing for the contactor rotor.

a. Mechanical Considerations

A wide range of mechanical factors must be considered in the development of a high-throughput contactor. These factors include (1) size and speed constraints, (2) operation below or above the first natural frequency, and (3) if above f_1 is chosen, the design for a steady bearing so that the rotor can easily pass through f_1 . Other mechanical factors have been discussed previously as a part of normal contactor design.²³

(1) Size and Speed Constraints

A normal contactor rotor has a separating zone with a length-to-diameter (L/D) ratio of about 2 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.). Since, as will be seen below, the weir sections must be increased as the contactor rotor is lengthened, we are maintaining the ratio of separating zone length to weir zone length at 4. Thus, if we increase the 10-cm rotor by a factor of four, its overall length will increase from 25 cm to 100 cm.

In this work, designs for high-throughput contactors up to 16 times their normal L/D ratio were evaluated. However, an important use of the high-throughput contactor is expected to be in glovebox operation. For this case, we have to worry about the contactor height relative to the glovebox height. This contactor height must be reduced even further if (1) a chain hoist is needed to lift the rotor out of the contactor housing, and (2) a drain space is needed for each contactor stage. Our first estimate is that four times the normal length of the rotor is the longest we can consider for glovebox operation. Since the height of a typical glovebox is about 2 m, we should have enough space to lift the rotor out of the contactor housing if we take the motor off first.

Initially, we had planned to limit rotor speed to 3600 rpm (60 Hz) and just increase the rotor length. For this situation, we can use off-the-shelf motors, which are desirable because of their availability, reliability, and low cost. However, because the initial high-throughput contactor design is being limited to four times its normal L/D ratio, we have decided to study rotor operation up to 7200 rpm (120 Hz). Since theoretical contactor throughput is directly proportional to both rotor length and rotor speed, this design for the high-throughput contactor has the potential for increasing contactor throughput by a factor of four to eight times.

If a rotor is operated at 3600 rpm (60 Hz), a 3600-rpm motor can be directly coupled to the rotor and the motor bearings used as the support bearings for the rotor. However, for such a motor-rotor combination, the rotor shaft would need two support bearings external to the motor. The frame that holds these support bearings would also hold the motor. The motor would be either behind the support bearings or above the support bearings but offset from it. The power from motor shaft to rotor shaft would be transmitted by a belt, gears, chain, or pulley. Figure II-9 illustrates these three motor options.

Fig. II-9. Schematic of High L/D Rotor Showing Options for Motor Location and Steady Bearing Position

(2) Vibration Analysis

The Beam worksheet (ANL-91/26, pp. 157-167) was used to evaluate generic designs for the 10-cm contactor both below and above the first natural frequency. As a basis for these designs, the rotor shaft was assumed to be held in place by two external bearings, as shown in Fig. II-10. The shaft, which connects the motor to the rotor, ends with a flexible coupling (not shown) between the shaft and the motor. This effectively isolates the motor from the rest of the rotating system; thus, the motor was not included in the vibration analysis. As the diameter of this connecting shaft is increased, the stiffness of the rotating system and the first natural frequency also increase.

Fig. II-10. Rotor and Shaft Design for Operating below the First Natural Frequency with High L/D Rotors

In particular, a generic 10-cm contactor was evaluated by varying the diameter of the connecting shaft and the length of the separating zone in the rotor. A first series of analyses was done to determine a satisfactory operating region below the first natural frequency. A second series of analyses was done to determine a satisfactory operating region between the first and second natural frequencies (f_1 and f_2 , respectively). The results of these analyses are given here. In addition, a test stand for evaluating steady bearings for good operation between f_1 and f_2 is discussed.

(a) Operation below First Natural Frequency

In contactor operation below f_1 , a distinction is made between the rotor shaft and the connecting shaft. The rotor shaft is assumed to screw into the connecting shaft. When the connecting shaft diameter is less than or equal to 41.3 mm (1.625 in.), the diameter of the connecting shaft is assumed to equal that of the rotor shaft. When the diameter of the connecting shaft is greater than 41.3 mm, the diameter of the rotor shaft is held at 41.3 mm for its 25.4-mm (1.0-in.) length just above the solid rotor body. As a result, the diameter of the rotor shaft does not become so large that it interferes with liquid flow over the more-dense-phase weir. Results of these calculations, plotted in Fig. II-11, show how the first natural frequency decreases as the separating zone length is increased for a given shaft diameter.

Fig. II-11. Effect of Connecting Shaft Diameter and Separating Zone Length on First Natural Frequency of Rotor

For an operating speed of 60 Hz (3600 rpm), good operation will be realized as long as the first natural frequency is greater than 20% above the operating speed. This lower limit for good contactor operation, 72 Hz, is indicated in the figure. The curves in Fig. II-11 show that a 10-cm rotor can be operated at 3600 rpm (60 Hz) with a separating zone that is almost twice the normal length of 20 cm (actually 208 mm in this case) if the connecting shaft diameter is 63.5 mm (2.5 in.) or more.

Operation at 7200 rpm (120 Hz) requires that f_1 for the rotating system be above 144 Hz, that is, 20% above 120 Hz. Figure II-11 indicates that this is possible if (1) the connecting

shaft diameter is 50.8 mm (2 in.) or greater, and (2) the length of the separating zone is that for a normal rotor. Note that increasing the connecting shaft diameter from 76.2 to 101.6 mm (3 to 4 in.) has very little effect on f_1 . Thus, further increases in this diameter are not effective since the controlling stiffness is the rotor shaft. If the connecting shaft diameter is 50.8 mm (2 in.) and its length between the two external bearings, normally 15.2 cm (6.0 in.), is doubled, f_1 increases 10%. If the length between these two bearings is cut in half, f_1 decreases 25%.

(b) Operation above First Natural Frequency

In operating above f_1 , the motor/rotor system must be at least 20% above f_1 but at least 20% below f_2 . For this design, it is assumed that a steady bearing, either a solid bushing or a pin as shown in Fig. II-9, 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, it is assumed that the bearing does not generate much friction so that the motor/rotor assembly passes through f_1 easily on its way to a final operating speed between f_1 and f_2 .

Results of calculations concerning contactor operation between f_1 and f_2 are plotted in Fig. II-12. In these calculations, the shaft diameter was varied from 22.2 to 41.3 mm (0.875 to 1.625 in.), while the separating zone length was varied from 1 to 16 times the normal length. Also shown in the figure is the range of natural frequencies to avoid for satisfactory operation at 60 and 120 Hz, i.e., $\pm 20\%$. As can be seen by keeping both error bands in mind, all three diameters allow vibration-free operation at 60 Hz (3600 rpm) with separating zone lengths from 4 to 16 times the normal length of 20 cm (actually 208 mm in this case). At 120 Hz (7200 rpm), operation between f_1 and f_2 is possible with separating zone lengths from 2 to 16 times the normal length if the shaft diameter is 31.8 mm (1.250 in.) or greater.

Fig. II-12. Effect of Connecting Shaft Diameter and Separating Zone Length on Region between the First and Second Natural Frequencies

(3) Use of Steady Bearing for Rotor

When designing a contactor to operate above f_1 , we assumed that a steady bearing could be found that would allow the rotor to pass through f_1 easily. To find under what conditions, if any, this assumption is true, a bearing test stand was built, as shown in Fig. II-13. We will also use this test stand to explore (1) the problem of bearing wear as it passes through f_1 and (2) the ability of the rotating system to recover from a mechanical shock while operating at full speed. The test stand was designed for rotors whose diameters are about 4 cm. Although the 4-cm rotor size is used in this test stand, we hope to discover general principles that will apply to all contactors. The dc motor used on the test stand has a variable speed controller with a range from 0 to 45 Hz (0 to 2700 rpm). A plate, located under the rotor in Fig. II-13, is available in several designs so that we can test either the pin bearing or one of the ring bearings. By using a series of plates designed like the one in Fig. II-13, we can test all three of the steady bearings options shown in Fig. II-9.

Fig. II-13. Test Stand for Rotor Steady Bearings

While the bearings on the rotor shaft are rolling bearings with low starting and running friction, the steady bearing options for the rotor body are sleeve bearings; thus, the bearings do not turn. For these bearings, the starting friction will be higher. In addition, because no liquid film, i.e., lubrication, is possible for solid bushings around the upper part of the rotor, running friction will also be high. Our plan in operating with these sleeve bearings between f_1 and f_2 is as follows. Except when passing through f_1 , the sleeve bearings will not be in contact with the rotor. The rotor is to be brought up to speed quickly so that little or no contact with the sleeve bearing occurs on startup. On shutdown, we expect some contact with the sleeve bearing as the motor/rotor system loses speed slowly and so will spend more time near f_1 . The total indicating runout (T.I.R.) of the rotor should be less than the gap between the rotor body and the bearing sleeve so that there will not normally be any contact between these two parts. Above f_1 , the motor/rotor system becomes self-centering. Thus, vibration analysis for the rotating system assumes that the sleeve bearing is not there, that is, it has no bearing stiffness because it provides no radial support.

Two test rotors were built with dimensions as listed in Table II-8. For each rotor, f_1 was measured without any sleeve bearing present. For rotor I, f_1 was low enough that it could be measured by visually counting the oscillations of the static rotor. For both rotors, the operating value for f_1 was measured by determining how close we could approach f_1 , both from below and above, without the rotating system starting to bang on the test plate located around the rotor body. The highest such operating speed below f_1 and the lowest such operating speed above f_1 were used to obtain the measured value for f_1 when the rotor was operating. As shown in Table II-9, these experimental f_1 values are in reasonable agreement with the calculated f_1 values. The calculated f_1 values typically have an error that is less than 20%. Rotor banging is expected only within 20% of the actual value for f_1 .

For each sleeve bearing, gaps of 0.03, 0.25, and 0.76 mm (1, 10, and 30 mils) were used. The gap is measured when the bearing and rotor are concentric. One material was used for the pin bearings: 304 stainless steel. Three materials were used for the ring bearings: 304 stainless steel, Hastelloy C-276, and tetrafluoroethylene (TFE). The ring bearing was located either at the very top of the rotor or 3.02 cm (1-3/16 in.) below the top of the rotor.

Table II-8. Dimensions of the Two Test Rotors

Test Rotor	Part	Length		Diameter		Wall		Notes
		inch	cm	inch	cm	inch	cm	
I	Motor Coupling	1.875	4.76	0.625	1.59	--	--	
	Rotor Shaft	18.13	46.0	0.290	0.74	--	--	
	Rotor	4.00	10.16	1.625	4.13	--	--	a
II	Motor Coupling	2.00	5.08	0.625	1.59	--	--	
	Rotor Shaft	1.00	2.54	0.500	1.27	--	--	
	Rotor	21.0	53.3	1.625	4.13	0.094	0.24	b

*The first test rotor is a solid stainless steel rotor.

^bThis hollow rotor has solid plugs at each end. The length of the top plug is 1.59 cm (0.625 in.); the length of the bottom plug is 0.95 cm (0.375 in.). These plug lengths are included in the overall length of the rotor shown.

Table II-9. Natural Frequencies of the Two Test Rotors

Rotor	Rotor Condition	First Natural Frequency, Hz		Calculated Second Natural Frequency, ^a Hz
		Measured	Calculated ^a	
I	Static	3.0	3.43	48.0
	Operating	3.9 ± 1.6	3.45	61.8
II	Operating	8.96 ± 1.29	7.57	249.5

^aCalculated using the Beam worksheet with 21 sections.

Results for rotor I were interesting but probably not useful for the design of a high-throughput contactor. This rotor had a long slender shaft so that we might be able to approach f_2 for the rotor without any steady bearing support. The vibration analysis shows that, if the sleeve bearing is in continuous contact with the rotor so that it does have some bearing stiffness, the first natural frequency will lie between f_1 and f_2 for the unsupported rotor. The new value for f_1 would give a measure of the stiffness of the support bearing. As rotor I was located so close to the bottom of the long rotor shaft, the T.I.R. was high, 1.52 mm (60 mils). Thus, all three bearing gaps were in contact with the rotor. The result was unsatisfactory sleeve bearing operation because of the noise (but not banging) and the high wear on the surface of the sleeve bearings.

Except for two cases, the results for rotor I showed that the lower bounds for the first natural frequencies were significantly above the f_1 value shown in Table II-9. The two exceptions were the stainless steel and Hastelloy ring bearings located 1-3/16 in. below the top of the bearing with 0.03 mm of clearance. These two rings bound up the rotor so that the motor could not turn at all. More typically, binding of the rotor did not occur, and the lower bound for f_1 was 10 Hz or greater. For the three ring bearings at the top of the rotor with a 0.03-mm clearance, the lower bound for f_1 was greater than 45 Hz, the top speed for the test stand motor. This suggests a bearing stiffness of $>1.7 \times 10^7$ N/m ($>10^5$ lb_f/in.). Other data are much more erratic, giving bearing stiffnesses down to 6.1×10^3 N/m (35 lb_f/in.) for the ring bearings located 1-3/16 in. below the top of the rotor with a 0.76-mm clearance and down to 1.14×10^4 N/m (65 lb_f/in.) for the pin bearing with a 0.76-mm clearance. The overall trend was for the bearing stiffness to drop as the gap between the rotor and the sleeve bearing was increased.

Based on these results, rotor II was designed and is now ready to be tested. Rotor II is a hollow rotor with a shape much closer to that envisioned in the final high-throughput contactor. Because the top of the rotor is much closer to the motor and the rotor shaft is larger, the T.I.R. at the top of the rotor is much less, about 0.25 mm (10 mils). Thus, we expect to see bearing stiffnesses for the upper sleeve bearings on the rotor that appear to be zero when the gap between the rotor and the ring bearing is large.

b. Hydraulic Considerations

In the development of the high-throughput contactor, we initially thought that the major problem would be contactor vibrations. While this certainly is true, vibrations are not the only problem. A review of rotor hydraulics has shown that simply making the rotor longer and running it faster are not enough to increase contactor throughput. One must also address some important hydraulic problems. These problems, both inside and outside of the rotor, are discussed below.

(1) Inside Rotor

The operation of a typical contactor rotor is shown in Fig. II-14. For this normal rotor, the L/D ratio of the separating zone is about 2.0, and the L/D ratio of the weir region is about 0.5. If the rotor diameter is 10 cm, this normal rotor operating at 60 Hz (3600 rpm) will have a maximum throughput of about 22 L/min. This is considerably higher than the nominal maximum throughput of about 11 L/min, which allows for satisfactory operation over a range of solution densities and a range of O/A flow ratios.

Fig. II-14. Cross Section of Operating Contactor with Normal L/D Rotor

If the L/D of the separating zone for this normal 10-cm rotor is increased by a factor of four, the design curves for various O/A flow ratios become widely divergent as contactor throughput increases above 20 L/min. For a normal rotor, such design curves, while not congruent, are close together (ANL-90/15, pp. 152-160). In addition, the region of satisfactory operation (i.e., the region where both effluents have less than 1% other-phase carryover) generally works for very low flow rates up to the maximum throughput for a normal rotor with a given radius for the more-dense-phase weir. However, as shown in Fig. II-15, especially for an O/A flow ratio of 0.2, the radius for the more-dense-

phase weir that works for one flow rate will not work for much higher or lower flow rates. For example, if the more-dense-phase weir has a radius of 35 mm, contactor operation is satisfactory only between 48 and 56 L/min of total flow when the O/A flow ratio is 0.2. This situation does not lead to a satisfactory design for a long rotor.

Fig. II-15. Effect of O/A Flow Ratio on Region of Satisfactory Operation for High L/D Rotor with Normal Design

This design problem was partially solved by increasing the cross-sectional area available to flow in the underflow to the upper weir and by increasing the vertical height of the riser leading to the upper weir. These increases are proportional to the increase in the length of the separating zone. Some small additional benefit was obtained by increasing the number of vanes in this riser and in the separating zone.

A fully satisfactory solution was only found when the length of the upper and lower weirs available for flow was increased proportionally with the increase in the length of the separating zone. To achieve this increase in the weir length without changing the weir radius, one must use multiple circular weirs for both the upper and lower weirs, as shown in Fig. II-16.

The use of multiple weirs creates two new problems because channels must be provided for the liquid so that all the weirs can be used. The first problem is that some of the more dense phase can be trapped in the channels for the less dense phase. This problem is solved, as shown in Fig. II-16, by providing weep holes that connect the less-dense-phase channels to the underflow for the more dense phase. The second problem is the need for complex machining, which increases construction costs. Because of this problem, a second weir design was developed. This new weir is a series of troughs with their openings at the level of the liquid surface and with each trough connected by a tube to the wall of the rotor. A cross section of the trough-on-tube weirs, which shows how they allow liquid to exit at the wall of the rotor, is given in Fig. II-17. A second cross section, which shows how the trough-on-tube weirs are arranged about the rotor axis, is given in Fig. II-18.

Fig. II-16. Contactor Cross Section Showing Multiple Circular Weirs for Both Phases

Fig. II-17. Rotor Cross Section Showing the Trough-on-Tube Weirs for Both Phases

Fig. II-18. Rotor Cross Section at the Trough-on-Tube Weirs in the Separating Zone

For the trough-on-tube weir, the long sides of each trough can be either parallel to the rotor axis (as shown in Figs. II-17 and II-18) or on a circle around the axis, as the weirs are in the normal design. In either case, the surface of the trough must have the same radius from the axis of the rotor for a given liquid phase. If the parallel design is used, and it looks the most attractive at present, some experimental tests will be needed so that our weir correlations can be revised for this new situation.

While the discussion above was for the contactor operating at 60 Hz (3600 rpm), it applies to a wide range of rotor speeds, since throughput is proportional to the rotor speed. If a rotor is designed so that its separating zone capacity is fully utilized at one rotor speed, one will also have full use of the separating zone capacity at other speeds. Thus, when rotor speed is doubled, the maximum throughput of the contactor will also be doubled.

(2) Outside Rotor

Outside the rotor, but inside the stationary contactor housing, the mixing zone should still be satisfactory, since it is lengthened as the rotor is lengthened. The increased cross-sectional area of the underflow will result in a rotor that has a larger diameter in this region. Since the collectors should be no larger than about 15 cm (6 in.) to have nuclear criticality safety by geometry, the larger underflow diameter reduces the cross-sectional area available for flow in the collector rings. For this reason, we are planning to include a slinger ring at the bottom of both collector rings. The lower slinger ring will be a part of the wider top portion of the rotor, as shown in Fig. II-16. The slinger ring limits the liquid escaping over the lip of the collector ring by its small gap. In addition, the slinger ring imparts momentum to the liquid in the ring so that the liquid flows out the tangential exit port of the collector ring easily. Note that, while two collector rings are shown for both sets of weirs, a single collector ring that can capture all the liquid from its set of weirs would also work.

3. Vibration Analysis

We have developed a relatively easy method to determine the first natural frequency of the rotating motor/rotor system in a centrifugal contactor. An evaluation of the calculations, which are done in an Excel worksheet called Beam, shows them to be accurate to within 20%. A report is being prepared on this worksheet and the general use of the method of transfer matrices in an Excel worksheet. A user manual for the Zonic Real Time Spectrum Analyzer (RTSA) is also being prepared to supplement the *6088 Multichannel Signal Processor User Manual* that comes with the Zonic 6088 Multichannel Signal Processor. It is intended that, using only the manual, one will be able to make routine measurements of natural frequencies in static motor/rotor assemblies for centrifugal contactors.

F. Monitoring and Controlling the TRUEX Processes (B. Misra and M. C. Regalbuto)

1. Introduction

Development of an optimized TRUEX process will depend, to a large extent, not only on selection of monitoring instruments for the critical process variables, but also on implementation of control strategies based on the inherent characteristics of multistage centrifugal contactors. It is expected that selection and placement of sensors will play a dominant role in gaining an insight into both the static and dynamic behavior of the separation process. Successful development of a control system will depend on use of on-line monitoring for such key variables as concentration and activity levels by the latest analytical techniques. Since the TRU concentration in the TRUEX feed solution is low, monitoring of the impurity concentrations in the product streams with the desired degree of accuracy may be, in many cases, beyond the capability of existing instruments.

As part of this development effort, we are evaluating the TRUEX process in the light of requirements for monitoring and control instruments, and are assessing via mathematical modeling the interrelationship among the various components and process variables. One of our goals is to develop a knowledge-based (expert) system which will be used to (1) analyze potential and hypothetical failure modes, (2) study propagation of failure modes and their consequences, (3) select instruments for detecting fault-initiating events, and (4) develop a control system for an optimized TRUEX process.

As a part of developing the instrumental control and monitoring requirements of the TRUEX process, we have focused on the needs associated with the use of centrifugal contactors. For this study, we chose a waste composition typical of that generated during plutonium scrap recovery operations at the Westinghouse Hanford Plutonium Finishing Plant (PFP). This composition is typical of many such TRU wastes found throughout the DOE complex from the recycle, purification, and recovery of plutonium, and its relatively simple composition makes sensitivity analysis easier and quicker.

Design of a monitoring and control system for the TRUEX process requires a general understanding of not only the process and its goals but also the role of major process variables in governing the mass transfer processes and the interactions among the process variables. This necessitates making distinction between:

1. Primary process variables such as the aqueous and organic flow rates, compositions of the feeds, and other-phase carryover.
2. Secondary process variables such as liquid levels in the contactor, liquid levels in process tanks, and temperature.

3. Tertiary process variables such as conductivity and density.

This distinction will provide a basis for sensor selection as outlined in a later section.

Since the TRUEX process involves solutions containing radioactive elements, the monitoring and control system is expected to be more complex than that of a conventional industrial chemical process. However, because of the operation of the processing equipment at essentially ambient temperature and pressure, the overall system is expected to be less complex. Table II-10 lists the key process variables and the corresponding upper and lower operating limits envisioned for the TRUEX process.

Table II-10. Operating Limits for Key Variables in TRUEX Process

	Operating Limits
Temperature	Ambient (15-60°C)
Pressure	Ambient (13-16 psia)
Liquid Level	0.005-7 m
Flow Rate	0.001-20 L/min
Density	0.8-1.2 g/mL
Actinide Concentration	1×10^{-2} - 1×10^{-10} M
H ⁺ Concentration	0.01-10M
α , β , γ activity	Varies (System Dependent)

2. Sensor Requirements

In the previous semiannual (ANL-92/25, pp. 78-85), equipment was suggested for the monitoring and control of a typical TRUEX process based on communication with commercial vendors, review of commercial and scientific literature, and conversations with DOE contractor personnel. Examination of instrument catalogs showed that several manufacturers supply sensors for monitoring parameters such as temperature, pressure, fluid flow rate, and liquid level. In addition, the same manufacturer often offers a wide choice of sensors of a given type with varying degrees of sophistication. For remote monitoring and control, the signals must be sent a great distance in a noisy electronic environment. Also, for process control the signals must interface with a computer system. Hence, it is desirable that all sensors provide a uniform signal.

To select a set of instruments for monitoring and control, the following factors will be taken into account:

Materials of Construction. The primary process fluids are aqueous nitric acid solution and the organic solvent. Hence, the materials of construction should be chosen based on the corrosive nature of the acidic solutions and the stability of sensors in contact with organic solvents. These materials include those in the primary structural members, i.e., the metering pumps, valves, flowmeters, and level probes. Also included are secondary materials such as seals, packing materials, liners, insulators, etc., that come in direct contact with the process fluids.

Physical Size. For a compact system such as the TRUEX process, the physical size of the sensors will have a major impact on the system design. Hence, their physical size is an important selection criterion.

Accuracy, Resolution, Repeatability, and Response. Since accuracy and resolution go hand in hand with cost, complexity, and reliability, the accuracy limits should be specified consistent with the design requirements. More emphasis should be placed on repeatability than accuracy since repeatability is more important for automatic control. The response time of each sensor depends on its specific design characteristics, operating principle, and installation. The response time must be based on the dynamic characteristics of the system.

Ruggedness and Reliability. These are some of the important considerations in sensor selection since the malfunction of a sensor may have important safety-related consequences.

Signal Output. In this age of microprocessors and digital technology, the output signal (analog, digital, or pneumatic) is not a deciding factor in instrument selection. In most cases, the manufacturers provide options (analog, digital, or both) for the output signal. In addition, signal conditioners or converters (analog-to-digital and vice versa) are widely available to meet the specific needs of a particular process.

Direct vs. Inferential Instruments. Selection of sensors based on direct vs. inferential considerations will have great impact on their accuracy, design complexity, initial cost, and operating and maintenance cost. Most monitoring instruments used in process industries are inferential type.

Intrusive vs. Non-Intrusive Sensors. This is an important consideration since it affects the design, installation, and replacement of the sensors.

Calibration. Since very few sensors are self-calibrating, frequency of instrument calibration is an important consideration.

Remote Operation and Maintenance. This is a very broad subject and needs to be considered separately in the overall design of a specific process.

Rangeability. As broad a measuring range as available from a specific vendor for a given sensor should be selected.

Radiation Environment. The life expectancy of a particular sensor in a radioactive environment is an important consideration. Since this is of primary importance to the TRUEX process, lifetime and radiation dose rates will be considered separately.

3. Analysis of Key Variables

Of the eight process variables in Table II-10, the liquid level, liquid flow rate, and actinide (also nitrate) concentration are the most important variables that must be monitored and controlled for an optimized TRUEX process. Hence, the measurement of these variables will be discussed in greater detail. A general discussion of other variables such as temperature, pressure, pH, and conductivity is not included here since sensors for these have well-established technology.

a. Volumetric and Mass Flow

Measurement of flow is fundamental to all process industries and one of the oldest technologies. Without measurement and control of this crucial process variable, there can be no automatic control for the overall process. Hence, selection of flow sensors is critical to effectively operating a TRUEX process. The physical, chemical, and hydrodynamic characteristics of the fluids are important to flowmeter selection. The fluid streams must be analyzed in terms of either mass flow or volumetric flow, with maximum and minimum flow rates set. Different flowmeters may be chosen depending on whether the stream is a pure liquid, a slurry, an acid, a base, or a solvent. Types of flowmeters suitable for flow monitoring for one or more streams include (1) those based on the conservation principle, such as the orifice plate, venturi tube, rotometer; (2) those based on rate equations, such as velocity, heat, and mass transfer; and (3) those based on some dynamic aspect of flow, such as vortex shedding and Coriolis effect. An examination of the literature data on flowmeters revealed ten broad classes. The salient features of eight of these classes are summarized in Table II-11. (The other two classes, target flowmeter and the open-channel flowmeters, are not included because they are unlikely candidates for the TRUEX process.) Of these flowmeters, the magnetic flowmeter, the Coriolis flowmeter, and the metering pump (positive displacement) are suitable for the TRUEX process.

b. Liquid Level

A typical TRUEX flowsheet (see Fig. II-19) has a number of locations where liquid-level monitoring and control are necessary. While the liquid level in the centrifugal contactor is set by the operating limit and is, therefore, not externally controlled, problems in operation of the centrifugal contactors are often revealed by changes in the liquid level in the annular zone of one or more stages. Monitoring of volume held in a tank can also be done using a liquid-level probe. There is a wide choice in sensors for monitoring liquid level (mechanical, electronic, and pneumatic), varying from very simple and inexpensive devices to very sophisticated and expensive ones which incorporate the latest electronic technology.

The liquid level in storage tanks, mixing vessels, settling tanks, etc., is one of the most widely measured process variables in industry. In general, the liquid-level probes are rather bulky; hence, most of them, with the exception of IR detecting probes, are unsuitable for the centrifugal contactors. Of the large number of level probes (see Table II-12), the RF admittance type is the most versatile and accurate for tanks and vessels, while the IR detector appears to be suitable for level monitoring in the centrifugal contactors.

c. Actinide and Nitrate Concentration

On-line monitoring of the activity levels of actinides at low concentrations presents a formidable task. A brief discussion of some of the on-line measuring techniques applicable to the TRUEX process is presented below.

(1) Ion-Selective Electrode (ISE)

Great advances have been made on the development of ion-sensitive electrodes (both anion and cation) as analytical tools to detect and measure quantitatively the ionic activity on ionic equilibrium across membranes.²⁴ A recent literature search on ISEs for the nitrate ion alone uncovered more than 700 references. The operating principle of ISEs is similar to that of a pH electrode. In fact, no additional measuring equipment are needed if one has the ISE and the appropriate instrument for the pH measurement. The ion exchanger (e.g., ammonium chloride for the nitrate-ion ISE) is enclosed in a

Table II-11. Characteristic Data of Fluid Flowmeters

Parameter	Differential	Magnetic	Coriolis	Oscillatory	Positive	Turbine	Ultrasonic	Variable Area
Pressure, psi (MPa)	Depends on Transducer	≤750 (±5)	±2800 (±19)	±3600 (±25)	±1400 (±9.5)	±3000 (±20)	±1000 (±6.8)	±750 (±5.0)
Temp., °F (°C)	Depends on Application	≤500 (±260)	-320 to 460 (-200 to 240)	±750 (±400)	±600 (±315)	-450 to 500 (-270 to 260)	-300 to 500 (-180 to 260)	±1000 (±540)
Service	Liquids, Gases	Conducting Liquids, Slurries	Liquids, Slurries	Liquids, Gases	Liquids, Gases	Liquids, Gases	Liquids	Liquids, Gases
Flow Regime ^a	Turbulent	All Regimes	Turbulent	Reduced Accuracy Re <20000	All Regimes	Reduced Accuracy Re <7000	Reduced Accuracy Re <4000	N/A
Flow Range, L/min (gpm)	≥0.001 (0.003) ^b	0.04-19x10 ⁵ (0.01-5x10 ⁵)	0.045-10,500 (0.1-23000)	10-19000 (3-5000)	0.001-120 0.0003-32	0.004-150,000 (0.001-40000)	0.025-2300 (0.007-600)	0.001-1200 (0-300)
Rangeability ^c	4:1	100:1	10:1	15:1	10:1	10:1	20:1	10:1
Output Signal	Analog, Local Indication	Analog, Digital	Analog, Digital	Analog, Digital	Analog, Local Indication	Analog Frequency	Analog, Digital	Analog, Digital, Pneumatic, Local Indication
Accuracy, ±%	0.5-2.0	0.2-1.0	0.1-0.5	0.5-1.0	0.2-1.0	0.5-1.0	1.0-2.0	2.0-3.0
Repeat., ±%	0.5	0.1-0.2	0.1-0.2	0.1-0.2	0.02-0.05	0.05-0.2	0.2-0.5	0.55-1.0
Dia, mm (in.)	13-2000 (0.5-80)	2.5-2500 (0.1-100)	1.5-150 (1/16-6)	13-200 (0.5-8.0)	3-300 (0.125-12)	13-600 (0.5-24)	6-3000 (1/4-120)	1-80 (0.04-300)
Calib.	Usually Not Required	Required	Required	Not Required	Required	Required	Usually Required	Not Required
Mat.	Widest among all Flowmeters	316 SS, Opts. Avail.	316 SS, Opts. Avail.	316 SS, Opts. Avail.	316 SS, Opts. Avail.	316 SS, Opts. Avail.	316 SS, Opts. Avail.	Wide Selection of Materials

^aRe=Reynolds number.^bAnd equivalent ΔP for gas.^cThe maximum-to-minimum range over which an instrument operates.

Fig. II-19. Flowsheet for Tests with Synthetic Plutonium Finishing Plant Waste. (Parenthetical entries indicate stream flow rates, which can be in any units of volumetric flow rate. The important factor is that flow rate is relative to that of the extraction feed.)

Table II-12. Sensors for Measurement of Liquid Level^a

Sensor Type	Measurement Type			Material Type	
	On/Off	Continuous	Liquid	Granular Solid	Slurry
RF Admittance	Yes	Yes	Yes	Yes	Yes
Nuclear	Yes	Yes	Yes	Yes	Yes
Microwave	Yes	Yes	Yes	Yes	Yes
Pressure	No	Yes	Yes	Yes	Yes
Strain Gauge	No	Yes	Yes	Yes	Yes
Sonic	Yes	No	Yes	Yes	Yes
Ultrasonic	No	Yes	Yes	?	Yes
Floats	No	Yes	Yes	Yes	?
Capacitance ^b	Yes	Yes	?	?	?
Diff. Pressure	No	Yes	Yes	Yes	Yes
Resistance Tape	No	Yes	Yes	Yes	Yes
Displacers	No	Yes	Yes	Yes	?
Optical (IR)	Yes	No	Yes	No	No

^aInstrument Society of America Directory of Instruments 1990 (published by IEEE) provides a comprehensive list of manufacturers of liquid-level sensors/controllers.

^bDepends on the particular application.

polymeric matrix, such as PVC, Teflon, or silicon. New materials for the ISEs and improvements in measuring technique, especially the use of field-effect transistors (ion-sensitive field-effect transistors), have increased the detection limits, response time, and selectivity coefficients. Like the pH probes, the ISEs are self-calibrating as long as the measurements remain in the Nernstian regime. However, they have several potential difficulties, such as

1. unavailability of longer-lasting polymeric materials,
2. interference from other ions than those being measured, and
3. limited range.

The characteristics of a typical ISE for NO_3^- are given in Table II-13.

Table II-13. Characteristics of Ion Selective Electrode^a

Parameter	Range
Temperature	0-100 °C (30-200 °F)
Pressure	Ambient to slightly above ambient
Length	100-130 mm (6-12 mm probe tip)
Accuracy	±0.5%
Range	A few ppm to 10,000 ppm
Output	Analog, digital
Response Time	30 ms to 2 min
Calibration	Self-calibrating
Replacement	Similar to that of pH electrode
Limitations	Short life, usually 2 months, and limited range of concentration
Cost	
Probe	\$500
Membrane	\$ 50

^aORION Research, Inc.

To overcome the limitations due to high nitrate concentrations (0.1 to 4.0M) in the TRUEX-process effluent and influent solutions, it may be possible to use a bypass stream which can be diluted 100 to 1000 fold by distilled water for the NO_3^- measurement. The current successful use of ISEs has been limited to the food/beverage industry and water treatment/monitoring.

(2) Solid Scintillators

Considerable effort has been devoted to develop an on-line α -particle monitor for nuclear waste solutions. For processing of nuclear waste streams, Savannah River Site (SRS) researchers have developed an on-line nuclide analyzer (monitor and a sodium iodide gamma detector). Discussions with the SRS personnel (S. R. Salaymeh) revealed that improved analytical techniques using solid scintillators hold promise for on-line monitoring of actinides at low concentrations ($<5 \times 10^{-8}$ g/L). However, successful application of these new detectors will require some development effort.

(3) Spectrophotometry

Methods based on absorption spectrophotometry have been developed and applied successfully at Savannah River Site to monitor uranium and nitrate concentrations. Discussions with personnel at Savannah River Site (P. E. O'Rourke) indicate that spectrophotometric techniques combined with fiber optics hold promise for on-line monitoring and control of transuranics. It should be noted that successful application of this technique to the TRUEX process will involve further development.

d. Effect of Nuclear Radiation

The TRUEX process is expected to have a broad range of waste solutions in which the concentration of the fission products and the transuranic elements may vary over a broad range. From the standpoint of irradiation damage to components, the primary source is ^{137}Cs for γ -radiation and ^{90}Sr for β -radiation. For purposes of calculating an approximate dose rate to components, a typical waste solution containing 2×10^{-3} Ci/mL is considered. The dose rate from a radiation source at a distance of one foot may be calculated (with $\pm 20\%$ accuracy) by the following approximate formula²⁵:

$$R = 6CEf/d^2 \quad (\text{II-16})$$

where R = Radiation dose rate, rad/h (1 rad = 100 erg/g)

C = Radioactive decay rate, Ci

E = Energy of the penetrating radiation, MeV

f = Fraction of the time the particle appears per disintegration

d = Distance from source, ft

The insulating materials, liners, and seals which are in contact with the fluid may be considered to be located within a few millimeters of the source; the electronic components, motors, and hydraulic actuators, which are outside the piping used to carry fluids, may be assumed to be located at a distance of 1 cm from the source. Hence, from Eq. II-16 with $C = 2 \times 10^{-3}$ Ci and $E = 0.662$ MeV (for ^{137}Cs), the dose rates may vary between 5 and 50 rad/h.

The TRUEX system materials that are expected to be exposed to a radiation environment are

1. Metals
2. Ceramics
3. Elastomers (seals, O-rings, packings, hoses)
4. Oils and lubricants
5. Motors, transformers, and magnets
6. Electronic components (capacitors, resistors, printed circuit boards, insulation, cables, semiconductors)

Based on radiation exposure data,²⁵ the materials most susceptible to radiation damage are the elastomers, lubricants, and electronic components. The expected life of these components is calculated to be

$$\frac{10^8 \text{ rad}}{500 \text{ rad/h}} = 2 \times 10^5 \text{ h (23 yr)}$$

for elastomers and lubricants, and

$$\frac{1 \times 10^5 \text{ rad}}{5 \text{ rad/h}} = 2 \times 10^4 \text{ h (2.3 yr)}$$

for electronic components. The latter may be increased by a factor of 10 by using radiation-hardened components.²⁶ In addition, there are a number of ways, primarily by design changes, one can increase the life expectancy for all three components. For example, sulfur or selenium additives will increase the life of oils and lubricants. Also, the electronic components could be placed as far away as possible from the radiation source to increase the instrument life. In addition, shielding materials (e.g., Pb) between the radiation source and the electronic components would decrease the radiation exposure rate. Design of components and placement of sensors will have great impact on life of components that are most susceptible to radiation damage.²⁷

e. Recommendations for TRUEX Process

The important process variables from the standpoint of measurement and control are fluid flow rate, liquid level, and concentrations. Acceptable instruments for flow and liquid level measurement are available to meet the needs of the TRUEX process. However, instruments for on-line measurement of Am, Pu, and NO₃ 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 ISEs. At present, spectrophotometric measurement of Pu and Am concentrations can be made down to 10⁻⁵M, 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. Table II-14 has been developed for an initial selection of fluid flowmeter, liquid level probe, and on-line monitors of liquid compositions.

Table II-14. Summary of Potential Instruments for TRUEX Process Measurement and Control*

	Flow Measurement			Level Measurement		Conc. Measurement		
	Magnetic	Corolis	Metering Pump	IR Probe	RF Admittance	Spectrophotometer	Ion-Selective Electrode	Solid Scintillator
Aqueous Flow	X							
Organic Flow		X						
Scrub			X					
Strip #1, #2			X					
Solvent Strip			X					
Solvent Wash, Rinse			X					
Storage Tank					X			
Centrifugal Contactor				X				
U, Pu						X		
NO ₃						X	X	
α, γ								X

*An "X" indicates instrument has promise for indicated measurement.

4. Sensitivity Analysis

Using the GTM, one can obtain the steady-state concentrations of all components present in the aqueous or organic phases in every stage for a specific flowsheet with a given number of sections and stages, feed flow rates and compositions, and back-mixing coefficients. The value of one or several of the feed variables (composition or flow rate) can be altered, the flowsheet re-evaluated, and a sensitivity analysis performed to identify an appropriate strategy for process monitoring and control. After establishing the process goals and base-case conditions, we performed a sensitivity analysis to determine the effect of changing variables in the base case.

a. Process Goals

An important consideration in designing a monitoring and control system for TRUEX processing is to look at what the process is supposed to do: which functions are priorities, which are useful but not essential to have, and which are unimportant to the facility needs. The goals of the TRUEX process are listed below in a generally accepted order of priority:

1. Reducing the TRU concentration in the extraction raffinate to less than 100 nCi/g of solid so that its solidified form can be classified as a nonTRU low-level waste. (A concentration of <10 nCi/g to make it less than class C low-level waste has also been stated as a process goal.)
2. Recovering >99% of the plutonium in a separate product stream for recycle to a plutonium purification process.
3. Recovering the remaining plutonium and other TRU elements in a waste stream suitable for inclusion in borosilicate glass or production of a waste form certifiable for disposal in the Waste Isolation Pilot Plant (WIPP).
4. Concentrating the plutonium and other TRU elements in their respective product streams to greater than their initial feed concentrations.
5. Recovering >99.99% of the TRU-element mass in the strip product streams, thus allowing the solvent cleanup sections to act as a sink for solvent degradation products and any uranium extracted into the solvent.
6. Purifying plutonium in the plutonium product stream.

Item 1 is certainly the primary function of the process. TRUEX processes are designed with this goal in mind, and the monitoring and control of the system are intended primarily to meet this function. Because of the high salt and acid concentrations in potential feeds to the TRUEX process, the final volume of solid TRU waste will be typically reduced by 20 to 200 times due to TRUEX processing. If immediate disposal is not intended, converting the bulk of the waste to nonTRU is also an important consideration if storage space for TRU waste is in short supply.

Item 2, recovery of plutonium, was once a higher priority than it appears to be currently because of less concern about nuclear weapons buildup. However, if plutonium inventories

need to be replenished, there are large quantities in stored wastes. Even at the low concentrations found in most waste streams, their large volumes contain significant quantities of plutonium.

Items 3 and 4 are also important considerations in designing a TRUEX process. Item 4 is designed into the process by setting flow rates and number of strip stages appropriately. Item 3 is designed into the process flowsheet and maintained during processing by monitoring feed, interstage, and effluent concentrations and by controlling feed flow rates and, perhaps, strip- and scrub-feed compositions.

Item 5, highly efficient stripping of the TRUEX solvent, is designed into the process and is an important concern for monitoring and control of the process. It is important for (1) keeping the TRU elements out of the solvent wash, thus allowing that section to function as a strip for solvent degradation products and uranium, and (2) maintaining a low TRU content in the solvent before its recycle to the extraction section, which is critical to producing a nonTRU raffinate.

Item 6 is a secondary consequence of specific TRUEX processing and is not a design criterion to be monitored or controlled.

b. Methodology

The sensitivity analysis was done using GTM version 2.1 and the TRUEX process flowsheet given in Fig. II-19. The base case, given in Fig. II-19, meets our four process criteria for treatment of this waste: the raffinate should be nonTRU ($[TRU] \leq 10 \text{ nCi-}\alpha/\text{g solid}$); 99.7% or more of the americium should report to strip 1; 98.9% or more of the plutonium should report to strip 2; and less than 0.01% of the TRU should be in the organic solvent as it leaves the second strip section with the solvent. The flow rates and compositions of the feeds and the effluent streams for the base case are shown in Table II-15.

After the base case was defined, some of the system variables were changed. After the base value was altered for a given variable, the model was rerun, and the results were analyzed to see if they met the process goals. Obviously, not every perturbation from the base case will lead to a flowsheet within process bounds. These are the cases for which monitoring and control become important. By analyzing the cases in which the process criteria do not hold anymore, it is possible to obtain the bounds for the observable process variables. Using these bounds, one can establish the specifications for monitoring and control.

The effect of varying important variables such as flow rate, concentration, and number of stages was analyzed in our sensitivity analysis. In each case, the four process criteria were examined and plotted versus the fractional change with respect to the base value of the variable perturbed. The first criterion is determined from the total nCi/mL that exits in this stream, which should be less than 10 nCi/mL. The second criterion is achieved when the mole percent of americium in the second strip is less than 0.3%. The third criterion is achieved when the mole percent of plutonium in the first strip is less than 1.1%. The fourth criterion is achieved when the "activity basis" (nCi- α) is less than 0.01% of the total in the feed.

c. Results and Discussion

As an example of the type of analysis that was performed, we will look in detail at the case in which the organic-feed flow rate was perturbed. After this example, we will include a summary of the results of all the cases studied.

Table II-15. Calculated Results Determined for Base Case with NPH as Diluent

Stream Identity ^a	Flow Rate ^b	Component Concentration, <u>M</u>					
		H	Fe	Ni	Al	Na	Ca
DX	150	1.00H-15	1.00H-15	1.00H-15	1.00H-15	1.00H-15	1.00H-15
DF	400	1.50E+00	3.00H-02	4.00H-04	4.30H-01	4.00H-02	6.00H-02
DS	40	4.00H-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
EF	150	4.00H-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
FF	75	1.00H-01	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
DW	440	1.26E+00	2.73H-02	3.64H-04	3.92H-01	3.64H-02	5.46H-02
EW	150	3.66H-01	9.74H-08	5.62H-13	5.11H-10	5.62H-11	8.43H-11
FW	75	5.37H-02	2.22H-14	3.29H-28	1.51H-25	3.29H-26	4.93H-26
FF	150	2.53H-02	1.33H-17	5.61H-37	3.54H-39	5.61H-35	8.42H-35

Stream Identity ^a	Flow Rate ^b	Component Concentration, <u>M</u>						
		Cu	Mg	UO ₂	Am	Pu(IV)	F	HSO ₄
DX	150	1.00H-15	1.00H-15	1.00H-15	1.00H-15	1.00H-15	1.00H-15	1.00H-15
DF	400	3.00H-04	6.00H-02	3.00H-06	6.00H-06	3.00H-05	9.00H-02	1.00H-02
DS	40	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
EF	150	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
FF	75	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	5.00H-02	0.00E+00
DW	440	2.73H-04	5.46H-02	2.15H-14	4.65H-11 ^c	1.25H-13 ^c	8.19H-02	9.11H-03
EW	150	4.22H-13	8.43H-11	3.54H-08	1.60H-05	6.69H-07	1.55H-04	1.08H-11
FW	75	2.46H-28	4.93H-26	6.86H-06	7.43H-08	1.57H-04	2.51H-03	3.28H-27
FP	150	4.21H-37	8.42H-35	4.50H-06	4.91H-11 ^d	2.63H-08 ^d	2.37H-02	1.62H-36

^aSee Fig. II-19 for identity of each stream.

^bFlow rates can be in any unit of volumetric flow rate. The important factor is that flow rate is relative to that of extraction feed (DF).

^cThis is equal to nCi/mL of α from TRU.

^dCorresponds to only 0.003% of TRU in this stream.

Variations in the organic-feed flow rate are generally the most drastic flow-rate-related perturbation of a solvent extraction flowsheet. In the TRU^{EX} process, increases in organic-feed flow tend to make the extraction section more effective in removing TRU elements from the aqueous feed. This is accomplished by increasing the extraction factor, the product of distribution ratio (D) and organic-to-aqueous phase ratio (Q). The method is to increase Q or increase D by decreasing solvent loading.* By the same means, the scrub and strip sections decrease in effectiveness in stripping nitric acid and actinides, respectively, from the solvent as the organic-feed flow rate is increased. Conversely, decreases in the organic-feed flow rate decrease the effectiveness of the extraction section and increase the effectiveness of the scrub and strip sections.

*Solvent loading is defined as extracting enough of a metal salt into the organic phase that its presence significantly decreases the concentration of CMPO available for extracting additional metal salts (CMPO_{free}). It is assumed that the extraction of one mole of Am(NO₃)₃ requires three moles of CMPO (n=3), and that the extraction of one mole of UO₂(NO₃)₂ and Pu(NO₃)₄ requires two moles of CMPO (n=2); thus, [CMPO_{free}]_{org} = [CMPO_{total}]_{org} - $\sum n[M]_{org}$, where M is the metal salt.

Over a $\pm 20\%$ range in organic-feed flow rate, the extraction raffinate was nonTRU (Fig. II-20), but the amount of TRU exiting strip 2 exceeded the limit of 0.01% (Fig. II-21). Figures II-22 and II-23 show the effect of a perturbation in the organic extraction feed flow rate on the amount of americium and plutonium being stripped. Also shown in Figs. II-22 and II-23 are horizontal lines that represent the PFP process criteria (0.3 mol % of americium present in strip 2 and 1.1 mol % of plutonium present in strip 1, respectively). Therefore, all points which lie below these lines are cases in which the perturbation in the organic feed flow rate still meets process criteria.

Fig. II-20. Concentration of TRU Elements in Raffinate as Function of Changes in Organic Extraction-Feed Flow Rate. Flow rates are relative to the base case shown in Fig. II-19.

Fig. II-21. Percentage of TRU Lost in the Organic Flow Exiting Strip 2 (activity basis) as Function of Changes in Organic Extraction-Feed Flow Rate. Flow rates are relative to the base case shown in Fig. II-19.

Fig. II-22. Percent Americium in Strip 2 Effluent as Function of Changes in Organic Extraction-Feed Flow Rate. Flow rates are relative to the base case shown in Fig. II-19.

Fig. II-23. Percent Plutonium in Strip 1 Effluent as Function of Changes in Organic Extraction-Feed Flow Rate. Flow rates are relative to the base case shown in Fig. II-19.

As can be deduced from Figs. II-22 and II-23, increasing the organic feed increases the limiting amount of americium lost in the second strip, but decreases the plutonium lost in the first strip, whereas decreasing the organic feed decreases the americium lost in the second strip but increases the plutonium lost in the first strip. This counter-balancing effect enables us to obtain upper and lower bounds for this variable as follows. Figures II-21, II-22, and II-23 all have intersection points for which the process criteria stop being accomplished, giving upper and lower bounds to the allowed variability of

the organic-feed flow rate. These bounds provide input to the selection of monitoring and control instruments. Based on the results shown in Figs. II-22 and II-23, the extractant organic feed needs to be controlled in the 0.935-1.01 range to meet the process criteria.

An expert system should be able to utilize this type of analysis. For example, the data shown in Figs. II-20 to II-23 can be represented in a mathematical form along with the intersection points for the bounds that set the operating range. These analyses can then be done automatically once a detailed data base is generated.

Tables II-16 to II-18 give a summary of the bounds obtained for every case studied. Also indicated are the process criteria that do not hold if the given bounds are exceeded. For every perturbation study we give the base value. Note that these perturbation values are relative, with the bounds being given in a fractional form.

Of all the perturbations analyzed, only one of them, the perturbation to the aqueous feed flow rate in the extraction section, was limited by the most important process goal, a TRU concentration in the raffinate of less than 10 nCi/mL. But even in this case, the flow rate can be up to four times greater than its base value of 400 mL/min without exceeding the process goals.

The tightest bound obtained were in the cases of (1) the organic-feed flow rate and (2) the concentration of HNO_3 in the aqueous feed in the scrub and in the first strip. For these cases, the upper value could not exceed 1% and 2%, respectively, of the base value before the percent of americium in the second strip exceeds 0.3%. In this circumstance, the basic flowsheet (base case) should be redesigned to increase the operating range of these two variables.

Also, the rate at which the process criteria stops being achieved, with respect to the changes in the perturbed variable, is of great importance. The slopes in figures similar to Fig. II-20 to II-23 should be as horizontal as possible. Nearly horizontal slopes appear when large changes from the base values can be made with a minimal effect in the process criteria.

Perturbation (or sensitivity) analysis is often tied up with flowsheet design. The use of this analysis early in the design stage will lead to a "robust" flowsheet, i.e., a flowsheet that will meet all process goals and allow for wide control bounds. Also important for designing a process is the instrumentation available to monitor and control it. The base case (Table II-15) and the control bounds obtained (Tables II-16 to II-18) will be used to illustrate how instrument selection can be accomplished.

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

The success of the TRUEX process and the development of models useful to designing flowsheets strongly depend on the quality and the retrievability of underlying measurements of distribution ratios for the many chemical species likely to be present. A data base has been developed using the software package 4th Dimension on a Macintosh computer. The design of the data base places strong emphasis on various modes of retrievability and anticipated report formats useful to the project. The data base is intended to be useful to at least four customer types: program managers, individual experimenters who measure distribution ratios, modelers who develop algorithms useful to the design of TRUEX flowsheets, and quality assurance auditors. The ability to rapidly identify categories of information in need of development is especially important to program managers and modelers. The data base now contains 612 data sets (corresponding to 6461 individual measurements of distribution ratios).

Table II-16. Control Bounds for Flow Rates

Variable (Base Case Value) ^a	Allowable Fractional Change ^b	Criterion 1	Criterion 2	Criterion 3	Criterion 4
		Range in Which the TRU Concentration in the Raffinate Is Less Than 10 nCi/mL	Range in Which the Am mol % in Strip 2 Effluent Is Less Than 0.3%	Range in Which the Pu mol % in Strip 1 Effluent Is Less Than 1.1%	Range in Which the TRU Lost in the Organic Flow Exiting Strip 2 Is Less Than 0.01%
Organic Extraction Feed (150)	0.935-1.01	Not Limiting	<1.01	>0.935	<1.08
Aqueous Extraction Feed (400)	0.1-4.03	<4.03	Not Limiting	>0.1	Not Limiting
Aqueous Scrub Feed (40)	0.959-1.17	Not Limiting	<0.959	<1.17	>0.477
Aqueous Strip 1 Feed (150)	0.986-1.133	Not Limiting	>0.986	<1.133	>0.842
Aqueous Strip 2 Feed (75)	>0.902 ^c	Not Limiting	Not Limiting	Not Limiting	>0.902

^aSee Fig. II-19.^bFractional change with respect to the base case for which the process goals still hold.^cHigher flow rates will be limited by equipment size.

Table II-17. Effect of Losing a Stage in a Given Section

Case Description	Effect
1 Stage - Extraction Section	No negative effect in the process goals, i.e., the TRU concentration in the raffinate is less than 10 nCi/mL, the Am mol % in strip 2 effluent is less than 0.3%, the Pu mol % in strip 1 effluent is less than 1.1 %, and the TRU lost in the organic flow exiting strip 2 is less than 0.01%.
2 Stages - Extraction Section	The TRU concentration in the raffinate is greater than 10 nCi/mL; therefore, the process goal is not met.
1 Stage - Scrub Section	The Am mol % in strip 2 effluent is greater than 0.3%, and the TRU lost in the organic flow exiting strip 2 is greater than 0.01%. Therefore, the process goal is not met.
1 Stage - First Strip Section	The Am mol % in strip 2 effluent is greater than 0.3%. Therefore, the process goal is not met.
1 Stage - Second Strip Section	No negative effect in the process goals, i.e., the TRU concentration in the raffinate is less than 10 nCi/mL, the Am mol % in strip 2 effluent is less than 0.3%, the Pu mol % in strip 1 effluent is less than 1.1 %, and the TRU lost in the organic flow exiting strip 2 is less than 0.01%.

We have identified 32 data sets in which distribution-ratio measurements were made without first pre-equilibrating the organic and aqueous phases. Thus, the acid concentrations currently reported for the aqueous phases are the before-contact values. Efforts are being made to obtain the post-contact acid concentrations.

Some difficulties were experienced with data obtained at 50 °C (total of 106 data sets, of which 16 were obtained without pre-equilibration). These data sets are being examined to determine whether clarifying notes are needed on some or all of them.

H. Waste Solution Processing for the New Brunswick Laboratory
(D. B. Chamberlain, J. A. Dow,* D. R. Fredrickson, J. C. Hutter,
E. H. Van Deventer, R. A. Leonard, 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 uranium, plutonium, neptunium, and americium. Originally destined for Idaho for temporary storage and eventual disposal at WIPP, these wastes now appear to have no place that 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 ANL Plant Facilities and Services, Waste Management Operations (PFS-WMO), for final disposal. The recovered plutonium will be converted into solid PuO₂ for return to NBL for storage and subsequent transport to the DOE defense complex.

*Co-op student, Purdue University.

Table II-18. Control Bounds for Concentration

Variable (Base Case Value)	Allowable Fractional Change ^a	Criterion 1	Criterion 2	Criterion 3	Criterion 4
		Range in Which the TRU Concentration in the Raffinate Is Less Than 10 nCi/mL	Range in Which the Am mol % in Strip 2 Effluent Is Less Than 0.3%	Range in Which the Pu mol % in Strip 1 Effluent Is Less Than 1.1%	Range in Which the TRU Lost in the Organic Flow Exiting Strip 2 Is Less Than 0.01%
Am in Aqueous Extraction Feed (6 x 10 ⁻⁶ M)	<12.7	<203	<12.7	<90.2	Not Limiting
Pu in Aqueous Extraction Feed (3 x 10 ⁻⁵ M)	<4.14	<689	Not Limiting	<103	<4.14
UO ₂ in Aqueous Extraction Feed (3 x 10 ⁻⁶ M)	<620	Not Limiting	Not Limiting	Not Limiting	<620
Al(NO ₃) ₃ in Aqueous Extraction Feed (0.43M)	0.904-1.15	Not Limiting	<1.15	>0.904	Not Limiting
Al(NO ₃) ₃ and F ⁻ in Aqueous Extraction Feed (0.43M and 0.09M)	<1.17	Not Limiting	<1.17	Not Limiting	Not Limiting
HNO ₃ in Aqueous Extraction Feed (1.5M)	0.435-1.11	Not Limiting	<1.11	>0.435	Not Limiting
HNO ₃ in Aqueous Scrub and Strip 1 Feed (0.04M)	0.43-1.02	Not Limiting	<1.02	>0.43	Not Limiting
F at Constant H ⁺ in Aqueous Strip 2 Feed (0.05M)	>0.886	Not Limiting	Not Limiting	Not Limiting	>0.886
HF at Constant HNO ₃ in Aqueous Strip 2 Feed (0.05M)	>0.745	Not Limiting	Not Limiting	Not Limiting	>0.745

^aFractional change with respect to the base case for which the process goals still hold.

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 Westinghouse Hanford site, and will act as a basis for considering this process as a future waste treatment process at ANL/NBL.

The bulk of the waste that will be processed is being stored by PFS-WMO. These wastes will be transported to CMT for processing. Because of the fissile-material limits in CMT, transfers and subsequent processing will be completed in eight to ten batches, with each batch containing a maximum of 50 g of fissile material. Since the composition of each batch differs, modifications will be made to each flowsheet (e.g., stages in each section, feed-stream flow rates) to optimize the process for each batch. Flowsheets will be developed and 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-24. The TRUEX 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 (nDD). The bulk of the waste generated by this program will be the nonTRU waste stream. Prior to transferring this waste to PFS-WMO for disposal, it will be neutralized so that PFS-WMO can feed it directly into their evaporator. The americium product stream shown in Fig. II-24 will be saved for use in ongoing laboratory experiments in CMT.

Fig. II-24. General Flowsheet for Processing Plutonium Waste Solutions from New Brunswick Laboratory

The plutonium product stream will be evaporated to dryness, then converted to an oxide by calcining in an oven at $>600^{\circ}\text{C}$. The product from the calcining operation, PuO_2 , will then be reduced to the metal and 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 in this program, this stream will be a TRU waste. Thus, this stream will be recycled back into the TRUEX process because PFS-WMO cannot handle or accept this solution for disposal. Procedures for handling this recycle stream are being developed.

1. Preliminary Tests

a. Batch Extraction/Strip Test for Plutonium

A procedure for completing a series of batch contacts was developed to evaluate the effectiveness of a TRUEX process in (1) generating a nonTRU raffinate and (2) stripping and recovering both Am and Pu. By completing this test prior to actually processing the waste solution, we hoped to identify and solve potential problems. Some steps in this procedure were completed inside a glovebox because they involved high alpha activity. Other steps were completed in a hood because they involved less activity and were easier to do in a hood than a glovebox.

A series of extraction contacts was completed with a sample of plutonium stock solution (from D. L. Bowers, CMT). The feed solution consisted of 1 mL of this stock solution diluted with 20 mL of 2M HNO_3 . In this test, four extraction contacts were completed with an O/A ratio of 1/4. Fresh TRUEX-nDD solvent was used for each contact. The organic phase from the initial extraction contact was used as the feed for americium strip tests. The strip solution was 0.04M HNO_3 , and four strip contacts were completed at an O/A ratio of 1/2. Each strip contact was completed with fresh 0.04M HNO_3 . The organic remaining from the four americium strip contacts was then used for three plutonium strip contacts at an O/A ratio of 1/1 with a solution of 0.1M $\text{H}_2\text{C}_2\text{O}_4/0.1\text{M}$ HNO_3 . Samples of each phase were collected following each contact. Aliquots were counted on both a liquid scintillation counter and a gamma counter.

Tables II-19 lists the gamma counting results from the extraction contacts. All samples were counted in duplicate, and the average of both counts and the standard deviation are reported. Americium distribution ratios were in the expected range, though the small drop for the last contact is puzzling. In four contacts, the americium concentration decreased by a factor of 2500.

Analysis of the scintillation results, given in Table II-20, is not so straightforward. Because ^{241}Am is also an alpha emitter, the scintillation results cannot be directly converted to a plutonium concentration. Therefore, the gamma counting results were used to calculate the amount of americium in solution, then the appropriate number of alpha counts for ^{241}Am was subtracted from the gross counts. This method is subject to large errors, as reflected by the aqueous phase activity due to plutonium after the first contact being a negative number (see Table II-20). A small change in the americium counting efficiency can have a very significant impact on the plutonium concentration. Calculated D values for the third and fourth contacts in Table II-20 are closer to those expected for americium, not the plutonium that we are supposedly counting.

The overall decrease in activity can readily be seen in Table II-20. The total alpha activity in the aqueous phase dropped from 1.22×10^5 dpm/ μL in the feed stream to 1.87 dpm/ μL in the aqueous phase following the fourth contact, a decrease of 65,000. After four extraction contacts, the

aqueous phase contained 0.84 nCi/mL of activity. This is well below the target of 10 nCi/g that we set initially for our process, but still above our new target of 0.1 nCi/mL.

Table II-19. Gamma Counting Results from the Batch Extraction Tests

		Volume, μL	Counts per sec^a	[Am-241], ^b $\text{dpm}/\mu\text{L}$	[Am-241], ^c g/L	D Value
Feed to Extraction Section	Aqueous	10	75.9			
		10	79.9			
			77.9 ± 2.83	4,340	5.69E-04	
Extraction: 1st Contact	Organic	10	282			
		10	270			
			276 ± 8.49	15,400	2.02E-03	26.0
	Aqueous	200	222			
			203			
			212.5 ± 13.4	592	7.77E-05	
Extraction: 2nd Contact	Organic	200	652			
		200	708			
			680 ± 39.6	1,890	2.49E-04	25.9
	Aqueous	200	25.6			
			27.0			
			26.3 ± 0.99	73.3	9.61E-06	
Extraction: 3rd Contact	Organic	200	89.0			
		200	89.0			
			89.0 ± 0	248	3.25E-05	24.8
	Aqueous	200	3.57			
		200	3.62			
			3.60 ± 0.04	10.0	1.31E-06	
Extraction: 4th Contact	Organic	100	6.16			
		100	5.52			
			5.84 ± 0.45	32.5	4.27E-06	18.4
	Aqueous	500	1.55			
		500	1.63			
			1.59 ± 0.06	1.8	2.32E-07	

^aAnalysis based upon the 59.5 keV peak for ^{241}Am .

^bConversion from counts per second to disintegrations per minute (dpm) was made using counter efficiency of 30% and ^{241}Am abundance for the 59.5 keV peak of 35.9%.

^cSpecific activity for ^{241}Am is 7.622×10^{12} dpm/g.

Table II-20. Scintillation Counting Results from Batch Extraction Tests

		Volume, μL	Disintegrations per min ^a	Adjusted ^b [Pu], dpm/ μL	[Pu-239], ^c g/L	Adjusted D Value
Feed to Extraction Section	Aqueous	10	1.222E+06	118,000	7.26E-01	
		10	1.216E+06 (1.22E±0.04)×10 ⁶			
Extraction: 1st Contact	Organic	0.4995	2.46E+05	452,000	2.79E+00	N/A
		0.4995	2.21E+05 (2.34±0.17)×10 ⁵			
	Aqueous	10	5820	-4.6	N/A	
		10	5920 5870±71			
Extraction: 2nd Contact	Organic	10	22,700	371	2.29E-03	2650
		10	22,600 22,600±75			
	Aqueous	10	758	1.0	5.88E-06	
		10	727 742±22			
Extraction: 3rd Contact	Organic	20	5250	15.4	9.52E-05	17.4
		20	5280 5270±22			
	Aqueous	200	2,180	0.9	5.58E-06	
		200	2,190 2,180±5			
Extraction: 4th Contact	Organic	20	681	2.0	1.21E-05	26.9
		20	699 690±12			
	Aqueous	200	373	0.1	6.07E-07	
		200	375 374±1			

^aThese counts are based upon a counting window of 80-600 keV.

^bThese counts are adjusted by subtracting the ²⁴¹Am activity from the gross counts. Americium activity is based upon gamma analysis (Table II-19).

^cSpecific activity of 1.62×10^{11} dpm/g used to convert dpm to g. This specific activity is based upon typical ²³⁹Pu/²⁴⁰Pu ratios.

The gamma counting results for the americium strip contacts are reported in Table II-21. Because of sample volume limitations in this test, only the aqueous phases were collected for analysis (until the last contact, where both phases were analyzed). With four strip contacts, the americium concentration in the organic phase dropped from 0.002 to 0.000004 g/L: a decrease by a factor of 515. In other words, only 0.2% of the initial americium remained in the organic phase after four strip contacts.

Table II-21. Gamma Counting Results from Americium Strip Contacts

		Volume, μL	Counts per sec^a	[Am-241], ^b $\text{dpm}/\mu\text{L}$	[Am-241], ^c g/L	D Value
Organic Feed to Strip	Organic	10	282.00	15,400	2.02E-03	
		10	270.00			
			276 $\pm$ 8			
Strip: 1st Contact	Aqueous	100	262.00	1,530	2.00E-04	
		100	286.00			
			274 $\pm$ 17			
Strip: 2nd Contact	Aqueous	100	713.00	4,006	5.26E-04	
		100	725.00			
			719 $\pm$ 8			
Strip: 3rd Contact	Aqueous	100	242.00	1,410	1.85E-04	
		100	265.00			
			254 $\pm$ 16			
Strip: 4th Contact	Organic	10	0.516	29.6	3.88E-06	0.220
		10	0.546			
			0.531 $\pm$ 0.021			
	Aqueous	100	24.20	134	1.76E-05	
		100	24.00			
			24.1 $\pm$ 0.1			

^aAnalysis based upon the 59.5 keV peak for ²⁴¹Am.

^bConversion from cps to dpm made using counter efficiency of 30% and ²⁴¹Am abundance for the 59.5 keV peak of 35.9%.

^cSpecific activity for ²⁴¹Am is 7.622×10^{12} dpm/g.

The scintillation results for the americium strip contacts are reported in Table II-22 and suffer from some of the same problems as the extraction data. However, some of the data should be fairly accurate because of the relative concentrations of plutonium to americium in these samples. The plutonium concentration in the organic feed to the first strip contact is equal to that for the extraction feed sample (Table II-20). The plutonium concentration in the extraction feed was 0.73 g/L; with the expected high D value for plutonium (assume all the plutonium extracts in one contact) and an O/A ratio of 4, the organic concentration would be approximately 4 times 0.73 g/L, or 2.9 g/L. The measured organic concentration was 2.8 g/L, and after four strip contacts, the organic plutonium concentration was 2.26 g/L. Thus, 19% of the plutonium was stripped from the organic phase in this section of the process. Analysis of the plutonium strip samples has not been completed; these data will be presented in future reports.

Table II-22. Scintillation Counting Results from Americium Strip Contacts

		Volume, μL	Counts, dpm	Adjusted, dpm/ μL	[Pu-239], g/L	Adjusted D Value
Organic Feed to Strip	Organic	0.4995	246000	452,000	2.79E+00	
		0.4995	221000			
			233697 $\pm$ 17700			
Strip: 1st Contact	Aqueous	4.9505	6730	-160	-1.01E-03	
		4.9505	6760			
			6750 $\pm$ 19.1			
Strip: 2nd Contact	Aqueous	4.9505	22100	320	1.97E-03	
		4.9505	20700			
			21400 $\pm$ 967			
Strip: 3rd Contact	Aqueous	4.9505	49600	8,300	5.15E-02	
		4.9505	46900			
			48300 $\pm$ 1890			
Strip: 4th Contact	Organic	0.4995	203000	366,000	2.26E+00	29.6
		0.4995	162000			
			183000 $\pm$ 29000			
	Aqueous	4.9505	70600	12,400	7.64E-02	
		4.9505	53200			
			61900 $\pm$ 12300			

b. Verification Run 14

The purpose of this test was to evaluate the scrub/strip sections in the TRUEX flowsheet for the NBL waste (Fig. II-25). This test was completed in an eleven-stage, 4-cm centrifugal contactor with a feed of 1.85M HNO_3 plus 0.007M Nd. The purpose of this run was to experimentally verify the GTM generated concentration profiles for acid and neodymium (simulant for americium) and to investigate possible third-phase formation. The FMI (Fluid Metering, Inc.) pumps were calibrated with clean water prior to the experiment.

(1) Run Summary

The checklist used in this run, shown in Table II-23, includes both the planned schedule and the actual times of the various events and operations. Startup of the system proceeded smoothly and on the planned schedule. However, a problem was quickly identified when the drain valves on each stage were adjusted to collect a continuous sample from each stage. This was attempted by opening each valve a very small amount and draining some solution into a small bottle. The plan was to collect these samples throughout the run, periodically changing each bottle in order to collect different samples over time. Flows of 1-2 mL/min from each stage were planned. Although previous attempts at this type of sampling proved successful, this time the liquid drops would not systematically fall directly out of the drain valves. Instead, the solution droplets stuck to the sides of the valve, and as the droplets fell, they missed the sample bottle openings. The sample bottle was moved under these droplets, but usually within only 10-20 s, the path that the droplets took as they disengaged from the valve changed.

After trying unsuccessfully over a 20-min period to collect these samples, we gave up and closed all of the bottom drain valves. Samples were then collected at the end of the run, as we had done in previous experiments.

In future experiments, either a smaller fitting will be placed in the discharge side of each drain valve, or a smaller diameter valve (and discharge tubing) will be installed to help direct the droplets into a sample bottle. We suspect that the presence of organic phase in the droplets changed the wetting characteristics of the solution (the drain valves were Teflon) so that operation during this run differed from that in our mockup tests with these same units. Sampling of the various raffinate solutions was not affected by the bottom drain problems. A second organic phase was not seen in this test, indicating that loading in the actual processing will not cause two phases to form.

Table II-23. Run Schedule for Verification Run 14

Planned Schedule ^a	Actual Times ^a	Action Required/Notes
-	-25:00	Sample feed solutions.
-30:00	-25:00	Measure feed solution temperatures, hood temperature. Record pump settings.
-10:00	-10:00	Verify CLOSED all stage drain valves.
-10:00	-10:00	Verify OPEN aqueous feed block valves.
-10:00	-25:00	DX mixer ON.
- 5:00	-10:00	Vent organic feed tank.
- 5:00	-10:00	Contactor motors ON.
- 3:00	-10:00	Verify OPEN line ball valves for organic feed/return.
0:00	0:00	EF pump ON (Scrub/Strip).
0:00	0:00	FF pump ON (Carbonate Wash).
2:40	3:02	FW raffinate detected (Carbonate Wash).
3:00		Check flow rate of FW stream.
6:30	6:23	EW overflow detected (1st Strip).
9:40	9:22	DW raffinate detected.
10:00		Check flow rate of DW stream.
11:00	10:50	EF, FF pumps OFF.
11:20	11:05	DX pump on (TRUEX solvent, about 20 s/stage).
11:30		Begin adjusting stage drip samples (1 drop/second). Measure flow rates of stage samples.
13:00	18:10	FP pump ON (TRUEX effluent).
14:40	18:53	FP effluent detected (TRUEX solvent).
15:00	19:16	Aqueous pumps ON (EF, FF).
20:00	21:30	DF pump ON (Extraction Feed).
20:20		Color change, DW raffinate.
22:00	22:40	Begin sampling period.
74:00	74:40	End of sampling.
74:30	77:10	Shut off all pumps and open drain valves.
+74:30	+77:10	Close drain valves.
+74:30	+77:10	Shut off rotors, collect stage samples.

^aMinutes:seconds.

Fig. II-25. Flowsheet for Testing the NBL Scrub/Strip Sections (Verification Run 14)

(2) Results and Discussion

The feed, effluent, and stage samples from Verification Run 14 were titrated with 0.1032M NaOH to determine the acid composition. The raw data for the feed samples are summarized in Table II-24. The average DF acid concentration was $1.87 \pm 0.026\text{M}$, while that for the strip feed was $0.0373 \pm 0.0004\text{M}$. The data for the effluent samples are summarized in Table II-25, and those for the stage samples are summarized in Table II-26. The NaOH was standardized by titration with potassium hydrogen phthalate.

Table II-24. Titration Results from Aqueous Feed Samples from Verification Run 14

Sample Identification	Molarity of Acid ^a
DF	1.82
DF	1.88
DF	1.89
DF	1.86
DF	1.87
DF	1.87
DF	1.90
EF	0.0378
EF	0.0371
EF	0.0375
EF	0.0366

^aAcid compositions determined from titration with 0.1032M NaOH.

Table II-25. Titration Results from Aqueous Effluent Samples from Verification Run 14

Sample Identification	Molarity of Acid
DW1	1.28
DW1	1.32
DW1	1.35
DW2	1.27
DW2	1.27
DW3	1.24
DW3	1.24
DW4	1.22
DW4	1.19
DW5	1.19
DW5	1.19
EW1	0.0677
EW1	0.0728
EW2	0.0678
EW2	0.0666
EW3	0.0613
EW3	0.0604
EW4	0.0611
EW4	0.0597

*Acid compositions determined from titration with 0.1032M NaOH.

Table II-26. Titration Results from Aqueous Stage Samples from Verification Run 14

Sample Stage Number	Molarity
1	1.16, 1.17
2	0.409, 0.393
3	0.136, 0.132
4	0.060, 0.0599
5	0.0441, 0.0431
6	0.0413, 0.0396
7	0.0413, 0.0401
8	0.0394, 0.0383
9	0.0395, 0.0383

*Acid compositions determined from titrations with 0.1032M NaOH.

The experimentally titrated compositions of the feed solutions and the measured flow rate of 173 mL/min for the DF pump were input to the GTM, and the contactor performance predicted. The results for the acid concentration profile were in excellent agreement with the model predictions of the stage-to-stage profile (Fig. II-26). There is a slight deviation between the predicted and experimental acid concentrations in stages 1, 2, and 3, which we suspect is due to the high neodymium concentration in these stages compared with that for the other stages in the system (10^{-2}M vs. 10^{-3} to 10^{-6}M). Neodymium can be titrated with a base due to its hydrolysis and precipitation as $\text{Nd}(\text{OH})_3$.

Fig. II-26. Experimental (squares) and GTM Predictions (curve) for Stage-to-Stage Acid Profile

The GTM predicted acid composition is only about 5% higher than the experimental values in stages 1, 2, and 3, as shown in Fig. II-26. In stages 4 through 9 the experimental values and GTM predicted acid compositions agree to within the experimental error of the measurements. The GTM-predicted acid and neodymium profiles are plotted in Figs. II-27 and II-28, respectively. Experimental neodymium results for comparison are not available yet.

Fig. II-27. Stage-to-Stage Acid Profile Predicted with GTM for Aqueous and Organic Phases

Fig. II-28. Stage-to-Stage Neodymium Profile Predicted with GTM for Aqueous and Organic Phases

The unsteady-state compositions of the acid in the EW and DW raffinate streams approached the GTM predicted values asymptotically, as shown in Figs. II-29 and II-30. After about 40 minutes, there is good agreement between the data and the GTM predictions.

Fig. II-29. Measured (squares) and Predicted (horizontal line) Acid Concentration for DW Stream (non-TRU raffinate)

Fig. II-30. Measured (squares) and Predicted (horizontal line) Acid Concentration for EW Stream (americium product)

c. Corrosion Experiment

Many of the NBL waste solutions that will be processed contain Cl^- , which could cause several problems. First, the centrifugal contactors are fabricated using 304 stainless steel, which are not resistant to high Cl^- concentrations. Because of the high-precision parts in the contactor rotor, high corrosion rates will have a detrimental effect on its operation. Second, high Cl^- concentrations may affect the chemistry of the process.

The Cl^- from these solutions could be removed by precipitation with silver. For special cases where the Cl^- concentration is very high, extraction of the metals from the aqueous phase in a batch process would be necessary. However, both these methods require additional operations and would increase the amount of waste generated. A third possibility is to process the waste without pre-treatment. This is discussed in more detail below.

Based upon data sheets from NBL, the Cl^- concentration will typically be around 0.1M. To determine if corrosion would be a problem, coupons were prepared by cutting five small strips of 304 stainless steel in half and then welding the halves back together in a "U" shape with the weld at the top of the "U." The welds were made to attain a heat-affected zone as present in normal welding of metals. Two solutions were prepared. Both solutions contained 0.1M HCl and 2M HNO_3 ; one solution also contained 0.1M $\text{Al}(\text{NO}_3)_3$. Two coupons were placed in each solution. The fifth coupon was a blank and was not placed in either solution. One coupon in each solution was removed after one day, while the second was removed after 2.7 days. A period of 2.7 days represents our initial estimate of the total time that we would be processing these solutions. After removal, the coupons were rinsed with water and dried. Analysis included reweighing the samples and analyzing a cross section by scanning electron microscopy (SEM).

The test data, shown in Table II-27, indicate that the initial corrosion is higher than the average over the 2.7-day period (because the weight loss over the longer period is not 2.7 times the weight loss over one day). Losses for the coupons placed in the solution containing $\text{Al}(\text{NO}_3)_3$ were slightly higher than those for HCl- HNO_3 solution. Some pitting was detected when the coupons were examined with SEM, but no major pits were seen. The surface did appear somewhat different from the blank coupon, but that was expected since some corrosion had occurred. Although we would not, in general, recommend processing large volumes of nitrate solutions containing Cl^- , we feel that the corrosion rates for this short duration are acceptable. Therefore, we will not routinely pre-treat the waste solutions by removing the Cl^- .

2. Processing of First Batch of Waste

a. Flowsheet Design

The flowsheet developed for processing the first batch of plutonium waste solution (designated CMT-NBL-1) is shown in Fig. II-31. This flowsheet was devised to concentrate the americium product stream by a factor of 80. This increases the amount of americium present in the contactors at the end of the run because the americium is stripped from the organic in the strip section, but only 2.5 mL/min of this solution is removed. The rest of the strip solution is passed back into the extraction section, where the americium is re-extracted. Over time, this process increases the americium concentration in the system. Therefore, a second flowsheet was developed to clean out the contactors at the end of the run, using as small an amount of flush solution as possible. Changes made for the "shutdown" flowsheet included (1) moving the americium product line from stage 9 to stage 7, (2) increasing the flow rate of the americium product stream from 2.5 to 100 mL/min (the same as for the

americium strip feed flow rate), (3) shutting off the first plutonium strip solution (to stage 15) after 10 min of flushing, and (4) introducing a nonradioactive flush solution to the DF feed tank in 1-L increments. This flowsheet should be adequate for cleaning out the system. (Unfortunately, 2M HNO₃ was used as the flush solution instead of the low-acid/high-salt solution planned. This was a mistake, since the high acid concentration probably prevented the americium from being stripped from the organic phase.)

Table II-27. Results of the Stainless Steel Corrosion Test

Coupon	Aqueous Solution Comp.	Days of Contact	Weight, g			Weight Loss, %
			Initial	Final	Loss	
1	Blank	0	1.2882	1.2879	0.0003	0.009%
2	0.1M HCl 2M HNO ₃	1	1.6286	1.6176	0.0110	0.675%
3	0.1M HCl 2M HNO ₃	2.7	1.5850	1.5716	0.0134	0.845%
4	0.1M HCl 2M HNO ₃ 0.1M Al(NO ₃) ₃	2.7	1.7579	1.7387	0.0192	1.09%
5	0.1M HCl 2M HNO ₃ 0.1M Al(NO ₃) ₃	1	1.6352	1.6164	0.0188	1.15%

Fig. II-31. Flowsheet for Processing First Batch of NBL Waste.
(Waste contains 12 g plutonium.)

b. Equipment Setup

Prior to the processing of waste solutions, a considerable amount of preparatory work, most of which was safety related, was required. The paragraphs below summarize these modifications.

Some additional protection against tornadoes was dictated. Thus, the legs of the glovebox frame were all bolted to the floor, and the glovebox was welded to the frame. This change should prevent the glovebox from being thrown about if a tornado should strike. However, it will not prevent the windows from being blown out and the box contents being scattered. Of particular concern is our use of a large plastic carboy, which will at times contain as much as 41 g plutonium in as much as 50 L of solution. To address this concern, a special stainless steel secondary container was obtained and modified. This container (Fig. II-32) is attached to the glovebox with steel bands and cables. Any time the carboy contains a plutonium solution, the lid of the secondary container must be securely attached at the end of the workday or at times when any tornado or severe thunderstorm activity is in the vicinity.

Fig. II-32. Secondary Containment Vessel for the Plutonium Feed Solution

Occasionally, liquids from the glovebox must be pumped to a Kewaunee hood. Since volumes as large as 10 L are pumped and this process is quite slow, we did not want any liquid overflows. Therefore, a liquid level alarm was built. This unit operates with a 6-V battery, is readily adjusted and tested, and transmits an audible alarm when a preset level is attained.

Positive displacement pumps (manufactured by Fluid Metering, Inc.) are used extensively for both the transfer and circulation of fluids in the glovebox. We observed that the rotating portion of these pumps might catch a glove and tear it while running. To prevent this, a snap-on plastic shield was fabricated by cutting the bottom from a 250 mL plastic bottle and fitting it to the pump. This shield effectively encases the rotating portion of the pump.

Titration of various solutions is sometimes required. Since the use of a conventional glass burette in our crowded glovebox is undesirable for several reasons, most notably it is breakable, cumbersome, and difficult to read, we decided to employ a plastic burette with a digital readout. For measurement of the pH, a stick pH meter was procured. With this arrangement, titration is simplified and reading errors are much less likely.

Calcination of the plutonium oxalate product will be accomplished with the aid of a small muffle furnace. Since this furnace has the ability to reach approximately 1200 °C, its temperature is limited by a Variac that prevents temperatures in excess of 650 °C. At this temperature, the maximum exterior temperature observed, as measured with a contact thermometer, was 95 °C. Thus, at the maximum temperature, there is no danger of loss of glove integrity, even if a glove touches any part of the muffle furnace.

c. Run Summary

The checklist used for this run, which was completed on January 3, 1991, is shown in Table II-28. Times of the various events in this test are also included in this table. Overall, this run went smoothly. The biggest potential problem was the formation of a Pu(IV) oxalate precipitate in the plutonium-strip section (stages 15-18). However, this precipitate did not create any operational problems (plugging of the rotor, emulsion formation, etc.) during the run. Some problems that were encountered included (1) sampling some feed streams, (2) setting the pumps at the desired flow, and (3) transferring samples in small glass vials to the hood.

Because of the translucent tubing used on the organic side, we could follow the high plutonium concentrations in the contactor by its dirty yellow color. This color first appeared in the organic effluent from stage 6 and continued up through the organic effluent from stage 14. The organic effluent from stage 15, the first plutonium strip stage, did not show any of the dirty yellow color. The aqueous raffinate for stage 15 did show this dirty yellow color. Some of this color was seen in the aqueous phase exiting stage 16. The aqueous phase exiting stages 17 and 18 looked clear. Thus, the general movement of the plutonium metal ions went as expected.

d. Flow-Rate Analysis

Because the flow rate of each process stream is important to understanding and modeling the process, the flow rates for each FMI pump were checked. To that end, the integrated volumes and total elapsed time of pump operation were used to calculate a flow rate for each pump. Some error is present in these data, since inadequate records forced us to estimate the flush time at the end of the run, and the total volume of feed solutions was not all accounted for in the product tanks. Despite this, in all but one case, reasonable agreement was found between the calibrated and estimated flow rates.

Table II-28. Run Schedule for Batch: CMT-NBL-1 (contains 12 g of plutonium)

Time Line ^a	Running Time ^a	Action Required/Noted
SYSTEM PREPARATION		
-		Sample feed solutions.
-		Measure feed solution and box temperatures.
-		Record pump settings.
SYSTEM STARTUP		
-10:00		Verify all stage drain valves CLOSED.
-10:00		Verify aqueous feed block valves OPEN.
-10:00		DX mixer ON.
-10:00		Vent organic feed tank.
- 5:00		Contactor motors ON.
0:00	0:00	DW, EW, FW, GW pumps ON (Raffinates).
0:00	1:00	GF pump ON (Pu Strip #2).
0:00	1:00	EF pump ON (Am Strip).
0:00	-14:00 ^b	FF pump ON (Pu Strip #1). Turn on only until solution enters stage #15. Then pump off.
6:15	c	EW overflow detected (Am Strip).
10:00	14:20	HF pump ON (Carbonate Wash #1).
10:00	14:20	IF pump ON (Carbonate Wash #2).
11:23	15:50	HW overflow detected (Carbonate Wash #1).
11:23	16:10	IW overflow detected (Carbonate Wash #2).
13:52	c	FW overflow detected (Pu Strip #1).
14:45	12:22	DW raffinate detected.
18:00	17:18	EF, GF, IF pumps OFF.
18:00	17:36	HF pump OFF.
18:00	17:48	DX pump on (TRUEX solvent, takes about 42 s/stage).
24:00	c	IP pump ON (TRUEX effluent).
32:40	32:19	IP effluent detected (TRUEX solvent).
33:00	33:20	Aqueous pumps ON (EF, FF, GF, HF, IF).
35:00	33:20-40:00	Verify effluent flow from all sections.
		Examine tubing/connections for leaks.
SYSTEM OPERATION		
0:00:00	41:00	DF pump ON (Extraction Feed).
0:01:00	c	Color change, DW raffinate.
0:45:00	93:00	Transfer DW raffinate solution to hood.
	121:00	Turn off DF feed pump momentarily to collect feed sample.
2:00:00	135:52	DF feed line ran dry--adjusted feed line into bottom of tank.
2:00:00	138:00	DF feed tank empty.
		END TRUEX PROCESSING: FIRST BATCH.
SYSTEM CLEANOUT AND SHUTDOWN		
0:00	139:00	Shut off DX, DF, EF, FF, GF, HF, and IF feed pumps.
		Shut off EW raffinate pump (Am Strip).
		Switch stage 7 to 6 connection so all aqueous discharges.
		Add 1-L flush sol'n. to DF feed tank (Extraction Feed).
5:00	174:00	Turn on DX, DF, EF, FF, GF, HF, and IF feed pumps.
10:00	179:00	Add 1-L flush sol'n. to DF feed tank (Extraction Feed).
15:00	190:00	Add 1-L flush sol'n. to DF feed tank (Extraction Feed).
15:00	c	Shut off FF feed pump (Pu Strip #1).
20:00	~ 200:00	Shut off DX, DF, EF, GF, HF, and IF feed pumps.

^aMinutes:seconds.^bThis pump turned on early to fill feed lines.^cData not available because event not witnessed or time of event not recorded.

(By "calibrated," we mean the flow rate that was set and measured below the start of the run.) The exception was the americium product pump (EW). This pump was set at 2.5 mL/min, and the integrated flow elapsed time value was found to be 3.3 mL/min, for a total displaced volume of 410 mL in 122.97 min. This pump was rechecked after the run, and the flow rate was found to be in agreement, 2.3 mL/min. The target and calibrated flow rates are summarized in Table II-29. The calibrated flow rates are the best numbers to use in any future analysis.

Table II-29. Pump Flow Rates for the NBL Waste Processing

Pump Identification	Flow Rate, mL/min	
	Calibrated	Actual
DF TRU Feed	200	205
EF Am Strip	100	105
FF Pu Strip 1	5	5
GF Pu Strip 2	30	30
HF Carb. Wash 1	75	75
IF Carb. Wash 2	75	75
DX TRUEX Solvent	75	75
EW Am Product	2.5	2.3
IP Recycle	>75	>75

During the run, we estimated the DF flow rate based on the change of the liquid level in the DF feed tank. These flow rate measurements are reported in Table II-30. The results (based on the last three readings) indicate that the flow rate for the DF feed was 210 ± 10 mL/min, which agrees with the flow rate reported in Table II-29.

Table II-30. Summary of Flow Rate Measurements for DF Feed

Time of Day	Vol., L	Rate, mL/min
1:59 pm	21	
2:34 pm	14.5	186
3:05 pm	6	227
3:16 pm	4	221
3:28 pm	2.7	206
3:31 pm	2.3	203
All five tests:	Average	209
	Std. Dev.	16
Last three tests:	Average	210
	Std. Dev.	10

e. Plutonium and Americium Analysis Method

Samples of the feed and product solutions were taken to complete a material balance for the Pu and Am processed. The liquid volumes of the feeds and products were measured so that the total Pu and Am amounts could be determined from the concentration measurements multiplied by the appropriate volumes.

The concentration of Am-241 was determined from the gamma counting results. The characteristic peak at 59.5 keV was used. At this energy, the counting efficiency is 0.310, and the abundance is 0.359. These data were used to calculate the disintegrations per second (DPS):

$$DPS = \frac{CPS}{(C. EFF) (ABD)} \quad (II-17)$$

where CPS = Measured counts per second
 C. EFF. = Counting efficiency of the intrinsic germanium detector at the gamma photon energy where CPS is measured (No. detected events/No. total events)
 ABD = Abundance (No. of gamma ray photons/disintegration event)

The calculated DPS was related to the amount of Am-241 in the sample by

$$\frac{dN}{dt} = -kN \quad (II-18)$$

where $\frac{dN}{dt}$ = Disintegration rate, mol/s (This number is determined from the value of DPS with the appropriate conversion factors.)
 k = First-order decay constant, $\ln(2/\text{half-life})$, s^{-1}
 N = Amount of radioisotope, mol

From Eq. II-18, the amount of Am-241 is calculated. The concentration is given by the amount of Am-241 divided by the sample volume. Since Am-241 decays primarily by alpha decay, only $3.8 \times 10^{-10}\%$ of the total decay events is by spontaneous fission. This analysis neglects the decay rate by spontaneous fission because it is so low. Only decay events that produce the characteristic gamma rays at 59.5 keV were used.

The amount of Pu-239 and Pu-240 was determined from the liquid scintillation results. In liquid scintillation, the scintillation cocktail essentially becomes part of the detector, and each decaying atom is surrounded on all sides by the cocktail. With this type of analysis, the counting efficiency is very close to 100% because all decay events are detected, except for a few which occur at the wall of the container and do not cause a light emission. Therefore, each count from a liquid scintillation measurement is the same as a disintegration, with very little error. The net alpha disintegration rate for both Pu-239 and Pu-240 is the total alpha disintegration determined from the liquid scintillation results minus the rate of alpha disintegration due to Am-241. The rate of disintegration of Am-241 was determined from the gamma analysis, as discussed above.

Once the net disintegrations for Pu-239 and Pu-240 were known, the plutonium concentration was determined from a weighted average of the specific activity for each identified plutonium isotope. The specific activity for plutonium was calculated from the published half-life of 2.41×10^4 years for Pu-239 and 6.56×10^3 years for Pu-240. We assumed that the ratio of Pu-239 to Pu-240 was 11.3 g to 0.7 g, as reported by PFS-WMO for the relative weights in the feed. This assumption yields an average specific activity of 1.59×10^{11} dpm per gram of plutonium. By dividing the net disintegration rate by this specific activity, the total amount of plutonium can be determined. The concentration of plutonium can then be determined by dividing this amount by the sample volume. In this analysis, we assumed that Pu-239 and Pu-240 were the only two isotopes of plutonium present in these samples. The presence of other isotopes can significantly affect the average specific activity and, therefore, the plutonium concentrations.

f. Preliminary Material Balance

Total alpha activity in samples collected from the DW raffinate stream are listed in Table II-31 and plotted in Fig. II-33. Based upon this analysis of the DW waste samples, the total alpha activity appeared to start out fairly high (40-50 cpm/ μ L), then slowly dropped throughout the run, eventually reaching approximately 4 cpm/ μ L. Since we made no adjustments during the run that would have this effect on the DW raffinate, the DF feed in the extraction section must have become contaminated during startup of the system. Then, during the run, this contamination was swept out of the system.

To explain this data further, we need to look at how the system was started up. First the extraction section was filled with the low acid scrub solution. Then, after every stage had been filled with both aqueous (first) and organic (second) solutions, the DF solution was started. The acid concentration in the extraction section apparently was not high enough to extract all of the Pu and Am into the organic phase before the last stage was reached. For future tests, the extraction section should be filled with a dummy feed that contains either (1) a high concentration acid, such as 2M HNO₃, or (2) a high concentration salt and low concentration acid, such as 3M NaNO₃ and 0.1M HNO₃, respectively. The material balance results from the CMT-NBL-1 run are summarized in Table II-32. Based upon this inventory, approximately 60% of the plutonium in the feed was located either in the product solutions or in the various waste solutions. The remaining 40%, or 4.7 g of plutonium, is suspected to be precipitated

Table II-31. Alpha Activity in DW Raffinate Samples
Collected during the Processing of Batch #1

Time, min	Alpha Activity, ^a cpm/100 μ L	
11	407	387
30	4950	4760
44	2770	2760
60	1090	1100
70	856	844
80	483	480
93	397	399

^aDuplicate samples collected for analysis.

Fig. II-33. Plot of Alpha Activity in DW Raffinate Samples for Batch #1. (Duplicate samples indicated by shaded and unshaded bars.)

plutonium that was in the contactor stage for the second strip and could not be removed. To be a viable process for these types of waste solutions (very high plutonium concentrations), these precipitates must be eliminated. Therefore, new strip solutions will be evaluated to eliminate this problem. Otherwise, the process seemed to work very well -- elimination of the activity spike in the DW raffinate at startup will also improve this process. A reduction in the amount of waste solutions listed in Table II-31 would also be beneficial, but not practical for such short duration tests. If the process had operated longer (several weeks), the volume of these wastes would still be about the same, making their plutonium content a very small fraction of the total.

g. Collection and Processing of Precipitates

The plutonium product (FW) will typically consist of approximately 9 L of plutonium oxalate, present as both dissolved plutonium and as a solid precipitate, in a solution of 0.05M oxalic and nitric acids. Initially, the plan was to filter this product to remove a majority of the plutonium precipitate and evaporate the filtrate to dryness. The solids from both operations would then be combined and calcined. Since problems were encountered in the initial filtration, we decided to eliminate the filtration step and merely evaporate to dryness and then calcine. Evaporation of the liquid portion was accomplished in a Teflon beaker, which resided upon a hot plate. When evaporation was complete, the beaker contents (plutonium oxalate) were transferred to a quartz crucible and calcination was begun. The crucible and its contents were initially heated at 590°C and held there for four hours. The furnace temperature was then elevated to 700°C and held at this temperature for an additional four hours. The weight was then measured, and the crucible was returned to the 700°C furnace for an additional four hours. There was no weight change after this additional heating. The oxidized product was a greenish yellow powder, which was easily removed from the crucible and showed no evidence of any reaction with the crucible.

A formal safety review which covers the evaporation and calcination of plutonium oxalate recovered from NBL waste, was conducted on November 28, 1990. No major problems were encountered, and approval to proceed was granted.

Table II-32. Summary of Plutonium Inventory for Batch CMP-NBL-1

Process Stream	Sol. Vol., L	Conc., g/L		Total Amount, g		Notes
		Pu	Am	Pu	Am	
FEED STREAMS						
DF Feed Solution	21	0.538	0.000422	11.298	0.0089	Feed sample (diluted)
DF Feed Sample (archived)	0.026	14.7		0.38	0	Archived undiluted feed (from D. L. Bowers, CMT)
TOTAL FEED INVENTORY						
				11.68	0.0089	
PRODUCT STREAMS						
Pu Oxide	--	--		5.6		
Am Product & Flush	2.71	0.0118	0.00188	3.20E-02	0.0051	All of Am strip solution
Pu Flush (Stage 15-18 Drains)	0.7	0.05	2E-07	3.50E-02	0.0000	Sol'n. from draining stages 15-18 (solids present)
Stage 1-14 Drain	0.8	0.0314	0.00031	2.51E-02	0.0002	Sol'n from draining stages 1-14
Acid Flush of Pu Section	0.422	0.034		1.43E-02	0.0000	6M HNO ₃ flush of stages 15-18 to dissolve Pu
Organic in Pu Acid Flush	0.007	46.4		3.25E-01	0.0000	Organic layer in 6M HNO ₃ flush sol'n.
Dissolved Black Solids	0.026	10.6	8.13E-06	2.76E-01	2.11E-07	Black solids dissolved (solids present)
Filtered Pu Oxalate Sol'n.	3.37	0.0242	1.89E-07	8.16E-02	6.37E-07	Filtered Pu product sol'n. (solids present)
TOTAL PRODUCT INVENTORY						
				6.433	0.0053	
DW WASTE STREAMS						
Neutralized DW Raffinate	80	0		0.00E+00		Reprocessed DW raffinate
Acidified Carbonate Sol'n.	51	0.00269	1.44E-05	1.37E-01	0.0007	Acidified carbonate solutions
TOTAL WASTE INVENTORY						
				0.137	0.0007	
UNRECOVERED MATERIAL (% of BATCH)						
				4.73 (40.5%)	2.78E-03 (31.4%)	

3. Results from pH Meter Titrations

For reprocessing the DW raffinate, we are planning on using an abbreviated TRUEX flowsheet that relies on the two sodium carbonate wash sections to remove americium, plutonium, and nitric acid from the organic solvent. Since the nitric acid being stripped from the solvent will react with the sodium carbonate, we need to develop a quick and simple method that can be used during the run for determining how much sodium carbonate remains. The following text is a description of this method development.

a. Titration Results Comparison

Aliquots from an HNO_3 stock solution (in duplicate) were titrated on the titroprocessor and pH meter. From previous titrations, the molarity of the acid was reported to be 0.0951. Titrant concentrations for the two instruments were slightly different, as shown in Table II-33. The fairly large discrepancy in the results for the two instruments is most likely due to the design of the digital buret. Since the volume in each drop of titrant released by the digital buret is 0.02 to 0.03 mL, the end-point volume at best can be ± 20 to 30 μL . Although this is not a major problem for our tests, a molarity accurate to four places cannot be expected with this method.

Table II-33. Comparison of Titration Results with pH Meter and Automatic Titroprocessor

Sample No.	Apparatus	Sample Volume, mL	Vol. Base Used, mL	Titrant Concentration, M	Acid Molarity
1	Titroprocessor	4.75	4.786	0.0963	0.0970
2	Titroprocessor	2.50	2.436	0.0963	0.0938
Average =					0.0954
3	pH meter	4.75	4.52	0.0953	0.0907
4	pH meter	2.50	2.35	0.0953	0.0896
Average =					0.0901
Difference =					0.0053
Percent Difference =					5.55%

b. Sodium Carbonate Titrations

Three solutions of varying amounts of Na_2CO_3 , partially neutralized with HNO_3 and $\text{H}_2\text{C}_2\text{O}_4$, were prepared. The compositions of each solution, plus the calculated concentration of Na_2CO_3 after partial neutralization, are listed in Table II-34. These solutions are similar to those likely to be obtained during the course of the NBL runs. Using a known molarity of HCl , we titrated these basic solutions to determine the sodium carbonate concentration. The solutions were titrated using both the pH meter and the automatic titrator. Results are listed in Table II-35.

Table II-34. Titration Results from Sodium Carbonate Solutions

Sample Number	Sample Volume, mL	Na ₂ CO ₃		H ₂ C ₂ O ₄		HNO ₃		Calculated [Na ₂ CO ₃] Not Neutralized, M
		g	M	g	M	g	M	
1	100	5.3	0.5	0.9	0.0714	0.629	0.1	0.3786
2	200	5.3	0.25	0.9	0.0714	0.629	0.05	0.1536
3	50	2.65	0.5	0.45	0.0714	1.5725	0.5	0.1786

Table II-35. Results from Titration of Partially Acidified Sodium Carbonate Solutions

Sample Number	Sample Volume, mL	Molarity	
		1st Endpoint	2nd Endpoint
Automatic Titrator			
1	1.00	0.361	0.393
	0.50	0.3568	0.378
	Average =	0.359	0.386
2	1.00	0.162	0.179
	0.50	0.177	0.188
	Average =	0.169	0.183
3	1.00	0.119	0.179
	0.50	0.133	0.241
	Average =	0.126	0.210
ph Meter			
1	1.00	0.34	a
	1.00	0.35	a
	1.00	0.34	a
	Average =	0.345	
2	0.50	0.167	0.202
	0.25	0.160	0.192
	Average =	0.164	0.197
3	0.50	0.124	0.166
	0.25	0.122	0.205
	Average =	0.123	0.186

*When sample 1 was titrated using the pH meter, difficulty was encountered with obtaining a stable pH.

When the results of pH vs. volume of base dispensed for Sample 1 were graphed, we found that concentration values could be calculated for the first endpoint, but in all three cases, the titration was stopped before the second endpoint was reached. The main reason for this problem is believed to be the release of CO_2 from solution. This problem was somewhat corrected in Samples 2 and 3 because they contained less sodium carbonate and were better mixed, and because the pH recorded after the addition of some acid was the lowest value seen before the pH started to rise.

When a strong base and strong acid are used in a titration (for example, NaOH and HNO_3), the single endpoint can often be derived from the data by (1) observing a pH change of 1.5 to 2, or (2) by examining a plot of pH versus volume of base dispensed, where the almost vertical pH jump indicates an endpoint. For Samples 2 and 3, two small endpoints could be seen in the plots (see Fig. II-34), but a more-accurate way of determining the endpoints was needed. This involved taking the data and calculating the first and second derivatives of pH as a function of volume dispensed. Plots of the first and second derivatives for Sample 2 are shown in Figs. II-35 and II-36, respectively. Endpoints can easily be obtained from the first-derivative plot by determining the volume where the curve reaches a maximum (peak), and from the second-derivative plot by determining where the curve crosses the x-axis. The second-derivative plot appears to contain more "noise" because any errors in the initial readings are significantly magnified by the time the second derivatives are calculated.

With these three tests completed, these instruments will soon be moved into the glovebox used for processing NBL waste and will be used for determining compositions of solutions that cannot be removed from the glovebox. Procedures for completing these titrations (and how to calibrate and use the equipment) were also generated.

Fig. II-34. Titration Curve for Sample 2 (First Trial)

Fig. II-35. First Derivative of pH Titration Curve for Sample 2 (First Trial)

Fig. II-36. Second Derivative of pH Titration Curve for Sample 2 (First Trial)

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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 Office of Environmental Restoration and Waste Management (EM). This program was initiated in 1989, and its purpose is to evaluate, before hot startup 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 (1) the long-term prediction of glass performance in a repository environment and (2) the determination of the relationship between the radionuclide release from a glass waste package and performance assessment of the repository are tasks that must be addressed, but that such tasks will not be completed 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 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 an Unsaturated Environment (J. J. Mazer)

The predicted repository environment at Yucca Mountain has been described by the YMP 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. Such a critical review is underway.

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 the temperature, radiation fields, glass composition, ratio of glass surface area to leachant volume (SA/V), and composition of alteration phases resulting from glass hydration. 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 compendium document. The results from this task will be used to support DWPF and WVDP startup.

The technical approach is to assemble all known and pertinent sources of scientific literature and then to objectively and critically consider the current state of knowledge as to how each critical parameter affects the 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. Existing data are synthesized, where possible, to provide a framework for comparing the results obtained from different studies. All references used in the critical reviews are collected in a computerized data base, which lists the reference, along with keywords and the ANL reviewer's comments regarding the reference. The references in the data base include published journal articles, symposia proceedings, unpublished technical reports, 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. The data base has a word-search capability that facilitates the review process and helps ensure that no known pertinent literature is overlooked.

A preliminary critical review was previously performed in order to provide a foundation for subsequent detailed reviews of each parameter.³ The first such report, detailing the effects of temperature on waste glass performance, has been issued.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 reaction process can be described by the Arrhenius equation, a relationship derived from empirical observations. In cases where the reaction mechanism changes as a function of time or temperature (i.e., the dominant reaction process changes), the Arrhenius equation is less useful in interpreting the temperature dependence of the overall reaction mechanism. Understanding the interplay of the reaction processes and their temperature dependences for nuclear waste glasses requires a clear understanding of the overall reaction mechanism, which has not yet been achieved. Until this understanding is attained, caution should be exercised in using temperature as an accelerating parameter in nuclear waste glass studies.

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 models of glass dissolution are combined with this information to form a basis for critically reviewing theoretical and empirical 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 field, SA/V ratio, surface layers, and unsaturated environments) are also being initiated, and drafts of each report will be completed in the near future. The process governing the execution of each review involves several steps. Each author(s) initially produces an outline listing the expected content of each section. The outline is then internally reviewed, and corrections and additions are made, as necessary. A draft of the manuscript is then prepared and submitted for internal review. After the comments from this review are addressed, the manuscript is then sent out for an external review by acknowledged experts in each field. After the comments from this review are received and incorporated into the manuscript, the final document is published and distributed.

2. Long-Term Testing of Fully Radioactive Glass
(J. K. Bates, J. W. Emery, T. J. Gerding, and J. C. Hoh)

These long-term tests will provide information that can be used to validate glass reaction models and to demonstrate an understanding of glass reaction processes occurring in an unsaturated environment. The results will also indicate whether differences exist in the reaction of fully radioactive glass compared to nonradioactive glass of the same nominal composition. This is important to

demonstrate because model development has generally been done using results from nonradioactive glass tests. The results of the radioactive and nonradioactive tests can be used to demonstrate glass reaction in an unsaturated environment, but by themselves should not be used to predict glass reaction to repository time frames.

a. Objective and Rationale

The objective of this task is to evaluate the performance of fully radioactive glasses, similar to those that will be produced by the DWPF, in meeting the performance objectives for glass storage in a high-level waste repository located in an unsaturated horizon. Specifically, long-term data will be generated such that (1) reaction of fully radioactive glass can be compared with that of nonradioactive glass of the same nominal composition; (2) interactions between waste package components that must be accounted for in independent reaction path models are identified; and (3) the long-term behavior of glass is established under anticipated unsaturated disposal conditions, such that validation of glass performance models can be achieved.

b. Technical Approach

To determine the long-term performance of glass under repository conditions, tests must be conducted such that the "final" reaction conditions (steady state) are achieved. The information obtained from these tests must include the solution composition as a function of time, combined with a description of the glass alteration. To meet these goals, three types of tests will be performed:

- (1) Long-term static tests (i.e., no water flow) at high SA/V ratios with monoliths and powders. These tests provide temporal solution trends, plus easy identification of secondary phases combined with the distribution of radionuclides in the reacted glass layers.
- (2) Long-term intermittent flow tests at high SA/V ratios following a modified version of the Unsaturated Test Procedure⁵ as applied to "aged" and fresh glass monoliths.
- (3) Long-term repository environment tests following the laboratory analog procedure as applied to "aged" and fresh glass monoliths.⁶

The tests are being performed with three different general groups of glass compositions: 165-, 200-, and 131-frit based glasses. Radioactive sludge-based glasses that were received from Westinghouse Savannah River Co. (WSRC) included 165/42R (165 frit and tank 42 sludge), 131/11R (131 frit and tank 11 sludge), and 200R (200-based frit and sludge from tanks 8 and 12). These glasses were remelted and both monolithic and powdered samples were prepared for testing. Nonradioactive, simulated glasses of the same nominal composition as the radioactive glasses are also being tested. These simulated glasses are designated 165/42S, 131/11S, and 200S. The status of each test category is given below.

(1) Long-Term Static Tests at High SA/V

The long-term static tests will be performed following the test matrix shown in Table III-1. The matrix is divided into three sections, based on the glass type (165, 131, and 200). Tests are done with monoliths at 340 m^{-1} and with powdered samples (100-200 mesh) at 2000 and $20,000 \text{ m}^{-1}$.

Table III-1. Test Matrix^a for Long-Term Static Tests at High SA/V Ratios

Reaction Progress ^d	131 Glass Type ^b						202 Glass Type ^c						165 Glass Type ^e						Blank ^b
	131/11			Simulated			200R			Simulated			165/42			Simulated			
	340	2000	340	2000	340	2000	340	2000	20,000	340	2000	20,000	340	2000	340	2000			
	SA/V (m ⁻¹) =																		
1,020																			3
2,380																			14
4,760							14					14							28
6,000								3				3							30
9,520																			56
14,000																			70
19,040							56					56							91
28,000								14					14						98
30,940																			140
60,000																			182
61,880							182					182							280
123,760							364					364							364
140,000								70					70						546
247,520							728					728							728
280,000											14								980
495,000							1456					1456							1456
560,000								280					280						1820
990,080							2912					2912							2912
1,120,000								560				56							TBD
1,960,000							980					98							TBD
3,649,000								1820				182							TBD
7,280,000												364							TBD
10,920,000												546							
14,560,000												728							
							TBD ^e	TBD	TBD	TBD	TBD		TBD	TBD	TBD	TBD	TBD	TBD	
							TBD	TBD	TBD	TBD	TBD		TBD	TBD	TBD	TBD	TBD	TBD	

^aThe entries in the table indicate the duration of a specific test in days. The tests done at 340 m⁻¹ use monoliths, the tests done at 2000 and 20,000 m⁻¹ use powder. The underlined tests have been terminated.

^bTests will be single tests.

^cTests will be duplicate.

^dReaction Progress in terms of SA/Vt (units of m⁻¹day⁻¹). No significance is implied to the use of this reaction progress indicator.

^eTBD = To be determined.

The tests to be performed with the 165 and 131 glasses are identical except for the number of replicates. The tests done with the 131 glass are not replicated due to the limited amount of 131/11 glass available for testing. The tests done with 165 and 200 glasses are done in duplicate. Twelve duplicate tests are performed with a termination period yet to be determined. It is hoped that enough data will be available to allow temporal trends to be established.

The tests with 131/11R glass were started on June 13, 1990, and the 131/11S glass is in the process of being made; thus no comparative results are yet available for this glass type.

The tests with 165/42R glass were started April 27, 1990, and those with 165/42S glass on April 20, 1990. Testing has been completed through the 91-day period for monoliths and the 140-day period for powders.

The 200R glass has just been received from WSRC, so no testing has been initiated with this glass. The glass samples are being made for testing.

(2) Long-Term Intermittent Flow Tests at High SA/V

The long-term intermittent flow tests will be conducted using the Unsaturated Test procedure developed by the YMP to assess glass performance in an unsaturated environment.^{5,7} The standard Unsaturated Test matrix was modified to include effects of aging both the glass and metal components to make the results more relevant to an actual storage environment. The tests will be performed with 200R glass, and the objectives of the tests are to provide (1) data that describe the release of radionuclides from a specifically designed waste package under strictly controlled test conditions and (2) information concerning synergistic effects that may occur between waste package components. A detailed description of these tests was given in the previous semiannual report (ANL-92/25, p. 160), but since the 200R glass has just been received, no testing has been initiated.

(3) Long-Term Repository Environment Tests

The laboratory analog test has been developed to relate the performance of glass as observed in the Unsaturated Test with a more repository-relevant environment.⁶ In the laboratory analog test, the waste package assemblage (WPA) as used in the Unsaturated Test is placed within a bored-out cavity in a tuff core. The dimensions of the WPA and the cavity are similar to those used in the Unsaturated Test. The tuff core and WPA are assembled, and an unsaturated flow of water is forced through the core by using a vapor pressure slightly above ambient.

The objective of this test is to evaluate glass performance in an environment that closely matches that expected in the repository. Emphasis is placed on measuring glass reaction by examining the reacted glass and surrounding tuff rock at the test termination, and by monitoring the radionuclide content of the groundwater as it is released from the test vessel.

Two analog tests will be performed, but have not yet been started because the glass forms have not yet been produced.

c. Future Progress

All of the 200R glass has been received, and the monoliths and powdered samples for the static tests are being produced. A batch of 200S glass will also be made so that the matrix of nonradioactive tests can be started.

Upon initiation of the static tests with 200R glass, effort will begin on starting the long-term intermittent flow tests with this glass. This will require making the required monolithic blocks, aging half of the monoliths under vapor hydration conditions, and adapting the Unsaturated Test apparatus to operate with fully radioactive glass. It is anticipated that the intermittent flow tests will be started in the third quarter of FY 1991.

The ongoing static tests will be continued, and emphasis will be placed on analysis of the reacted samples. Each sample will be examined by optical microscopy to identify regions of interest for microscopic analysis and to obtain a visual description of the sample. Analyses will then be conducted using scanning electron microscopy (SEM), analytical electron microscopy (AEM), and/or secondary ion mass spectroscopy (SIMS) based on the information required. Data will be generated to compare the reactivity of the radioactive and nonradioactive glasses and to provide a data base for validation of glass performance models.

3. Effect of Radiation (D. J. Wronkiewicz)

The objective of this task is to determine the effects of radiation on the leaching and vapor-phase aging of DWPF glass under the unsaturated conditions expected at the potential Yucca Mountain repository. The task is divided into two subtasks, one to examine the formation of radiolytic products in moist air environments exposed to either an alpha or gamma radiation field, and the other to determine what influence these radiolytic products have on the performance of waste glasses and their alteration phases. Experimental conditions and preliminary results are given in Refs. 8 and 9.

Two sets of "blank" experiments were conducted in the absence of glass to determine the effects of either gamma or alpha radiation fields on moist air environments at room temperature. Results indicate that the extent of nitrogen fixation, measured as a function of nitrate plus nitrite production, varies at a rate that is linear with respect to exposure time and dose rate, and is similar to a previously determined rate of 1.9 molecules produced for every 100 eV of energy absorbed by the system.¹⁰ The fixed nitrogen species produced in these systems may combine with dissociated water molecules to produce nitric acid, which, in turn, may adversely affect the glass performance in the repository. In both the alpha and gamma blank tests, the radiolytic products that formed were concentrated in thin films of water that condensed on the test vessel walls and/or Am-241 foils (for alpha blank tests only). Increases were also noted for formate, oxalate, and inorganic carbon in solutions rinsed from the test vessel walls.

Gamma radiolysis blank tests (dose rate of 0.003 MR/h and times up to 180 days) were also conducted at 90 and 200 °C to determine the influence of temperature on the formation/stability of fixed nitrogen in the system. A comparison of results obtained at these high temperatures with the 25 °C results indicates an inverse temperature dependence on the concentration of nitrate and nitrite species in solution (Fig. III-1). The 90 and 200 °C tests display 65 and 80% decreases in nitrate plus nitrite concentration, respectively, relative to the 25 °C tests. These trends indicate that either the stability or the rate of formation of fixed nitrogen species or both are suppressed as the temperature is increased. These data are important in that the period of highest gamma radiation in the repository will also be the period of greatest heat flux from the radioactive waste material. The influence of high gamma flux on the formation of nitric acid may, therefore, be negated by the high temperatures that will exist during early repository operation.

Experiments were also conducted to examine the cumulative effects of radiolytic product formation on the performance of a simulated borosilicate waste glass. Several different glass compositions (202A, 202U, 165A, and 131U, where A and U indicate actinide and uranium doping,

Fig. III-1. Average Nitrogen Fixation (Nitrate plus Nitrite) in Gamma Blank Radiolysis Tests Measured as a Function of Time and Temperature. "Pre-rinse" refers to solution aliquot collected from bottom of test vessel. "Rinse" fraction includes portion rinsed from the vessel walls with deionized water plus the pre-rinse fraction. The $G(\text{NO}_x) = 1.9$ line is from experimentally determined data of Linacre and Marsh.¹⁰

respectively, were reacted for up to 56 days under gamma-irradiated and nonirradiated steam environments (150 °C and 200 °C). The reacted samples were then examined for the presence of secondary mineral precipitates, and the thicknesses of the reaction layers were measured. The differences observed between the irradiated and nonirradiated samples indicate the influence of irradiation on the stability of the glass waste form.

The thin films of water in contact with the glass in the irradiated tests were so corrosive that the samples had reacted completely through their 1-mm thicknesses after just 35 to 56 days of exposure. By contrast, the 35- and 56-day samples exposed in a nonirradiated environment have reacted layer thicknesses of $55 \pm 11 \mu\text{m}$ and $132 \pm 15 \mu\text{m}$, respectively (Fig. III-2). This preliminary comparison suggests that glass reaction rates in a radiation field exceed glass reactions in a nonradiation field by a factor of ~15. Reaction layer thicknesses of $5.1 \pm 0.9 \mu\text{m}$ have also been measured for 131 composition glasses reacted up to 14 days in a nonirradiated environment. Comparative tests of these glasses in an irradiated field have yet to be completed.

Detailed surface examinations by optical microscopy and scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) have been completed for all 202U, 165U, and 131U glasses reacted in nonirradiated steam environments. X-ray diffraction (XRD) examinations have been completed for many phases, while more still await analysis. Three new secondary phases have been identified on the altered glass surfaces, namely, phillipsite ($[\text{K}, \text{Na}]_{10}[\text{Al}_{10}\text{Si}_{22}\text{O}_{62} \cdot 20\text{H}_2\text{O}]$), herschelinite ($\text{Na}_4\text{Al}_4\text{Si}_8\text{O}_{24} \cdot 12\text{H}_2\text{O}$; a variety of chabazite), and calcite (CaCO_3). Small spherical K-Al-Si buttons previously identified as the K-feldspar mineral orthoclase¹¹ may instead be the K-feldspar polymorph adularia. This reclassification is based on expected temperature-pressure formational conditions of the two respective phases, with adularia being the phase expected to occur under hydrothermal conditions.¹²

Fig. III-2.

Alteration Layer Thickness Measurements from 202U and 131U Glasses Reacted in 200 and 150 °C Steam Environments, Respectively. Error bars indicate $\pm 1 \sigma$ standard deviation.

Positive differentiation of the two K-feldspar varieties is impossible using conventional XRD and SEM/EDS techniques. Other phases that commonly occur on the samples include analcime [$\text{NaAlSi}_2\text{O}_8 \cdot \text{H}_2\text{O}$], weberite [$\text{K}_2(\text{UO}_2)_2(\text{Si}_2\text{O}_5)_3 \cdot 4\text{H}_2\text{O}$], an acicular calcium silicate phase [tobermorite?; $\text{Ca}_5(\text{OH})_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$], and a bladed rosette-shaped calcium silicate phase [gyrolite?; $\text{Ca}_4(\text{Si}_6\text{O}_{16})(\text{OH})_2 \cdot 3\text{H}_2\text{O}$]. Numerous other phases have been detected but have yet to be positively identified. These phases include sodium silicate radiating fibers; Ca-K-Si, Na-Si, and Ca-Si radiating acicular growths; several different morphologies of Ca-Sr (carbonate?) phases; and numerous alkali uranyl silicate or phosphosilicate phases.

Initial examinations of the samples exposed to an irradiation field indicate that radiolysis reactions may have influenced the development of secondary mineral precipitates on the glass surfaces; however, it is not certain whether the irradiated environment has just accelerated the development of certain phases or has influenced the reaction to an extent where entirely different phases are being formed. Continued examinations of the reacted surfaces, especially those exposed to an irradiated atmosphere, will attempt to answer these questions.

Several saturated leach tests at 90 °C with 202A, 165A, and 131A glasses have been terminated on schedule for irradiation runs up to 91 days duration. These experiments provide a comparative analysis for glass performance in both steam and saturated water environments and also provide for testing of a "worst-case" scenario for the maximum water influx expected in the potential repository. A rise in pH values, to between 9 and 10, is detected for most tests conducted thus far, indicating that the glass is reacted in the solutions. All remaining scheduled saturated leach tests have been initiated, with a maximum sampling interval of two years.

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

The objective of this task is to characterize the extent and nature of glass reaction at different SA/V ratios through analyses of both the leachate solutions and the reacted solids. These tests are being performed to determine the relationship, if any, between MCC-1 tests, which are performed at low SA/V

ratios (10 m^{-1}), and tests such as the PCT and MCC-3, which are performed at higher SA/V ratios (2000 and $20,000 \text{ m}^{-1}$) more representative of the potential Yucca Mountain repository. Tests are performed at overlapping values of SA/V multiplied by the reaction time to determine if $\text{SA/V} \cdot t$ scaling can be applied to these reactions.

In our tests, actinide-doped SRL 131 and SRL 202 glasses (referred to as SRL 131A and SRL 202A, respectively) as powders or monoliths are reacted in pre-equilibrated J-13 groundwater in stainless steel vessels at 90°C for times of a few days to several years at SA/V values of 10, 340, 2000, or $20,000 \text{ m}^{-1}$. Leachates are analyzed for pH, anions, carbon, cations, and actinides. Actinide analysis is performed on the unfiltered leachates and on leachates filtered through $0.4 \mu\text{m}$ and $60 \text{ \AA}$ filters. An acid strip solution of each reaction vessel is also analyzed for sorbed actinides. The reacted solids are characterized using SEM/EDS, AEM, XRD, SIMS, and other surface sensitive techniques to identify secondary phases and characterize the reacted glass.

Table III-2 summarizes the tests to be performed at 90°C . Reaction times differ for all series and range from 3 days to several years. Tests at SA/V ratios of 10, 2000, and $20,000 \text{ m}^{-1}$ have been initiated, and all tests of 200 days or less have been completed. Tests at 340 m^{-1} are scheduled to be initiated in June 1991. Tests using a nonradioactive analog of SRL 202A glass are to be performed in Teflon vessels to assess the effects of the vessel material on the reaction and to provide data for comparison to YMP computer simulations. Several trends in the reaction progress can be seen in the leachate analyses of tests completed to date.

Table III-2. Test Matrix to Evaluate Effect of SA/V Ratio on Glass Reaction

Glass Type	SA/V, m^{-1}			
	10	340	2000	20,000
SRL 131A	X	Y	X	X
SRL 202A	X	Y	X	X
SRL 202U ^b		Y		Y

*X = all scheduled tests in progress. Y = scheduled to be initiated in June 1991.

^bNonradioactive analog of SRL 202A to be reacted in Teflon vessels.

a. Results for pH Effects

The measured pH (at room temperature) for tests with SRL 202A and SRL 131A glass vs. reaction time is shown in Fig. III-3. The pH is seen to approach a constant value beyond about 50 days and is higher in tests at higher SA/V ratios for both glass types. Also, the tests with SRL 131A glass have higher pH values than tests with SRL 202A glass at equivalent SA/V and reaction times. This suggests that SRL 131A glass is more reactive.

The increase in the pH with SA/V can be attributed, in part, to dilution effects. If the same volume of glass reacts at 2000 and $20,000 \text{ m}^{-1}$, the solution in the former will be diluted ten times more than the latter. Thus, the pH is expected to be one unit lower in tests at 2000 m^{-1} than in tests at

Fig. III-3.

Leachate pH for Tests with (a) SRL 202A Glass and (b) SRL 131A Glass vs. Reaction Time

20,000 m^{-1} due to dilution effects. In fact, the observed difference in pH at 2000 and 20,000 m^{-1} is greater than one unit for both glasses. This indicates that the effect of SA/V on the reaction is beyond that of simple dilution.

b. Results from Cation Analysis

Cation analysis is performed on the leachates passed through 0.4 μm filters for each test. The unfiltered leachate and the leachate passed through 60 $\text{\AA}$ filters are also analyzed for some tests to assess the effect of filtration. Transport through 0.4 μm filters was seen to remove suspended material rich in Al, Fe, Mn, and U in tests at 20,000 m^{-1} . Further filtration through 60 $\text{\AA}$ filters did not remove additional material. The data presented below were obtained from leachate passed through 0.4 μm filters.

Figure III-4 shows the normalized elemental releases* of B, K, Li, Na, Si, and U from SRL 202A glass vs. the reaction time at SA/V ratios of 10, 2000, and 20,000 m^{-1} . Note that tests at 2000 m^{-1} have NL(i) values greater than those of tests at 20,000 m^{-1} at equivalent reaction times for all these species. This suggests that the reaction rate is higher at 2000 m^{-1} than 20,000 m^{-1} . Also, the uranium release patterns at 2000 and 20,000 m^{-1} show an initial increase through about 20 days followed by a decrease. This is consistent with the presence of suspended material at these high SA/V ratios, which

*Represented as NL(i), where i is the leached species.

Fig. III-4. Normalized Elemental Mass Loss from Tests with SRL 202A Glass vs. Reaction Time for Boron, Potassium, Lithium, Sodium, Silicon, and Uranium. Reaction times given in units of days. The SA/V ratios are represented by circles (10 m^{-1}), squares (2000 m^{-1}), and diamonds ($20,000 \text{ m}^{-1}$), which are labeled as BX, BY, and BZ, respectively.

is removed by filtration. If the solubility limit of uranium is the same in tests at 2000 and 20,000 m^{-1} , then the NL(U) values should differ by an order of magnitude. Indeed, the NL(U) values differ by about an order of magnitude beyond about 20 days.

Boron is known to be highly soluble in leach tests of borosilicate glasses and is often used as a measure of the extent of glass reaction. The measured boron concentration is plotted against SA/V*t in Fig. III-5 for tests with SRL 202A and SRL 131A glass. Note first that the boron concentrations are greater for tests at higher SA/V at all reaction times. Tests run at different SA/V but equivalent SA/V*t show greater release at the higher SA/V. These plots clearly show that a single curve cannot fit the data, and SA/V*t scaling does not apply to these test conditions. The boron concentration in tests with SRL 131A glass is higher than in tests with SRL 202A glass at equivalent SA/V*t. This indicates that the SRL 131A glass is more reactive than the SRL 202A glass. Tests at 2000 and 20,000 m^{-1} show a decreasing boron release rate for both glasses, indicating the reactions are slowing down. Tests with SRL 131A appear to be slowed more than tests with SRL 202A glass, especially at 2000 m^{-1} .

Fig. III-5.

Boron Concentration in 0.4 μm Filtrate vs. Reaction Time (in days) Multiplied by SA/V (in m^{-1}) for (a) SRL 202A Glass and (b) SRL 131A Glass. The SA/V ratios are 10 m^{-1} (circles), 2000 m^{-1} (squares), and 20,000 m^{-1} (diamonds). These are labeled as BX, BY, and BZ for the SRL 202A glass, and PX, PY, and PZ for the SRL 131A glass.

c. Results from Actinide Analysis

The unfiltered and filtered leachates were analyzed using alpha spectroscopy to quantify the amounts of Np, Pu, and Am in colloidal and dissolved fractions and in an acid strip of the

vessel and to determine the total amounts of these actinides released from the glass. Figure III-6 shows the normalized actinide releases vs. the reaction time for tests with SRL 131A and SRL 202A glass at 10, 2000, and 20,000 m^{-1} . Similar to the results in Fig. III-5, tests at 2000 m^{-1} show greater total actinide release than tests at 20,000 m^{-1} for both glass types. In most cases, duplicate tests show similar results. The large difference between some duplicate tests is due to different extents of colloid formation. Plutonium and americium are known to become incorporated in suspended material, which complicates the analyses.

Fig. III-6. Normalized Elemental Mass Loss of Np, Pu, and Am from Tests with SRL 131A Glass (left side) and SRL 202A Glass (right side) vs. Reaction Time (in days). The SA/V ratios are 10 m^{-1} (circles), 2000 m^{-1} (squares), and 20,000 m^{-1} (diamonds). These symbols are labeled as PX, PY, and PZ, respectively, for SRL 131A Glass and BX, BY, and BZ, respectively, for SRL 202A Glass.

d. Results from Solids Analyses

Analyses of the recovered solids showed a chalky-white residue covering all SRL 131A glass grains reacted at 2000 or 20,000 m⁻¹. The residue contains high levels of Al, Mn, and Fe, which were found to be removed from the leachate by filtration. The residue is believed to have settled out of solution while the reaction was occurring, or as the reacted glass was dried, or both. No change in the surface character of SRL 202A grains was observed after 200 days. More detailed analyses using AEM are planned.

5. Natural Analogs
(J. J. Mazer)

Recent results produced at ANL suggest that the intrinsic total water content of obsidians is the dominant hydration rate-controlling parameter.¹³ These results indicate that archaeologists will be able to use the intrinsic water content of the obsidian to simplify the task of obsidian hydration dating, since there appears to be a direct empirical relationship between obsidian hydration rates and their water contents. It is currently unknown whether water contents of obsidian from a single field source are constant. Variable water contents in obsidians from a single source could lead to different rate determinations and can have profound implications for obsidian hydration dating. By using IR spectroscopic techniques as described by Newman et al.,¹⁴ the homogeneity of the water contents of obsidians can be characterized.

With respect to nuclear waste glasses, understanding the effects and magnitude of molecular water diffusion will lead to a better understanding of the reaction mechanisms responsible for forming the complex alteration assemblages observed on hydrated nuclear waste glasses. Also, measurements of the intrinsic water content of nuclear waste glasses can be used to estimate the magnitude of the rate of molecular water diffusion and compare it to the rates of other processes to assess its importance and understand the overall reaction.

The goal of this study is to examine the homogeneity of the total water content of obsidians in an entire volcanic region, within each flow, and within hand samples. The volcanic field at Coso, California, is suited for this study because it has been well characterized and studied in the past with respect to geology^{15,16} and obsidian hydration dating.^{13,17-19} Specifically, for the obsidian in the Coso field in California, 15 different hydration rates have been reported.²⁰ The quarries can be divided into two types: primary deposits (sources proximal to the original vitrification location) and lag deposits (sources removed from the original place of vitrification by processes such as explosive ejection or river transport). It has been presumed that lag deposits contain greater amounts of water due to the explosive events associated with them.

Amy Galbreath (Far Western Research) provided 100 mapped samples from the Coso field. These samples are from three separate geographic regions: West Cactus, Sugarloaf, and Joshua Ridge (Fig. III-7). Approximately ten samples were collected from the nine distinct quarries. An additional 100 unmapped samples from Sugarloaf, West Sugarloaf, and Joshua Ridge lag deposits were also provided. Precise locations for these additional samples have been requested from Far Western Research.

Each obsidian was mounted and cut using a low-concentration diamond wafering blade with water as a lubricant. The samples have approximately 1-cm² area and are 1-mm thick, depending on the size of the hand samples. These thin samples are initially polished using 600 grit paper with water as a lubricant, then they undergo a final diamond polish, which results in a 6 μm finish. Using the molar absorptivities for the IR bands corresponding to the presence of OH⁻ and H₂O reported by Newman

et al.,¹⁴ along with the measured density and thickness of the sample, the water content of each sample was computed. All of the IR measurements were taken on a Perkin Elmer Hitachi 340 recording spectrophotometer.

Fig. III-7. Map of Coso Field, CA, with Exact Locations of Mapped Samples. Provided by Far Western Research. Mapped locations for FW-35, FW-6, FW-89, FW-92, FW-95, FW-12, FW-37, and INY-1824 have been requested from Far Western Research.

An infrared spectroscopy measurement and a water content determination were performed for a slice from each hand sample in each quarry. A nitrogen atmosphere was used to reduce the humidity in the chamber where the sample was placed, thereby limiting the amount of sorbed water on the sample. To avoid phenocrysts, a 1-mm dia aperture was used to collect spectra. The detailed results will be presented later.

In the past, many workers assumed that all of the obsidian from the same field had the same intrinsic water contents. They found many different hydration rates for a single field, however, and could not determine the cause for the different rates. As has been shown in this and earlier studies, the Coso Field, in particular, contains a range of different intrinsic water contents.

The intrinsic water contents over the entire Coso Field are far from homogeneous, ranging from 0.31 to 2.34 wt % H₂O. By examining the water contents within each quarry, we determined that only one quarry is relatively homogeneous, even though the obsidians from these quarries are believed to be from the same volcanic flow. Within a single sample, the water contents are homogeneous, except for those from sites FW-416, FW-462, and INY-2826.

Table III-3 presents the average water contents for each quarry. The average ranges from $0.46 \pm 18\%$ to $1.26 \pm 16\%$ wt % H₂O, suggesting that water contents from obsidians in these quarries are not homogeneous. The two highest average water contents were measured for a lag deposit from the West Cactus region and a lag deposit from the Joshua Ridge region. The lowest average water content is also a lag deposit, FW-12. This site is located in the West Sugarloaf area. The general trend shows that the lag deposits have higher intrinsic water contents than the primary deposits. Unfortunately, it is difficult to draw any firmer conclusions regarding the relationships between the various quarries without more detailed information on their locations and geology. Far Western Research is in the process of gathering these data.

Table III-3. Average Total Water Contents for Each Quarry from the Coso Field, California

Site No.	Average H ₂ O Content, wt %
FW-416	$0.48 \pm 15\%$
FW-432	$1.26 \pm 16\%$
FW-462	$1.21 \pm 15\%$
FW-33	$1.16 \pm 16\%$
FW-35	$0.96 \pm 14\%$
FW-6	$0.87 \pm 19\%$
INY-2826	$0.47 \pm 20\%$
INY-2827	$0.88 \pm 25\%$
FW-102	$0.62 \pm 18\%$
FW-4	$0.50 \pm 24\%$
FW-5	$1.26 \pm 17\%$
FW-89	$1.00 \pm 17\%$
FW-92	$0.77 \pm 20\%$
FW-95	$1.19 \pm 32\%$
FW-12	$0.46 \pm 18\%$
FW-37	$0.68 \pm 14\%$
INY-1824	$0.74 \pm 19\%$

The results of this preliminary study suggest that variable water contents could lead to different hydration rates, which would have profound implications for obsidian hydration dating. In the past, obsidian hydration dating has been doubted as a useful chronometric dating tool. However, through further investigation of the relationship between the intrinsic water content, the hydration rate, and the hydration rate coefficient, obsidian hydration dating could become a simple and accurate method for age determination.

The infrared spectroscopy technique was used to determine the water contents of all of the Coso Field samples. The IR technique has many desirable features: (1) it is nondestructive; (2) the IR beam can be aimed at spots as small as a few tenths of micrometers in diameter, thereby avoiding most crystals, vesicles, or alteration; (3) the concentrations of OH^- or H_2O species can be measured individually, in addition to the total dissolved water content; and (4) it has a large range.¹⁴ In future studies, experimental studies to determine hydration rate should consider initially measuring the intrinsic water content of each sample using the IR technique to ensure that homogeneous samples are being used. This technique would avoid extraneous results.

Future research on intrinsic water content and its relationship to obsidian hydration dating could investigate several possible areas. Individual obsidian artifacts could be analyzed for water content (possibly even the same section used for hydration rim measurement) and then dated using empirical relationships. A geologic investigation of the relationship between primary and lag deposits would greatly aid in the understanding of the present results. Hydration rate experiments could be performed on samples with known intrinsic water contents to investigate whether a correlation exists between these two parameters. Finally, other volcanic fields could be examined to determine if any have homogeneous water contents.

6. Analytical Electron Microscopy
(C. R. Bradley, N. L. Dietz, and J. K. Bates)

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 using EDS, EELS, and ED is about 200 Å. The AEM is a very powerful tool for the investigation of inhomogeneous samples with very small inclusions, small crystallites, colloidal size particles, and thin layers.

Samples for AEM studies must be extremely thin, no more than 500 to 800 Å thick. As a result, considerable effort is expended in preparing these electron transparent specimens. The Appendix lists the samples prepared and surveyed in this reporting period. These samples include glasses from long-term testing (Sec.III.A.2), radiation-effect testing (Sec.III.A.3), and high SA/V testing (Sec.III.A.4), other glasses, and tektites.

Hydration reactions of naturally occurring glasses are interesting for several reasons. Most important to us is that they serve as a method for establishing that laboratory conditions designed to accelerate glass reaction do so without altering the mechanism of the reaction. They are also of interest for other reasons; for example, the hydration rim of obsidian, a volcanic glass, is used for dating artifacts, and tektites are evidence of past meteoritic impacts. Meteoritic impact and the weathering of features produced by such an impact are topics of great current interest because the effects of such an impact can have wide-ranging consequences.

We have examined an Indochinite tektite which has been altered as a result of natural weathering processes and has been reacted in vapor phase conditions in the laboratory. Similar phases have been identified; in both cases a glauconite-like clay was observed (Fig. III-8). Hydration reaction of nuclear waste glass is a complicated process, representing a balance between several competing mechanisms. Studies of natural analogues provide clues useful in evaluating the importance of individual reaction mechanisms in nuclear waste glasses.²¹ This finding with the tektite sample lends credibility to the argument that tests of nuclear waste glass done in the laboratory under controlled conditions and over comparatively short times really do accelerate reactions without changing the balance between individual mechanisms. The tektite results (see Appendix) are also interesting because they demonstrate that tektites do not react exclusively by dissolution; depending on reaction conditions, tektites may form clays as a result of weathering processes.

Fig. III-8.

Tektite Glass Reacted in the Laboratory.
A glauconite-like alteration layer developed
on the surface.

During this reporting period, we also completed some initial EELS studies of uranium in a variety of oxides. The objective was to determine if the oxidation state and local structure of uranium expresses itself in observable structure at the edge of an absorption threshold (near edge structure) accessible to EELS. The O and N thresholds are easily observed, but display no structure. The M_4 and M_5 edges are difficult to observe because at this high energy loss (3552 and 3728 eV, respectively) the count rate is extremely low. It has been possible, however, to acquire spectra of these edges with good signal-to-noise ratio by using a parallel detector. These spectra (Fig. III-9) compare reasonably well with X-ray absorption data acquired at a synchrotron.^{22,23} Multiple scattering artifacts, however, obscure the region of the spectrum, where differences due to the electronic state are expected. If this artifact can be removed and if resolution and signal-to-noise ratio are adequate, this will provide a method of determining uranium oxidation state with a small (less than 1- μ m dia) probe.

Initial scoping experiments have also been performed to identify colloidal particles, which develop in the reaction effluent.²⁴ Some of these small particles have been found to incorporate radionuclides, and this may be significant to eventual repository performance. Experiments were done to examine the leachate from reacted glass samples and identify the size fraction of the colloidal particles associated with radionuclides. Samples suitable for TEM examination were prepared by wicking a small amount of the leachate through a holey carbon grid, which is a special sample support grid with micron and sub-micron holes in a 200-500 Å carbon substrate. Examination of these particles shows very different types of particles. Some particles (Fig. III-10a) appear to be exfoliated material from the glass

surface. Others (Fig. III-10b) may nucleate and grow in the leachate solution. These particles are electron transparent, and future work will include analysis of these particles.

Fig. III-9. Uranium M Electron Energy Loss Absorption Edge

Fig. III-10. Colloidal Particles Collected on Holey Carbon Grids and Imaged with Transmission Electron Microscopy. (a) This particle was probably the result of exfoliation of the alteration layer. (b) These particles may have nucleated and grown within the solution. Particles in this size range have been shown to be associated with the radionuclide content of the effluent.

In the future, detailed characterizations of phases found in the experiments discussed in Sec. III.A.2, 3, and 4 will be started. This detailed characterization will entail identification of the secondary phases produced on the glass surface and observation of compositional gradients within the glass caused by the reaction process. Colloidal studies will continue with identification of the phases that make up this particulate matter and a search for those colloidal phases which bear radionuclides and elements of potential environmental impact.

B. Glass Studies for Yucca Mountain Project

The Yucca Mountain Site Characterization Project is evaluating the suitability of Yucca Mountain as a site for a potential high-level waste repository. Discussed below are results from tests involving reaction of waste glass under simulated repository conditions.

1. YMP Unsaturated Test Method (J. K. Bates and T. J. Gerding)

The YMP Unsaturated Test Method (see ANL-91/26, pp. 188-189) is being used in the N2 and N3 test series, which are being conducted with actinide-doped glasses (SRL 165 and ATM-10, respectively). Because of the alpha decay of the predominant radionuclides, these tests can be conducted in a contained area but without shielding. The N4 test series will be conducted with "fully" radioactive sludge-based glass, and modifications to the test method will have to be made. These tests will be performed as part of the effort discussed in Sec. III.A.2.

a. N2 Unsaturated Tests

The N2 continuing tests (SRL 165 glass) have been completed through the 260-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.

b. N3 Unsaturated Tests

The N3 Unsaturated Test uses ATM-10 glass (simulated West Valley glass containing actinides plus ^{99}Tc) that was received from the Materials Characterization Center (MCC) and remelted to obtain the required form of the glass. This ongoing test was started July 6, 1987, according to the Unsaturated Test matrix, and has been completed through the 245-week sampling period.

During this period, sampling from the ongoing unsaturated tests was done. Particular emphasis was placed on determining the distribution of actinide elements in solution. Selected recent results are discussed below.

The current reference design²⁵ for the Yucca Mountain site calls for spent nuclear fuel from commercial reactors and high-level waste glass to be contained in an engineered barrier system (EBS) that is surrounded by the natural host rock. Ideally, this multiple barrier system (waste form, EBS, rock) will limit radionuclide release from the waste material. In addition, radionuclide migration will be retarded due to chemical and physical interactions with the rock.

Evaluation of the total repository performance has been based on two premises: the release of actinides (e.g., Pu and Am)* from the waste form will be controlled by the solubility of

*For the time period after 1000 years, Pu and Am are the dominant radionuclides based on curie content of the waste. Resolution of their behavior must be established to predict repository performance.

individual elements in groundwater, and subsequent radionuclide transport will be determined by factors such as water flow and radionuclide retardation processes (e.g., sorption). Under this scenario, the waste form itself can react relatively rapidly, yet the transport of radionuclides will be limited by geohydrologic factors.

We have examined limitations of the solubility-controlled assumption by examining the release of Np, Pu, and Am from waste glass under simulated storage conditions. While radionuclides may form colloids that could affect transport properties,^{26,27} it is generally assumed that colloids result either from hydrolysis of dissolved species in solution (radiocolloids), or from adsorption of dissolved radionuclides onto suspended mineral particles existing in the groundwater (pseudocolloids). Both of these processes of colloid formation occur independently of the waste form and EBS and may be considered as secondary processes. However, since glass is a metastable solid, it may transform into a more stable phase assemblage under repository storage conditions.^{28,29} This assemblage may be a new source of colloidal material, i.e., primary colloids, and would form via a process that is waste-form dependent. The radionuclide content of these colloids, their sources, and the mechanism of formation must be accurately known to assess the transport of radionuclides from the EBS to the accessible environment. Thus, we have studied the primary colloids that form during glass reaction. The results provide insight into the dynamics of radionuclide mobilization in a high-level waste repository.

Glass may be exposed to a variety of conditions after disposal in a geologic repository, since the EBS environment changes as the waste cools. For example, at the potential Yucca Mountain site, depending upon when the outer containment barrier is breached, glass may be contacted by water vapor, small amounts of sorbed liquid water, or small amounts of flowing water if water enters and trickles through the metal container. We developed a test method to simulate these conditions,³⁰ and it has been applied to a prototype glass.³¹ The method involves dripping water onto a cylindrically shaped glass-metal assemblage that is suspended in an enclosed test vessel. The water that collects in the bottom of the test vessel provides information regarding (1) the form and rate by which radionuclides are released from the glass and (2) synergistic effects that occur in the glass-metal-water system.

Tests have been ongoing for 50 months. During the most recent liquid collection period, the test solution was filtered to determine whether the actinide fraction was associated with particulate material or could be considered truly dissolved in solution. Solution was passed sequentially through filters having pores ranging from 1.0 μm to 1 nm in size. The liquid that passed through each filter and the filters themselves were analyzed for radionuclides. The filters were then dissolved; the resulting suspension was dried and exposed to alpha-particle sensitive films to locate the source of alpha activity. When alpha tracks were observed, the specific particles producing those tracks were identified and transferred to a TEM grid. The structure and composition of the radioactive particle were then determined.

The radionuclide concentrations on the filters and in the liquid that passed through each filter were determined with alpha spectroscopy. The results of the tests (Table III-4) indicate that 70% of the neptunium passed through all filter sizes and can be considered truly dissolved in solution. On the contrary, over 99% of the Am and Pu was retained as colloidal solids. In these tests, most of the alpha radiation was due to the ²⁴¹Am decay; however, in samples where ²³⁹Pu was also detected, its behavior mirrored that of americium. Thus, we discuss Pu and Am release together. In general, the ratio of radioactivity in the filtered to dissolved fraction was greater than 1000:1.

We employed a combination of particle micromanipulation procedures, autoradiography, and AEM to characterize the colloidal particles. A 1 μm polycarbonate filter (including

Table III-4. Masses of Np and (Pu + Am) in the Unfiltered Solution and the Percent of the Starting Radioactivity after Each Pass through Filters of Decreasing Pore Size. Error in the absolute measurements is ~15% of the amount present. Absolute radioactivity levels in the test solutions differ between Tests 1 and 2 because water flow patterns were different.

	Np		Pu + Am	
	Test #1	Test #2	Test #1	Test #2
Mass in Test Solution (unfiltered), 10^{-3} g	17.4	6.0	108	1087
<u>Percent Passage</u>				
→ 1 μ m Filter	100	100	4	0.6
→ 0.4 μ m Filter	100	100	4	0.6
→ 0.1 μ m Filter	100	100	3	0.4
→ 0.05 μ m Filter	85	100	2	0.3
→ 0.015 μ m Filter	85	72	2	0.3
→ 0.003 μ m Filter	70	70	1	0.01
→ 0.001 μ m Filter	70	65	0.05	0.00

particles) was dissolved in chloroform, and the (colloid) residue that remained was dispersed within a thin ($\sim 1 \mu\text{m}$) collodion film. The film was exposed to nuclear emulsion for up to 30 days. The photosensitive emulsion was developed, and the positions and orientations of nuclear tracks (in the emulsion) relative to specific colloidal particles (in the collodion) were recorded. The collodion film was then mounted on a carbon-coated TEM grid, and the collodion dissolved. Because the relative positions of colloidal particles were preserved during transfer onto a TEM grid, it was possible to locate and analyze particles responsible for specific tracks in the emulsion (Fig. III-11).

The compositions and mineralogy of the alpha-emitting particles on the TEM grids were determined using AEM. Compositional analyses were performed using EDS, and crystal structures were investigated using lattice fringe imaging and electron diffraction. A sample of colloid-containing residue was also analyzed by XRD. The colloids were found to be a matrix of clay that contains submicrometer inclusions (Fig. III-12). The clay is a Na- and Fe-rich aluminosilicate (with minor amounts of Ca, Ti, and Ni), which exhibits a basal lattice spacing of $1012 \text{ \AA}$. This basal spacing, combined with XRD data, suggests that the clay is Na-rich smectite.³² The submicrometer inclusions contain major amounts of Ca, Th, P, and O and minor amounts of U and Pb. Electron diffraction (Table III-5) and XRD indicate that the inclusions are the mineral brockite (ideally $[\text{Ca,Th}](\text{PO}_4) \cdot \text{H}_2\text{O}$).³³

We compared the densities of the alpha tracks originating from brockite-rich vs. clay-rich material and established that the Am (and Pu) is carried in the brockite inclusions rather than the clay matrix. (Both Am and Pu are present at levels $\ll 0.1 \text{ wt } \%$ and are, therefore, undetectable by EDS.) Figure III-11c shows tracks emanating from two colloid particles. Particle i is almost four times larger than particle ii, yet it produces only a third as many tracks as particle ii. Brightfield and backscattered electron images (Figs. III-11a and -11b) and EDS analyses indicate that particle i is clay-rich, whereas particle ii is brockite-rich. Thus, the alpha activity and hence Am (and Pu) concentrations are associated with the brockite and not the clay.

Fig. III-11. Brightfield Electron Micrographs (left) and Corresponding Backscattered Images (right) of Two Colloid Particles. The images in (A) indicate that particle i contains mostly clay with minor brockite; the images in (B) indicate that particle ii is dominated by brockite. Image C shows alpha tracks in nuclear emulsion (with extrapolated trajectories) superimposed on a brightfield image of particles i and ii. The smaller particle (ii) contains the most (Pu- and Am-bearing) brockite and, therefore, produces the most tracks.

Fig. III-12. Brightfield (transmission) Electron Micrograph (left) and Corresponding Backscattered Electron Image (right) of Dispersed Colloid Residue Supported on Thin (<20 nm) Carbon Film. The residue is a mixture of clay and brockite (ideally Ca, Th phosphate). The bright spots in the backscattered electron image indicate the distribution of submicrometer brockite inclusions within the clay matrix.

Table III-5. Measured Electron Diffraction Results from a Pu- and Am-Bearing Inclusion along with Those of Brockite $[(Ca,Th)(PO_4) \cdot H_2O]$

Inclusion Spacing, ^a Å	Brockite Spacing, ^b Å
6.06	6.06
4.32	4.37
3.25	3.47
2.94	3.03
2.72	2.83
2.29	2.37
	2.15
2.05	1.92
	1.86
1.78	1.75
	1.69
1.65	1.67
	1.55
1.49	1.46
	1.35
	1.31

^aError of $\pm 2.5\%$.

^bFrom Ref. 33.

The Am (and Pu) bearing colloidal particles form by a different mechanism than radiocolloids and pseudocolloids. Whereas radiocolloids and pseudocolloids develop from solution, the colloids studied here are fragments of a hydrated layer that spalled from the glass surface during aqueous alteration. This spallation mechanism can generate primary colloidal particles with highly elevated radionuclide levels. Whereas radiocolloids and pseudocolloids typically are expected to incorporate only a small fraction of the actinide content of the waste,²⁶ the radioactivity associated with primary colloids can be highly concentrated within specific actinide-rich compounds that form directly from the waste.

We examined the spallation mechanism of colloid formation by exposing a glass to water vapor. Exposure to water vapor is known to accelerate glass reaction³⁴ and thus provides an ideal method to examine redistribution of elements during glass reaction. Additionally, water vapor is also likely to be more prevalent in the Yucca Mountain environment than liquid water. In the presence of water vapor, a thin film of water sorbs onto the glass surface, where it becomes concentrated in cations leached from the glass. Mineral phases nucleate from the film and form on the surface of the glass and, at the same time, a hydrated or leached layer penetrates into the glass (Fig. III-13).³⁵ Since this layer is analogous to the hydrated layer that forms during the dripping-water tests, its mineralogy should be similar to that of the primary colloids filtered from the groundwater. Scanning electron microscopy and AEM were used to study polished thick and ultramicrotomed thin sections of the vapor-exposed specimen. We found inclusions that exhibited the same compositional and diffraction characteristics as the Pu- and Am-bearing inclusions in the colloids, and determined that the clay in the hydrated layer was Na-rich smectite (Fig. III-13). This correspondence in phases confirms that the reacted glass layer is the source of the primary colloidal particles.

Fig. III-13.

Backscattered Electron Image of Cross Section of Glass Exposed to Water Vapor. As the glass hydrates, elemental segregation occurs, secondary phases (1) form on the original surface (2) of the glass, and a hydrated layer (3) simultaneously penetrates into the glass. Calcium, phosphorus, thorium, and other actinides redistribute within the hydrated layer to form discrete brockite inclusions (4) as small as 10 nm. Actinide redistribution preferentially concentrates Th, U, Pu, and Am from the glass into the inclusions, which are subsequently mobilized as colloids.

These results provide insight into the process of actinide release from glass waste forms. They also highlight the importance of engineered and natural barriers in retarding radionuclide migration. The majority of neptunium is truly in solution, as shown by its passage through the smallest filter size. Therefore, neptunium performance in the repository appears to be adequately treated using current assumptions of solubility-controlled transport. However, nearly 100% of the Pu and Am was found in small (<200 nm) insoluble inclusions associated with colloidal-sized clay particles. This observation has two ramifications. First, since the colloids form from the glass, as opposed to forming by

precipitation in solution, the actinides in the glass become highly concentrated in these colloids. In addition, these colloids are readily generated from reacted glass, and transport of Pu and Am from the glass may be dominated by their movement. Thus, the EBS should be designed to inhibit colloid transport in the case of unexpected liquid water contact with the waste. Assessments of the ability of the environment near the repository to retard radionuclide transport should also consider colloid migration and trapping processes. Secondly, a conservative performance assessment should be based on the identity and transport properties of specific actinide-bearing phases that result from waste-form reaction. The colloid phases generated will likely vary depending on the type of waste form (spent fuel or glass) and on the glass composition.

The approach taken in the present study (i.e., examination of actual radionuclide-bearing waste, combined with use of methods for identifying and characterizing sub-micrometer colloidal particles) also has applications to cleanup of sites contaminated with hazardous wastes.³⁶ The identity of small radionuclide-bearing phases may help in determining transport rates, developing remediation methods, and supporting risk assessment studies.

2. Parametric Experiments (A. B. Woodland)

Because the Unsaturated Test Method rigidly sets many of the test parameters, the effect that each parameter may have on the final radionuclide release needs to be studied. This is being done in parametric experiments. A description, purpose, and status of the parametric experiments in progress were given in detail in a previous semiannual (ANL-91/26, p. 188). The experiments are continuing as scheduled. A topical report describing the results of all of the parametric experiments is being prepared.

C. Radiation Studies for Yucca Mountain Project (D. T. Reed)

The YMP is investigating the feasibility of locating a nuclear high-level waste repository in the tuff formations in southern Nevada. The placement of high-level waste containers in the underground facility will perturb the pre-emplacement environment by raising the ambient temperature and exposing the environment to gamma radiation levels that initially may be in excess of 0.1 MR/h. Determining the effect of both of these perturbations on the gaseous/aqueous environment of the waste package is important to characterizing the performance of the high-level waste package during the containment period of repository history.

Experimental work in this area continues to focus on the radiation chemistry of air containing high levels of water vapor at elevated temperatures. To support the data collection activities, an effort has been initiated to model the effect of radiation on the expected air/steam environment. Further consideration has been given to the relationship between repository/waste package design and radiolytic effects.

1. Modeling Effects of Ionizing Radiation in Air-Water Vapor System

A number of studies have used fast reaction kinetic programs (simultaneous differential equation solvers) to model the effect of radiolysis on systems of interest to high-level nuclear waste. These efforts have dealt primarily with aqueous systems and focused on the actinide chemistry associated with release from the waste package during the controlled release period of repository history. They have, however, never been successfully applied to predict the chemistry observed in real systems from first principles (i.e., without going back and adding "missing" reaction steps). An evaluation of this modeling approach to the YMP is being performed.

The expected environment of the waste package in the potential high-level waste (HLW) repository is an air-water vapor gas phase. No data base has been critically assembled for modeling the expected environment in the HLW effort. In the results reported here, we use the data base compiled by Matzing³⁷ in connection with flue gas irradiation studies. The yields (G's) in this data base are given in Table III-6, and the reaction set used, along with the rate constants at 25 °C, are given in Table III-7. The code used in this investigation is designated as WR87, which is a differential solver developed by Klaus H. Schmidt at ANL based on the differential solver developed by A. C. Hindmarsh (Lawrence Livermore National Laboratory).

As a first step in modeling the complex gas phase system of the expected environment (Matzing³⁷ lists over 800 reaction steps), two simplified systems were investigated: (1) pure nitrogen and (2) nitrogen with variable amounts of oxygen with a limited reaction set for oxygen.

Table III-6. Radiolytic Yield (G) and Input Conditions for Modeling^a

Primary Yields	G Value
$N_2 \longrightarrow N_2^*$	0.29
$\longrightarrow N(2d)$	0.885
$\longrightarrow N(2p)$	0.295
$\longrightarrow N(4s)$	1.18
$\longrightarrow N_2^+ + e^-$	2.27
$\longrightarrow N^+ + N + e^-$	0.69
Pure Nitrogen: $[N_2] = 2.16 \times 10^{19}$ molec/cm ³	
Air: $[N_2] = 1.73 \times 10^{19}$ molec/cm ³	
$[O_2] = 4.32 \times 10^{18}$ molec/cm ³	
Dose Rate: 1.17×10^7 eV/cm ³ •s (rad/h)	

^aFrom Ref. 37.

a. Effect of Dose Rate in Pure Nitrogen

An important difference between the conditions used to generate the data in Table III-7 and those expected in the actual waste package environment is that the dose rate for the latter will be several orders of magnitude lower. As we have previously argued,³⁸ the key transient in nitrogen fixation (ammonia or NO_x formation) is atomic nitrogen. Developing an accurate model for the concentration and yield of this species is, therefore, an essential first step in successfully modeling the overall system of interest.

Atomic nitrogen exists as three distinguishable species in the irradiated system. The ground state species, N(4s), is represented simply as N in Table III-7. Two excited states, N(2d) and N(2p), are also formed and contribute to the overall chemistry observed. Their most important reaction is conversion to the ground state atom. Atomic nitrogen is produced directly due to the interaction ionizing radiation and indirectly through reactions 6-11. In the absence of a scavenger for this species, it is reconsumed according to reactions 1-5 and will approach a steady state if enough time is given.

Table III-7. Reactions Used in Modeling Parametric Effects on Nitrogen Yields^a

No.	Reactions	Rate Constant @ 25 °C
1	$N_2^+ + N \longrightarrow N^+ + N_2$	1.000E-11
2 ^b	$N_2^+ + N \longrightarrow N_3^+$	2.160E-10
3 ^b	$N^+ + N \longrightarrow N_2^+$	2.160E-10
4	$N_3^+ + N \longrightarrow N_2^+ + N_2$	4.000E-07
5 ^b	$N + N \longrightarrow N_2$	9.490E-14
6	$N_2^+ + e^- \longrightarrow N + N(d)$	2.200E-07
7	$N^+ + e^- \longrightarrow N$	3.520E-12
8	$N_3^+ + e^- \longrightarrow N_2 + N$	7.050E-07
9	$N(2d) + N_2 \longrightarrow N + N_2$	1.700E-14
10	$N_2^* + N \longrightarrow N_2 + N$	5.000E-11
11	$N(2p) + N_2 \longrightarrow N_2 + N$	2.000E-18
12	$N_2^+ + e^- \longrightarrow N_2$	4.020E-12
13	$N_4^+ + e^- \longrightarrow N_2 + N_2$	2.010E-06
14 ^b	$N_2^+ + N_2 \longrightarrow N_4^+$	1.070E-09
15 ^b	$N^+ + N_2 \longrightarrow N_3^+$	3.870E-10
16	$N_2^* + N_2 \longrightarrow N_2 + N_2$	2.700E-11
17	$N(2p) + O_2 \longrightarrow NO + O$	2.000E-12
18	$N(2d) + O_2 \longrightarrow NO + O$	6.040E-12
19	$N + O_2 \longrightarrow NO + O$	8.980E-17

^aFrom Ref. 37.^bThree-body reactions. The N_2 pressure at 660 torr (80 kPa) is already factored into the rate constant listed.

Figure III-14 shows nitrogen concentration vs. time for dose rates of 100, 1000, and 10,000 rad/h. For a duration of 200 s, a steady-state nitrogen concentration, $[N]_{ss}$, was established at 10,000 rad/h only. This occurred at approximately 125 s, with $[N]_{ss} = 1.2 \times 10^{11}$ atom/cm³. Longer times are needed to reach equilibration at the lower dose rates.

Fig. III-14.

Plot of Nitrogen Concentration vs. Time at Dose Rates of 100, 1000, and 10,000 rad/h in Pure Nitrogen

A plot of nitrogen concentration vs. time is shown in Fig. III-15 for dose rates of 10^4 , 10^5 , 10^7 , and 10^{10} rad/h. In all cases, the nitrogen concentration reached a steady state within 60 s, and the time to steady state decreased with dose rate. The steady-state nitrogen concentration at the different dose rates is given in Table III-8.

Fig. III-15.

Nitrogen Concentration vs. Time at Dose Rates of 10^4 , 10^5 , 10^7 , and 10^{10} rad/h in Pure Nitrogen

Table III-8. Steady-State Concentration of Atomic Nitrogen as Function of Dose Rate

Dose Rate, rad/h	Steady-State N Conc., atom/cm ³
10^4	1.2×10^{11}
10^5	3.9×10^{11}
10^7	3.9×10^{12}
10^{10}	1.2×10^{14}

The yield of N, $G(N)$, varies with time and dose rate. Figure III-16 shows a plot of $G(N)$ vs. time at 10^5 rad/h. Initially, there is an increase in $G(N)$ followed by a slow decrease as the back reaction becomes more favorable. At this dose rate, the maximum $G(N)$, 2.19 atoms/100 eV, is obtained at 0.005 s. In the absence of a scavenger, this is reduced to zero at long times (i.e., a steady-state concentration is reached). The same behavior was observed at 10^2 and 10^{10} rad/h, with the maximum yield being 2.42 and 2.16 atom/100 eV, respectively. In general, the apparent yield available for reaction decreased as the dose rate was increased. The maxima obtained are affected by the time steps taken in the WR87 code and need to be redetermined in the presence of high scavenger concentrations.

b. Relative Concentration of Nitrogenous Intermediates

In the pure nitrogen system, three general types of species contribute to the overall chemistry observed: (1) free radicals such as N, (2) excited states of free radicals and molecules, and (3) ions (nitrogenous cations and electrons). The effect of dose rate on atomic nitrogen was just discussed. The effect of dose rate on the concentration of the last two types of species is discussed in this section. The concentrations as a function of time are listed in Table III-9.

Fig. III-16. Nitrogen Yield as Function of Time for 10^5 rad/h in Pure Nitrogen

Table III-9. Concentration of Various Species Generated as Function of Time for Dose Rate of 10^5 rad/h in Pure Nitrogen

Species	Conc., molecules/cm ³				
	0.6 s	6 s	15 s	30 s	60 s
N	1.8×10^{10}	1.6×10^{11}	3.1×10^{11}	3.8×10^{11}	3.9×10^{11}
N(2d)	4.2×10^4	→			
N(2p)	1.2×10^8	→			
N ₂ [*]	8.6 →				
N ⁺	1.4 →				
N ₂ ⁺	2.2 →				
N ₃ ⁺	1.6×10^6	1.8×10^5	9.4×10^4	7.8×10^4	7.7×10^4
N ₄ ⁺ *	1.6×10^8 →				

*Slow increase in concentration was detectable but only at the fourth significant figure.

Three excited states are listed in Table III-7: N₂^{*}, N(2d), and N(2p). Note that N₂^{*} is not an important transient in the reactions denoted in Table III-7, since it is quenched by molecular or atomic nitrogen, leading to no net change in species concentrations. The excited states of atomic nitrogen are, however, important because they contribute directly to its production. At the pressures of interest to the YMP, steady-state concentrations of all three excited states are established rapidly and are quenched by reaction with molecular nitrogen. The concentrations of these species are directly proportional to the dose rate.

Four nitrogenous ionic species contribute to the overall mechanism: N^+ , N_2^+ , N_3^+ , and N_4^+ . The most important mechanism through which this contribution occurs is ion recombination with the electron. That is, N^+ and N_2^+ react readily with molecular nitrogen to reach a low steady-state concentration. Reaction of N_2^+ with nitrogen to generate N_4^+ leads to the reformation of molecular nitrogen and does not significantly contribute to the overall reaction progress. Reaction of N^+ with nitrogen results in the formation of N_3^+ and, subsequently, atomic nitrogen (reaction 9). The concentration of N^+ is higher initially and decreases with time as the electron and atomic nitrogen concentrations approach steady state.

c. Effect of Oxygen Concentration

The formation of NO_x is the reaction of interest when oxygen interacts with atomic nitrogen. The presence of oxygen will affect the net fixation process by (1) interfering with reactions that lead to the formation of atomic nitrogen and (2) reacting with atomic nitrogen, thereby reducing the tendency for a back reaction. Reactions 17-19 in Table III-7 correspond to the excited states of atomic nitrogen reacted with oxygen. This is an oversimplification of the system and is designed to help establish the extent to which oxygen concentration affects $G(N)$ and the role of oxygen in initial fixation of nitrogen (formation of NO).

Table III-10 lists the concentrations of N and NO as a function of time and oxygen concentration at 10^4 rad/h. At high concentrations of oxygen (e.g., air), nitrogen reaches very rapidly a steady-state concentration that is four orders of magnitude lower than when no oxygen is present due to reaction of atomic nitrogen with oxygen (reactions 17-19). The steady-state concentration of nitrogen increases to 10% of the pure nitrogen value at $[O_2] = 0.01$ mol%.

The concentration of NO as a function of time and oxygen concentration is shown in Fig. III-17. As shown in that figure, NO production is linear with time at oxygen concentration ≥ 0.1 mol%. At lower concentrations, the rate at which NO was generated increased with time and approached a linear rate of production at long times. The $G(NO)$ for air was 2.96 molecules/100 eV, which is higher than $G(N)$ obtained when oxygen was absent. This finding indicates that the oxygen present was scavenging atomic nitrogen which would otherwise react with the nitrogenous ions present.

Fig. III-17. Nitric Oxide Concentration vs. Time for 20 mol% O_2 , 0.1 mol% O_2 , and 0.001 mol% O_2 at 10^4 rad/h

Table III-10. Nitrogen and Nitric Oxide Concentration as a Function of Time and Oxygen Concentration (dose rate of 10^4 rad/h)

System	Species	Conc., molecules/cm ³						
		0.02 s	0.1 s	0.2 s	0.4 s	0.6 s	0.8 s	1.0 s
Pure N ₂ (528 torr)	N	7.5×10^7	3.6×10^8	6.8×10^8	1.3×10^9	1.9×10^9	2.5×10^9	3.1×10^9
	NO	0	→					
20% O ₂ in N ₂	N	6.6×10^6	7.8×10^6	7.9×10^6	→			
	NO	8.0×10^7	4.8×10^8	9.8×10^8				
1% O ₂ in N ₂	N	4.13×10^7	1.0×10^8	1.1×10^8	→			
	NO	4.3×10^7	3.1×10^8	7.0×10^8	1.5×10^9	2.3×10^9	3.1×10^9	3.9×10^9
0.1% O ₂ in N ₂	N	6.3×10^7	2.6×10^8	9.3×10^8	6.6×10^8	8.0×10^8	8.9×10^8	9.5×10^8
	NO	2.1×10^7	1.2×10^8	2.9×10^8	7.0×10^8	1.2×10^9	1.7×10^9	2.3×10^9
0.01% O ₂ in N ₂	N	7.1×10^7	3.1×10^8	5.7×10^8	1.0×10^9	1.5×10^9	1.9×10^9	2.3×10^9
	NO	1.1×10^7	5.9×10^7	1.3×10^8	2.7×10^8	4.3×10^8	6.1×10^8	8.1×10^8

2. Design Issues for Radiolytic Waste Package

We have also considered the relationship between the radiation chemistry of the moist air system and waste package design. Unlike many technical concerns in the YMP, those related to radiolysis can be substantially controlled through modifications in the design of both the repository and waste package. The most important aspects of the design are (1) self-shielding to reduce the gamma flux, (2) the free volume present in the environment near the waste package, and (3) the overall repository temperature, which depends on the spacing and heat loading of the high-level waste packages.

a. Self-Shielding

Self-shielding is primarily accomplished by increasing the thickness of the container wall but could also include other design modifications, such as placing filler material in the container. The idea of lowering the gamma dose rate by increasing the container thickness is not a new one. In a Swedish-designed waste package that was approved for licensing, a 20-cm-thick container was proposed to attenuate the gamma flux and remove radiolysis as a concern. In the Basalt Waste Isolation Project, which was concerned with the high-level waste site formerly considered at Hanford, a thickness of 8.5 cm was proposed. This thickness was also selected on the basis of the need to attenuate the gamma radiation flux outside the container.

The container thickness proposed by the YMP in the past is 1 to 3 cm, with 1 cm as the thickness that is most referenced. This yields an initial dose rate that is as high as 0.1 Mrad/h, corresponding to absorbed doses of 50,000 Mrad during the first 300 yr of repository history. This radiation level would have a significantly detrimental effect on the corrosion of copper-based materials and could also lead to enhanced corrosion of stainless steels. Lowering this dose should be considered in the development of future design concepts, even if radiation-tolerant materials are selected.

Although cost is not considered an important factor in preliminary design considerations, it becomes increasingly important in the latter stages of design. An excessively thick container, therefore, will have a substantial impact on overall costs and may introduce complications related to material weldability. In this context, a design guideline that recognizes the relationship between the radiation chemistry of the expected environment and the most likely degradation mode for the container material needs to be developed. This does not exist for the YMP, and past efforts in this area in other U.S. high-level waste projects have been inadequate.

b. Free Volume Outside the Waste Container

In an unsaturated repository system, the radiolytic products are generated in the free volume or air gap between the container and the host rock. Minimization of the volume of this air gap would proportionally decrease the yield of radiolytic products and reduce the potential for radiolysis to affect container material degradation.

Although the YMP waste package design is not yet firm, in our estimation, the gap between the borehole wall and the emplaced container would probably not exceed 10 cm. This corresponds to a free volume of approximately 1200 L for each spent fuel waste package. Minimization of this volume, to a substantial extent, could greatly reduce the detrimental effects of radiolysis.

c. Overall Repository Temperature

The temperature in the waste package depends, in part, on the thermal loading of each container and the arrangement of the containers in the repository. The Nuclear Waste Technical Review

Board (NWTRB), in its first report to Congress, has proposed that consideration be given to lowering the overall temperatures in the proposed repository. This was based on repository performance considerations.

From the perspective of corrosion in an irradiated air-water vapor system, higher rather than lower temperatures are preferred. This will lower the relative humidity at the surface of the container and, therefore, reduce the likelihood of localized effects, since the radiolytic products generated will not condense on the container surface. It is our estimation that keeping the relative humidity below 15-40% will keep the corrosion low, which will benefit the overall durability of the container.

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

Experiments are continuing to investigate the reaction behavior of Zircaloy clad- UO_2 pellets exposed to dripping EJ-13 water in an oxidizing environment. These tests are being conducted at 90°C and at variable SA/V ratios to simulate potential Yucca Mountain repository conditions. The test matrix includes a total of eight experiments, four of which have been terminated and the remaining four have been in progress for nearly six years. The experiments are designed to develop procedures for tests to be conducted with spent fuel, identify secondary alteration phases, and describe parameters that control the release of uranium from the waste package assembly.

Several different pellet configurations and water injection rates were employed to examine the effects of variable SA/V ratios. Despite the different SA/V ratios used in the tests, most samples appear to have achieved a similar uranium release pattern. Release trends are characterized by a large pulse of uranium occurring between one and two years of reaction time (Fig. III-18). After this interval, the rates of uranium release decrease to a relatively constant level; this trend has continued up to the present six years of reaction time.

Leachate cation analyses were first begun after two years of testing, with reaction patterns indicating a continued depletion of silicon, alkalis, and alkaline earths. Calcium, potassium, and magnesium display the greatest amount of decrease relative to the original EJ-13 leachant. These elements are combining with uranium from the UO_2 pellets to form secondary uranyl mineral phases on the sample surfaces.

Leachate pH values (average, 6.9 ± 0.5) are also decreased relative to the EJ-13 starting solution (pH = 8.2). The acidity of the leachate in contact with the UO_{2+x} surface may play an important, but complex role in the dissolution of uranium from the samples. Decreasing pH in near-neutral solutions may lead to the instability of several uranyl oxide hydrate mineral phases and the promotion of $\text{UO}_2(\text{OH})^+$ or UO_2^{2+} in solution.³⁹ Decreasing pH values may also influence the stability of several uranyl carbonate complexes; however, the importance of these species is rapidly diminished as temperatures approach the 90°C levels of the present experiments.⁴⁰

E. Investigation of Radionuclide Speciation
(S. Okajima and D. T. Reed)

The study of Pu(VI) speciation in environmental systems by spectroscopic methods is being extended to include its complexation behavior and redox stability under conditions anticipated in DOE-relevant groundwaters. These studies utilize the high-sensitivity spectroscopic methods of laser photoacoustic spectroscopy (LPAS) and ultraviolet-visible-infrared absorption spectrometry. This work is

Fig. III-18. Cumulative Release of Uranium from PMP8U Experiments with Teflon Support Stands. All tests use a leachant injection schedule of 0.075 mL of EJ-13 well water every 3.5 days, except for experiments 7 and 8, which use an injection rate of 0.0375 mL every 7 days. Darkened symbols indicate tests that have been terminated. (a) Experiments 1 and 2, 11 UO_2 discs; (b) experiments 3 and 4, crushed UO_2 pellets; (c) experiments 5 and 6, three UO_2 pellets; (d) experiments 7 and 8, three UO_2 pellets.

a continuation of past studies in which both laser-induced fluorescence and LPAS⁴¹⁻⁴⁴ were used to investigate radionuclide speciation in groundwater-relevant systems.

1. Background

There has been recent emphasis within DOE on problems associated with organic, metal ion, and radionuclide waste sites located on DOE lands. The restoration and remediation of these sites is a major issue that will be faced by DOE for several decades. Fundamental research on the migration of these species in geologic media is being conducted within DOE's Office of Energy Research by the Subsurface Science Program.

The speciation of radionuclides is a key consideration in defining their mobility in groundwater systems and establishing their interaction with subsurface materials. Here, "speciation" is used to mean the chemical form (i.e., oxidation state, complexation, and aggregation) of a particular radionuclide in the aqueous medium of interest. Speciation, in this context, has been the subject of many past investigations related to specific waste sites, including the characterization of high-level waste sites within the U.S. and abroad, and the distribution of radionuclides due to atmospheric fallout from nuclear testing.

While great progress has been made in understanding radionuclide speciation in aqueous systems, information is inadequate to predict aqueous speciation of relevant radionuclides over the broad range of geochemical conditions found in soils and groundwater on DOE sites. This situation is further complicated by the frequent occurrence of both anthropogenic and natural organic compounds along with radionuclides in terrestrial DOE disposal sites and associated subsurface environments.

2. Plutonium(VI) Speciation in Real Groundwaters and in the Presence of Organic Contaminants

We are investigating Pu(VI) speciation in increasingly complex systems. This effort has just recently been initiated with only preliminary results available. Increased system complexity is being attained by (1) the systematic addition of organics as complexants that compete with hydrolysis and (2) the addition of Pu(VI) to real groundwaters from DOE sites and/or sites that are being investigated by other researchers in the Subsurface Science Program. Some real-groundwater studies were initiated but the data are still being processed.

Since relatively few data exist for the complexation of Pu(VI) with organic ligands in environmental systems, the question of the general effect of organic ligands on Pu(VI) speciation is being addressed by determining the formation constant for organics that represent the various classes of complexants that exist at DOE sites. Emphasis in these studies is being placed on the redox reaction of plutonium species by organics and the resulting complex formation as it competes with the hydrolytic and inorganic species present. A perturbation to the hydrolytic system was investigated by adding an organic ligand to the hydrolytic system and comparing the spectra obtained. The effect of inorganic ligands on the organic complexes formed was then investigated by (1) placing the organic-radionuclide complex in real groundwater systems and (2) determining the specific contribution of inorganic constituents by including them as a perturbation to the simplified organic-radionuclide system.

The two organic ligands selected were citric acid and acetohydroxamic acid. The former is a tri-carboxylic acid that is representative of organic acids and has also been frequently identified as a contaminant in groundwater on DOE lands. There is no complexation data in the literature on the Pu(VI)-citrate complex. Acetohydroxamic acid is a building block for siderophores (sequestering agents) associated with microbes in subsurface media. It is also structurally similar to amines frequently used as reducing agents for actinides in laboratory applications.

Solutions with 1:1 mole ratios of organic to Pu(VI) were prepared to look for spectroscopic evidence of complexation. Solution pH in these systems was initially 1.5. The initial ultraviolet-visible spectra are shown in Fig. III-19. For citric acid, a red-shifted shoulder at 625 nm is evident, indicating complexation with citrate. A more systematic evaluation of the formation constant for this ligand was therefore initiated. Acetohydroxamic acid, however, rapidly reduced the Pu(VI) to Pu(V), as shown in the initial spectrum given in Fig. III-19 (bottom). The Pu(V), within a matter of a few days, was further reduced to Pu(III). Some additional studies at a higher pH and lower amine concentrations are planned, even though the redox kinetics of this system are too rapid for complexation studies.

Fig. III-19.

Absorption Spectrum of Pu(VI) (a) as Aquo Ion, (b) as Complex with Citrate, and (c) after Addition of Acetohydroxamic Acid. The latter is actually Pu(V).

3. The LPAS Sensitivity to Cr, UO_2^{2+} , and PuO_2^{2+}

In contrast to work that we did before this project, we are now using our LPAS system to generate spectra that are rigorously quantitative rather than simply qualitative. Therefore, it is necessary to establish the general photo-physics of the species of interest and ensure that the acoustic signal intensity obtained is directly proportional to the aqueous concentration of the species of interest. Since this physics is frequently altered by complexation and changes in the speciation of the radionuclide of interest, frequent reassessment of this aspect is needed.

For the reasons just discussed, an important, albeit secondary, objective of our research effort is to evaluate the applicability of this spectroscopic technique to systems of interest to the Subsurface Science Program. This entails studies with new metal/radionuclide ions and ions that we have previously investigated in systems of increasing complexity. There are primarily two steps in this evaluation. First, the laser power dependence of the acoustic signal for each absorption band of interest is established. This determines the laser energy at which signal saturation occurs and defines the laser power range over which we can operate the photoacoustic spectrometer. The second step involves determining the sensitivity of the LPAS system to the aqueous species. This is done by plotting the LPAS signal against the concentration of the absorbing species to establish the linearity of the response.

Since initiation of this project, we have evaluated the sensitivity and signal saturation of the LPAS system for uranyl, plutonyl, and the chromium system. Our most recent emphasis has been on

investigating Cr^{3+} . The results we obtained for 10^{-3} to 10^{-7}M Cr^{3+} in perchlorate medium at room temperature are briefly described here. The absorption spectrum for this species is shown in Fig. III-20. For both absorption maxima in noncomplexing media (580 and 425 nm), the power dependence of the signal obtained was linear with laser energy (see Fig. III-21). The dependence of the signal at 580 nm as a function of Cr^{3+} concentration is shown in Fig. III-22. Our sensitivity to chromium, based on this, was $8 \times 10^{-7}\text{M}$. As is evident in this figure, the reproducibility becomes much poorer as the concentration drops below $1 \times 10^{-6}\text{M}$. The LPAS spectra at low concentrations (compare Fig. III-23) have the appearance of a noisy baseline with no real features. For this particular species, although sensitivity is quite good, the low selectivity, because of the broad-band nature of the absorbance, limits general application of LPAS to chromium detection in more complex systems.

Fig. III-20.

Ultraviolet-Visible Absorption Spectrum
of Cr^{3+} in Perchlorate Media

Fig. III-21. Dependence of LPAS Signal on Laser Energy for Cr^{3+}
in Perchlorate Media at (a) 580 nm and (b) 425 nm

Fig. III-22.

Dependence of LPAS Signal on Cr^{3+}
Concentration in Perchlorate Media at 580 nm

Fig. III-23. Dependence of LPAS Spectra on Wavelength for Cr^{3+} in Perchlorate Media at (a) $1.7 \times 10^{-4} \text{ M}$ and (b) $5 \times 10^{-6} \text{ M}$

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APPENDIX

SAMPLE SURVEY RESULTS

Samples surveyed during this reporting period are listed below, along with a basic outline of the results of the surveys. The aim of the survey is to produce publication-quality micrographs, data on the mechanism of glass reaction, and information on the best samples produced. This information is also used to select specific samples for further detailed analysis.

Task II. Long-Term Testing

DP-20	A good section of several particles of glass bound together with clay layers was produced. A good section showing an extremely thin reaction layer was obtained.
DP-21	A good section showing an extremely thin reaction layer was obtained, and in another case, sections showed several particles of glass bound together with clay layers.
DP-74	Samples were intact. Very little alteration material.
DP-76	Samples were intact. Lattice fringes were visible.
DP-77	Samples were intact. Lattice fringes were visible.
DP-78	Samples were intact. Lattice fringes were visible.
DP-79	Samples were intact with a layer around 20-nm thick. Lattice fringes were visible.

Task IV. Steam Hydration Tests. The layers on these samples were usually very large (several microns). This has resulted in specimen preparation difficulties.

IVE202U-14	Good results were obtained for two of the outer layers. No glass layer interface has been prepared as yet. In some cases, remnants of a precipitate on the outer surface have been observed. No clear precipitate layer interface has been prepared.
IVE202U-14	Some cases produced good sections of the layer parts of the precipitate. However, some distorted interface appeared. Further effort will be required to obtain an undistorted interface in a section.

ATM Samples

ATM-1C567	Heavy chatter, some layer. Relationships between layer and glass unclear.
ATM-1C568	Mostly glass. Shattered layer. Sodium depletion in "grainy" layer.

ATM-1C572 Reaction layers, but relationships between layer and glass unclear. Sodium depletion. Reaction layers clearly visible. Chattered and plucked out. Some reaction layer present.

ATM-1C575 Heavy chatter, thin reaction layer. Layer present, glass plucked out, sodium depletion.

ATM-1C575 Thin outer layer beginning to form.

ATM-1C579 Plucked out. Some shards remain. Clay layer just beginning to form.

ATM-1C579 Extensive disruption. Suggestion of possibly three layers. Glass only. No layer present.

ATM-1C579 The clay layer was around 300-nm thick, with an alteration layer of 1.5 mm. A complete layer structure was not found.

P-150-2 A thin (20-50 nm) reaction layer was observed.

Tektites. The tektites are geologically ancient glasses formed as a result of meteoric impact on the earth's surface.

Tektite Layer and glass interface not intact. Only the layer was visible.

1C2010-04 These sections showed a reaction layer, a second layer where glass had been grossly etched, and possibly a third layer of subtly modified glass. Further work will be required to determine whether this third layer is real or an artifact of sample preparation.

SRL Samples

1099 165/TDS This was a brine reacted sample from SRL.

SRL 165/16 A small region of etched glass - no layers of reaction products. Glass, etched glass, and small clay-like particles distributed on the surface of the etched glass were observed. Some samples were nearly all glass, others had a small region of etched glass.

SRL U 421 A backbone layer was visible: a gap, etched glass, and then fresh glass.

Other Samples. This section shows the results of the sectioning of samples which were not from glass tests.

Mrazek sample An effort to prepare samples of fuel cell electrode has been made. There was extensive chatter and plucking out in these samples. In addition, the diamond knife was scratched during the sectioning. The shards that remained were electron transparent and gave good diffraction and EDS spectra.

U1,U2,U3 These were various uranium oxide samples. They sectioned well to yield samples which will be used to investigate whether the EELS system can provide oxidation state data.

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