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Chemical Technology Division

Annual Technical Report

1995

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Cover Description

1. Extensive glovebox facilities built in CMT for conducting experiments in the electrometallurgical treatment of spent nuclear fuel.
2. Nickel/metal hydride battery modules being evaluated for performance and lifetime under simulated electric-vehicle driving conditions.
3. Nuclear magnetic resonance apparatus used for studying catalytic chemistry in supercritical fluids at high temperatures and pressures.
4. Analytical transmission electron microscope used in the analyses of nuclear waste glass and spent fuel tested under conditions anticipated for high-level waste repository.
5. Testing of catalysts used in the partial-oxidation reforming of hydrocarbon fuel for advanced fuel cells.

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CHEMICAL TECHNOLOGY DIVISION
ANNUAL TECHNICAL REPORT
1995

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MASTER

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**CHEMICAL TECHNOLOGY DIVISION
ANNUAL TECHNICAL REPORT
1995**

ABSTRACT

Highlights of the Chemical Technology (CMT) Division's activities during 1995 are presented. In this period, CMT conducted research and development in the following areas: (1) electrochemical technology, including advanced batteries and fuel cells; (2) methods for treatment of hazardous waste and mixed hazardous/radioactive waste; (3) the reaction of nuclear waste glass and spent fuel under conditions expected for an unsaturated repository; (4) processes for separating and recovering selected elements from waste streams, concentrating low-level radioactive waste streams with advanced evaporator technology, and producing ^{99}Mo from low-enriched uranium; (5) electrometallurgical treatment of different types of spent nuclear fuel in storage at Department of Energy sites; and (6) physical chemistry of selected materials in environments simulating those of fission and fusion energy systems. The Division also conducts basic research in catalytic chemistry associated with molecular energy resources and novel ceramic precursors; materials chemistry of electrified metal/solution interfaces, molecular sieve structures, and diamond thin films; and the geochemical processes involved in mineral/fluid interfaces and in water-rock interactions occurring in active hydrothermal systems. In addition, the Analytical Chemistry Laboratory in CMT provides a broad range of analytical chemistry support services to the technical programs at Argonne National Laboratory (ANL).

SUMMARY

Current programs within CMT are briefly summarized below. These programs are discussed in greater detail in the remainder of the report.

1. *Electrochemical Technology*

The CMT Division is engaged in a variety of activities related to the development of advanced batteries for vehicle propulsion, utility load-leveling, and other energy storage applications. These activities include research, performance and lifetime testing, post-test examinations, modeling, and technology transfer. Work is also being conducted on advanced fuel cells for power plant and transportation applications. The technical management of industrial contracts for the Department of Energy (DOE) is also carried out on the development of fuel cells for transportation applications.

The CMT electrochemical technology program continued to receive support from the U.S. Advanced Battery Consortium (USABC). The USABC is a partnership among DOE, the U.S. automobile industry, and the U.S. electric utility industry and was formed with the objective

of accelerating the development of advanced batteries for electric vehicles. Under Cooperative Research and Development Agreements (CRADAs), the Division has been developing bipolar Li/FeS₂ batteries, developing lithium-polymer electrolyte batteries, and testing advanced batteries in CMT's Analysis and Diagnostics Laboratory.

The CRADA on the Li/FeS₂ system is a collaborative effort with SAFT America to develop a bipolar battery that will meet the long-term goals of the USABC. This battery system has a molten salt electrolyte and operates at temperatures above 375°C. During 1995, the project was redirected toward increasing the performance of full-scale engineering cells, in lieu of cell scaleup to bipolar stacks and modules. Researchers in CMT identified chemically active and inactive additives for the electrodes, as well as additives for the salt electrolyte, that significantly increase the power, active-material utilization, and overcharge tolerance of engineering-scale cells. These performance improvements should result in greater vehicle range under demanding driving profiles, hill climbing, and high-speed driving.

Under a separate CRADA, CMT is working with 3M Corp. and Hydro-Québec to develop lithium-polymer batteries for the USABC. These batteries show promise for meeting the demanding performance requirements of electric vehicles and operate at low temperature (typically 60°C). The battery's flexible, multilaminate structure makes possible very high power and energy. Recent effort has focused on the synthesis and characterization of α -MnO₂ cathodes, which show promise of electrochemical behavior superior to state-of-the-art materials. Button cells made with composite electrodes of α -MnO₂ yielded initial discharge capacities of 180-200 mAh/g. This amount of stored, rechargeable energy translates to a projected full-size battery module having a specific energy of 180 Wh/kg, which is near to the long-term goal of the USABC.

The Analysis and Diagnostics Laboratory in CMT includes a test laboratory to conduct battery evaluations under simulated application conditions. During 1995, performance and life evaluations were conducted for nickel/metal hydride and advanced lead-acid systems fabricated by industrial firms. In addition, nickel/metal hydride cells were subjected to post-test analyses after life evaluations. The information gained from these evaluations and tests provides a measure of the technical progress made by the battery developers and identifies specific areas where changes in design or the materials of construction would improve battery performance.

Several advanced fuel cells are under development at CMT: high-temperature solid oxide and molten carbonate fuel cells for utility applications, and low-temperature solid oxide and polymer electrolyte fuel cells for transportation applications. Also being studied are methods for reforming hydrocarbon fuels to produce the hydrogen needed by the fuel cells.

For the solid oxide fuel cell, we are developing electronically insulating sealants for sealing the edges and gas-supply and exhaust manifolds. These sealants must be compatible with the fuel cell materials under the aggressive fuel-cell operating conditions (including temperatures of 800-1000°C). We are developing a glass-ceramic sealant with the desired properties. Conductivity testing and long-term compatibility testing (up to 100 h at 1000°C) with cell components have confirmed the promise of this composite material. Samples of the high-temperature sealants were sent to several fuel-cell manufacturers for evaluation. Favorable results were reported for both a high-temperature

(1000°C) and an intermediate-temperature (800°C) version of the sealant. Work is also underway to develop technology for the operation of solid oxide fuel cells at 450-500°C directly on methanol and air. Tests of a small cell with a La-Sr-Fe-Co-O cathode and a thin, ceria-based electrolyte indicated that it is capable of achieving the desired performance at 500°C.

In molten carbonate fuel cells, the present NiO cathodes have dissolution/precipitation problems that limit cell lifetime under pressurized operating conditions, and a search is underway for alternative conductive materials that are stable in the high-temperature (650°C) cell environment. Tests of two alternative stable materials (double doped LiFeO_2 and LiCoO_2) showed them to have comparable performance and longer lifetimes than the conventional NiO cathode. In other research, modeling of a new design of molten carbonate fuel cell stack (a multiply manifolded concept) showed it to have potential for significantly increased power density, which was confirmed in cell tests. Corrosion resistance tests were started on the different compositions of stainless steel that could be used as components in the molten carbonate fuel cell.

Research has continued on the polymer electrolyte fuel cell, which operates at low temperature (<100°C). In one option being considered for the transportation application of the polymer electrolyte fuel cell, the hydrogen fuel would be produced by reforming methanol. However, the carbon monoxide in the reformat degrades the platinum catalyst used in the anode. A group of alloy catalysts has been found to improve the CO tolerance of platinum. There is also interest in eliminating the need for a separate fuel reformer with the polymer fuel cell. Currently being evaluated is use of a Pt-Ru electrocatalyst in the anode for the direct oxidation of methanol. Further, a computer model is being developed for optimization of a polymer fuel cell directly fed by liquid methanol fuel.

The low-temperature fuel cells for the transportation application require fuel reformers for converting alcohols to hydrogen. A bench-top [10 kW(e)] methanol reformer based on partial oxidation has been built and is being tested. These tests have demonstrated that the reformer can provide rapid startup and a reformat containing about 50% hydrogen. There was no detectable methane found in the reformat. This reformer is much smaller and lighter than existing technology and represents a radical departure in reformer technology. General Motors Corp. has initiated a new R&D program based on the success of this CMT project. In another project, systems analysis and modeling have shown that the startup of a steam reformer for methanol has a detrimental effect on the efficiency of the overall fuel cell system if the average operating time after each cold start is much less than about 20 min.

The CMT electrochemical technology program continues its support of the DOE Office of Transportation Technologies by reviewing the progress of the industrial contractors and assisting in the startup of new programs. Major ongoing programs managed by CMT include DOE contracts with General Motors, Ford, Chrysler, and fuel-cell component suppliers. Together with Georgetown University, CMT has also been managing a development program for an urban bus powered by phosphoric acid fuel cells. In late 1995, effort was initiated to develop a fuel cell test facility at ANL.

2. Hazardous and Mixed Waste Research

This research includes studies on methods for treating hazardous waste and mixed hazardous/radioactive waste.

One project in this area involves developing aqueous biphasic extraction (ABE) processes for large-scale treatment of contaminated soil, solid radioactive wastes, industrial wastewater, and mineral ores. The biphasic system combines aqueous solutions of polymers [e.g., polyethylene glycol (PEG)] with aqueous salt solutions $[(\text{NH}_4)_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{or } \text{Na}_2\text{CO}_3]$. Fundamental studies of the solution microstructure were conducted by use of small angle neutron scattering (SANS). The SANS measurements indicated that the presence of biphasic-forming salts leads to the formation of PEG aggregates, whose size increases with increasing salt concentration up to the point of biphasic formation, where the PEG-rich phase forms an entangled mesh with loss of polymer chain identity. Also, the SANS measurements, coupled with cloud point data of PEG in H_2O and D_2O , suggest that increased structuring of water by lyotropic ions provides the driving force behind polymer aggregation and phase separation.

A pilot-scale column (2.5-cm ID, 3.6-m height) has been installed to test aqueous biphasic extraction with uranium-contaminated soils. In recent tests, the uranium concentration in the soil was reduced from 500 mg/kg to about 77 mg/kg. In contrast, carbonate leaching alone was able to reduce uranium concentrations only to 146 mg/kg. Another significant finding from the column tests is that ^{234}Th (a daughter of ^{238}U) can be extracted from the soil and recovered in the fraction of solids that partition into the salt-rich phase. A preliminary flowsheet has been developed for uranium removal from soils by use of an ABE system.

Work has continued to investigate the effects of ionizing radiation on gas production in environments similar to those expected in the Waste Isolation Pilot Plant (WIPP), which is DOE's proposed long-term transuranic waste disposal facility. In this area, a new project was initiated to provide experimental data on actinide solubility and oxidation state distribution. These data will be used to test the Actinide Source Term model being developed for the WIPP project. There are no experimental data yet to report.

Efforts were continued to investigate the speciation of radionuclides under conditions relevant to subsurface groundwaters on DOE lands. The current focus is on the environmental chemistry of plutonium-organic mixtures in the presence of microbes. One study involved examining the interactions of the plutonium-nitrilotriacetic acid (NTA) complex with the *Chelatobacter heintzii* microbe, a known degrader of the NTA complexant. Results showed that increased concentrations of plutonium (up to 0.01 mM) resulted in a lower rate of NTA degradation. Also, the NTA bound in the Pu-NTA complex was not directly accessible to the microbe for degradation, and the interaction of ionizing radiation with microbes reduced the bacterium survivability.

During the past year, technical support was provided to the privatization effort for processing the tank wastes at the DOE Hanford site (approximately 1.4×10^8 Ci of radioactivity dispersed in over 230,000 metric tons of process chemicals). This support involved developing specifications for the immobilized low-activity waste products that are to be produced. These

products will be in the form of solidified waste and optional matrix and filler materials enclosed in sealed metal boxes.

A new project was initiated to develop a modeling capability for assessing the performance of proposed waste disposal systems for geological repositories. Although the primary application of this capability is as a regulatory tool in the licensing of waste disposal systems, it can also serve as a tool for identifying and evaluating technical issues that need to be resolved during the identification of waste solidification/stabilization options and during the design of the disposal systems.

3. *Nuclear Waste Programs*

Work is being performed to support programs on the disposal of high-level nuclear waste and spent fuel in the candidate repository site at Yucca Mountain in southwestern Nevada. Several series of laboratory tests are being performed to determine the corrosion behavior of high-level waste glasses upon exposure to liquid water or water vapor. These tests are being conducted to determine the corrosion behavior of various high-level radioactive waste forms under the hydrologically unsaturated conditions anticipated at the proposed Yucca Mountain site and are designed to assist DOE in demonstrating that the Defense Waste Processing Facility (DWPF) and the West Valley Demonstration Project (WVDP) will produce a waste glass product that will perform well in an unsaturated environment typical of what may be expected at Yucca Mountain.

In one series, long-term tests are underway with radioactive sludge-based and simulated nuclear waste glasses having three compositions (SRL 131, 165, and 200). Test conditions include a temperature of 90°C and ratios of glass surface area to water volume (S/V) of 340, 2000, and 20,000 m⁻¹. In tests up to 1456 days at S/V of 340 or 2000 m⁻¹, little difference was found between the radioactive and simulated glasses. However, in tests with the 200-type glass at the S/V of 20,000 m⁻¹, the simulated glass corroded faster than the radioactive counterpart after about one year. This accelerated corrosion rate is associated with the formation of crystalline phases on the glass surface and a slight rise in solution pH.

The fully radioactive SRL 200 glass is also undergoing drip tests with the Unsaturated Test Method. Some of the glass samples were pre-aged by reacting them in a water vapor environment at 200°C before testing. In drip testing up to five years, results show a significant difference in the reaction and subsequent solution composition of the as-cast and aged glass. For example, the solution pH values for the aged glass were consistently in the 11.0 to 11.7 range, while the test solutions for the as-cast glass had pH values of about 8. Differences were also observed in the release to solution of other glass constituents.

In another series, static dissolution tests at S/V of 10 to 20,000 m⁻¹ with actinide-doped SRL glasses have been in progress for up to 2000 days. It was found that lower glass corrosion rates were initially attained for the high S/V (≥ 2000 m⁻¹) because higher concentrations of H₄SiO₄ form and decrease the reaction rate. However, after one year with high S/V, new alteration products form on the glass and increase the reaction rate. While this increase in reaction rate affects the release of radionuclides from the glass, the disposition of each of the radionuclides is controlled by

the chemistry. For example, the sparingly soluble Pu and Am are found primarily fixed on the steel reaction vessel, whereas the U and Np are moderately soluble and are found in solution and associated with colloids. These results indicate the importance of using actual radioactive glasses to determine the long-term behavior of radionuclides rather than relying solely on surrogates. Static dissolution tests are also in progress to assess the dissolution behavior of Environmental Assessment (EA) glass, which is the benchmark for DWPF glasses, and a radioactive glass made from the sludge in Tank 51 at the Savannah River Plant. In addition, long-term drip tests are underway with glasses representative of those that may be produced at DWPF and WVDP.

Several alternatives are being considered for disposal of surplus plutonium resulting from the dismantlement of nuclear weapons and the cleanup of weapons production sites. One method is incorporating plutonium into a glass. An alkali-tin-silicate glass was developed in CMT for this purpose. Testing indicated that this glass melts at a relatively low temperature, dissolves more than 5 wt% of its own weight in plutonium, and resists reaction with water under storage conditions. Continued tests are planned to confirm these promising findings.

Energy loss spectrometry was used to detect trace levels of transuranics and rare earths in the alteration phases of reacted waste glasses from earlier tests. The high-energy M-absorption edge in the electron energy loss spectrum (>3500 eV) indicated the presence of plutonium in a phosphate alteration phase structurally related to apatite, as well as neptunium in the uranyl silicate alteration phase. Energy loss spectrometry will continue to be used to provide new information on the microstructure of reacted nuclear waste materials.

Besides the glass studies, long-term tests with unirradiated UO_2 pellets and spent fuel are in progress to determine radionuclide release rates when these materials are exposed to repository-relevant conditions. Results from drip tests with UO_2 pellets for 10 years indicated a large decrease in the uranium release rate compared with the initial 1- to 2-year period. The majority of the uranium released from the UO_2 samples was sorbed or precipitated on the stainless steel walls of the test vessel and the Teflon support stand. Tests have also been ongoing for three years with two types of spent fuel (ATM-103 and ATM-106) under drip conditions. The release fractions for ^{238}U , ^{137}Cs , ^{90}Sr , ^{129}I , and ^{99}Tc in the leachate were examined to determine if any of them reflected the rate of fuel-matrix dissolution under unsaturated conditions. The results suggest that the release of ^{99}Tc may serve as an indicator of matrix dissolution, though continued tests are needed to confirm this finding.

Other work is being performed to investigate the use of vitrification for treating mixed and low-level wastes. Tests are in progress to develop and analyze glass and glass/ceramic waste forms for remediation of contaminated materials, including waste generated from ANL research activities, storage tank waste from the DOE Hanford site, and incinerator residues. Many of the testing and analytical techniques developed for the high-level waste form are being applied to the low-level waste form so that its long-term durability can be assessed during development efforts.

A project was successfully completed to characterize the radioactive phases in contaminated soil resulting from uranium processing at the DOE Fernald site in Ohio and from weapons testing at the Johnston Atoll in the Pacific Ocean.

4. *Separation Science and Technology*

The Division's work in separation science and technology is concerned with developing methods for treating radioactive, mixed, and hazardous waste. The TRUEX (transuranic extraction) process continues to be developed for removing and concentrating actinides from acidic waste streams contaminated with transuranic elements. An important part of this effort is the development and application of the Generic TRUEX Model (GTM), which allows users to design multistage flowsheets for specific waste streams and estimate the cost and space requirements for implementing a site- and feed-specific TRUEX process. During this past year, the GTM was enhanced for use with two types of high-level waste at Idaho National Engineering Laboratory, sodium-bearing waste and calcined waste.

An effort was begun to evaluate a solvent extraction flowsheet being developed by the ANL Chemistry Division for the pretreatment of nuclear waste before final disposal. A flowsheet for the CSEX-SREX (Cs and Sr extraction) process was evaluated by using the GTM and data from a batch countercurrent test. The evaluation indicated that the CSEX-SREX flowsheet is attractive for removing Cs and Sr from nuclear waste.

A new evaporator system has been fabricated for Oak Ridge National Laboratory by Delta Thermal Systems, Inc. This evaporator is to be used for volume reduction of the low-level radioactive waste in the Melton Valley Storage Tanks. Our involvement in this project included (1) review of the specifications, bids, and design, (2) review of the as-manufactured equipment, (3) aid in oversight of the systems' operability, performance, and startup testing, and (4) completion of tests in a laboratory-scale evaporator. Testing of the new evaporator is scheduled for next year at Oak Ridge.

In support of Argonne's waste management effort, CMT staff are designing a facility for treating waste solutions with a transuranic content of 10^2 - 10^7 nCi per gram and assisting in the installation, testing, and operation of evaporators and concentrators for treating ANL wastewaters.

The Division continues its effort in determining the feasibility of substituting low-enriched uranium (LEU) for the high-enriched uranium (HEU) currently used in the production of ^{99}Mo for medical applications. Two LEU target materials are being studied: uranium-metal foil and uranium silicide. In the past, the Cintichem process has been employed to produce ^{99}Mo from HEU targets consisting of a UO_2 film, and it is now being modified to process LEU targets consisting of uranium foil. Small-scale dissolver tests indicated that the required uranium foil dissolution should be carried out at 92 to 103°C with an initial dissolver solution of 3 M HNO_3 and 2 M H_2SO_4 . A large-scale dissolver constructed of stainless steel was designed, built, and successfully tested. Collaborative work with the University of Illinois has focused on the precipitation of molybdenum from uranium solution containing α -benzoin oxime. Results indicate that the required purity levels for molybdenum can be reached with the LEU-modified Cintichem process. In other work on LEU targets, a two-step basic dissolution method is being developed for silicide targets. Also under investigation is a new basic dissolution method for LEU metal foils. The use of sodium hydroxide with sodium peroxide appears very promising as a means of dissolving a foil target in less than an hour.

Development efforts are underway on the concentration of plutonium-containing liquids generated from decontamination and decommissioning (D&D) activities. Pilot-scale tests were completed to assess the operation of an agitated-film concentrator system for use as a portable concentrator of D&D waste solutions. Two simulated-waste solutions were tested. With both solutions, >90% evaporation rates were achieved without operational problems. In another D&D project, six processes were tested for their ability to decontaminate stainless steel coupons containing simulated contaminants (Am, Pu, Gd, Sr, and Cs). The best decontamination results were achieved with use of either HNO_3 -HF solution or HBF_4 .

5. *Electrometallurgical Technology*

The CMT Division is developing electrometallurgical technology for treating spent nuclear fuels. The process uses electrorefining in molten salt to isolate pure uranium and to dispose of the transuranic (TRU) elements and the fission products. Where appropriate, isotopic dilution of uranium is easily incorporated into the treatment. After electrorefining of the spent fuel, the fuel cladding and the fission products are placed in two stable waste forms (one ceramic, the other metal), which are suitable for disposal in a geologic repository. There are no other high level wastes, and only negligible amounts of low level waste are generated. Past research effort has focused on the use of electrometallurgical technology for the treatment of stainless-steel-clad metal fuel from fast nuclear reactors. Current effort is being directed toward adapting this technology to the wide variety of fuel types that make up the DOE inventory of spent nuclear fuel.

During this last year, development of the electrometallurgical technology continued at the laboratory scale (electrorefiner capable of transporting 300 g of uranium to a solid cathode). In electrorefining of spent nuclear fuel, it is periodically necessary to lower the amount of heat generated in the electrorefiner by removing fission products from the electrolyte. The first step in this process is the removal of the TRU chlorides and the bulk of the uranium chloride from the salt. The "drawdown" operation consists of electrotransport using a Li-Cd anode. Experimental results indicated that about 90% of the U and Pu in the salt can be reduced by the Li-Cd alloy prior to removal of the rare-earth fission products.

After the actinide chloride concentration is reduced in the salt, the active metal fission products will be removed by ion exchange with zeolite A in a column, and the column contents will be disposed of as a ceramic waste form. In experiments to determine the uptake of plutonium by zeolite A, it was shown that when chloride salts containing PuCl_3 are contacted with solid zeolite, plutonium is absorbed into the zeolite. Zeolite pellets containing up to 26 wt% plutonium were produced in this manner.

The behavior of the fission products Se, Te, and Sb is of importance in the electrorefining process. Their behavior was therefore studied in a laboratory-scale electrorefiner. The potential problem is that these elements could form intermetallics that might be soluble in the electrolyte salt. However, the experimental results indicated that Se, Te, and Sb will act as noble metals during electrorefining and, therefore, should remain with the metal waste in the anode basket after fuel dissolution and electrotransport.

New projects were initiated to study the application of electrometallurgical technology to single-pass reactor (SPR) fuel and the uranium-containing salt from the Molten Salt Reactor Experiment (MSRE). The SPR fuel consists of aluminum-clad uranium slugs bonded with an Al-Si braze. Decladding of this fuel using a mechanical device was successfully tested with a mock fuel pin composed of a brass cylinder in an aluminum can. In electrorefining tests with a small test cell, it was shown that uranium can be anodically dissolved in the presence of metallic aluminum. The aluminum remained untouched at voltages that dissolved the uranium. Testing of SPR fuel treatment will be continued in an engineering-scale electrorefiner.

In the MSRE, a uranium fluoride fuel was dissolved in a mixture of molten fluoride salts ($\text{LiF-BeF}_2\text{-ZrF}_4$). A flowsheet has been developed for treating this MSRE salt. The proposed flowsheet has an electrorefining step that recovers uranium and TRU elements from the fluoride melt by transport to a liquid bismuth cathode. Experiments carried out with our present laboratory-scale electrorefiner (suitable only for chloride salts and limited to temperatures below 550°C) indicated that the present design of liquid cathode should be suitable for recovering uranium from the MSRE salt. This electrorefiner is being modified for testing of the proposed flowsheet with a fluoride salt at $600\text{-}700^\circ\text{C}$.

Ceramic and metal waste forms are being developed for handling the waste streams from the electrorefining of spent nuclear fuel. A new Waste Form Development Laboratory has been built for this effort. It houses engineering-scale waste removal and waste form preparation equipment. In this facility, metal waste development is now carried out on a 2.5-kg scale in a large glovebox with a tilt-pour furnace that allows molten salt fluxing of the waste form ingot. A four-stage "pyrocontactor" (high-temperature centrifugal contactor used for extracting actinides and fission products between molten salts and liquid metal alloys) is housed in another glovebox. A third glovebox contains a zeolite column test facility that handles columns up to 5 cm (2 in.) in diameter and 35 cm (14 in.) in length. Grinding and excess salt removal equipment are also located in this glovebox. Drying, blending, and other necessary equipment are in separate locations. Also installed is a hot isostatic press and related can loading, evacuating, and welding equipment, providing a complete facility for fabrication and study of the ceramic waste form.

Development of the ceramic waste form is proceeding on two fronts. First, zeolite column studies, including development of a mathematical model, are beginning to identify conditions for optimal operation and scaleup. The partition of fission products from salt to zeolite has been shown to be quite effective and is reasonably well understood, except for kinetic effects. Second, waste form fabrication is being investigated in parallel with the column work. Fabrication steps tested during this period included the dehydration of zeolite A (which is extremely hydrophilic) and the blending of zeolite A with simulated waste salt. Preparations are underway to test hot isostatic pressing in the fabrication of glass-bonded zeolite.

Development of the metal alloy (stainless steel-zirconium) waste form is at a relatively advanced stage. Scaleup to multi-kilogram ingots has been accomplished, the alloy metallurgy at the microscopic scale is beginning to be understood, the alloys have been demonstrated to be corrosion resistant, and waste-form processing under appropriate fluxes is about to begin.

6. *Treatment of Spent Oxide Fuel*

The electrometallurgical treatment of spent oxide fuels requires that the oxides first be reduced to metals that can be processed in the electrolyzer. A lithium reduction process has been selected to convert the spent oxide fuels into metals. In this process, the spent oxide fuel is reduced by reaction with lithium at 650°C in the presence of molten LiCl.

Work has been initiated on adapting the lithium process for the treatment of core debris from the reactor accident at Three Mile Island unit 2. This debris has been divided into four parts, depending on the position in the core and the degree of damage sustained in the accident. A portion of the fuel, near the bottom of the reactor, was essentially undamaged, and hence its treatment would be similar to that of normal light water reactor fuel. A portion of the fuel in the center of the core, which melted, is a mixture of (U, Zr)O₂ ceramic phases. Surrounding the central region are the upper and lower crust regions, which are mixtures of the ceramic phases and metallic reactor components that melted during the accident. Flowsheets have been developed for the treatment of all four components of the fuel debris.

The reduction salt used in the lithium process must be recycled to minimize the process wastes. This requires removal by electrowinning of the Li₂O that forms in the salt. Oxygen-evolving anodes have been chosen for this process because graphite anodes, which liberate oxygen as CO₂, contaminated the salt with carbon. Most of the experimental work on the electrowinning step of the process has been conducted with a Pt-10% Rh anode. Experiments have demonstrated that the electrowinning and reduction steps could be combined in a single operation. This was accomplished by making the cathode a basket which contains the UO₂ material. During electrolysis the lithium is produced on the UO₂ in the basket, where it reacts and generates Li₂O, which is subsequently decomposed at the anode.

Work has continued on the development of stable anode materials for the replacement of the expensive platinum presently used. Because these anodes liberate oxygen, the search has focused on oxide ceramic materials. On the basis of experimental evidence and material properties, the primary candidates are Fe₃O₄ and lithium-doped NiO. Both of these materials appeared to be stable in the salt system when used in laboratory-scale experiments. Because thermal shock is a serious problem in using ceramic electrodes, a method was developed for improving the thermal shock resistance of these ceramic materials. This method consisted of incorporating MgO shards into the anode during fabrication. The shards interfere with crack propagation and effectively eliminate it.

Engineering-scale experiments have been conducted in a newly completed argon-atmosphere glovebox. The first experiment combined the reduction of TRU-containing simulated fuel with the recovery of the spent salt and reductant by electrowinning. This experiment was run at 650°C using a pure LiCl salt and 10 kg of simulated fuel to proof test the newly installed equipment and to verify the effectiveness of procedures and personnel training. The fuel reduction was successful, and the procedures and training were shown to be satisfactory. However, the electrowinning step did not regenerate the spent salt and reductant because of design and material

deficiencies in the anode that were not apparent during the earlier laboratory-scale testing. A second experiment with a redesigned anode was also unable to regenerate the spent salt.

7. *Applied Physical Chemistry*

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

Measurements and calculational analyses are being performed to provide needed information on the thermophysical properties of metallic nuclear fuel and related waste and plutonium-handling issues. Thermodynamic analysis of phase equilibria in metallic fuel has progressed from the study of binary systems (Pu-U, U-Zr, and Zr-Pu) to the ternary Pu-U-Zr system. Thermodynamic expressions for the Gibbs energy of all phases in the Pu-U-Zr system have been derived. The phase diagram calculated from these optimized thermodynamic expressions is believed to be the best presently available for the Pu-U-Zr system.

Because of disagreements among published phase diagrams for the binary Fe-Zr system, differential thermal analysis and scanning electron microscopy studies have been undertaken with annealed and quenched samples of Fe-Zr. As a result, some important regions of the Fe-Zr phase diagram have been clarified.

Work is in progress to develop a microanalytical facility that will allow simultaneous X-ray diffraction and X-ray fluorescence examination of materials on a microscopic scale. For this facility, a dedicated synchrotron beam line is being prepared at the Center for Advanced Microstructures and Devices, Louisiana State University. To date, equipment suitable for microfluorescence studies has been installed and tested. This work will ultimately lead to a unique facility for the microscopic X-ray examination of a wide range of technologically important systems.

A critical element in the development of the fusion reactor is the blanket for breeding tritium fuel. Lithium ceramics are being considered for the tritium breeder material. The use of vanadium alloy as a structural material with either Li_2O or Li_2TiO_3 as the breeder appears to be attractive for the blanket design because of vanadium's low activation. A thermodynamic evaluation indicated no apparent compatibility problem between the ceramics and vanadium metal or alloys. However, compatibility problems may occur when small amounts of moisture are present in the breeder blanket system. The partial pressure of moisture generated during irradiation of lithium ceramics in a breeder blanket could be very close to that required thermodynamically for oxidation of vanadium to occur. More experimental data are needed on the kinetics of vanadium oxidation. In a separate study, experimental and calculation studies were conducted to determine the interaction of water vapor with lithium zirconate, another candidate ceramic for the breeder blanket. The results indicated very little interaction.

In past experiments, small amounts of hydrogen in the helium purge gas were found to increase tritium release from Li_2O surfaces. A mechanistic model has been developed to better understand the mechanism through which hydrogen enhances tritium release. The model was derived

from *ab initio* calculations concerning hydrogen chemisorption on Li_2O surfaces under typical breeder blanket conditions.

8. Basic Chemistry Research

Fluid Catalysis. This program explores catalytic reaction chemistry of small molecules that serve as precursors in many industrial processes. Precursors of interest include those of the C_1 chemical industry, e.g., CO , CO_2 , and CH_4 ; the ammonia synthesis precursors, H_2 and N_2 ; and the ceramic precursors, e.g., $(\text{CH}_3)_4\text{Si}$ and $(\text{CH}_3)_3\text{B}$. The efficient utilization of these molecules is potentially of great economic significance; however, in many cases the required conversion chemistry is difficult to achieve by present strategies. Recent CMT research in fluid catalysis encompasses the catalytic chemistry of (1) phosphine-modified catalysts for the hydroformylation of olefins in supercritical fluids and (2) the extremely robust polyfluorophthalocyanine catalysts for hydrocarbon activation processes. Also, in a new initiative associated with the advancement of the lithium-polymer battery, ion transport mechanisms are being investigated by use of the *in situ* spectroscopic techniques developed for the catalysis research.

The homogeneous catalysis research investigates the chemistry associated with the conversion of some key industrial catalytic processes to more energy efficient and more environmentally benign supercritical ones. The various processes designed to achieve the commercial hydroformylation of olefins comprise the largest scale use of homogeneous catalysts and are the subject of the current efforts in this area. Olefin hydroformylation catalysts based on dicobaltoctacarbonyl can be modified with tertiary phosphines to achieve greater stability and higher selectivity. These catalysts are used commercially to produce agricultural chemicals, industrial solvents, and detergents from olefinic feedstocks. Using *in situ* nuclear magnetic resonance (NMR) measurements that for the first time encompass the high pressure and high temperature conditions of the process, CMT researchers have determined the thermodynamics associated with a key salt-forming step for the phosphine-modified catalyst.

Research in hydrocarbon activation is aimed at achieving the controlled catalytic functionalization of methane and other hydrocarbons via activation of their C-H bonds. Current research focuses on developing catalytic strategies based on the extremely robust phthalocyanine nucleus. Metallophthalocyanines can be tuned (with fluorocarbon substituents) to achieve very high electrophilicities, which, combined with their high thermal and oxidative stabilities, offer some attractive possibilities for achieving homogeneous catalytic oxidations, oxidative couplings, substitution reactions, and other potentially beneficial hydrocarbon conversion processes. During the past year, CMT researchers synthesized and characterized several new organometallic complexes based on this polyfluorinated phthalocyanine strategy.

The goal of the new advanced battery project is to investigate the mechanism(s) of ion transport in lithium-polymer electrolyte battery materials by using *in situ* magnetic resonance imaging developed in the catalysis research. During the past year, the toroid cavity NMR device developed in CMT was shown to have ample sensitivity and distance resolution in measuring concentration profiles within a working electrochemical cell. By this means, the triflate (CF_3SO_3^-) concentration gradient was measured both before and after electrodepositing lithium from samples

of $\text{CF}_3\text{SO}_3\text{Li}$ in polyethylene oxide. Typically, the electrolyte was depleted over a distance range of approximately 450 μm following the electrodeposition of 5 μmol of lithium. These direct observations of the salt depletion zones allow, for the first time, the measurement of lithium ion transference numbers by a nondestructive *in situ* spectroscopic technique.

Materials Chemistry. The Division's materials chemistry program continues to explore corrosion and interfacial science and entails (1) development and implementation of *in situ* synchrotron X-ray methods to elucidate issues related to metal/aqueous solution interfaces, (2) theoretical studies of materials that emphasize both method development and application, and (3) integration of theoretical studies with laboratory experiments.

In the first area, synchrotron far- and mid-infrared spectroscopy has been used to study film formation on copper in alkaline media. The spectra reveal that Cu_2O gives way to a hydrated CuO species as the potential is increased from -0.05 to $+0.3$ V. Specular and diffuse X-ray scattering have been employed to examine the morphology of electrodeposited copper in NaHCO_3 solution. In contrast to earlier investigations of copper pitting, it was found that the deposition of copper occurs in a random, uncorrelated manner. X-ray absorption fine structure measurements were conducted to study the anodic corrosion films on nickel in alkaline solution. The results have provided information on the bond lengths and coordination numbers for the $\text{Ni}(\text{OH})_2$ and NiOOH species that exist in discharge deposits on nickel electrode surfaces. Finally, *in situ* X-ray reflectivity studies of incipient pore formation on luminescent silicon surfaces have revealed a unique funnel-shaped pore structure near the electrolyte/silicon interface. Porous silicon is potentially a very important material because of its luminescence at visible frequencies.

Considerable progress has been made in the ongoing investigation of the temperature dependence of the electron transfer reaction sequence involving $\text{Cu}^{2+}/\text{Cu}^+/\text{Cu}^0$, an important cathodic reaction occurring during stress corrosion cracking in light water reactors. The $\text{Cu}^{2+}/\text{Cu}^+$ reaction rate was found to increase 100-fold on going from 25 to 200°C, with no evidence of a temperature-dependent transfer coefficient. In parallel theoretical studies, the interaction distances and electronic coupling effects for bromine- and fluorine-bridged transition structures were found to be similar to water-bridged transition structures. This finding indicates that the coupling strength is determined by copper-copper distance parameters, not the chemical nature of the bridging ligand.

The materials-chemistry theoretical research has centered around the further development and implementation of Gaussian-2 (G-2) theory for the accurate calculation of thermochemical data. The theory itself has been extended to include the third-row elements Ga through Kr and has been successfully tested on over 40 reactions involving these elements. In another study, calculations were undertaken to study the interaction of a single H_2O molecule with the acid site (Z) in a zeolite cluster embodiment resembling ZSM-5. The results revealed that $\text{Z}\cdots\text{H}_3\text{O}^+$ is a transition state that facilitates H^+ transfer from one acid site to another. Also calculated was the potential energy surface for addition of C_2 to a hydrogen-terminated diamond surface. These results suggested little or no energy barrier to this particular mechanism of diamond growth.

Geochemistry. The geochemistry research program is focused on chemical processes occurring at mineral-fluid interfaces that play a crucial role in geochemical transport processes.

Several *in situ* X-ray scattering studies of the calcite-fluid interface are underway by CMT researchers at the National Synchrotron Light Source. One such study has demonstrated a new and accurate approach for measuring *in situ* precipitation rates and growth mechanisms in calcite-water systems. This approach involves X-ray standing wave measurements at the calcite-water interface. Results from these measurements indicated that lead preferentially adsorbs onto the calcite surface from aqueous solution.

9. *Analytical Chemistry Laboratory*

The Analytical Chemistry Laboratory (ACL) is administratively within CMT, its principal client, but collaborates as a full-cost-recovery service center with many technical divisions and programs at ANL. In addition, the ACL conducts research in analytical chemistry and provides analytical services for governmental, educational, and industrial organizations.

During the past year, ACL was involved in a diverse array of activities, including the following: analyses in support of the ANL project to develop an electrometallurgical process for treating spent nuclear fuel; development of a Fourier transform infrared spectrometer for continuously monitoring the organic effluents of waste incinerators; characterization of products from recycling of automobile shredder "fluff"; analyses in support of the development of high-temperature superconductors; development and implementation of a comprehensive program to provide DOE with information on data quality from laboratories analyzing environmental and waste samples; determination of platinum content in the inner-ear fluid of guinea pigs treated with the antitumor drug cisplatin and the antibiotic gentamycin; testing of a wide variety of oils for their ability to remove radon from air; development of automated methods for real-time analysis of chemical sensor data from environmental samples; sample preparation and development of analytical methods in support of the Waste Isolation Pilot Plant; development of methods for reducing the secondary waste and turnaround time for analyses of environmental and mixed-waste samples; characterization of used laboratory exhaust filters for disposal; development of a method for determining whether waste oil contains hazardous metals; development of a method for separating mercury from americium in radioactive waste analysis; analyses of environmental samples (water, soils, sediments, filters, etc.) and waste samples for ANL and other DOE sites; determination of the reaction products from molten sodium and chlorinated hydrocarbons; determination of uranium in dissolver solutions for production of ^{99}Mo from low-enriched uranium; development of analytical procedures that will be used to characterize the lability of transition metals in textile mill wastewater; research in support of a U.S. Army program on stand-off detection of chemical plumes; analysis of U.S. currency bills for the presence of cocaine; analysis of samples from a pilot-scale test of a process to recycle aluminum salt cake; and determination of arsenic species in soil samples from the Rocky Mountain Arsenal.

I. ELECTROCHEMICAL TECHNOLOGY

The ANL Electrochemical Technology Program in CMT undertakes (1) in-house research, development, testing, post-test analysis, and technical evaluation studies of advanced battery and fuel cell systems and (2) support research, technology transfer, and technical management for industrial R&D contracts to develop these systems. During the past year, in-house battery R&D has focused on lithium/iron disulfide and lithium-polymer systems. The testing, evaluation, and post-test analysis of a variety of advanced batteries (e.g., lead-acid, nickel/metal hydride, lithium/iron sulfide, sodium/sulfur) fabricated by industrial firms are performed in CMT's Analysis and Diagnostics Laboratory. Potential uses of these battery systems include vehicle propulsion, utility load-leveling, and other energy storage applications. In-house R&D is also being conducted on fuel cells, where the CMT Division continues to be the premier DOE laboratory in fuel-cell technology development. We are engaged in R&D on the solid oxide fuel cell and the molten carbonate fuel cell, which are targeted for utility applications, and we are becoming increasingly involved with R&D on the polymer electrolyte fuel cell for transportation applications.

A. *Battery Research and Development*

1. U.S. Advanced Battery Consortium

The U.S. Advanced Battery Consortium (USABC) was formed in 1991 to accelerate the development and commercialization of advanced battery technologies for electric vehicle applications. The USABC is a government-industry partnership among the U.S. Department of Energy, the U.S. automobile industry (Chrysler Corp., Ford Motor Co., and General Motors Corp.), and the U.S. electric utility industry through the Electric Power Research Institute. In 1995, CMT continued its advanced battery R&D activities under three Cooperative Research and Development Agreements (CRADAs) with the USABC. One of the CRADAs involves the independent evaluation of advanced batteries in CMT's Analysis and Diagnostic Laboratory and technical support to the USABC's Technical Advisory Committee (see Sec. I.B). The other two CRADAs involve the development of advanced batteries to meet the long-term performance targets of the USABC. These targets include performance of 300 Wh/L and 600 W/L, lifetime of >1000 cycles, and cost of <\$100/kWh. One CRADA is to work with Saft America to develop bipolar Li-alloy/FeS₂ batteries (Sec. I.A.2), while the other CRADA is to work with 3M Corp. and Hydro-Québec's to develop lithium-polymer batteries (Sec. I.A.3).

2. Bipolar Lithium/Iron Sulfide System

Under this CRADA, CMT researchers have been working with Saft America on the development of the bipolar lithium/iron sulfide battery system. The basic design for this system employs disk-shaped cells assembled into a series-connected stack in which adjacent cells share a common current collector, denoted the bipolar plate.¹ The cells employ lithium-alloy negative electrodes, dense FeS₂ positive electrodes, molten LiCl-LiBr-KBr electrolyte, and MgO powder

¹ G. L. Henriksen, "Lithium Sulfide Batteries," in *Handbook of Batteries*, 2nd ed., Chapter 39 (1995).

separators. Cells are sealed around their periphery by using a chalcogenide-based ceramic-to-metal seal. Final assembly is accomplished with metal-to-metal peripheral welds. Cells are operated in the temperature range of 375-450°C to maintain the electrolyte in a molten state. Cylindrical bipolar stacks will be housed inside thermal enclosures to form integrated modules that are engineered to maintain acceptable operating temperatures throughout. Vacuum multifoil thermal enclosures are being developed to achieve low thermal losses in lightweight, low-volume packages.

During 1995, the project was redirected toward increasing the performance of full-scale engineering cells, in lieu of cell scaleup to bipolar stacks and integrated modules. The Electrochemical Technology Program in CMT chose to pursue cell-level performance enhancements through the development of electrode and electrolyte additives. It successfully identified chemically active and inactive electrode additives, as well as electrolyte salt additives, that significantly increase the power, active material utilization, and overcharge tolerance of engineering-scale cells. Figure I-1 illustrates the cell-level performance improvements demonstrated in full-size electric-vehicle cells fabricated with the new additives. The increased specific energy at high power levels corresponds to greater vehicle range under demanding driving profiles, hill climbing, and high-speed driving. No further development work on this battery system is planned for 1996.

Fig. I-1. Specific Energy vs. Power for Li-Al/FeS₂ Cells with and without Newly Developed Additives

3. Lithium-Polymer Electrolyte System

a. Project Overview

The lithium-polymer battery (LPB) is a lightweight, high-energy system that can operate at moderate temperatures (typically 60°C). With a polymer electrolyte, this all-solid-state battery can be manufactured by using high-speed film-laminate technology. The battery's low weight translates into high specific energy. The Li/Li⁺ redox reaction (negative electrode, -3.0 V)

gives the battery its high power. As mentioned earlier, the LPB for electric-vehicle applications is being developed under a CRADA with 3M and Hydro-Québec. Under the CRADA, ANL provides technical support related to all aspects of battery development, including component, cell, and battery testing and characterization; post-test diagnostic analysis; electrochemical cell modeling and battery design; and electrode materials evaluation and optimization.

Component and cell testing and characterization are carried out with electrochemical techniques such as DC methods (e.g., constant-current or -power discharge, peak power measurements, and current interruptions), Dynamic Stress Tests, and AC impedance methods. The purpose of these scientific investigations is to develop a better understanding of the cell characteristics and to provide the critical information needed to focus the future research efforts on improving and optimizing the LPB performance.

In the post-test studies, the initial focus has been the destructive evaluation of fractured and/or peeled cells by electron and optical microscopy. The investigation of state-of-the-art nondestructive techniques has also begun. These newer methods may provide us with a better means for conducting post-test analysis. The overall goal is to precisely determine the factors affecting the electrochemical performance of cells.

Electrochemical modeling studies of LPB cells have been initiated to elucidate the phenomena occurring in the cells during operation. The time constant for the lithium transport in the lithium polymer cells is relatively large when compared to liquid-electrolyte battery systems. This is a result of the slow ionic transport in the polymer electrolyte and the cathode active material. The long time constant; the fact that the cathode is a composite structure of carbon, electrolyte, and active material; and the thin cell geometry make it difficult to separate and examine these phenomena experimentally.

The overall development effort includes design of electric-vehicle batteries for three levels of technical development. The Mark I design involves a battery assembled of cylindrical wound cells having compositions and fabrication procedures which are essentially those for the cells now being tested at ANL's and Hydro-Québec's laboratories. The Mark II design will involve the use of cells to be developed in the next phase of this program. These future cells will have higher specific energy and a prismatic shape to improve the packing density of the battery assembly. The Mark III design will be based on improvements in the cell expected in the longer range.

b. System Description

Rechargeable lithium batteries with either metallic lithium or lithium carbon as the anode use transition metal oxides as the cathode, for example, oxides of V, Mn, Co, or Ni. These transition metal oxide electrodes have host structures into which lithium can be inserted during electrochemical discharge; the insertion of lithium is accompanied by a concomitant reduction of the transition metal ion. The reverse process occurs during charge.

The structural stability of a host electrode to the repeated insertion and extraction of lithium is undoubtedly one of the key properties for ensuring that a lithium cell operates

with good electrochemical efficiency. In transition metal oxides, both stability of the oxygen-ion array and minimum displacements of the transition metal cations in the host are required to ensure good reversibility. For example, structures with a cubic-close-packed oxygen array are more stable to lithium insertion/extraction than hexagonal-close-packed structures, which tend to shear on lithium insertion in response to electrostatic interactions between the incoming lithium ions and transition metal cations in face-shared octahedral sites. The shear process is often accompanied by displacements of the transition metal cations within the oxygen lattice. These structural modifications tend to degrade the integrity of the insertion electrode, particularly when it is subjected to repeated charge and discharge.

Structures of transition metal oxide insertion electrodes are, in general, not tolerant to overcharge or overdischarge. It is, therefore, critically important to carefully control fabrication conditions so that the composition of the electrode corresponds to that of the most stable host structure of the metal oxide system. Furthermore, cell operating conditions, such as voltage limits and current drain, must be carefully controlled to ensure that the structural integrity of the electrodes is not destroyed on cycling.

c. Progress

Materials development within the LPB project is focused on the synthesis and characterization of metal oxide electrodes that offer superior electrochemical behavior to state-of-the-art materials. A specific intercalation transition metal oxide for LPBs examined in this laboratory is alpha manganese dioxide ($\alpha\text{-MnO}_2 \cdot n\text{H}_2\text{O}$, where $n = 0.2\text{-}0.3$). The $\alpha\text{-MnO}_2$ phase is made up of a unique arrangement of corner- and edge-shared MnO_6 octahedra. A perspective drawing of the structure is depicted in Fig. I-2. The octahedra are situated such that the material contains 2×2 tunnels arranged in an infinite chain down the c-axis of the tetragonal unit cell of the framework structure.

During cathode discharge, lithium cations are inserted preferentially into the 2×2 tunnels of the structure, and the valence state of manganese in the material is reduced from four

Fig. I-2.

Perspective Drawing of $\alpha\text{-MnO}_2$ Structure
as Viewed Down the c-Axis of Tetragonal
Unit Cell

to three. The unit-cell volume for the discharged product expands only 7.1%. There is no distortion along the c-axis of the unit cell. Consequently, the discharged (i.e., lithiated) α -MnO₂ material demonstrates an inherent resistance against crystallographic distortion. Resistance to crystallographic distortion is important because it promotes good, repetitive insertion/extraction of lithium cations.

The discharge voltage profile has an average of 2.7 V vs. metallic lithium. It is indicative of an intercalation process. Button cells made with composite electrodes of α -MnO₂ yield initial discharge capacities of 180-200 mAh/g. This amount of stored, rechargeable energy translates to a projected full-size battery module that would possess a specific energy of 180 Wh/kg, which is near to the long-term target of the USABC.

Current efforts are focused on both applied and basic research. Specific attention is being paid to processing conditions, chemical composition, and structure. Structure analyses of electrode materials at various states of charge and discharge are undertaken with neutron-diffraction data from ANL's Intense Pulsed Neutron Source and with X-ray diffraction data. Such studies provide valuable information about the stability of the host structures to lithium insertion/extraction, the mechanisms by which the cells operate, and most important, clues about how to modify the structures to enhance their electrochemical properties.

B. *Analysis and Diagnostics Laboratory*

The Analysis and Diagnostics Laboratory was established at ANL to study advanced battery systems for applications such as electric vehicles and utility load-leveling. The facilities include a test laboratory to conduct battery experimental evaluations under simulated application conditions and a post-test analysis laboratory to determine, in a protected atmosphere if needed, component compositional changes and failure mechanisms. Evaluations are performed for DOE, USABC, Electric Power Research Institute (EPRI), and others to provide insight into those factors that limit the performance and life of advanced battery systems. The results of these evaluations help identify the most-promising R&D approaches for overcoming these limitations and provide battery users, developers, and program managers with a measure of the progress being made in battery R&D programs, a comparison of battery technologies, and basic data for modeling.

As mentioned in Sec. I.A.1, performance and life evaluations were continued under a CRADA with the USABC. These evaluations included (1) nickel/metal hydride (Ni/MH) cells and multi-cell modules from a USABC contract with Ovonic Battery Co. (OBC) and (2) nickel electrodes from Yardney Technical Products. In 1995, our activities under this CRADA were expanded to include the development of a thermal model for the Ovonic nickel/metal hydride technology and evaluation of advanced nickel/metal hydride cells and modules. The results of these tests and analyses will be released by the USABC at a later date.

Advanced lead-acid battery technologies are being evaluated by ANL for EPRI. These evaluations include batteries manufactured by Electrosources, Inc. (ELSI); Yuasa/Exide, Inc.; Optima Batteries, Inc.; Hawker Energy Products, Inc.; and GNB Industrial Battery Co. The performance and life data gathered from testing these technologies will be made available through an EPRI report in early 1996.

A number of Ovonic Ni/MH cells have undergone post-test analysis after life evaluation in the Analysis and Diagnostics Laboratory. This activity is being sponsored by the USABC to assist Ovonic in identifying and focusing their resources on critical issues facing their technology. Many of the activities performed at ANL have been a joint effort between ANL and Ovonic.

Besides battery testing and evaluation, ANL has supported the USABC by having representatives on the Technical Advisory Committee, the Ni/MH Working Group, the Nickel-Based Component Cost Reduction Group, and the Battery Testing Procedures Tiger Team. Argonne has also participated in battery readiness review meetings for the USABC. These meetings are held prior to the initiation of unique battery tests to verify proper test planning, instrumentation, and data acquisition.

In 1996, performance and life evaluations, as well as post-test analyses, will be continued on cells, modules, and batteries for the USABC and EPRI.

C. *Fuel Cell Research and Development*

Fuel cell technology could become a significant part of the economy in the U.S. and other countries. Following the U.S. lead, Japan has mounted a major initiative to develop the molten carbonate fuel cell (MCFC) for dispersed utility applications. Europe is concentrating its efforts on development of the solid oxide fuel cell (SOFC) and has reoriented the R&D programs in some of its national laboratories from nuclear to SOFC technology. Furthermore, Daimler-Benz AG in Germany and Toyota Motor Corp. in Japan have begun major programs to explore the potential of the polymer electrolyte fuel cell (PEFC) for automobiles.

Being a pioneer in fuel cell technology since the 1970s, the CMT Division continues to conduct R&D on the SOFC and MCFC, which are targeted for utility applications, and on the PEFC for transportation applications.

All fuel cells convert the chemical energy of fuels such as hydrogen, methane, methanol, ethanol, or other hydrogen-bearing compounds to electricity with little or no pollution and with greater efficiency than heat engines. For efficient operation of the low-temperature PEFC, hydrogen must be used as the fuel, and fuels other than hydrogen need to be converted to hydrogen in separate reforming reactions. For this fuel conversion, we have developed an innovative new reformer based on partial oxidation instead of the conventional steam-reforming reaction. This reformer is much smaller than existing technology, which is an important asset for transportation applications. We are also investigating the mechanisms of direct electrochemical oxidation of methanol in a PEFC to improve performance of such direct methanol fuel cells.

1. Solid Oxide Fuel Cells

The present SOFC technology has an oxide-ion-conducting electrolyte material, yttria-stabilized zirconia; a cathode of strontium-doped lanthanum manganite; an anode of nickel/yttria-stabilized zirconia; and a cell interconnect of strontium-doped lanthanum chromite. The typical cell operating temperature is 800-1000°C. Recent research in CMT has focused on developing (1) improved sealing materials for sealing the edges and gas-supply and exhaust

manifolds in solid oxide fuel cells and stacks, (2) electrolyte and electrode materials that allow operation at lower temperatures (400-800°C), and (3) anode/electrolyte bilayers with improved mechanical strength.

a. Sealant Materials

The materials under development in this project are glass-ceramic sealants for high-temperature SOFC applications, based on a five-component oxide system: SrO, La₂O₃, Al₂O₃, SiO₂, and B₂O₃. Basic requirements for the sealant are good bonding to the materials of interest, chemical stability in the operating environment, and low gas permeability. For high-temperature operation, the sealant must also have a thermal expansion which is reasonably close to that of the other materials involved and must have some compliance, or softness, to allow for some mismatch between the components to be joined. Past work has shown that these materials have excellent bonding characteristics to SOFC materials and low gas permeabilities.² It has also been shown that the expansion coefficients of these sealants can be matched to SOFC materials, and that compositions can be chosen which provide mechanical compliance through viscous flow at the operating temperature.

While some testing had previously been done on the chemical stability of the candidate sealants in fuel cell environments, additional long-term testing was performed this year. These tests focused on the sealant compatibility with the electrolyte and interconnect, since these are the two materials which must be joined by an air-tight seal. The porous anode and cathode materials, while uninvolved in sealing, may also come into contact with the sealant; thus, some tests were also performed on these materials.

Of the four cell components, only the electrolyte showed significant changes after long-term exposure to the sealant in reducing conditions. The growth of large, yttria-depleted crystals within the electrolyte was seen at the sealant interface when the materials were held in moist hydrogen at 1000°C for 500 h. However, the bond between the materials remained intact and mechanically sound, and changes in the electrolyte were restricted to the immediate area of the sealant interface. Thus, this reaction may not be detrimental to fuel cell performance, as the sealant will not be present in an electrochemically active area of the electrolyte.

A study was also performed on the interactions between the sealant and interconnect under a voltage gradient. In these tests, a one-volt bias was applied between two interconnect samples with a layer of the sealant in between, simulating stack operating conditions. The conductivity of the sealant was monitored with reference electrodes while these structures were held at 1000°C. We found that the conductivity decreased initially and then rose very gradually for the next 100 h. This increase still left the sealant more than sufficiently insulating for manifolding applications. In post-test analysis using scanning electron microscopy (SEM), we found that the positive-biased sealant interface was high in Sr and Ca, and that some chromium had migrated into the sealant. This finding may account for the gradual increase in conductivity toward the end of the

² J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, pp. 22-23 (1995).

test. The sealant/interconnect interface most likely contains strontium borate crystals, which were predicted to be present by thermodynamic calculations. Also, SEM analysis revealed that faceted crystals high in strontium occur at the sealant/interconnect interface.

Long-term stability tests (up to 100 h at 1000°C) of the five-component sealant in humidified hydrogen were also performed. Some weight loss and porosity formation in the sealant were detected in these tests. Using a cold finger trap in the furnace exhaust, we collected some crystalline material during these tests, which under X-ray diffraction analysis proved to be boric acid. Compositions of the sealant system that would possess reduced boric acid volatility were predicted by thermodynamic calculation, and many compositions were produced and tested. A low-silica composition was found to have greatly improved boric acid stability, and the temperature-viscosity behavior and thermal expansion were found to remain suitable for SOFC use.

In an effort to create a data base for the prediction of thermal expansion and other properties, several series of sealants were produced and tested. Linear regression analysis was performed on the expansion data to determine first-order effects from the variations in composition. For simplicity, pure strontia was used as the y-intercept (plot of weight percent additive vs. thermal expansion), since strontia has the highest thermal expansion of the five pure components ($12.5 \times 10^{-6}/^{\circ}\text{C}$). Lanthana, alumina, silica, and boria weight percentages were used as independent variables. The best fit gave an intercept of $13 \times 10^{-6}/^{\circ}\text{C}$ for pure strontia, while effects for addition of the other oxides were all slightly negative, with coefficients (per percent of additive) ranging from $-0.01 \times 10^{-6}/^{\circ}\text{C}$ for lanthana to $-0.04 \times 10^{-6}/^{\circ}\text{C}$ for alumina. Higher-order analyses failed to significantly improve the fit. The most convenient way to control the thermal expansion, then, is the strontia content, while the next most effective change is the alumina percentage. Other considerations, such as the viscosity behavior, determine which substitutions should be made.

Two glass manufacturers were contracted to produce commercial quantities of promising sealants. Both vendors had difficulty in maintaining the proper composition of the material when large batch processing was used. The two-phase nature of the molten sealant, after several tries, was judged to be unsuitable for production by standard downspout casting. Tilt pouring was also tried by the second manufacturer, but this method caused composition variations owing to large-scale segregation of crystalline material within the melt. These problems remain unsolved at present, and production is limited to small batches.

Samples of our high-temperature sealants were sent to several fuel cell manufacturers for evaluation. Favorable results were reported for both a high-temperature (1000°C) and an intermediate-temperature (800°C) version of the sealant. We will continue to work with these fuel cell developers to address their needs and concerns. Scaled-up production remains the main difficulty to further utilization of these sealants, as demand for large test quantities continues.

b. Solid Oxide Fuel Cell Fueled Directly by Methanol

The purpose of this effort is to develop technology for the operation of SOFCs at 450-500°C directly on methanol and air. At these low temperatures, the stack sealing problem would be eased, cell lifetimes could be increased, and the SOFC technology would be more attractive for transportation applications. Last year, we reported the development of a ceria-gadolinia

electrolyte with higher conductivity than the conventional zirconia electrolyte. Currently, we are developing cathodes with higher performance than conventional ones to be used at 500°C and below. Effort this past year has focused on cathode material development, electrolyte thickness reduction, confirmation of equivalent performance whether the SOFC is fueled by methanol or hydrogen, and improvements in the overall cell performance.

Tests with the ceria-based SOFC showed that near theoretical open-circuit voltage (OCV) of 0.98 V could be obtained at 500°C in air/H₂. The OCV declines with increasing temperature due to the onset of electronic conductivity in the electrolyte. Further, we showed that the fuel cell performed nearly the same with methanol as it did with hydrogen at 500, 600, and 700°C. Since then, our effort has been aimed at improving the cell performance in air/hydrogen. Performance was increased by improvements in the cathode material composition, resulting in lower cathode overpotentials, and by reductions of the electrolyte thickness, resulting in lower voltage drop due to ohmic resistance.

While the La_{1-x}Sr_xMnO₃ cathode exhibits good performance in high temperature (>800°C) SOFCs, it is not adequate for operation at low temperatures because of the significantly higher polarization. Therefore, use of other cathode materials, such as those from the La-Sr-Fe-Co-O system, were investigated. One of the compositions (Cathode A) was found to give good performance at 700 and 600°C. At 500°C, it exhibited a cathodic polarization resistance between 5.1 and 6.9 W·cm². The performance data in Fig. I-3 were obtained with Cathode A. While this performance is better than that of any material reported in the literature, it is inadequate for our application. Therefore, further work is being conducted to reduce the cathode polarization resistance to a target value of 1 W·cm² or less.

The electrolytes used in our fuel cell tests were prepared by pressing and sintering pellets that were about 2.5 cm in diameter. The pellets were fired at 1600°C for several hours. Initially, the pellet thickness was over 1.1 mm. Cells made with these electrolytes exhibited high OCV (0.98 V) at 500°C. To decrease the ohmic drop across the electrolyte, thinner electrolytes

Fig. I-3.

Performance of a Ceria-Based Solid Oxide Fuel Cell in Air/H₂. Cell has La-Sr-Fe-Co-O cathode and thin electrolyte.

(0.4-0.7 mm) were made and tested in cells. These electrolytes resulted in lower ohmic resistance but also lower OCV (0.8-0.85 V) at 500°C, as seen in Fig. I-3. Post-test microstructural examinations indicated that the decreased OCV was due to a small amount of interconnected porosity within the electrolyte. Part of our future effort will be devoted to improving electrolyte densification. This can be achieved by improving the morphology of the starting electrolyte powder. A smaller effort will be directed to increasing the OCV by decreasing the electronic conductivity. It appears from our research efforts that the desired SOFC performance at 500°C is achievable by continued improvements in the cathode material and decreases in electrolyte thickness.

c. Improved Anode Substrates for Thin Electrolytes

The objective of this effort is to improve the mechanical and electrochemical properties of anode/electrolyte bilayers so that they become reliable components for full-scale cells. With large cell areas, current fabrication techniques are limited in their ability to provide defect-free cells that have adequate mechanical properties yet still maintain good electrochemical properties. A key problem, then, is to improve mechanical strength and cell uniformity without compromising layer thicknesses or interfacial morphology. With regard to cell stacking, two difficulties are the high electrical resistance of bond layers adjoining the interconnect and the lack of mechanical compliance in current planar stack designs. These conditions lead to large voltage losses and/or poor mechanical integrity of stacks. In this effort, alternative fabrication methods and component microstructures are used to build and test planar stacks designed to overcome the above problems.

The need for both good mechanical and good electrochemical properties has usually led to SOFC (anode/electrolyte/cathode) designs which seriously compromise one property or the other. If a free-standing electrolyte is used as the substrate for electrode deposition, poor mechanical properties can result even when the electrolyte is 300- μm thick or greater, the thicknesses at which the conductivity is severely compromised. Designs with thin electrolytes on porous supporting anodes also may have poor mechanical properties, caused by the low volume fraction of zirconia in the electrolyte and the reduction of the nickel oxide anode during processing (both of these conditions create a lack of strong particle-particle bonding). In both thin and thick electrolyte designs, interfacial morphology may be impossible to optimize if the wrong ceramic processing techniques are used to join the materials, leading to high electrode overpotentials or poor structural strength of the assembly.

At CMT, we are pursuing the approach of supporting a thin electrolyte with a strong composite anode. The anode has been fabricated to optimize both the gas permeability and electrical conductivity, while at the same time offering far superior strength to conventional porous cermet anodes. In this way both the conductivity and the mechanical properties of the trilayer (anode/electrolyte/cathode) are uncompromised. We also make use of ceramic fabrication techniques that allow better control over the interfacial morphology, leading to superior electrochemical performance.

We have experimented with optimized pore formers to provide our anode with excellent gas permeability at low volume fractions of porosity. In addition, we have the capability to fabricate conductive nickel paths along these same pore networks. This capability allows us to create conductive materials at nickel volume fractions far below the percolation limit. With these

reductions in the necessary volume of nickel and pore phases, we can produce an anode that contains up to 80 vol% of a dense zirconia "backbone," with no large crack-like defects, leading to very strong components. The high volume of zirconia also makes these anodes excellent supports for zirconia electrolytes, in terms of matched thermal expansion and mechanical properties.

By using a novel technique, we have screen-printed a very thin (20 μm) zirconia electrolyte onto an anode; this technique yields an anode/electrolyte bilayer which has optimized electrochemical properties. A porous interlayer is used to grade the properties from the dense electrolyte to the anode. Within this interlayer, the microstructure is controlled to provide a large gas/electrolyte/electrode interface area for electrode reactions. The components are co-fired and shrinkages are matched. Work continues on the electrochemical characterization of these cells.

2. Molten Carbonate Fuel Cells

The present molten carbonate fuel cell (MCFC) has a porous nickel anode, a porous nickel oxide cathode, a liquid electrolyte of lithium and potassium carbonates retained by a porous ceramic matrix of LiAlO_2 , and an appropriate metal separator. The operating temperature is 650°C . Our MCFC program is engaged in efforts to (1) develop alternative cathodes that will extend the lifetime of the fuel cell, (2) develop a simpler design based on a multiply manifolded concept that has the potential for significantly reduced cost and increased power density, and (3) improve the corrosion resistance of the metal components of the fuel cell. The goals are extended life, increased power density, and decreased cost for the MCFC.

a. Improved Cathodes

The cathode presently being employed by commercial MCFC developers is lithiated nickel oxide ($\text{Li}_{0.05}\text{Ni}_{0.95}\text{O}$). Because of its low resistivity ($0.1\ \Omega\cdot\text{cm}$ at 650°C), this cathode has high power capabilities. However, its life is limited by transport toward the nickel anode, particularly in pressurized cells. The transport mechanism is dissolution of NiO and migration of Ni^{2+} through the molten alkali-carbonate electrolyte toward the anode followed by deposition of the Ni^{2+} as metallic nickel in the electrolyte- LiAlO_2 matrix.^{3,4} This deposition degrades the cell performance by forming an electronically conducting bridge between the cathode and anode. The NiO solubility and, consequently, the rate of nickel transport increases linearly with increasing CO_2 pressure, as indicated by the reaction $\text{NiO} + \text{CO}_2 \rightarrow \text{Ni}^{2+} + \text{CO}_3^{2-}$.

We have been investigating the use of lithium cobaltate (LiCoO_2) and lithium ferrate (LiFeO_2) cathodes as substitutes for the NiO cathode. These alternative cathodes originated in early work at ANL.⁵ A recent study⁶ has revealed a potential problem with the LiCoO_2 cathode.

³ W. M. Vogel, L. J. Bregoli, H. R. Kung, and S. W. Smith, "Stability of NiO Cathodes in Molten Carbonate Fuel Cells," Proc. of the 166th Electrochem. Soc. Meeting, Vol. 84-12, pp. 443-451 (1984).

⁴ H. R. Kunz and J. W. Pandolfo, J. Electrochem. Soc. **139**, 1549-1556 (1992).

⁵ G. H. Kucera, J. L. Smith, and J. W. Sim, "Electronically Conductive Ceramics for High Temperature Oxidizing Environments," U.S. Patent No. 4,564,567 (January 14, 1986).

⁶ K. Ota, Y. Takeishi, S. Shibata, H. Yoshitake, and N. Kamiya, J. Electrochem. Soc. **142**, 3322-3326 (1995).

In this study, the cobalt solubility was shown to increase with increasing CO₂ pressure because of the reaction $\text{LiCoO}_2 + 1.5 \text{CO}_2 \rightarrow \text{Co}^{2+} + \text{CO}_3^{2-} + 0.5 \text{Li}_2\text{CO}_3 + 0.25 \text{O}_2$. The high CO₂ pressure dependence of this reaction (CO₂ pressure raised to the 1.5 power) leads to a LiCoO₂ solubility approaching that of NiO in pressurized cells. In addition, thermodynamic calculations indicated that cobalt, like nickel, will be transported from the cathode as a metal. In our cell tests to date (up to 2000 h), we have found the cobalt in small islands distributed throughout the electrolyte between the cathode and anode. Thus, because of its increased solubility at higher CO₂ pressures, the LiCoO₂ cathode may not be an acceptable substitute for the NiO cathode in pressurized cells. Although a reaction similar to the above reaction for LiCoO₂ dissolution can be written for LiFeO₂ dissolution, the subsequent reduction of Fe²⁺ to metallic iron (either in the electrolyte or at the anode) is not expected to occur because of thermodynamic considerations. Consequently, the LiFeO₂ cathode may have a greater life expectancy than either of the other two cathodes, particularly in pressurized cells.

The problem that has prevented adoption of the LiFeO₂ cathode by commercial MCFC developers to date has been its poor performance in MCFCs because of its high resistivity (300 Ω·cm at 650°C). As discussed in the previous report,⁷ double doping has decreased the resistivity of LiFeO₂ to 0.3 Ω·cm at 650°C and has produced a LiFeO₂ cathode capable of high power density in MCFCs. Both the doubly doped LiFeO₂ cathode and the LiCoO₂ cathode (resistivity of 1 Ω·cm at 650°C) now exhibit power capabilities equivalent to that of the lithiated NiO cathode.

During 1995, we evaluated the relative lifetimes of the NiO, LiCoO₂, and LiFeO₂ cathodes, using mixtures of CO₂ and O₂ as the cathode gas (this simulated pressurized operation with air-CO₂ mixtures). Results from cathode tests at 160 mA/cm² are shown in Fig. I-4. The data suggest a superior life for the LiCoO₂ cathode in spite of the high solubility of LiCoO₂ at high CO₂ pressures. These and other data collected to date suggest that both LiCoO₂ and LiFeO₂ may have a longer life than the NiO cathode, but additional study is needed.

During 1995, optimization studies of the doubly doped LiFeO₂ cathode were continued. The solubilities of the two dopants in LiFeO₂ were measured, and the data are being used to modify the composition of the doubly doped LiFeO₂. Dopant migration was evaluated by post-test examinations of cells. These results are also being employed to modify the composition of the doubly doped LiFeO₂. In 1996, the lifetime comparisons of the three cathode materials and the optimization of the doubly doped LiFeO₂ cathode will be continued.

b. Multiply Manifoldd Fuel Cells

During the past year, we continued modeling and experimental studies of the multiply manifolded MCFC concept.⁸ This design employs a number of gas inlet and exit manifolds distributed across the plane of the MCFC. Because the gas flow is two dimensional, existing one-dimensional models do not adequately describe its features. Therefore, we developed a

⁷ J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, pp. 28-32 (1995).

⁸ G. B. Kirby Meacham, "Multiple Manifold Fuel Cell," U.S. Patent No. 5,268,241 (December 7, 1993).

Fig. I-4. Potential vs. Operating Time for Cathodes in MCFCs (area, 25 cm²) Operated at 160 mA/cm² and 650°C (D. D. = double doped)

two-dimensional model that relies on first principles and employs overpotential relationships reported by Wilemski et al.⁹ In 1994, the model was used to calculate the performance of various flow configurations in rectangular MCFC designs.⁷ In 1995, the studies were extended to cylindrical designs because they are best suited to pressurized MCFC operation within a cylindrical pressure vessel. These studies emphasized maximizing the power density of the MCFC while minimizing the peak temperature within the MCFC (the lowest possible peak temperature is desired for extended life).

As depicted in Fig. I-5, four cylindrical (Cyl) and four square (Sq) flow patterns were modeled. The calculated peak temperatures vs. specific powers for six of these flow patterns (and the standard cathode oxidant of 70% air-30% CO₂) are shown in Fig. I-6. The two flows not plotted in Fig. I-6 ("Corner Sq" and "AO-CO Cyl") are nearly identical to two that are plotted ("Cross Sq" and "Co-Flow Sq," respectively). From this study, the best designs are those that employ co-flow of the anode and cathode gases. The best of these, because it yields the lowest peak temperature for any specific power, is the cylindrical design with both the anode and cathode gases flowing inward (AI-CI Cyl). These modeling results have been incorporated in a novel cylindrical design for a high-power-density MCFC that integrates a fuel reformer and heat exchangers within the MCFC pressure vessel.

⁹ G. Wilemski, N. H. Kemp, and A. Gelb, *Molten Carbonate Fuel Cell Performance Model Update: Final Report*, Department of Energy Report DOE/FE/15078-1742 (1985).

Fig. I-5. Types of Rectangular and Cylindrical Flows Modeled for MCFC (AI = anode in, AO = anode out, CI = cathode in, CO = cathode out)

Fig. I-6. Calculated Peak Temperature vs. Specific Power for MCFC Flow Patterns in Fig. I-5

During 1995, we tested nine MCFCs (square design, 25×25 cm) employing the multiply manifolded concept. The cell design included flat metal current collectors and dimpling of the nickel anodes and NiO cathodes to form the gas flow channels. The volumetric power density of the best of these MCFCs exceeded 300 kW/m^3 at 200 mA/cm^2 , which is a factor of ten higher than previous MCFC designs. During 1996, studies of both the rectangular and cylindrical versions of this concept will be continued.

c. Pitting Corrosion of Stainless Steels in the Fuel Cell

Stainless steels are generally employed to form the current collectors, gas-distribution channels, and wet seals of the MCFC. The wet seals are formed between the molten-carbonate electrolyte and the steel, and are used to form gas-tight seals at the periphery of the MCFC and around the gas manifolds that deliver fuel and oxidant to the MCFC anode and cathode, respectively. Type 316 stainless steel is one of the candidate materials for these applications. Others are Type 316L (a low-carbon version of Type 316) and Type 310S (also a low-carbon stainless steel). These steels are generally clad with nickel on the anode side of the MCFC to minimize anode-side corrosion; they are also aluminized in the wet-seal areas of the MCFC to minimize both corrosion and shunting currents between the anode and cathode.

Severe pitting corrosion of Type 316 stainless steel exposed to a combination of simulated exhaust anode gas (CO_2 -3% H_2 -20% H_2O) and molten Li_2CO_3 - K_2CO_3 electrolyte was described in the previous report.⁷ Similar pitting has since been seen on the same stainless steel exposed to a combination of cathode gas (either dry or humidified) and the Li_2CO_3 - K_2CO_3 electrolyte. The pits were found by polishing off the duplex corrosion layer and examining the cleaned surface beneath it with an optical microscope.

During 1995, corrosion tests were conducted with Type 316L and 310S stainless steels in $(\text{Li},\text{K})_2\text{CO}_3$ and $(\text{Li},\text{Na})_2\text{CO}_3$ melts. Test conditions included exposure to the electrode exhaust gases and a potential (-800 mV vs. an O_2 - CO_2 reference electrode) where pitting had been previously observed with the Type 316 stainless steel. No pitting of the steels was seen after 4 days. This suggests that the initial concentration of carbon in the steel plays a role in pitting corrosion.

Severe pitting (millimeter-sized pits) was found when nickel-clad stainless steel was exposed to exhaust anode gas and the $(\text{Li},\text{K})_2\text{CO}_3$ melt at -800 mV vs. an O_2 - CO_2 reference electrode. A sheet of Type 200 nickel similarly exposed showed no pitting after 4 days. Additional study is needed to confirm these observations, since no such pitting of nickel-clad steel has been seen by the commercial MCFC developers.

The corrosion of aluminized Type 310S stainless steel in the $(\text{Li},\text{K})_2\text{CO}_3$ melt was examined at a potential of -800 mV vs. an O_2 - CO_2 reference electrode under exhaust anode gas conditions. After a 4-day exposure, the aluminum formed a tenacious oxide scale. Some interdiffusion of aluminum into the steel was also observed, possibly forming an intermetallic phase. No pitting was detectable in these samples; the tenacious scale and the interdiffusion may have interfered with detection of pitting.

Future work in this area will include testing of the nickel-clad and aluminized stainless steels under a variety of potentials and gas mixtures. Pulse methods will also be employed to promote pit formation for further study of the corrosion mechanism. In addition, samples of stainless steels from long-term cell tests are being supplied by two commercial developers. These samples will be tested and examined for evidence of pitting and other corrosion phenomena.

3. Polymer Electrolyte Fuel Cells

The polymer electrolyte fuel cell is based on a proton-conducting solid polymer membrane and uses platinum or platinum alloy electrocatalysts for hydrogen oxidation at the anode and oxygen reduction at the cathode. In some designs, the catalysts are supported on carbon and may use specially prepared carbon cloth or carbon paper to facilitate reactant gas diffusion to the electrodes and to act as a current collector. The polymer electrolyte membrane used in most laboratories is Nafion, developed by DuPont Corp. for the chlor-alkali process, although developmental membranes by DuPont and other manufacturers are also being investigated. The goal of our program is to advance the technology of power systems based on PEFCs so that they meet the performance demands of transportation applications. Advantages of these fuel cells include a high power density and a low operating temperature (typically, below 100°C).

a. Carbon Monoxide-Tolerant Anode Electrocatalysts

In one option being considered for the transportation application of the PEFC, the hydrogen fuel would be produced by the reforming of methanol. The reforming of carbonaceous on-board fuels produces substantial quantities of carbon dioxide and small amounts of carbon monoxide in the reformat. This carbon monoxide, even at a parts-per-million level, acts as a poison for the platinum catalyst in the anode and substantially reduces cell performance. We are investigating alternative anode electrocatalysts that are not easily poisoned by the carbon monoxide.

We have tested a group of alloy catalysts in which the alloying element is oxidized at a lower potential than the platinum-group metals, forms a stable oxide at the pH of the Nafion electrolyte, and has a lower work function than platinum. The objective is to enhance the CO tolerance of the hydrogen oxidation catalyst (e.g., platinum) by alloying it with an element that would decrease the strength of the CO-platinum bond or would provide an oxidant to remove CO adsorbed on the platinum. We fabricated membrane-electrode assemblies (MEAs) from these catalysts, using a slight modification of the thin-film technique. The MEA polarization tests showed that the alloying element improved the CO tolerance of platinum: a 100 mV improvement in cell voltage (at 400 mA/cm²) when operating on fuel contaminated with 155 ppm of carbon monoxide. This improvement is believed to result from a shift in the onset potential for CO oxidation rather than from a decrease in the coverage of platinum by the CO. Efforts are underway to enhance this CO tolerance by varying the catalyst composition, catalyst support, and the catalyst particle size.

b. Anode Electrocatalysts for Direct Methanol Fuel Cell

There is a great deal of interest in developing a direct methanol PEFC that would eliminate the need for a separate reformer. At present, however, such fuel cells suffer from high anodic polarizations, methanol crossover across the electrolyte membrane, and a reduced cell voltage due to the mixed potential at the cathode. We are conducting an electrochemical, X-ray diffraction (XRD), and X-ray absorption investigation (using the Synchrotron National Light Source at Brookhaven National Laboratory) of Pt-Ru, currently the best catalyst for the electrochemical oxidation of methanol. The objective of these studies is to determine the correlation, if any, between the effect of ruthenium on platinum's electronic structure and the effect of ruthenium in enhancing platinum's activity for electrochemically oxidizing methanol. Supported and unsupported Pt-Ru

catalysts were characterized by using XRD, extended X-ray absorption fine structure (EXAFS), and X-ray absorption near edge structure (XANES) techniques. The XRD data showed that the ruthenium was alloyed with the platinum, but that there was no change in the Pt-Pt bond length. However, alloying with ruthenium did decrease the d-band electronic occupancy of platinum.

The catalysts are currently being evaluated in a single cell using liquid methanol as the fuel and oxygen gas as the oxidant at ambient pressure and temperatures above 80°C. For these tests, MEAs with Pt-Ru anodes (3-10 mg/cm²), Pt/C cathodes (1-4 mg/cm²), and Nafion 117 electrolyte were fabricated by the ink technique. The open-circuit potential was approximately 0.7 V, and the current density at short circuit was greater than 1000 mA/cm². This is comparable to the best such performance reported in the literature. In these tests, however, the catalyst utilization is rather low. Also, any electronic properties affected by the methanol oxidation would not be readily apparent in the X-ray studies since EXAFS and XANES are averaging techniques. A specially designed *in situ* X-ray absorption fuel cell is being modified to obtain high catalyst utilization and enhanced X-ray data. To date, this cell has shown an open-circuit potential of 0.7 V and a current density of 500 mA/cm² at short circuit, a somewhat lower performance than in the *ex situ* cells but considerably improved over our first *in situ* cells. Additional experiments are planned at Brookhaven with the improved cell to elucidate the effects of catalyst structural and electronic properties on fuel cell performance.

c. Optimization and Modeling of Direct Methanol Fuel Cells

The goal of this work is to develop and verify a computer model for a polymer electrolyte fuel cell fed by liquid methanol fuel. A preliminary computer program has been devised to track fuel and oxidant utilizations as a function of the cell current. Another program has been developed to permit sizing of the cell block heaters for a given set of operating parameters. These parameters include the temperatures and pressures for the fuel and air inlets, the flow rate and molar concentration of the methanol feed, the flow rate of the oxygen gas, the cell block geometry, and the cell current. The program relates the applied current to the electrochemical consumption of methanol and oxygen, as well as the utilization of each feed given the flow rates and methanol solution concentration. The heat loss is calculated by taking into consideration the temperature differential between the inlet streams (methanol and oxygen) and the cell block, the vaporization of methanol (crossover) and water produced at the cathode into the exiting oxygen gas stream, and free convection at the surfaces of the cell block. For our cell test fixture, the largest single heat requirement was calculated to be due to the temperature difference between the methanol feed and the fuel cell; the heater power requirement can be reduced by heating the methanol feed before its introduction into the cell, especially for cells at high test temperatures. The second highest loss of heat was calculated to be caused by the vaporization of methanol and water on the cathode side. These results are consistent with the observed cell temperatures and block heater power consumption. The computer program is being expanded to model mass transport effects through the cell and, ultimately, to predict the performance of a given fuel cell.

4. Fuel Reforming Technology

The objective of this work is to develop catalytic partial-oxidation reformers for the generation of hydrogen from methanol and hydrocarbon fuels for use with the low-temperature fuel

cells (polymer electrolyte and phosphoric acid fuel cells) being developed for transportation applications. Such fuel processors need to be compact, lightweight, efficient, and capable of rapid startup and good dynamic response to changing fuel processing rates. We are addressing the reforming of methanol and hydrocarbons separately.

a. Partial-Oxidation Reforming of Methanol

For the partial-oxidation reforming of methanol, a copper-zinc-oxide catalyst has been selected to facilitate the desired reactions and suppress the formation of the unwanted methane and carbon monoxide. The desired partial oxidation of methanol can be expressed by the idealized general reaction,

where x is the oxygen/methanol molar ratio (for $x \leq 0.5$), and the oxygen is derived from air. The carbon monoxide produced can be converted via the water-gas shift reaction to produce carbon dioxide and additional hydrogen,

The net reaction can then be represented as,

Therefore, for a given value of x , the minimum amount of water required to ensure complete conversion of all the carbon in the fuel to carbon dioxide is $(1-2x)$. As x increases, the required amount of water and the hydrogen yield decrease. The enthalpy change for the overall reaction, Eq. 3, also depends on x . At $x=0$, the reaction is strongly endothermic. As x increases, the reaction becomes less endothermic. At a certain value of x , the reaction becomes thermally neutral. Above that ratio of oxygen to methanol, the reaction becomes exothermic. Depending on the feed and product temperatures and on the amount of excess water in the feed, Eq. 3 is thermally neutral for $x \approx 0.27$. This is the preferred reformer operating condition since at this value of x there is little or no requirement for heat transfer into or out of the reaction process.

We have built a bench-scale [nominal 10 kW(e)] reformer, shown schematically in Fig. I-7. In this reformer, the methanol-water mixture is injected as a fine spray through a nozzle at the top of the reactor. The spray is allowed to mix with air and flows past an electrically heated igniter coil. The partially vaporized mixture flows into the catalyst bed, where it reacts to produce a hydrogen-rich reformat product. The product gas is analyzed by on-line non-dispersive infrared analyzers for CO , CO_2 , and CH_4 ; an on-line thermal conductivity analyzer for H_2 ; and a gas chromatograph for these and other chemical species.

Fig. I-7.

Schematic of Catalytic Partial-Oxidation Reformer for Methanol

The composition of the reformer product gas obtained during eight test runs conducted over several days is shown in Fig. I-8. The methanol feed rates were varied from 30 to 55 mL/min; the air flow was controlled to obtain an oxygen-to-methanol molar ratio of 0.27 to 0.31; and the water feed rate was held constant at 10 mL/min (which is greater than, or equal to, the minimum amount of water required for the reaction in Eq. 3). A product composition of 50% H₂, 20% CO₂, and less than 5% CO (on a dry basis) was typical. There was no detectable methane found in the reformat. Reformer testing is continuing to evaluate the present catalyst and some other commercial catalysts to determine their performance with respect to activity, product distribution, and catalyst life

Fig. I-8. Composition (dry basis) of Product Gas from Methanol Partial-Oxidation Reformer

b. Partial-Oxidation Reforming of Hydrocarbon Fuels

The overall partial oxidation of hydrocarbons to generate hydrogen may be represented by the following unbalanced reaction (using pentane as a surrogate):

The CO may subsequently be reacted with water *in situ* or *ex situ* to produce additional hydrogen via the reaction in Eq. 2.

The objective of our present work is to identify promising catalysts that offer the desired product distribution, i.e., high H_2 , low CO, and very little, if any, CH_4 , at a reasonably low temperature and high activity. Analogous to the catalyst selection for methanol reforming, catalysts which are used to form a material may be useful in breaking it down. The classic method to produce hydrocarbons from mixtures of H_2 and CO is Fischer-Tropsch synthesis (FTS). Thus, FTS catalysts (or variants) may potentially be active for the partial-oxidation reforming of hydrocarbons.

We have begun preliminary experiments with pentane because this hydrocarbon is volatile enough to make handling easy in the experimental apparatus and yet incorporates the important chemistry needed to reform the heavier hydrocarbons, such as those present in gasoline and other distillate fuels. For these tests, pentane vapor was mixed with water and oxygen and fed to a microreactor loaded with a small amount of the test catalyst material and placed in a furnace. The product gas was analyzed by a gas chromatograph for H_2 , CO, CO_2 , CH_4 , and other chemical species.

We found that the product distribution is sensitive to the promoter used in the catalyst. For example, one FTS catalyst in its usual composition produced 3% H_2 , 15% CO, 41% CO_2 , and 41% H_2O . With a more acidic, electron-deficient promoter, the product gas composition changed to 19% H_2 , 3% CO, 67% CO_2 , 1% CH_4 , and 10% H_2O . Clearly, this product gas mixture does not contain enough hydrogen for a practical application. However, the results illustrate the promise of the approach. Work is continuing to evaluate different promoters for the FTS catalysts, as well as different catalytic schemes.

c. Systems Modeling and Analysis

In this activity, we develop computer simulations of various fuel cell system designs for transportation applications. The different types of simulations range from complex but idealized spreadsheet models to much more rigorous simulations that use the GPS systems analysis code.¹⁰ The major activity is related to the design and analysis of PEFC systems and components; other fuel cell systems, such as the phosphoric acid fuel cell (PAFC), are also modeled, as needed.

In methanol-fueled PEFC and PAFC systems, the methanol is first converted to a hydrogen-rich gas, which is then fed to the fuel cell stack (except in the case of the direct methanol fuel cell). Steam reforming of methanol is presently used in the PAFC buses developed by H-Power Corp. and in the PEFC light-duty vehicles being developed by General Motors. The dynamic response of the fuel reformer is likely to govern the dynamic performance of the complete fuel cell system. We have, therefore, begun developing a dynamic model of a generic steam reformer

¹⁰ R. Kumar, R. Ahluwalia, H. K. Geyer, and M. Krumpelt, "Modeling of Polymer Electrolyte Fuel Cell Systems," Proc. of the Annual Automotive Technology Development Contractors' Coordination Meeting, SAE Publication P-278, Society of Automotive Engineers, Warrendale, PA, pp. 409-417 (May 1994).

for methanol. This model has been used to simulate three types of operations: constant temperature, steady state, and startup and transient conditions. Some of the results obtained from the reformer simulation are summarized below.

We found that methanol conversion on the copper-zinc-oxide catalysts is affected most strongly by the reaction temperature, while the amount of catalyst has a much weaker influence. The conversion of methanol is $\geq 99\%$ at temperatures $\geq 250^\circ\text{C}$ and a molar ratio of water to methanol of ≥ 1.0 . In a steam reformer the heat of reaction is provided by hot combustion gases. Therefore, significant variations occur in the catalyst temperature in the radial and axial directions. Since the reaction kinetics are strongly affected by temperature, these temperature variations have a pronounced effect on methanol conversion. Further, although the reformer is essentially a heat exchanger, the reaction energies greatly affect the temperature distribution, compared to that obtained for a simple heat exchanger; without the endothermic reaction, no heat exchange occurs beyond about 50% of the catalyst bed length, while with the reaction, heat transfer occurs over the entire bed length. Methanol conversion is also strongly influenced by the ratio of the flow rate of the hot combustion gas to the flow rate of the process gas; a ratio greater than three is needed to obtain nearly 100% conversion. Finally, small-diameter (e.g., 1-cm-dia) catalyst tubes have a smaller radial temperature difference than large-diameter (e.g., 5-cm-dia) catalyst tubes and provide more complete conversion of methanol.

Simulating startup from room temperature, we found that with 5-cm-dia catalyst tubes, a significant warmup time of over 900 s was required to reach 50% methanol conversion, and that even after 1500 s, only 81% of the feed methanol was converted. In 2-cm-dia catalyst tubes, methanol conversion reached 50% in 520 s and 96% in 1500 s. Increasing the flow rate and the temperature of the hot gas can reduce the time needed for startup. If the hot gas temperature is increased from 625 to 925°C , and its flow rate increased to three times that needed at normal operating conditions, methanol conversion of greater than 80% can be obtained in approximately 3 min. However, the methanol consumed during startup (to provide the energy required to raise the reformer to the operating temperature) decreases the fuel cell system's efficiency over the driving cycle. This decrease in efficiency is a function of the operating time (at full load) after each startup, as shown in Fig. I-9; for example, an operating time of 300 s after startup reduces the system's efficiency to about 70% of its normal efficiency. The dynamic steam reformer model will be incorporated into the PEFC system model to examine the dynamic performance of the total system on one or more standardized driving cycles.

Fig. I-9.

Overall System Efficiency vs. Operating Time after Startup for Steam Reformer with 2-cm Catalyst Tubes

5. Technical Management

The CMT Division, through the ANL Electrochemical Technology Program, provides support to the DOE Office of Transportation Technologies. This support is in the form of technical management of R&D contracts with industrial developers of fuel cells and related components. In this capacity, we prepare work statements, evaluate proposals, and conduct progress reviews. Major ongoing projects managed by CMT include DOE contracts with General Motors, Ford, Chrysler, and fuel-cell component suppliers.

The Electrochemical Technology Program is managing a multi-year DOE contract with General Motors for development of a methanol-fueled PEFC propulsion system for automotive applications. General Motors continued work toward designing and developing a 50-kW fuel cell engine scheduled for delivery to ANL in early 1997. In 1995, a 30-kW PEFC stack was built, and several 10-kW size methanol reformers were built and tested.

The Electrochemical Technology Program also manages two contracts awarded by DOE in 1994 to teams headed by Ford and Chrysler. The goal is to develop PEFC propulsion systems for passenger cars fueled directly by hydrogen carried on the vehicle. In 1995, Ford and Chrysler (1) developed conceptual designs of passenger vehicles powered by PEFC systems, (2) investigated on-board hydrogen storage technologies, and (3) conducted R&D programs to develop fuel cell technology.

The Electrochemical Technology Program, together with Georgetown University, manages a fuel cell bus development program sponsored by DOE, the U.S. Department of Transportation, and the California South Coast Air Quality Management District. During 1995, H-Power Corp., the prime contractor, fabricated the second and third U.S.-built buses powered by fuel cells. The buses have a capacity of 25 passengers and meet all applicable standards for transit buses, including wheelchair lifts and air conditioning. Phosphoric acid fuel cells (50-kW capacity) supply all the vehicles' energy needs. The fuel cells operate on methanol fuel at over 40% fuel efficiency. The buses emit carbon monoxide and nitrogen oxides at levels that are more than 30 times lower than the 1998 federal standards for heavy-duty diesel emissions, with essentially no hydrocarbon or particulate emissions.

The Electrochemical Technology Program also continues to manage a DOE contract (co-funded by the State of Illinois) with Arthur D. Little, Inc. (ADL) to develop a multifuel fuel reformer. In 1995, ADL developed a prototype partial oxidation reformer and demonstrated its capabilities to reform ethanol, methanol, natural gas, and gasoline into a hydrogen-rich gas stream. The goal of the 1996 work is to develop a complete, integrated partial oxidation reformer for gasoline and similar fuels.

In late 1995, we initiated development of a DOE fuel cell test facility at ANL, building upon and augmenting our existing extensive battery testing capabilities (see Sec. I.B). We also initiated development of fuel cell testing standards through a DOE-sponsored working group to establish a set of metrics for evaluating fuel cells on a common basis.

II. HAZARDOUS AND MIXED WASTE RESEARCH

A major challenge facing the Department of Energy (DOE) is management of the massive quantity of hazardous and mixed (hazardous/radioactive) waste that has accumulated at various DOE sites as a result of nuclear-defense production conducted for more than four decades at these sites. Cleanup and disposal of this waste in an environmentally sound and cost-effective manner is now a major DOE mission. In addition, minimization of hazardous waste production and safe and efficient management of any hazardous waste that is produced are becoming increasingly important considerations in the commercial sector. We are conducting a variety of projects aimed at treating and disposing of hazardous and mixed wastes in support of DOE's waste management mission. In addition, we are investigating whether the technologies developed for DOE applications could also be used for hazardous waste minimization in industry.

A. *Development of Aqueous Biphasic Extraction Processes*

We have been evaluating the possible application of aqueous biphasic extraction (ABE) to the large-scale treatment of contaminated soils, solid radioactive wastes, industrial wastewater, and mineral ores. The ABE systems are heterogeneous liquid/liquid solutions composed of immiscible combinations of inorganic salts and water-soluble polymers, such as polyethylene glycol (PEG). Inorganic salts that promote biphasic formation with PEG solutions include the sodium/potassium salts of carbonate, nitrate, sulfate, phosphate, and hydroxide.¹ In addition to pilot-scale studies of extraction systems, we have been conducting fundamental studies of the microstructure of aqueous PEG solutions. This effort is directed toward furthering our understanding of the factors governing biphasic formation and partitioning behavior of ionic species in ABE systems.

1. Fundamental Studies of Aqueous Biphasic Formation

In collaboration with the ANL Intense Pulsed Neutron Source and the Los Alamos Neutron Science Center, we carried out small angle neutron scattering (SANS) studies of various PEG/salt solutions.² Variables included polymer molecular weight and salt type and concentration. In addition, anion effects on biphasic formation were investigated by cloud-point measurements in H₂O and D₂O.

The SANS results indicated that, in the presence of NaNO₃, PEG behaves like a random coil with no evidence of aggregation, whereas the presence of either Na₃PO₄ or Na₂CO₃ leads to aggregate formation. The aggregate size increased with increasing salt concentration until a discontinuity appeared at the point of biphasic formation, where the polymer in the PEG-rich phase formed an entangled mesh with loss of chain identity. In the monophasic regime, the aggregates were

¹ D. J. Chaiko, Deepak, J. Gartelmann, Y. Voyta, E. Thuillet, and C. J. Mertz, "Issues in the Scale-Up of Aqueous Biphasic Extraction of Uranium from Contaminated Soils," in *Separations of Elements*, Eds., K. L. Nash and G. R. Choppin, Plenum Press, New York, p. 225 (1995).

² P. Thiagarajan, D. J. Chaiko, and R. P. Hjelm, Jr., *Macromolecules* **28**, 7730 (1995).

elongated with a radius of approximately 19 Å and a length which varied with salt type and concentration and polymer molecular weight.

Analysis of the effects of electrolytes on the cloud points of PEG in H₂O and D₂O suggests that the polymer phase behavior in solution is entropy driven, in agreement with results from earlier studies.^{3,4} Salt effects on cloud points and biphasic formation follow the well-known Hofmeister series.⁵ That is, salt anions leading to increased structuring of water lower the cloud point. We have found that this cloud-point lowering of PEG correlates linearly with the change in water entropy (ΔS_{H}) upon the addition of electrolytes.² This is illustrated in Fig. II-1, where the cloud points of PEG-3400 are plotted as a function of ΔS_{H} for a variety of single- and multiple-charged anions. While the linear fit to the data is quite good, the cloud point for the PEG/Na₂CO₃ system deviates somewhat from the behavior of the other sodium salts. The reason for the discrepancy is not known at this time, but we are investigating a possible error in the entropy data and will be making extensive measurements of cloud points as a function of polymer concentrations, molecular weight, and salt concentration.

Fig. II-1. Effect of Sodium Salts on the Cloud Points of PEG-3400. The solution compositions were kept constant at 7 wt% PEG/5 wt% salt.

Just as the addition of structure-making ions lowers the cloud point of PEGs, so too does the substitution of D₂O for H₂O. This effect is illustrated in Fig. II-2, where the cloud points in H₂O and D₂O are compared for various PEG-3400 salt solutions. The linear fit of the data indicates that the effects of salt and D₂O are additive, suggesting that both influence the cloud point

³ W. A. P. Luck, Topics Current Chem. **64**, 113 (1976).

⁴ R. Kjellander and E. Florin, J. Chem. Soc., Faraday Trans. I **77**, 2053 (1981).

⁵ K. P. Ananthapmanabhan and E. D. Goddard, Langmuir **3**, 25 (1987).

Fig. II-2. Cloud Points of PEG-3400 in H₂O and D₂O as Function of Anion Type. The solution compositions were fixed at 7 wt% PEG/ 5 wt% salt.

through a mechanism of increasing water structure. As shown in Fig. II-2, the difference between the cloud point in D₂O and that in H₂O decreases with increasing temperature. This behavior mirrors the strength and magnitude of the hydrogen-bond network of D₂O as a function of temperature, which breaks down faster than that of H₂O as temperature increases.

Our experimental results also indicated that the effects of sodium salts (e.g., Na₃PO₄, Na₂CO₃, Na₂SO₄, Na₂SO₃, Na₂CrO₄, Na₂WO₄, and Na₂MoO₄) on the cloud points of linear PEGs, branched PEGs, and polyvinylpyrrolidone (PVP) all correlate linearly with the changes in water entropy caused by the formation of the hydrated anion. This implies that the conformation of the polymer chain (e.g., linear or branched PEG) and its chemical structure (e.g., PEG vs. PVP) is not the dominant factor in salt-induced clouding and aqueous biphasic formation.

We also found that it should be possible to predict the partitioning behavior of tracer-level ions in PEG/salt systems. Published thermodynamic data indicate that ions with highly negative ΔS_{H} values should exhibit partition coefficients (*D*) that are either equal to, or less than, those of the biphasic-forming salts (e.g., *D* ~ 0.1-0.2), while ions that are structure-breaking (e.g., those exhibiting only slightly negative and positive ΔS_{H} values) should have *D* values close to 1. For example, we have found that the partition coefficient of Pu(IV) (ΔS_{H} for Pu(IV) = -1462.3 J·K⁻¹·mol⁻¹) in the PEG-3400/Na₂SO₄ system at 25°C is about 0.17, while that of polymeric Pu(IV) under the same conditions is about 0.001.⁶ Similarly, low partition coefficients (i.e., 0.004) were measured for uranyl

⁶ D. J. Chaiko, R. Mensah-Biney, C. J. Mertz, and A. N. Rollins, *Actinide Recovery Using Aqueous Biphasic Extraction: Initial Developmental Studies*, Argonne National Laboratory Report ANL-92/36 (1992).

carbonate (ΔS_{H} for $\text{UO}_2^{2+} = -106.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$) complexes in the PEG-3400/ Na_2CO_3 system.⁷ The extremely low partition coefficients for complex species like uranyl carbonate and polymeric plutonium reflect an additional entropy loss caused by a large rotational contribution.

As a result of our work, past attempts to approximate the PEG molecule as a non-interacting, hard sphere in modeling partition behavior will have to be reevaluated. Future development of thermodynamic models of partitioning behavior will need to explicitly account for the heretofore unrecognized effects of salt on PEG aggregation.

2. Removal of Uranium and Thorium from Contaminated Soils

We are evaluating the use of ABE systems for the recovery of radionuclides from contaminated soils. The contaminated soils used in this work were provided by DOE's Fernald Environmental Management Project (FEMP) at Fernald, OH. The Fernald site had at one time been employed for production of uranium metal for use in defense reactors. During operation of the defense production facility, the soil at the site became contaminated with uranium from a variety of sources, including deposition of airborne uranium particulates, spills of solvents, and escape of process effluents.

The ABE process for contaminated soil involves the selective partitioning of fine particulates and dissolved species between two immiscible aqueous phases. The contaminated soil is suspended in an aqueous polymer solution (e.g., polyethylene glycol) and is contacted in a countercurrent fashion with an aqueous salt solution (e.g., sodium carbonate). The liquid/liquid extraction is carried out in a Karr column because of its ability to handle solids without blockage. During the liquid/liquid contact, heavy-metal contaminants, such as U and Th, are selectively partitioned from the polymer solution to the salt solution, while the cleaned soil particles remain dispersed in the polymer phase. Typically, 99 to 99.5% of the soil is recovered in the cleaned soil fraction, while only 0.5 to 1% is recovered in the contaminant concentrate.

The selective partitioning of particulates in the ABE systems is based on physicochemical interactions between the particle surface and the liquid phases, rather than on bulk phase properties such as density. Consequently, particle size should be small enough that the rate of particle settling due to gravity is slow compared to the rate of liquid/liquid phase separation. In general, we have found that an upper particle size of about 150-200 μm can be accommodated during continuous, countercurrent extractions.

Test-tube-scale experiments have shown that, in general, ultrafine metal oxide particulates (such as PuO_2 , UO_2 , CeO_2 , Fe_2O_3 , TiO_2 , and Al_2O_3) partition preferentially into the salt-rich phase in PEG/salt systems. The only exceptions that we have found so far are the crystalline silicates (e.g., quartz and cristobalite), layered silicates (e.g., clays such as kaolinite and montmorillonite), and glass. Clays partition into the PEG-rich phase with partition coefficients of about 100, regardless of pH in the aqueous phase (we investigated pH values ranging from 2 to 12). On the other

⁷ D. J. Chaiko, R. Mensah-Biney, and E. Van Deventer, in *Removal of Uranium from Uranium-Contaminated Soils, Phase 1: Bench-Scale Testing*, Oak Ridge National Laboratory Report ORNL-6762 (1993).

hand, the partition behavior of crystalline silicates and glass depends on the degree of surface ionization. At pH values near the point-of-zero charge (PZC), these materials partition into the PEG-rich phase, while partitioning into the salt-rich phase occurs when the pH is either above or below the PZC.

The aqueous biphasic extraction of soil samples from the Fernald site was tested in a pilot-scale Karr column (2.5-cm ID, 3.6-m height). In these tests, we were able to reduce the uranium concentration in the -100 mesh soil fraction from about 500 mg/kg to about 77 mg/kg. In contrast, carbonate leaching alone was able to reduce the uranium concentration only to 146 mg/kg. We also found that dissolved soil organics (e.g., humates) and dissolved uranium species can be recovered from the salt phase by selective precipitation with methanol. This process produces an easily filtered solid residue and can reduce the residual uranium concentration in the salt stream to below 1 mg/kg. The methanol would be recovered for recycle from the methanol/salt solution by distillation.

Another significant finding from the Karr column tests is that ^{234}Th (a daughter product of ^{238}U) can be extracted from the soil and recovered in the fraction of solids that partition into the salt-rich phase. The thorium was concentrated by 6- to 16-fold, a result demonstrating that refractory materials can be extracted and concentrated by the ABE process.

We have developed a preliminary flowsheet for uranium removal from soils by use of an ABE system (dry soil capacity of 20 tons per hour). Treatment costs with this flowsheet were estimated as \$160 per ton of dry soil. We are confident that the processing costs can be reduced even further by continued technology development and by process scaleup to treatment rates of 100 to 200 tons per hour.

The most expensive component for the flowsheet, in terms of both capital and operating costs, is the methanol precipitation/distillation step. This operation is energy-intensive and consumes a significant fraction of carbonate from the biphasic system. Further development work on alternative methods for the removal of dissolved uranium from concentrated sodium carbonate solutions is recommended. Advances in techniques for radionuclide removal from carbonate solutions with high ionic strength would not only be of benefit to soil washing, but would also be of use in the treatment of process solutions generated in decontamination and decommissioning operations. In this regard, a new solvent extraction process developed at CMT shows great promise in its ability to remove actinides from concentrated (>5 wt%) carbonate solutions. It should be pointed out that this secondary treatment of the salt-rich phase is necessary only because a significant portion of the uranium present in the Fernald soil is easily dissolved in the salt-rich phase.

B. *Laboratory Studies in Support of the Waste Isolation Pilot Plant*

The Waste Isolation Pilot Plant (WIPP) in Carlsbad, NM, has been selected as a possible disposal site for transuranic radioactive wastes resulting from defense-related activities at DOE sites. Over the past few years, we have conducted a number of studies in support of WIPP. These studies were centered on the potential effects of ionizing radiation on repository performance and actinide speciation/solubility issues. In this past year, a new project was begun to study actinide stability and solubility in simulated WIPP brine. This work is part of an overall effort, coordinated through Sandia

National Laboratories (SNL), to help evaluate the long-term performance of WIPP for the disposal of transuranic waste.

The objective of the new project is to provide experimental data on actinide solubility and oxidation state distribution to test the Actinide Source-Term (AST) model being developed for the WIPP project. The experimental plan consists of determining the stability of actinides in two synthetic WIPP brines (G-Seep and ERDA-6) and measuring the solubility of selected actinides in these brines. The effects of carbonate and three organic complexants (oxalate, citrate, and ethylenediaminetetraacetic acid) on actinide solubility will also be evaluated. In addition to providing a test for the AST model, the solubility measurements serve as a backup. In the event certain parts of the model cannot be completed by the deadline for submission of the WIPP compliance application to the Environmental Protection Agency (EPA), the empirical data will be used to supplement the AST model and provide a complete data set for actinide solubility.

Two sets of experiments were initiated during 1995: (1) stability/solubility experiments with U(VI), Np(VI), and Pu(VI) in an aqueous solution with and without carbonate and (2) experimental determination of the effects of the three organic complexants (oxalate, citrate, and ethylenediaminetetraacetic acid) on the stability of the VI oxidation state. There are no data yet to report. The studies will be extended to include the IV and V oxidation states, as well as the long-term solubility of actinides in the presence of selected organics.

During the past year, studies were also continued on the effects of ionizing radiation on gas production in environments similar to those expected in WIPP. Experiments were conducted in which ^{238}Pu was spiked into WIPP brine A held in titanium high-pressure autoclaves, and the pressure buildup was monitored. The objective is to establish the equilibration hydrogen overpressure caused by alpha-particle degradation of the WIPP brine. Figure II-3 shows the pressure buildup measured in two experiments with $\sim 10^{-3}$ and 10^{-4} M plutonium concentrations in WIPP brine A. Gas generation, up to ~ 1000 psi (~ 7 MPa), has been linear with time and absorbed dose. These experiments will be continued until an equilibration pressure is established, or the expected hydrostatic pressure in the WIPP, 2200 psi (15 MPa), is exceeded.

Fig. II-3.

Pressure Buildup due to Alpha Particle Degradation of WIPP Brine A with Plutonium-238 Concentrations of 10^{-3} M (■) and 10^{-4} M (●)

C. Laboratory Studies on Actinide Speciation in Groundwater

The speciation (i.e., complexation, oxidation state, and aggregation) of radionuclides is being investigated under conditions relevant to subsurface groundwaters on DOE lands. Emphasis is on factors that affect both the mobilization and immobilization of plutonium species. As a result of this work, we expect to more clearly establish the key factors that define the speciation of plutonium in the subsurface. This is expected to lead to new concepts for the mobilization/immobilization of plutonium and an improved capability to predict the migration of co-contaminant mixtures in the subsurface. This work is part of a multi-investigator effort, which includes collaborations with investigators at Northwestern University, Pacific Northwest Laboratory, Brookhaven National Laboratory, and Lawrence Berkeley Laboratory.

Our recent work has centered on the interactions of the plutonium-nitrilotriacetic acid (NTA) complex with *Chelatobacter heintzii* in a near-neutral solution. The *C. heintzii* bacterium is an NTA degrader and is a candidate for *in situ* bioremediation of contaminated DOE sites. Specific issues addressed were the effect of plutonium on the degradation of the NTA complex, the fate of plutonium in the microbial system, and the radiation tolerance of the bacterium.

The interactions of the Pu(IV)-NTA complex with *C. heintzii* were investigated in a series of experiments performed at near-neutral pH (pH ~ 6.2) with 0.01 M PIPES [1,4-piperazinebis (ethane-sulfonic) acid] buffer solution. In these experiments, 15-25 mL of test solution was held in gas-tight serum bottles for 3-14 days. Plutonium concentration was established by alpha scintillation counting, NTA concentration was determined with an ion chromatograph, and the Pu(IV)-NTA complex was monitored in the 475-520 nm range by absorption spectrometry. The viability of the bacterium was established by bioassay. The measured plutonium concentrations were initially in the range of 10^{-9} to 10^{-5} M with NTA concentrations fixed at $\sim 10^{-4}$ M, corresponding to ligand-to-metal ratios of 20 to 200,000.

The degradation of NTA as a function of time and plutonium concentration is shown in Fig. II-4. Increased concentrations of plutonium resulted in a lower rate of NTA degradation. Furthermore, the NTA bound in the Pu-NTA complex was not directly accessible to the microbe for degradation. At a high concentration of plutonium (10^{-5} M), where we could directly monitor the Pu(IV)-NTA complex spectroscopically, the Pu-NTA complex persisted well past the time when microbial degradation of the NTA had stopped (~ 100 h in Fig. II-4).

The fate of plutonium in the Pu-NTA system was also related to the concentration of plutonium present in solution. The partitioning of the plutonium species between the aqueous complex and the microbial fraction (defined as the fraction of the plutonium that could not go through a 0.2- μ m filter) is shown in Fig. II-5. At low concentrations of plutonium (10^{-7} to 10^{-9} M), where very high ligand/metal ratios existed, almost all the plutonium was very quickly associated with the microbial fraction. In contrast, at higher plutonium concentration ($\sim 10^{-5}$ M), most of the plutonium remained in solution as a Pu-NTA complex. This finding is not consistent with our initial hypothesis that the plutonium reduces the availability of the NTA in that the Pu-NTA complex becomes more strongly associated with the microbial fractions when it is stabilized at the low plutonium concentrations. We now hypothesize that a small but significant interaction occurs between the complex and the bacterium, which is overwhelmed at the higher plutonium concentration.

Fig. II-4. Effect of Plutonium Concentration on Degradation of NTA by *Chelatobacter heintzii* Microbe

Fig. II-5. Distribution of Plutonium in *Chelatobacter heintzii*-NTA System

The radiation tolerance of *C. heintzii*, defined as the ability of the bacterium to survive in the presence of ionizing radiation, was evaluated by exposure to both external radiation (gamma rays) and internal radiation (alpha particles from the decay of plutonium) in high purity water and 0.01 M PIPES solution. The interaction of ionizing radiation with microbes, whether it be gamma rays or alpha particles, reduced the microbe survivability, which was established by bioassay. The results for gamma irradiation are shown in Fig. II-6. For the *C. heintzii* microbe suspended in water and 0.01 M PIPES, the radiation tolerance was low, with less than 10% survivability after 0.03 Mrad. When plutonium was used as the source of ionizing radiation, the decreased survivability could only be explained if the plutonium was assumed to be strongly associated with the bacterium. The observed radiation tolerance of the bacterium was less than expected but is known to depend on the microbe's history (e.g., how/where the bacterium was grown), as well as the aqueous environment in which the microbe exists. Future work will focus on isotope-variable studies and Pu(V)-NTA interactions, where biotic transformation will be examined along with actinide interactions and toxicity.

Fig. II-6.

Effect of Gamma Radiation on the Survivability of *Chelatobacter heintzii* Suspended in High Purity Water (HPW) and 0.01 M PIPES Solution. Survivability expressed as number of colony-forming units (CFU).

D. Development of Acceptance Specifications for Hanford Low-Activity Waste

The legacy of past defense reprocessing operations at the DOE Hanford site includes over 140 MCi of radioactivity dispersed in over 230,000 metric tons of process chemicals, currently stored underground as sludge, saltcake, and highly alkaline solutions in 149 single-shell and 28 double-shell tanks. The overall strategy for management of these wastes is to remove them from the tanks, then separate them into a high-activity fraction containing most of the radionuclide inventory and a low-activity fraction containing most of the nonradioactive solids. These separated fractions are to be converted into forms suitable for subsequent storage, transport, and disposal. During 1995, the decision was made to "privatize" the treatment and solidification steps. Under privatization, contractors from the private sector will be responsible for performing the waste separations and for converting the separate fractions into forms that meet the requirements of pre-established specifications. The DOE will contract with private companies for the waste treatment and solidification services involved and will pay for these services based on a pre-established price for the delivered products that meet or exceed the requirements in the product specifications.

During 1995, we provided technical support to the privatization effort for the Hanford tank waste by developing specifications for the immobilized low-activity waste (ILAW) products that are

to be produced. The ILAW products will be in the form of solidification waste and optional matrix and filler materials enclosed in sealed metal boxes. The specifications were developed with due consideration of the regulatory requirements that will govern the transportation, storage, and disposal of these products. They identify the characteristics of the products that are to be controlled, the acceptance criteria, and the testing methods that are to be employed for assessing compliance with these criteria. The acceptance criteria cover the physical characteristics of the containers, the chemical and physical characteristics of the waste form and other materials that may be included in the container, the waste loading, and the radionuclide leaching performance of the waste form. The criteria also include requirements to ensure that, if the ILAW products are hazardous or dangerous wastes as defined by the Resource Conservation and Recovery Act or the State of Washington Dangerous Waste Regulations, they must meet applicable requirements for land disposal. The specifications will be completed in 1996.

E. *Performance Assessment of Waste Disposal Facilities*

We have initiated a new task to develop a modeling capability for assessing the performance of proposed waste disposal systems for geological repositories. Performance assessment involves the use of mathematical models (computer codes) that simulate the long-term degradation of final waste forms and subsequent release and transport of radionuclides from these waste forms through engineered barriers and the surrounding natural environment. Although the primary application of this capability is as a regulatory tool in the licensing of waste disposal systems, it can also serve as an important tool for identifying and evaluating technical issues that need to be resolved during the formulation of waste solidification/stabilization options and during the design of the disposal systems.

Our approach to developing a performance assessment capability is to build on past knowledge and technologies that have been developed for disposal of radioactive waste. It includes the following three general steps: (1) evaluate the existing computer models on geotransport, geochemical behavior, and waste form and repository performance, focusing on the principles used to derive the various models, the uncertainties in both the model as a whole and model parameters, and the applicability of a given model to a specific repository design or site; (2) develop improved models that address uncertainties and deficiencies in existing models; and (3) link the various models together in an integral framework that enables the long-term projection of the impact of a proposed waste repository on the surrounding environment.

In 1995, we focused part of our effort on evaluating current models for subsurface flow, geotransport, and waste-form and disposal-system performance. We have also developed a model for diffusive transport through the low-permeability engineered barriers (e.g., compact clay layers) often used in disposal systems. In the model, an effective diffusion coefficient is used to account for chemical and microstructural effects involved in the transport through these barriers. Chemical effects are manifested as the result of sorption of leached contaminants onto the interior pore surfaces of the barrier materials. Microstructural effects, such as porosity and connectivity, on transport are accounted for by measuring the electrical conductivity of fluid-bearing rocks and using a differential effective medium model to derive the diffusivity from the measured conductivity. In 1996, work will continue on evaluating current models and further development of our diffusive transport model.

F. *Waste Minimization Technologies*

For about a decade, nuclear power utilities have been implementing waste-minimization strategies and employing volume-reduction technologies because of the diminishing access to disposal sites and the escalating disposal costs. Over the past decade, these utilities have reduced the annual volume of low-level waste shipped for disposal to one-fifth of the original volume. The lessons from industrial experience in this area are of direct relevance to DOE's needs in waste minimization.

In this project, information from various sources was analyzed, including technical reports from the Electric Power Research Institute and the National Low-Level Radioactive Waste Management Program, operational waste management reports from reactor utilities, relevant literature reviews, and DOE reports. Reactor utilities were visited to examine firsthand the waste minimization strategies and practices in operation. These included McGuire Station of Duke Power Co., Pilgrim Nuclear Station of Boston Edison, Monticello and Prairie Island Stations of Northern States Power Co., and the volume reduction facilities of the Scientific Ecology Group at Oak Ridge, Tennessee. Results from this project, as well as the recommendations for application of waste minimization technologies, are to be issued in a formal report to DOE.

III. NUCLEAR WASTE MANAGEMENT

Before nuclear waste can be buried in a geologic repository, its corrosion behavior over extremely long time frames must be known. In the CMT nuclear waste programs, a variety of laboratory tests with simulated and fully radioactive waste glasses are performed to obtain corrosion information that is used to support development of a geologic repository in an unsaturated environment similar to that expected for the candidate site at Yucca Mountain in southwestern Nevada. These tests are primarily directed at determining the interactions between groundwater and various nuclear waste forms, including high-level waste glasses and spent nuclear fuel, under unsaturated conditions. Tests are also underway to support development of vitrified forms of low-level waste generated at Argonne and the DOE Hanford site, as well as glasses for the disposal of surplus plutonium and plutonium-bearing wastes. Our work to characterize the radioactive phases in contaminated soil and other materials was successfully completed.

A. *Preparation of Review Documents*

In this effort, we are compiling and interpreting previously published data that address the effects of several important parameters on the reactions between glass and repository groundwater. During 1994, critical reviews were completed on glass reaction modeling, glass composition, and ratio of glass surface area to water volume (S/V) on glass reaction. Although no critical reviews were completed in 1995, two reports are due to be completed in 1996: one on the effects of unsaturated conditions on glass durability, and the other on the corrosion behavior of natural analogues to the waste glass.

B. *Testing of High-Level Waste Glasses*

Projects have been ongoing for many years to support DOE in efforts to qualify vitrified high-level nuclear wastes for geologic disposal. The work has been aimed primarily at glass compositions similar to those to be produced at the Savannah River Site in the Defense Waste Processing Facility (DWPF) and at the West Valley Demonstration Project (WVDP). In this work, important information is being gathered on the reaction of the glass waste forms with groundwater. This information is useful to performance assessments in which the long-term behavior of glass exposed to water must be known. In another project, tests are being conducted to measure the durability of vitrified waste forms developed at Lockheed Idaho Technology Co. (LITCO) for the immobilization of calcined radioactive wastes at Idaho National Engineering Laboratory.

1. Static Tests of Savannah River Glass

The long half-life periods of the transuranic elements in high-level nuclear waste require a stable final waste form for a long time frame (>10,000 years). The chosen vitrification material, borosilicate glass, will confine the transuranic elements, and understanding its corrosion mechanism is important to evaluate the performance of glass destined for a repository. The performance of glass scheduled for production at the DWPF must be evaluated experimentally. However, the time frame for opening a repository site obviously excludes any long-term experimentation that would involve hundreds of years of data collection. Thus, the corrosion

behavior must be experimentally evaluated in a more realistic time frame. The glass corrosion mechanism is being studied by varying physical parameters to accelerate the glass reaction. The variation of the S/V ratio is one parameter used jointly with elevated temperature to accelerate glass reaction.

Static dissolution tests with simulated high-level waste glasses that may be produced at the DWPF are in progress at various S/V ratios and 90°C. The objectives are to (1) compare the corrosion behavior of three fully radioactive glasses with that of analogous nonradioactive glasses, (2) determine the effects of S/V on the corrosion behavior of two radionuclide-doped glasses and on the disposition of released radionuclides, (3) measure the long-term dissolution rate and study the corrosion behavior of Environmental Assessment glass, which is the benchmark glass for DWPF glasses, and (4) measure the long-term dissolution rate and study the corrosion behavior of radioactive glass made from the sludge in DWPF Tank 51. Results from these ongoing tests are summarized below.

a. Corrosion Behavior of Fully Radioactive vs. Simulated Glasses

Static dissolution tests with fully radioactive glasses (SRL 131, SRL 165, and SRL 200 frits plus actual DWPF sludge) and nonradioactive homologues are being conducted at 90°C and S/V ratios of 340, 2000, and 20,000 m⁻¹ to determine the effect of radionuclides on the glass dissolution and the rates of elemental release. Each S/V ratio is designed to provide information on the different stages of glass reaction. The S/V ratios of 340, 2000, and 20,000 m⁻¹ provide information regarding the initial, interim, and long-term stages of glass reaction, respectively. The corrosion mechanism of the glass is inferred from the release rate of the glass matrix elements (Li, Na, B, and Si) and the radionuclides, solution pH, and alteration phases that form on the glass surface. Tests have been in progress for up to 1456 days.

The following observations were made from the test results obtained to date. The dissolution rates of the fully radioactive glasses are similar to those of the corresponding nonradioactive glasses in tests at low S/V (340 and 2000 m⁻¹) and at short test duration (365 days). However, alteration phases that increase the glass dissolution rates form after about one year in tests at 20,000 m⁻¹ with the nonradioactive glasses, but not in the tests with the fully radioactive glasses. Radiolysis of the air and solution in the tests with the fully radioactive glass results in solutions that have lower pH values (differences of between 0.5 and 1.0 pH unit). Also, the solutions in tests with radioactive glasses do not become saturated with respect to those alteration phases that form with nonradioactive glasses.

The fully radioactive SRL 200 glass is also undergoing tests with the Unsaturated Test Method, which involves slowly dripping groundwater onto a glass sample supported above the leachate in a test vessel at 90°C. Some of the glass samples had been pre-aged by reacting them in a water vapor environment at 200°C before testing. In testing up to 5 years, results show a significant difference in the reaction and subsequent solution composition for the as-cast and aged glass. The solution pH values for the aged glass were consistently in the 11.0 to 11.7 range, while the test solutions for the as-cast glass had pH values of about 8. Differences in the release to solution of anions, cations, carbon, and radionuclides were also significant.

Major glass elements (such as Li, B, Na, and Si) were initially detected in solution at levels several hundred times greater for the aged glass than for the as-cast glass. This probably occurred because not all of the major elements are incorporated into stable alteration products as the glass is aged and forms a hydrated layer; thus, these elements are readily rinsed from the surface during initial contact with liquid water. In fact, the amounts of Li and B in solution have steadily decreased throughout the test.

The measured amount of actinides in solution for the first two sampling periods (at 18 and 55 months) with the radioactive SRL 200 glass was given previously.¹ Alpha and gamma spectroscopy of the leachates was initially used to measure the actinide release levels; however, owing to problems caused by the salt content in the aged samples, additional analytical methods have been employed. Over the past year, the radionuclide contents in leachates and in filtered samples of the leachates have been analyzed by use of alpha spectroscopy combined with evaporation and electroplating methods, gamma spectroscopy, and inductively coupled plasma/mass spectroscopy (ICP/MS). A combination of all analyses will be used to ensure that we report correct and consistent values for actinide release. Considerable data are available from test solutions that were passed through filters of decreasing pore size. Both the filters and filtrates have been analyzed. The results of these analyses are not yet correlated and thus are not reported here.

Some indication of the distribution of radionuclides and other species in solution has been obtained by isolating particles on perforated carbon grids and then analyzing them with transmission electron microscopy (TEM). The solutions from tests with the as-cast glass wicked easily through the grid and produced good samples for analysis. The solutions from the aged-glass tests contained a large salt content and were wicked with more difficulty through the grid. While the salt content disrupts the clear distinction of colloidal particles, some discrete colloids were identified. The particles identified are summarized in Table III-1. The results show the presence of various metal oxides. The surfaces of oxides are amphoteric; as a result, the surface charge is dependent on the pH and will vary depending on the type of oxide. In most groundwaters, the surface charge (i.e., zeta potential) will be negative for clay colloids, whereas the sols of metal hydroxides mostly carry positive charges in groundwaters. Hence, there will be an electrostatic attraction between the metal hydroxide sols and clay colloids. This behavior was observed in our drip tests with the SRL 200 glass, where corrosion took place in the test vessel. Particles of iron oxide from the container vessel were attracted to the smectite clay particles; this created larger agglomerates, which may be less able to remain in solution.

b. Effects of S/V Ratio

Tests with SRL 131 and SRL 202 glasses doped with Tc, Np, U, Pu, and Am are being used to determine the effects of the S/V ratio on the glass dissolution rate and the release

¹ J. K. Bates, W. L. Bourcier, C. R. Bradley, E. C. Buck, J. C. Cunnane, N. L. Dietz, W. L. Ebert, J. W. Emery, R. C. Ewing, X. Feng, T. J. Gerding, M. Gong, J. C. Hoh, H. Li, J. J. Mazer, L. E. Morgan, L. Newton, J. K. Nielsen, B. L. Phillips, M. Tomozawa, L. Wang, and D. J. Wronkiewicz, *ANL Technical Support Program for DOE Environmental Restoration and Waste Management, Annual Report, October 1991-September 1992*, Argonne National Laboratory Report ANL-93/13, pp. 25-32 (1993).

Table III-1. Results of Surveys from Transmission Electron Microscopy of Colloidal Particles in Test Solutions

	Observations
As-Cast Samples	Large agglomerates on grid; calcium-rich regions in the agglomerates; Cr-Pb and Fe-Cr-Mn particles.
	Agglomerates of particles; CaF_2 particle; some clays containing lead and uranium; FeCrO_x particles.
	Calcium oxide particles and a nickel-rich clay.
Aged Samples	Barium sulfate particles; clays containing Mn-Fe and Zn-Mn particles; Ca-Al silicates with trace strontium; a magnesium aluminosilicate phase.
	Calcium aluminosilicate phases and iron-rich clay.
	A large amount of clay material; evidence of iron chromium particles, possibly corrosion products.
	Calcium silicate phosphorus phase, possibly nagelschmidite; small amount of strontium in this phase, which may have been background contamination; nickel-rich clay (smectite).
	Silicate agglomerates; electron diffraction patterns indicating presence of clay.

behaviors of these radionuclides. Static dissolution tests at $S/V = 10, 340, 2000$, and $20,000 \text{ m}^{-1}$ and $T = 90^\circ\text{C}$ have been in progress for up to about 2000 days. Lower glass corrosion rates were initially attained in tests at high S/V (2000 and $20,000 \text{ m}^{-1}$) because higher concentrations of H_4SiO_4 form and decrease the reaction rate. However, at long reaction times (>1 year) and high S/V , new alteration products form and increase the reaction rate. While this increase in reaction rate affects the release of radionuclides from the glass, the disposition of each of the doped radionuclides is controlled by its chemistry. Sparingly soluble Pu and Am are found primarily fixed on the steel reaction vessel, whereas U and Np are moderately soluble and are found in solution and associated with colloids. Also, technetium is highly soluble and is released into solution as fast as the glass dissolves. However, the amount of technetium in solution decreases significantly under test conditions in which the solution Eh decreases, presumably because of the effects of radiolysis and glass corrosion. This shows the importance of using actual radioactive glasses to determine the long-term behavior of radionuclides rather than relying solely on the behavior of surrogates.

c. Long-Term Corrosion Behavior of Environmental Assessment Glass

We have conducted static dissolution tests at S/V ratios of 2000 and $20,000 \text{ m}^{-1}$ and 90°C with Environmental Assessment (EA) glass to measure its corrosion rate in the presence of alteration phases. The EA glass has been identified as the benchmark glass for waste glasses to be produced at the DWPF. These tests were conducted to determine if the short-term durability of the EA glass is representative of its long-term durability after alteration phases have formed. Alteration phases that increase the glass dissolution rate (including analcime, gmelinite, calcium silicates, and sodium aluminum silicate hydrates) formed within 1 year in tests conducted at an S/V of 2000 m^{-1} and within 56 days in tests at $20,000 \text{ m}^{-1}$. The glass dissolution rate in the presence of these alteration phases is $0.07 \text{ g}/(\text{m}^2\cdot\text{d})$ at 2000 m^{-1} and $0.2 \text{ g}/(\text{m}^2\cdot\text{d})$ at $20,000 \text{ m}^{-1}$. These

rates are less than that measured in a 7-day test, which was $0.7 \text{ g}/(\text{m}^2\cdot\text{d})$. Therefore, the corrosion rate of EA glass measured with a 7-day test provides an upper bound to the corrosion rate, even after alteration phases form.

d. Long-Term Corrosion Behavior of Tank 51 Sludge-Based Glass

Static dissolution tests are being conducted with a radioactive glass made during a demonstration of the DWPF process (sludge from Tank 51 at Hanford) and with a nonradioactive homologue glass. The objective is to measure the long-term dissolution rate of the sludge-based glass and to determine if alteration phases that increase the dissolution rate form under the same test conditions as occur for other DWPF glasses. Tests are being conducted at 90°C and S/V ratios of 2000 and $20,000 \text{ m}^{-1}$. Tests with the nonradioactive glass completed through 140 days show it to have a durability similar to that of the SRL 202-based glass (see Sec. III.B.1.b). Alteration phases are expected to form after about 1 year in tests conducted at $20,000 \text{ m}^{-1}$. Tests with the fully radioactive glass have been started, and results of 7-day tests with the radioactive and nonradioactive glasses are similar.

2. Drip Tests of Savannah River Glass

Unsaturated Glass Tests (designated the N2 tests) were initiated in February 1986 on actinide- and technetium-doped SRL 165 glass, which is representative of the glass to be produced at the DWPF. These tests are still in progress, and the test solutions have been sampled intermittently over the ensuing period of nearly nine years, with regular sampling at 26-week intervals since December 1993. In these tests, designed to simulate potential conditions at the proposed Yucca Mountain Repository, groundwater representative of the site (EJ-13 water) is slowly dripped onto the waste glass sample at 90°C in a closed stainless steel test vessel. Periodic analysis of the leachate water is performed to monitor release of glass components, including actinides. Particulate and colloidal materials released to solution are also analyzed with TEM (for structure) and with sequential filtering and alpha spectroscopy (for transuranic content). These combined data indicate that insoluble elements, including U, Pu, and Am, are incorporated into alteration phases as the glass reacts and are subsequently released with particulate or colloidal matter as the alteration products spall from the glass. Ultimately, the transport of these actinides in the repository will be determined by the transport of the particulates suspended in solution.

3. Drip Tests of West Valley Glass

Unsaturated Glass Tests, designated the N3 tests (similar to the N2 tests described in Sec. III.B.2), are being conducted with an actinide- and technetium-doped glass (ATM-10). These tests were started in July 1987 and remain ongoing, with regular sampling at 26-week intervals. The ATM-10 glass is a former reference glass for the WVDP, and its composition differs only slightly from the present West Valley reference glass. Test results to date indicate that the release of actinide elements, besides neptunium, is controlled by their incorporation into alteration phases that may subsequently spall from the glass and become suspended in solution. The ATM-10 glass, like other West Valley glasses, contains substantial amounts of thorium, which has been found to cause extensive formation of an actinide-bearing phase called brockite [nominally, $\text{Ca}^{2+}\text{Th}^{4+}\text{PO}_4)_2^{3-}$]. Brockite is known to incorporate rare earth elements and uranium, as well as americium and possibly plutonium,

into its crystal structure. Its appearance as an alteration phase may explain the low initial release rates of actinides observed in the N3 tests.

Laboratory tests are being conducted with a nonradioactive homologue of WVDP reference glass to characterize its corrosion behavior and assess its long-term durability. The nonradioactive glass is referred to as WV6. The fully radioactive glass will be tested when it becomes available. Static dissolution tests are being conducted at 90°C and S/V ratios of 10, 2000, and 20,000 m⁻¹. Vapor hydration tests (200°C under saturated vapor) have been completed. The results available to date indicate that the WV6 glass is at least as durable as other high-level waste reference glasses. A variety of alteration phases were observed to form during corrosion in the vapor hydration tests, including zeolites, phosphates, and uranium silicate phases. These alteration phases will likely incorporate some radionuclides.

In the static dissolution tests with WV6 glass, no alteration phases that increase the dissolution rate have formed through two years; only a thin layer of clay has formed. However, the results of the vapor hydration tests indicate that these alteration phases should form after longer reaction times. Long-term tests are ongoing.

4. Immobilization of Plutonium Glass

Several alternatives are being considered for disposal of surplus plutonium resulting from the dismantlement of nuclear weapons and the cleanup of weapon production sites. One method is incorporating plutonium into glass. This year, we have studied the corrosion behavior of an alkali-tin-silicate glass containing plutonium, as well as DWPF reference glasses containing plutonium. The test data will be used as input to performance assessment calculations being performed for the Yucca Mountain Project. The alkali-tin-silicate glass was developed at CMT as a low processing temperature (1150°C) alternative to other commercially available glasses that can dissolve high levels of plutonium. A glass with low processing temperature addresses several melter options for waste form production and will take on added importance if surplus plutonium and scrap material (e.g., ash from Rocky Flats) need to be vitrified. The alkali-tin-silicate glass was engineered to accommodate a high plutonium loading and to be durable under all test conditions, especially those conditions that have been found to be deleterious to the durability of some high-level waste glasses. The glass dissolved about 7 wt% Pu together with the neutron absorber gadolinium, and under test conditions expected to accelerate the glass reaction with water, this glass was resistant to corrosion. In vapor hydration tests (200°C under saturated vapor), the Pu and Gd were released from the glass at nearly the same rate as in static dissolution tests and were not segregated into surface alteration phases. This release behavior suggests that criticality should not be an important issue for the disposal of high-plutonium-loaded glass. Similar results for the release behavior of Pu and Gd were obtained for the DWPF reference glasses, although the reaction for the reference glasses under vapor-hydration conditions was more rapid than for the alkali-tin-silicate glass. Continued tests are planned to confirm these findings.

5. Testing of LITCO Glass

Argonne National Laboratory has completed a testing program in support of the efforts of LITCO to vitrify high-level waste calcines from Idaho National Engineering Laboratory.

Both Product Consistency (PC) tests and Vapor Hydration (VH) tests were performed on ten glasses supplied by LITCO. Nine of these contained 3-11 wt% fluorine, and so differ substantially in composition from other high-level waste glass candidates developed at DOE laboratories. The PC tests include temperatures of 90°C and S/V ratios of 2000 and 20,000 m⁻¹, and have been in progress for up to 182 days. The VH tests expose the samples to water vapor (relative humidity above 90%) and 200°C and have been run for up to 56 days.

The primary conclusions from the testing program are as follows:

- All glasses contain primary crystalline phases, which affect, to varying degrees, the composition of the residual glass and the way that the glass and crystal react with water. In the fluoride-bearing glass, the main crystalline phase is fluorite, CaF₂, whereas in fluoride-free glass, the main crystalline phases are virgilite (LiAlSi₃O₈), a copper titanium oxide (Cu₃TiO₄), and rutile (TiO₂). The degree of crystallinity and the distribution of crystals throughout the glass matrix vary with glass composition and with processing conditions.
- In PC tests of 7-day duration, normalized releases of major glass-forming elements are comparable to, or lower than, normalized releases obtained from other candidate waste glasses.
- The fluoride-free glass forms alteration phases (zeolite) relatively early in its reaction with water. The zeolite acts as a sink for Na, Al, and Si and increases the rate of glass reaction. However, even after 182 days at an S/V of 20,000 m⁻¹ in the PC tests, the normalized releases of B, Li, Na, and Si are still four times lower than those obtained from EA glass in only 7 days.
- The fluoride-bearing glasses are highly durable and form alteration phases only after prolonged exposure to water. Alteration phases formed during tests on one fluoride-bearing glass but had little effect on the rate of glass corrosion. The duration of the longest PC tests for the remaining fluoride glasses was insufficient to cause formation of alteration phases. Zeolites formed during VH tests of these glasses, however, indicating that zeolites would eventually form in PC tests as well. In VH tests, zeolites increase the rate of fluoride glass reaction.
- The corrosion behaviors of mixed-alkali glasses and single-alkali glasses are similar. Using normalized releases of B and Li obtained from PC tests, we determined that the mixed-alkali glasses react at a somewhat higher rate than the single-alkali glasses. In vapor hydration tests, both single- and mixed-alkali glasses form zeolite phases, which increase the rate of glass reaction.

6. Use of Energy Loss Spectrometry to Analyze Glasses

Although the presence of transuranic elements in alteration phases on reacted glass (and spent fuel) has been determined indirectly using autoradiography, these elements have never

been detected directly, as the levels are often too small for detection with elemental analytical X-ray methods. We are exploring the use of energy loss spectrometry to detect trace levels of transuranics and rare earths in the alteration phases of reacted waste glass. Using the high-energy M-absorption edges of the transuranics (>3500 eV), we have been able to detect plutonium in a phosphate alteration phase structurally related to apatite, as well as neptunium in the uranyl silicate alteration phase weeksite (Fig. III-1). The release of neptunium from reacted glass has been generally considered to be solubility controlled, yet here we have direct evidence of its incorporation into an alteration phase. Energy loss spectrometry will continue to be used in glass testing efforts to provide new information on the microstructure of reacted nuclear waste materials.

Fig. III-1.

Electron Energy Loss Spectrum of
M-edges for Np and U in Weeksite
from Tests of SRL 131 Glass

C. *Testing of Spent Fuel*

Spent nuclear fuel contained in an engineered barrier system surrounded by consolidated volcanic tuff is the current reference design for the potential repository at Yucca Mountain. This multiple barrier system will be designed to limit the radionuclide release from the spent fuel, which is irradiated UO_2 . Long-term tests with both unirradiated UO_2 and spent fuel are in progress to determine the behavior and radionuclide release characteristics of spent fuel under unsaturated conditions.

1. Unsaturated Tests with UO_2 Samples

The objective of this program is to evaluate the reaction of unirradiated UO_2 pellets after long-term exposure to dripping EJ-13 water at 90°C . Results from these tests will be used to characterize the dissolution behavior of UO_2 , formation of alteration phases, and rates and mechanisms of uranium release and will provide input to drip tests with spent nuclear fuel (see Sec. III.C.2).

Drip tests of UO_2 pellets supported by a Teflon test stand are continuing into their eleventh year. Reactions of the test samples analyzed during the past decade are characterized by a rapid period of uranium release between one and two years of testing, followed by relatively low amounts of release over the following eight years. Calculated uranium release rates (normalized to

sample surface area) during the last year were also similar to earlier results. For example, sample PMP8U-3 (geometric surface area = 0.0486 m^2) has a normalized uranium release rate of $0.0163 \text{ mg}/(\text{m}^2\cdot\text{day})$ during the interval of 9 to 10 years. This rate is similar to that observed over the past several years and is the lowest rate observed from all of the original eight tests. Sample PMP8U-6 (surface area = 0.0022 m^2) has continued to display an increase in uranium release, from $0.0925 \text{ mg}/(\text{m}^2\cdot\text{day})$ for the 4.5-5.5 year interval, to the present value of $0.4402 \text{ mg}/(\text{m}^2\cdot\text{day})$ for the 9-10 year interval.

An analysis of the uranium release trends indicated that 87-99% of the uranium released from the samples was recovered from a solution aliquot obtained by soaking the inside of the test vessel in dilute nitric acid for ~10 min. Less than 2% of the uranium passed through a filter with a pore-size opening of 5 nm, whereas 1-12% of the uranium was present as particulates that did not pass through the same filters. This finding indicates that the majority of the uranium released from the UO_2 samples is sorbed or precipitated on the stainless steel walls of the test vessel and the Teflon support stand.

Cation analyses indicated that alkalis, alkaline earths, and silicon continue to be depleted from the EJ-13 leachant. Previous analyses with scanning electron microscopy and X-ray energy dispersive spectroscopy revealed that these elements were incorporated into secondary uranyl phases on the sample surfaces, with the uranium being derived from the dissolution of the UO_2 pellets.² Our recent analyses indicated that magnesium was generally depleted to the greatest extent, with leachate concentrations typically reduced to ~10% of the initial EJ-13 values. Calcium and potassium were depleted to ~30% of the original EJ-13 compositions, while silicon was depleted to a level that is within 50-60% of the original EJ-13 composition. Sodium concentrations were depleted to the least extent, at a value that was ~90% of the EJ-13 composition.

Four tests are in progress with UO_2 pellets supported by stainless steel stands. After six years of testing, these samples visually appeared to be much less reacted than their Teflon-support-stand counterparts were after the same extent of testing. Greenish patches of what appeared to be dehydrated schoepite ($\text{UO}_3\cdot 0.8\text{H}_2\text{O}$) were observed on the surfaces of some samples, although detailed characterization studies have yet to be conducted. Solution aliquots were collected from these tests for determination of cations, anions, pH, carbon, and uranium (obtained after solution passed through 5-nm filter). These aliquots fractions are currently being analyzed.

2. Unsaturated Tests with Spent Fuel Samples

To provide input with which to evaluate the reaction of spent fuel for the unsaturated conditions that may be expected in the Yucca Mountain candidate repository, we have ongoing tests at 90°C in which EJ-13 groundwater is dripped at 0.75 mL every 3.5 days on spent fuel samples, ATM-103 and ATM-106. The leachate is characterized at intervals of approximately six months. These tests have been in progress for nearly 3 years. This year, the release fractions for ^{238}U , ^{137}Cs , ^{90}Sr , ^{129}I , and ^{99}Tc were examined to determine if any of them reflected the rate of matrix dissolution

² J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, p. 61 (1995).

under unsaturated conditions. (Release fraction is the ratio of the material collected divided by the total amount of material in the fuel sample. Material in alteration products is not included.) The dissolution results reported from flow-through tests by others^{3,4} were used to provide a measure of the magnitude of fuel matrix dissolution.

The release fraction for ^{238}U was smaller than that for any of the other radionuclides. This finding can be correlated with the formation of large amounts of alteration products on the spent fuel, including a billietite-related phase (uranyl oxide hydrate) containing Mo, Ba, Cs, and Sr (very small amount). The formula of the new phase is considered to be $\text{Cs}(\text{UO}_2)_5\text{O}_4(\text{MoO}_2)(\text{OH})\cdot x\text{H}_2\text{O}$. The incorporation of Cs and Sr in alteration products reduced their measured release. For both ATM fuels, the ^{90}Sr fractional release rates were comparable to the ^{137}Cs fractional release rates, ranging between 10^{-5} and 10^{-7} /day in the ATM-106 test and falling from an initial value of 2×10^{-4} /day to 4×10^{-6} /day in the ATM-103 test.

The ^{129}I fractions, which were very large in the first two test intervals (up to about 275 days), decreased during later time intervals. The cause of the major part of the decrease may be exhaustion of the ^{129}I inventory in the Zircaloy/fuel gap. The ATM-103 contains large amounts of the fission gas xenon in particles along the grain boundaries, and this finding suggests that ^{129}I is located there. The ATM-106 fuel has a large fission gas release (11.2%), which suggests a large ^{129}I release to the gap.

Large ^{99}Tc fractions, which were comparable to those reported by Gray et al.^{3,4} for fuel matrix dissolution, were found for ATM-103 fuel throughout the first 1.6 years of testing. For the ATM-106 fuel at the 1.6-year test interval, the fractional release rate for ^{99}Tc , 1×10^{-4} /day, was orders of magnitude larger than that for ^{137}Cs , 2×10^{-6} /day. For the ATM-103 fuel at the 1.6-year interval, the fractional release rate for ^{99}Tc , 6×10^{-4} /day, was also higher than that for ^{137}Cs , 2×10^{-6} /day. In flow-through tests at 25°C by Gray et al.,³ the dissolution rate for ^{99}Tc in the fuel matrix was the same order of magnitude as that of ^{238}U . The rate for matrix dissolution at 90°C for an activation energy of 30 kJ/mol (taken from Ref. 3) was calculated to be 9×10^{-5} /day, a rate comparable to our measured ^{99}Tc rates at 90°C . Thus, the release of ^{99}Tc may reflect the dissolution rate of the spent fuel matrix under the conditions of our tests. If the ^{99}Tc release behavior is maintained in future test intervals, then ^{99}Tc release may be used as an indicator of the magnitude of fuel matrix dissolution.

D. *Vitrification of Low-Level Waste*

1. Development of Low-Level Glass Waste Forms

The objective of this study is to identify and produce glass formulations that can be used to vitrify low-level radioactive mixed waste (LLMW). We have developed a compositional envelope of glass formulations that could eventually be used by DOE's Environmental Management

³ W. J. Gray, D. M. Strachan, and C. N. Wilson, *Mater. Res. Soc. Symp. Proc.* **257**, 353-360 (1992).

⁴ W. J. Gray, H. R. Leider, and S. A. Steward, *J. Nucl. Mater.* **190**, 46-52 (1992).

Operations in the full-scale vitrification of LLMW. Several criteria were used to select glass formulations for inclusion in the compositional envelope:

- the formulation melts and pours at temperatures consistent with commercially available vitrification systems;
- the melted mixture has a viscosity amenable to pouring at the melt temperature; and
- the resultant waste form passes the Environmental Protection Agency (EPA) Toxicity Characteristic Leaching Procedure (TCLP), the regulatory basis for determining whether the LLMW materials have the characteristic of being hazardous.

The waste streams used in developing the compositional envelope included storage tank sludge, evaporator concentrator bottom sludge, HEPA (High Efficiency Particulate Air) filter media, and contaminated soils. These waste streams contained various radioactive elements (e.g., ^{232}U , $^{239/240}\text{Pu}$, ^{237}Np , ^{210}Po , ^{241}Am , ^{137}Cs , ^{60}Co) and hazardous components (e.g., Ag, As, Ba, Cd, Cr, Hg, Se, Pb) at levels above the EPA limits as determined with the TCLP.

The compositional envelope for waste vitrification covers a range of alkali borosilicate glasses. The glasses within the compositional envelope were produced with relatively small amounts (7 to 28 wt%) of glass-forming additives; these additives, borax, diatomaceous earth, boric acid, and sodium carbonate, were easily handled. The overall waste volume was reduced by a factor of eight to a factor of four during vitrification, depending on the glass formulation and the degree of pretreatment. Characterization of the glass waste forms within the compositional envelope indicated that they are homogeneous on a millimeter scale. Furthermore, TCLP results with glasses produced with added amounts of hazardous metals provided compelling evidence that alkali borosilicate glasses could potentially be used in treating a wide range of ANL waste streams.

2. Development and Testing of Glass-Crystal Composite Waste Forms

Glass-crystal composite (GCC) waste forms have been examined for their potential use in the immobilization of mixed low-level nuclear and toxic waste materials. Approximately 40 samples were produced as crucible melts with both simulated and actual DOE wastes. Processing temperatures ranged from 1300 to 1500°C, with crystal formation being induced by the proper blending of the simulated waste streams, slow cooling of the molten waste material, and addition of chemical additives such as Zr, Ti, and P. The formation of iron-rich spinels was the primary requirement for the high melt temperatures, which may be reduced when large amounts of metal components are not included in the waste stream. Melting of the actual waste materials also reduced waste volume by 80% relative to the original air-dried and pulverized feed material.

The hazardous elements U, Pu, Sr (analogue for ^{90}Sr), Cr, Cd, Pb, As, Ba, and Ni were incorporated into corrosion-resistant crystalline phases such as zirconolite ($\text{CaZrTi}_2\text{O}_7$), monazite $[(\text{Ce,Th})\text{PO}_4]$, perovskite $[(\text{Ca,Na,Fe,Ce,Sr})\text{TiO}_3]$, spinel $[(\text{Mg,Fe,Zn,Mn,Ni})(\text{Al,Fe,Cr,Ti})_2\text{O}_4]$, titanite $[\text{CaTiSiO}_4(\text{F,O,OH})]$, baddeleyite (ZrO_2), and apatite $[\text{Ca}_5(\text{PO}_4)_3(\text{F,Cl,OH})]$. This versatility suggests that GCCs can be applied to a much wider range of waste stream compositions than would

be amenable to homogeneous glass production alone. The crystal phases also incorporated Fe, P, and F, thereby showing promise for the processing of waste streams containing large proportions of scrap metals and other components undesirable for glass formation. Determination of partition coefficients for the crystal/glass matrix indicate that U and Ce are preferentially partitioned into zirconolite, perovskite, baddeleyite, monazite, and apatite; Cr, Ni, and Cd into spinels; and As and Sr into apatite. Lead also displays a limited partitioning into apatite.

The GCCs passed the TCLP for toxic metal components, despite loadings that were up to 11 element wt% of hazardous metals. In Product Consistency tests at 90°C for intervals of 7 to 365 days, the GCCs also have uranium-retention capacities that are up to 300-fold better than those of SRL 202U, a simulated high-level nuclear waste glass. The GCCs thus combine advantageous features of both the excellent durability exhibited by predominantly crystalline waste forms, such as Synroc, with the ease in processing offered by use of commercially available vitrification facilities. No future work is planned.

3. Testing of Glass Waste Forms for Low-Level Waste

Both Product Consistency (PC) and Vapor Hydration (VH) tests are being conducted to assess the long-term behavior of a sodium borosilicate waste glass (LD6-5412) that has been developed as a reference glass for stabilizing low-level radioactive wastes generated during the remediation of tank wastes from the DOE Hanford site. This testing program supports performance assessment calculations by measuring long-term corrosion rates and identifying alteration phases that form as the glass corrodes. The PC tests were conducted at temperatures of 20, 40, 70, and 90°C; at S/V ratios of 2000 and 20,000 m⁻¹; and for reaction times from 28 days to more than one year. The VH tests were performed at 70, 120, 150, 175, and 200°C with durations from one day to more than one year. The measured rates were then extrapolated to low temperatures for comparison with the rates measured in the PC tests.

Release rates of Si and B from the glass matrix in the PC tests were nearly identical, while the release rate of sodium was always higher. The persistently high sodium release may have profound implications regarding the dissolution model⁵ used to assess the disposal site performance. It is usually assumed that ion exchange of alkali elements is a transient phenomenon that occurs soon after water contacts the glass, and that continued glass dissolution is controlled by matrix dissolution. The results obtained in this study suggest that, while the ion exchange might be a transient phenomenon at 90°C, it may affect glass dissolution much longer at 20°C. An understanding of the glass dissolution mechanism is necessary to calculate the release of radionuclides over long disposal times. Testing of a glass containing radionuclide surrogate elements will be conducted during 1996 to provide deeper insight into the release behavior of radionuclides at low temperatures.

Alteration phases, including analcime and gobbinsite, were formed in PC tests conducted at 90°C and 20,000 m⁻¹ for 98 days and longer. The precipitation of these phases increases the glass dissolution rate because they are more stable and have lower solubilities than the glass. The glass dissolution rate was 0.003 g/(m²·d) before these phases formed and increased to

⁵ B. P. McGrail, M. J. Apted, D. W. Engel, and A. M. Liebetrau, Mater. Res. Soc. Symp. Proc. 176, 785-792 (1990).

0.5 g/(m²·d) after they formed. Alteration-phase formation has previously been found to increase the dissolution rates of high-level waste glasses.^{6,7}

In the VH tests, the same alteration phases formed as in the PC tests. Similar to the PC tests, much higher glass dissolution rates occurred after the alteration phases formed. Using an Arrhenius plot, we extrapolated the VH results to lower temperature and obtained the following: 2 g/(m²·d) at 90°C, 0.5 g/(m²·d) at 70°C, 0.02 g/(m²·d) at 40°C, and 0.003 g/(m²·d) at 20°C. The extrapolated rate at 90°C is consistent with that measured in the PC tests.

The dissolution rate of the LD6-5412 glass at 90°C was measured in a newly developed test, the Accelerated Dissolution test. In this new test, the dissolution rate of a sample is measured after it is placed in a solution generated by a PC test along with a VH test sample of the same glass. The dissolution rate at 90°C was measured to be about 1.8 g/(m²·d), which is in good agreement with the rates measured using the PC test and extrapolated from the VH test. Accelerated Dissolution tests are in progress at 40 and 70°C. Also, PC and MCC-1 (Materials Characterization Center) tests are being conducted with the LD6-5412 glass to measure its dissolution rate under highly dilute solution conditions.

E. *Characterization of Contaminated Materials*

1. Fernald

The Fernald site in Ohio has become heavily contaminated with uranium as a result of uranium processing operations. To assist in developing remediation techniques, we determined the composition of the uranium in the soil. We developed a new sample preparation method for examining the sub-micrometer phases present in the soils by transmission electron microscopy.⁸ The analytical results indicate that uranium exists in several forms in the soils. The major uranium-bearing phase in the site soils was identified as meta-autunite, a calcium uranyl phosphate.⁹ Also found in the soils were phosphate phases, which possibly arose from the widespread use of tributyl phosphate for uranium purification. This completes our characterization of the contaminated Fernald soil. The results should be useful in the site remediation efforts at Fernald.

2. Johnston Atoll

We have completed our examination of the Pu and U contamination that resulted from the abort of a nuclear weapon on Johnston Atoll in the Pacific Ocean in the early 1960s. Detailed analyses of fragments of bomb components indicated that the Pu and U in these fragments have oxidized and formed carbonate complexes, facilitating their migration to surrounding soil surfaces. Results from this investigation are being submitted for journal publication.

⁶ W. L. Ebert, J. K. Bates, E. C. Buck, and C. R. Bradley, Mater. Res. Soc. Symp. Proc. **294**, 569-576 (1993).

⁷ P. Van Iseghem and B. Grambow, Mater. Res. Soc. Symp. Proc. **112**, 631-639 (1988).

⁸ E. C. Buck, N. L. Dietz, and J. K. Bates, Microsc. Res. Tech. **31**, 174-181 (1995).

⁹ E. C. Buck, N. R. Brown, and N. L. Dietz, "Contaminant Uranium Phases and Leaching at the Fernald Site in Ohio," Environ. Sci. and Technol., in press.

3. Cement Work

Leach tests have been conducted on cement mortar formulations from Applied Innovation Inc. The objective is to elucidate the capacities of these formulations to retain radioactive elements from radioactive waste, toxic waste, and mixed waste. If successful, these Portland cement-based mortars could find wide applications in the immobilization and containment of radioactive, toxic, and mixed wastes. We have determined the leachability indices of mortars containing Tc, Cs, Sr, transuranic elements, and hazardous metals. These mortars were subjected to the American Nuclear Society ANS 16.1 test, and the leachates were analyzed by inductively coupled plasma/mass spectroscopic and gamma spectroscopic analyses. The Nuclear Regulatory Commission has suggested that a low-level waste form should have an effective diffusivity of less than $1 \times 10^{-6} \text{ cm}^2/\text{s}$ or a leachability index of 6. Thus, only leachability index values of 6 or greater are acceptable for a low-level waste form. Test results for Cs and Sr in chloride and carbonate salts cured for 30 days showed that the leachability indices for these elements are promising, 7 and 12, respectively. Radioactive cement mortars were prepared by using a low-level waste sulfide sludge (11 wt% in mortar) generated by ANL Waste Management Operations and demonstrated leachability indices for Tc, Cs, Sr, U, and Cd of 15, 14, 11, 17, and 15, respectively. These excellent results are attributed to the reducing nature of the waste stream itself. These results are encouraging for the development of materials for immobilization of low-level waste. The next series of studies will yield information on the leachability of radionuclides and hazardous metals in mortar prepared with a variety of curing times, waste loadings, and low-level waste content.

IV. SEPARATION SCIENCE AND TECHNOLOGY

The Division's work in separation science and technology during the past year was in three areas:

- Treatment of radioactive, mixed, and hazardous waste
- Substitution of low-enriched uranium for high-enriched uranium in the production of ^{99}Mo
- Radionuclide decontamination of facilities undergoing decommissioning

The main project in the first area involves R&D on solvent extraction processes, namely, TRUEX (transuranic extraction) and CSEX (cesium extraction) combined with SREX (strontium extraction). These processes are designed for the cleanup of acidic nuclear waste solutions. In another project, we are developing evaporator/concentrator systems for treating low-level radioactive waste at Oak Ridge National Laboratory and the Savannah River Technical Center. We also continue to provide technical support for ANL's Waste Management Organization; our major task in 1995 was designing and starting up a waste treatment facility for liquid transuranic (TRU) waste.

In the second area, we are developing a low-enriched uranium target and a processing method for production of ^{99}Mo to be used for medical applications. The third area entails developing radionuclide cleanup processes applicable to the decontamination and decommissioning activities in progress throughout the DOE complex.

A. *Solvent Extraction Technology*

Although our separation science and technology activities have broadened into many new areas, solvent extraction R&D remains a significant fraction of our development work. In earlier tests,¹ the TRUEX solvent extraction process was demonstrated to be capable of recovering TRU elements from nuclear waste solutions containing a wide range of nitric acid and nitrate salt concentrations. The TRUEX extractant is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (abbreviated as CMPO), which is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX solvent. The Generic TRUEX Model (GTM) was developed in the CMT Division for designing TRUEX flowsheets for specific waste streams. Work during the past year was focused on modifying the GTM for use with two types of high-level waste at Idaho National Engineering Laboratory (INEL): (1) sodium-bearing waste, which is a highly acidic waste solution currently stored in stainless steel tanks, and (2) calcined waste, which is stored in silos in a dry form and must be dissolved in nitric acid before treatment. In a collaborative project with the ANL Chemistry Division, we are also providing engineering and modeling support and testing countercurrent flowsheets for the combined CSEX-SREX process, which was invented in the ANL Chemistry

¹ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, p. 78 (1994).

Division. This solvent extraction process is applicable to removing ^{137}Cs and ^{90}Sr from acidic waste solution, such as that presently stored at INEL.

1. TRUEX Process

The TRUEX process was selected as a reference technology for the removal of actinides from the high-level sodium-bearing and calcined wastes at INEL. While the TRUEX process is predominantly designed to remove actinides from acidic nitrate solutions, the extraction behavior of these waste components by TRUEX solvent will be affected by the presence of the significant quantities of chloride, mercury, and zirconium in the INEL waste.

Experimental studies at INEL have shown that mercury is effectively extracted as a chlorocomplex from nitric acid and simulated sodium-bearing waste when chloride is present.² Batch extraction experiments were performed at CMT to derive a model for mercury extraction by the TRUEX process. Data were collected to measure the mercury distribution ratio (concentration in the organic phase divided by that in aqueous phase) as a function of the concentrations of HNO_3 , NaCl , and HCl in the aqueous phase and the concentrations of CMPO and TBP in the organic phase. The mercury distribution ratio was found to be highly dependent on both the chloride and acid concentrations. Figure IV-1 shows the mercury distribution ratios as a function of HCl and NaCl concentrations. Initial modeling of mercury distribution ratios was performed with speciation results from the Environmental Simulation Program (ESP, a product of OLI Systems, Inc.), which resulted in good fits to the data. The dichloromercuric complex was shown to be extracted well by the TRUEX solvent at low concentrations of acid and chloride, while the tetrachloromercuric complex

Fig. IV-1.

Distribution Ratio of Mercury as Function of HCl and NaCl Concentrations. Mercury extractions were performed with 0.2 M CMPO and 1.4 M TBP in dodecane at 25°C. Lines through points were fit by a model using speciation results from the Environmental Simulation Program.

² R. S. Herbst, K. N. Brewer, J. D. Law, T. J. Tranter, and T. A. Todd, *TRUEX Partitioning Studies Applied to ICPP Sodium-Bearing Waste*, Idaho National Engineering Laboratory Report WINCO-1206 (May 1994).

was extracted as a neutral acid at high chloride concentrations. (Note that the chloride concentration was greater than the mercury concentration.) Mercury complexation constants for Cl^- , F^- , NO_3^- , and SO_4^{2-} have been incorporated into the GTM, and the GTM now accounts for over ten aqueous-phase mercury species. In the future, GTM-derived speciation will be used to calculate mercury(II) distribution ratios.

We continued our efforts in the modeling of the extraction behavior of Zr/F (major components in the INEL waste) for use in the GTM. Two different models that fit the previously collected experimental zirconium distribution ratios were tested. The first model assumed the extractability of ZrF_2 and produced poor results at high HNO_3 concentration ($> 2 \text{ M}$). The second model assumed the extractability of $\text{ZrF}_2(\text{NO}_3)_2$, and although more accurate than the first, it did not accurately predict the distribution ratio of zirconium over a wide range of F/Zr ratios (0 to 6) and HNO_3 concentrations (0.1 to 5 M). To increase GTM accuracy, we assumed the extractability of both ZrF_2 and $\text{ZrF}_2(\text{NO}_3)_2$ and fit the model using all available data. Future plans are to assist INEL in demonstrating the TRUEX processing of actual sodium-bearing high-level waste.

2. CSEX-SREX Process

Pretreatment of nuclear waste before final disposal would greatly reduce the amount of nuclear waste that has to be disposed in a high-level waste repository, with an attendant major reduction in waste disposal costs. We are working with the ANL Chemistry Division on the development and demonstration of new solvent extraction flowsheets for the cleanup of nuclear waste. The flowsheet evaluated during this reporting period was the CSEX-SREX process, which combines the SREX and CSEX extractants. The SREX extractant is a crown ether called 4,4'(5')-di-*t*-butylcyclohexano-18-crown-6, which selectively extracts and partitions Sr, Pb, and, to some extent, Tc. The CSEX extractant is a new crown ether (designated CE_Cs) that selectively extracts cesium and, to some extent, sodium. Combining these extractants reduces the number of steps needed in the pretreatment of nuclear waste from Idaho and Hanford, while the overall extraction process is made more effective. Our work includes an evaluation of the combined process in a batch countercurrent test and the extension of the results to continuous countercurrent operation. In 1996, we expect to have enough of the CE_Cs extractant for a process demonstration to be conducted with a multistage 2-cm centrifugal contactor (minicontactor) of the Argonne design. The centrifugal contactor is an excellent device for testing solvent extraction flowsheets because it allows process evaluation under conditions very close to those that might be expected in a full-scale plant. Thus, if the process runs well in the minicontactor, one can be reasonably sure that it will work in a full-scale plant.

In our work with the Chemistry Division, we developed a mathematical correlation for their data on the distribution ratios of Cs and Sr for CSEX-SREX solvent and used this correlation to analyze a batch countercurrent test being done in the Chemistry Division. To do this analysis, we needed to obtain distribution ratios for nitric acid from the GTM. Our analysis indicated that the batch countercurrent test was close to steady-state conditions. We used the analysis of the batch test to improve the distribution-ratio correlations for Cs and Sr. These correlations were then used to evaluate the operation of continuous countercurrent flowsheets. For this evaluation, we used the SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) worksheet from the GTM. Extraction efficiency was found to be especially important. The evaluation showed that, even if stage efficiencies for Cs and Sr are low in the extraction section, the desired decontamination factors can

be achieved by adding more extraction stages. Overall, our analysis of the batch countercurrent test indicates that the CSEX-SREX flowsheet is an attractive process for removing Cs and Sr from nuclear waste.

B. *Advanced Evaporator Technology*

A new evaporator system (capacity of 340 L/h) has been fabricated for ORNL by Delta Thermal Systems, Inc. (Mobile, AL). The new evaporator system is to be used for volume reduction of the supernatant liquid (low-level radioactive waste) from ORNL's Melton Valley Storage Tanks under the Out-of-Tank Evaporation Demonstration. Our involvement in the project during 1995 has included (1) review of the specifications, bids, and design of the evaporator, (2) review of the as-manufactured equipment, (3) aid in oversight of the systems operability, performance, and startup testing, and (4) completion of laboratory tests in our evaporator manufactured by LICON, Inc. (Model FVP-C3, capacity of 12 L/h).

Tests of a Melton Valley simulated waste in our laboratory-scale evaporator indicated that a volume reduction of 25% can be achieved in ORNL's evaporator system without difficulty. Boiling point elevations seen in ANL's tests under these conditions were less than 7°C. Although some foaming in the form of large bubbles was encountered, it will most likely not cause problems in ORNL's system. No measurable scaling of the tubes was encountered. Overall heat transfer coefficients of 3.1 kW/(m²·K) were measured, which are typical for wastes processed in this type of equipment. Very high decontamination factors (in the range of 10⁶) were attained.

Although one test showed solids forming in the process concentrate at volume reductions as low as 30%, all other indications are that solidification should not start until about 65% volume reduction. Solids formation in cooled concentrate was not seen below volume reductions of about 50%. Should solids formation result from a process upset, redissolution of these solids with fresh feed should be relatively straightforward, although the mixing efficiency for the concentrate recirculation system and/or flushing system should be investigated.

On-site testing and radioactive operation of the Delta Thermal evaporator at ORNL are scheduled for 1996. We will again have a small program to support this task.

In a new project, we will determine the feasibility of concentrating blowdown waste from the Consolidated Incineration Facility (CIF) at Savannah River Technical Center. This waste stream, consisting mainly of sodium chloride and fly ash, is generated during scrubbing of the off-gas from the CIF. In an evaporation study, we will determine the composition and physical properties of the condensate, concentrate, and feed streams during concentration, including boiling temperature, density, viscosity, and composition. In addition, we will observe and measure evaporation behavior with (1) increasing waste concentration and (2) variable ash loading. Also determined will be the potential for scale formation, foaming tendencies, and decontamination factors. Some modeling work will be completed to compare predicted solubilities with experimental data. Modeling will be done with the Environmental Simulation Program of OLI Systems. This work will be completed in 1996.

C. Technical Support to ANL Waste Management

Argonne's Waste Management Organization is storing waste solutions with a TRU content of 10^2 - 10^7 nCi/g because no disposal site will currently accept them. Much of this TRU waste is in highly acidic solution that requires stabilization for storage until a disposal site is available. The process developed in CMT to treat these wastes uses coprecipitation of the TRU elements with magnetite ($\text{FeO} \cdot \text{Fe}_2\text{O}_3$), a mixture of ferric and ferrous oxides. The magnetite is formed by making the waste alkaline and then adding ferric and ferrous salts in a 2:1 stoichiometric ratio. Magnetite precipitates, carrying the TRU elements with it. In laboratory tests with simple acid solutions, very high decontamination factors ($> 10^6$) for Pu and Am have been achieved. The goal is to reduce the TRU content in the bulk of the waste below 100 nCi/g so that it can be disposed of in the low-level waste system at ANL. The precipitate, containing most of the TRU elements, is suitable for long-term storage.

A block diagram showing the overall process steps for treatment of TRU-containing waste is shown in Fig. IV-2. A glovebox facility is being built to perform the magnetite carrier precipitation and filter the resultant slurry. The chemical treatment module will consist of a semiautomated system to make the waste solution alkaline and to add the ferric and ferrous salts. Once the waste has been processed in the chemical treatment module, it will be passed through the filtration module. The filtration module consists of a 5- μm bag filter to remove the bulk of the solids, then 1- μm and 0.1- μm cartridge filters to remove any fine particulate. After passing through the filtration module, the supernatant is collected and analyzed for radioactivity before being processed in an evaporator/concentrator system. If the supernatant still contains >100 nCi/g of TRU, then it may be processed again to reduce the radioactivity even further. The solids can be mixed with sufficient absorbent to absorb any remaining liquid and placed in storage until a disposal site is available. The TRU waste glovebox will be installed, tested, and placed into operation during 1996.

Argonne's Waste Management Organization currently has a low-level waste evaporator/concentrator system that is more than 30 years old. We are assisting in replacement of the evaporator

Fig. IV-2. Block Diagram of TRU Waste Treatment Process

and concentrator with up-to-date technology by providing technical support, including assistance in purchasing, design, installation, and startup. Two new evaporators (from LICON, Inc.), rated for distillate production of 340 L/h (90 gal/h), and two agitated-film concentrators (Rototherms from Artisan Industries, Inc.), rated for a distillate production rate of 0.5 L/h (0.15 gal/h), have been purchased and installed. The equipment is undergoing operability testing before being placed in service. Once in service, the old equipment will be decommissioned.

During operation of the LICON evaporators, scale is formed on their titanium heat exchangers. A nitric-acid cleaning solution is used to remove this scale. Since one of the components of the scale is calcium fluoride, a corrosive nitric/hydrofluoric acid solution is generated. This solution is particularly aggressive to titanium. To reduce the corrosivity of this solution, Al or Zr can be used to complex the fluoride. We developed a chemical model that includes accurate aqueous-phase speciation in acidic fluoride solutions containing Al or Zr. This was accomplished by use of two thermodynamic software programs: the Generic TRUEX Model (version 3.1.1) developed by CMT and ESP developed by OLI Systems. The chemical model predicts the distributions of Al, Zr, H, and F species in acidic fluoride solutions containing Al or Zr. Various molar ratios (up to 6:1) at several temperatures (25, 50, and 80°C) were investigated with the model. In addition, using a polarization resistance method, we measured corrosion rates for titanium in nitric/hydrofluoric acid solutions containing Al or Zr as a complexant. The experimental and calculated values indicate that, with regard to titanium corrosivity, the optimal Al/F ratio is 1:3, and the optimal Zr/F ratio is 1:4. This information can be used in determining the amount of aluminum or zirconium nitrate that should be added to the acid cleaning solution in order to control titanium corrosion.

D. *Production of Molybdenum-99 from Low-Enriched Uranium*

Molybdenum-99 ($t_{1/2} = 66.02$ h) decays by beta emission to ^{99m}Tc ($t_{1/2} = 6.02$ h). The latter nuclide is used in many nuclear medicine applications. For clinical use, it is prepared first in the form of TcO_4^- and then suitably changed to other chemical forms, depending upon the intended application. The TcO_4^- is washed from an alumina-column generator that contains the parent ^{99}Mo by elution with a saline solution. Much of the world's supply of ^{99}Mo is produced from fissioning of high-enriched uranium (HEU).

The Reduced Enrichment for Research and Test Reactors (RERTR) program has been active for 18 years at ANL and many countries throughout the world to modify reactor and fuel designs so that reactors could switch from HEU to low-enriched uranium (LEU) with no or little loss in flux. Many reactors have converted to LEU, and many more are in progress. While conversions of reactor fuel have proceeded, the amount of HEU being exported from the United States for use in ^{99}Mo production has become an ever more visible proliferation concern.

As a part of the RERTR program, we are studying two LEU target designs, uranium metal foil and uranium silicide (U_3Si_2). At present, either UO_2 or various UAl_x alloys are used in HEU targets. The silicide fuel is being developed as the LEU substitute for UAl_x alloys, and the uranium metal foil is being primarily developed as the LEU substitute for UO_2 . We are also looking into the possibility of substituting the LEU metal foil target for all current HEU targets.

1. Cintichem Processing of LEU Targets

The Cintichem process produces, recovers, and purifies ^{99}Mo from HEU targets that consist of a thin coating of UO_2 on the inside of a cylindrical target, which is also used as a dissolver vessel for the irradiated HEU. Our R&D effort is focused on modifying the target and the recovery and purification procedures so that they can be used to process LEU targets consisting of uranium metal foil that is 0.13-mm thick. The new chemical procedures are expected to resemble closely the original Cintichem process. The initial chemical procedure is to dissolve the uranium, release the gases generated during dissolution in an appropriate manner, and separate ^{99}Mo from the uranium and fission and activation products by a series of purification steps. The key purification step is the precipitation of molybdenum from the dissolver solution by use of α -benzoin oxime.

Work in CMT has continued to measure the dissolution rate for uranium foil in nitric/sulfuric acid mixtures over a wide range of conditions. Most of these measurements were done with less than 1 g of uranium foil in a 15-mL test tube held in a constant-temperature bath. From the data obtained, we developed a mathematical correlation that gives the dissolution rate for uranium foil as a function of temperature, nitric acid concentration, and sulfuric acid concentration. The correlation indicates that the required uranium foil dissolution should be carried out at 92 to 103°C with an initial dissolver solution of 3 M HNO_3 and 2 M H_2SO_4 . Also, we determined that the volume of dissolver solution should be such that the final concentration of uranium is 1 M.

To carry out large-scale dissolver tests that would allow this technology to be demonstrated at the PUSPIPTK facilities of the National Atomic Energy Agency in Indonesia (Badan Tenaga Atom Nasional), a stainless steel (Type 304) dissolver was designed at ANL, and two units were built. The dissolver units have a length of 457 mm, an outside diameter of 31.8 mm, and a wall thickness of 0.89 mm. This design allows for a maximum operating pressure of 4.8 MPa (700 psig), about twice the pressure expected when 80 mL of solution is used to dissolve 18 g of uranium foil. A flange at the open end of the dissolver allows the uranium foil to be inserted easily. After a successful first test of the large-scale dissolver at ANL, the second unit was used at PUSPIPTK to do further tests. Figure IV-3 gives typical results for 3 to 18 g of uranium foil. As shown, the dissolver pressure became steady in 30 to 40 min after the start of dissolution. This finding indicates that the dissolution of the uranium foil is complete well within the 60 min required. For high amounts of uranium foil (5 to 18 g), the pressure curve shows a distinct peak. This peak indicates that the dissolution becomes self-heating. This heat greatly speeds up the dissolution; otherwise, our calculations show that these dissolutions would have taken much longer than 60 min. Because of our success with the stainless steel dissolver, we are planning to extend its use to (1) uranium foil dissolution using only HNO_3 , (2) uranium foil dissolution using H_2O_2 and NaOH , and (3) U_3Si_2 particle dissolution using H_2O_2 and NaOH .

Collaborative work at the University of Illinois has focused on the precipitation of molybdenum from a dissolver solution containing α -benzoin oxime. The precipitation was studied for a wide range of conditions, including (1) nitric- and sulfuric-acid concentrations, (2) partial neutralization of the acids, (3) molybdenum and uranium concentrations, and (4) the ratio of α -benzoin oxime to molybdenum. Decontamination factors were measured for U, Np, and various fission products, and the results were presented at the 1995 international RERTR meeting. Three

Fig. IV-3. Variation of Pressure with Time during Dissolution of Uranium Foil in Stainless Steel Dissolver. Tests carried out by Badan Tenaga Atom Nasional (BATAN) and ANL, as indicated by legend.

mock demonstrations were conducted with tracer levels of irradiated LEU (i.e., low-level radioactivity compared with the ^{99}Mo production process) to test molybdenum recovery and purification during each step of the Cintichem process. A sampling procedure and gamma-counting technique were developed for this purpose. The results indicate that the required purity levels can be reached with the LEU-modified Cintichem process.

During 1996, we plan to demonstrate the LEU-modified Cintichem process on a full-size, fully irradiated target in PUSPIPTEK. After that, we will begin collecting all necessary data for the approval of the ^{99}Mo product by the Federal Drug Administration.

2. Basic Processing of U_3Si_2 Targets

Over the last several years, uranium silicide fuels have been under development as LEU targets for ^{99}Mo production. The LEU silicide is aimed to replace the UAl_x in the HEU dissolution process used throughout the world.^{3,4} Replacement of UAl_x with U_3Si_2 targets requires development of an aggressive dissolution process. Unlike UAl_x , U_3Si_2 targets do not readily dissolve

³ J. Salacz, "Reprocessing of Irradiated U-235 for the Production of Mo-99, I-131, and Xe-133 Radioisotopes," in *Fission Molybdenum for Medical Use, Proceedings of the Technical Committee*, International Atomic Energy Agency, Karlsruhe, Germany, IAEA-TECDOC-515, pp. 149-154 (1987).

⁴ R. O. Marques, P. R. Cristini, H. Fernandez, and D. Marziale, "Operation of the Installation for Fission Mo-99 Production in Argentina," in *Fission Molybdenum for Medical Use, Proceedings of the Technical Committee*, International Atomic Energy Agency, Karlsruhe, Germany, IAEA-TECDOC-515, pp. 23-33 (1987).

in base. In acid dissolution tests run in Canada, silica was precipitated, and the ^{99}Mo was recovered from the solution in very low yield.⁵

We employ a two-step process to dissolve the silicide targets. First, the aluminum alloy cladding and matrix aluminum are dissolved in 3 M NaOH-3 M NaNO₃. Then, the dispersed U₃Si₂ particles are dissolved in a mixture of 5 M H₂O₂ and 0.1-2 M NaOH. The procedure to remove the aluminum cladding was developed in the fifties at ORNL,⁶ and slight variations of it are practiced all over the world. It has worked well for removing cladding from nonirradiated and unannealed ("cold") targets, as well as thermally annealed and irradiated targets. However, the aluminum powder in the meat of the thermally annealed and irradiated targets did not dissolve well after the cladding was removed. Also, the silicide particles did not disperse but remained affixed with matrix aluminum powder in a thin wafer. The annealed targets required approximately double the time of the cold targets to dissolve the matrix aluminum and disperse the particles. After the silicide dispersed, it dissolved readily, as in the cold targets.

Target dissolution continues to be the primary development need for the replacement of conventional HEU aluminide with LEU silicide targets for ^{99}Mo production. We found that aluminum alloy cladding dissolved easily in base, but sintering of matrix aluminum powder and adhesion of gas bubbles to the silicide matrix during dissolution retarded aluminum dissolution and prevented silicide particle dispersion. Once dispersed, silicide particles dissolved in solutions of alkaline hydrogen peroxide. Reduction of base concentrations from 5 to 0.1 M NaOH yielded similar silicide dissolution and peroxide destruction rates, simplifying later processing. The kinetics of the dissolution process was shown to favor a plug-flow reactor configuration that frequently replaces a small volume of the dissolving solution or continuously replenishes hydrogen peroxide. Downstream process development remains to be done, including ion chromatographic recovery of ^{99}Mo and waste disposal. We are hoping to demonstrate this process in the future in either Argentina or South Africa.

3. Basic Dissolution of LEU Metal Foil

During 1995, we started studies on a new process for the use of LEU metal foil targets in ^{99}Mo production. The LEU metal foil target is aimed at replacing the HEU-UA1_x and HEU-UO₂ targets. In this process, an irradiated LEU metal foil target is dissolved in a mixture of hydrogen peroxide and sodium hydroxide. The ^{99}Mo is then recovered from the dissolved solution and is decontaminated. A literature survey revealed that dissolution of uranium metal with alkaline peroxide solutions has received little study. Our R&D efforts have been focused on chemical kinetic studies and dissolution optimization.

During 1995, we completed uranium dissolution experiments over a wide range of base concentrations (0.01 to 5.0 M) and hydrogen peroxide concentrations (1 to 4.0 M) under various

⁵ K. A. Burrill and R. J. Harrison, "Development of the Mo-99 Process at CRNL," in *Fission Molybdenum for Medical Use, Proceedings of the Technical Committee*, International Atomic Energy Agency, Karlsruhe, Germany, IAEA-TECDOC-515, pp. 35-46 (1987).

⁶ S. Stoller and R. Richards, Eds., *Reactor Handbook: Fuel Reprocessing*, Interscience Publishers, New York (1961).

temperatures in an open, batch-type reactor. It was found that uranium dissolution in an alkaline H_2O_2 solution is a 0.25th order reaction with respect to equilibrium hydrogen peroxide concentration and can be divided into a low-base ($<0.2 \text{ M}$ hydroxide) and a high-base ($>0.2 \text{ M}$ hydroxide) process. In the low-base process, the equilibrium concentrations of hydrogen peroxide and hydroxide affect the rate of uranium dissolution. In the high-base process, uranium dissolution is independent of alkali concentration, and the presence of base affects only the equilibrium concentration of hydrogen peroxide. We have developed a chemical kinetics model that fits the experimental data:

$$R_u = A \left(e^{\frac{-E_a}{RT}} \right) \left(\frac{K_a [\text{OH}^-]^{n''}}{1 + K_a [\text{OH}^-]^{n''}} \right) [\text{H}_2\text{O}_2]_{\text{equilibrium}}^n \quad (1)$$

where R_u is the rate of uranium dissolution ($\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$), T is temperature in Kelvin, E_a ($= 48.8 \text{ kJ/mol}$) is the activation energy, A ($= 1.65 \times 10^3$) is a pre-exponential factor, R is the gas constant, K_a ($= 20.4$) is a constant, $[\text{OH}^-]$ is the initial (total) hydroxide concentration, n'' and n are constants (2 and 0.25, respectively), and $[\text{H}_2\text{O}_2]_{\text{equilibrium}}$ is the equilibrium concentration of hydrogen peroxide ($\text{mol}\cdot\text{L}^{-1}$). Equation 1 will be used in designing the dissolution process and equipment. Present plans are to (1) design the equipment necessary to dissolve the foil in alkaline peroxide, (2) develop means to destroy excess peroxide, and (3) recover and purify ^{99}Mo from the dissolved uranium under conditions similar to those used for base-dissolved HEU targets. We will also be seeking a partner to undertake full-scale demonstration of the process on an irradiated LEU target.

E. *Decontamination and Decommissioning*

With the change in focus from weapons production to cleanup and environmental restoration at many DOE sites, technologies are needed to expedite decontamination and decommissioning (D&D) of plants and equipment. Development efforts are underway on the concentration of plutonium-containing liquids generated from D&D activities and the *in situ* decontamination of equipment (piping systems, storage tanks) in production plants.

1. Concentrator Application

In this activity, we investigated the operation of an agitated-film concentrator system (fabricated by Artisan Industries, Inc.) for use as a portable, modular concentrator of D&D waste solutions. Pilot-scale tests at Artisan were completed to (1) determine the concentration factor achieved with different waste streams and (2) estimate the process conditions at which stable operation can be achieved. Two solutions were tested. The first solution simulated a decontamination reagent that is proposed for use in the nuclear industry. The main components are 4 M nitric acid and 0.1 M hydrofluoric acid. The metals present (iron, chrome, and nickel) are from the dissolution of stainless steel. Aluminum was added to complex the fluoride ions and thereby reduce the corrosiveness of the solution. The second solution simulated the plutonium-nitric acid solutions that are generated during the processing of plutonium. This solution contains only two components, nitric acid and bismuth; the bismuth served as a stand-in for plutonium.

For the decontamination solution, a processing rate of 13 L/h was achieved in the Artisan concentrator. The bottoms product was well behaved when the concentrator was operated at less than a 93% evaporation rate. At higher rates, the bottoms solidified upon cooling. We encountered no major problems that would prevent scaleup to a production system. For the plutonium solution, a processing rate of 10 L/h was achieved. At a 97% evaporation rate, a "wet" powder was generated, and 12 M nitric acid was recovered in the distillate. Although some solids tended to build up in the concentrator body, the bottoms stream was well behaved. Extended steady-state tests are needed to establish operating limits for this concentrator system. A report is being drafted on the application of the Artisan system for concentrating D&D waste solutions.

2. Evaluation of *In Situ* Chemical Decontamination

In another D&D project, we are evaluating methods for the *in situ* decontamination of equipment interiors. On the basis of an extensive literature survey, six decontamination processes were selected and tested in the laboratory; for a base-case comparison, nitric acid decontamination was also tested. The seven solutions tested were as follows:

- Nitric Acid
- Nitric Acid plus Hydrofluoric Acid
- Fluoboric Acid
- Alkaline Persulfate Followed by Citric Acid plus Oxalic Acid (CITROX)
- Hydrogen Peroxide plus Oxalic Acid plus Hydrofluoric Acid
- Silver(II) Persulfate
- Electropolishing with Nitric Acid Electrolyte

For the process testing, Type 304 stainless steel coupons were contaminated with either Pu, Am, or a mixture of Cs, Sr, and Gd. Then, decontamination factors for these contaminants were measured for each of the seven decontamination processes. The decontamination factors given in Fig. IV-4 are for the conditions that appeared to produce the best results; these test conditions are reported in Table IV-1.

In general, the higher the temperature and the longer the contact time, the higher the decontamination factor. The nitric/hydrofluoric acid and fluoboric acid solutions achieved consistently high decontamination factors for the five isotopes tested and are much higher than the decontamination factor for the nitric acid solution (base case). For most of the processes, decontamination factors were highest for strontium and lowest for cesium, with the other three isotopes falling in between. For the processes involving the silver(II) persulfate and the oxalate-peroxide-hydrofluoric acid, tests showed that the solutions must be used immediately after preparation. Even a delay in 30 min caused a significant decrease in the measured decontamination factor. Because of this time constraint, implementation of either process for remote, *in situ* decontamination would be difficult.

Fig. IV-4. Decontamination Factors for the Seven Processes Evaluated in the Laboratory. Values represent the average decontamination factor for the best results.

Table IV-1. Best Conditions^a Tested for Each Decontamination Process Represented in Fig. IV-4

Decontamination Processes	Solution Composition	Best Decontamination Conditions
Nitric Acid	4 <u>M</u> HNO ₃	6 h at 80°C
Nitric-Hydrofluoric Acids	4 <u>M</u> HNO ₃ 0.1 <u>M</u> HF	6 h at 80°C
Fluoboric Acid	4 <u>M</u> HBF ₄	6 h at 80°C
Alkaline-Persulfate CITROX (two-step)	0.2 <u>M</u> K ₂ S ₂ O ₈ 1 <u>M</u> NaOH 50 g/L Oxalic Acid 100 g/L Citric Acid	4 h at 80°C 6 h at 80°C
Oxalate-Peroxide-Hydrofluoric Acids	0.4 <u>M</u> H ₂ C ₂ O ₄ 0.1 <u>M</u> HF 0.01 <u>M</u> H ₂ O ₂	3 h at 80°C
Silver(II) Persulfate	0.5 <u>M</u> K ₂ S ₂ O ₈ 0.2 <u>M</u> AgNO ₃ 3 <u>M</u> HNO ₃	3 h at 40°C
Electropolishing	4-6 <u>M</u> HNO ₃	400 mA/cm ² 10 min at 25°C

^aBest condition was selected from the limited number of laboratory tests completed.

Coupon weight loss follows these same trends, with increased contact time and temperature relating to higher corrosion rates. The highest corrosion rates, 7-17 $\mu\text{m/h}$, were achieved with the nitric/hydrofluoric acid and fluoboric acid solutions at 80°C; for comparison, the corrosion rates measured with the nitric acid process are $\leq 0.3 \mu\text{m/h}$. While corrosion rates with the fluoboric solutions appeared to be fairly constant over the time evaluated (6 h), corrosion rates for the nitric/hydrofluoric solutions appear to decrease slightly. Continuation of this work awaits additional funding.

V. ELECTROMETALLURGICAL TECHNOLOGY

The CMT Division is developing an electrometallurgical treatment for spent nuclear fuels. The process uses electrolysis in a molten salt to isolate pure uranium and to dispose of the transuranic (TRU) elements and fission products.¹ Where appropriate, isotopic dilution of uranium is easily incorporated into the treatment. After electrolysis of the spent fuel, the fuel cladding and the fission products are placed in two stable waste forms (one a glass-bonded zeolite, the other a metal matrix), which are suitable for disposal in a geologic repository. There are no other high-level wastes, and only negligible amounts of low-level waste are generated. Waste volumes are low because the treatment uses electrotransport for separation, rather than chemical additions, which generate additional residues that must be disposed of, and because the cladding hulls form the matrix for much of the waste.

Past effort has been focused on the development of electrometallurgical technology for the treatment of stainless-steel-clad metal fuel from fast nuclear reactors, such as the Experimental Breeder Reactor-II (EBR-II) and Integral Fast Reactor (IFR). Much of this technology (with some variation) can be applied to other spent nuclear fuels that exist in the DOE complex. Spent "N" reactor fuel is an example. This fuel is Zircaloy clad, and with slight process modification the fuel will anodically dissolve in molten salt. Aluminum-clad metal fuel is a similar example. Coupled with a lithium reduction step, the electrometallurgical technology is also able to process spent oxide fuel (see Sec. VI). Development of the electrometallurgical technology for treatment of DOE spent fuel will require a large scaleup. Select topics from the electrometallurgical programs in CMT are discussed below.

A. *Process Development*

1. Drawdown Experiments

The electrometallurgical process involves electrolysis of spent nuclear fuel in a molten salt (LiCl-KCl-U/PuCl_3) at 500°C (773 K). At some point, the concentrations of alkali, alkaline earth, and rare earth fission products that accumulate in the salt must be reduced in order to lower the amount of heat generated in the electrolyzer. The heavy metal concentration in the salt must be reduced before fission products are removed from the salt.

In the drawdown operation, a Li-Cd alloy that is solid at 500°C (773 K) is loaded into anodic dissolution baskets and rotated in a molten electrolyte salt; current is driven from the anodic dissolution baskets to a solid-mandrel cathode (see Fig. V-1), where nearly pure uranium metal is collected, or to a liquid cadmium cathode (liquid cadmium in ceramic crucible), where a mixture of uranium and plutonium is collected.

¹ J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, pp. 86-92 (1995).

Fig. V-1. Schematic of Electrorefiner for Drawdown Operation with Solid Cathode

Engineering-scale tests conducted earlier¹ demonstrated that this reduction step proceeds quite satisfactorily when a Li-Cd alloy (6 wt% Li) is used as an anode and when the electrolyte contains UCl_3 and representative fission product chlorides. However, because these tests did not involve plutonium, it was necessary to demonstrate that a similar reduction would take place in the presence of plutonium. Because of limits to the amount of plutonium available for testing, we were restricted to <150 g plutonium.

Five scouting tests with our laboratory-scale electrorefiner (capable of transporting 300 g of uranium to a solid cathode) were conducted in the past year. In the first four tests, a liquid cadmium "pounder" cathode was used to collect the reduced metals. In the last test, the same "pounder" design was used but without the liquid cadmium in the ceramic crucible. (The details of the "pounder" cathode have been presented earlier¹ and will not be repeated here.) Of importance, the design allows operation of the electrorefiner in either the solid cathode mode to collect uranium alone or the liquid cathode mode to collect a TRU-U product.

Results from these tests are summarized in Table V-1. To ensure that the results could be compared from test to test, the electrolyte composition was maintained constant for each test by returning the recovered cathode product from each test back into the electrorefiner, and then adding CdCl_2 as oxidant in amounts sufficient to convert all the reduced metals to their corresponding trihalides.

The optimum lithium content in the Li-Cd alloy could not be determined from the results of only five tests. Nevertheless, the results demonstrate that we can safely draw down the U and Pu concentration in the electrolyte by greater than 90% before starting to draw down the rare earth elements. Because these tests support the earlier engineering-scale results,¹ we plan no further work in this area.

Table V-1. Results from Drawdown Experiments

Test Number	Purpose	Results
1	Decrease (UCl_3 and PuCl_3) concentration in electrolyte using Li-Cd alloy (6 wt% Li) as anode material.	UCl_3 and PuCl_3 concentration reduced by a factor of 150, while rare earths reduced by factor of 4. Cell temperature increased during operation, which can be accounted for by chemical reaction of Li-Cd alloy with electrolyte. Coulombic efficiency not as high as expected.
2	Same as above except current not passed.	UCl_3 and PuCl_3 concentration decreased by a factor of 3.2, while rare earths decreased by <1.4.
3	Same as 1 except that lithium content of Li-Cd alloy reduced to 2 wt%.	Product contained U, Pu, and rare earths. Amount recovered greater than can be accounted for by electrochemistry. Thus, chemical reduction still taking place, but at reduced rate.
4	Repeat 3.	Experimental difficulty but data sufficient to allow calculation of collection efficiency to be ~67%.
5	Collect the reduced metals using "pounder" in solid cathode mode (no cadmium in ceramic crucible).	Weight of recovered product greater than can be accounted for by electrochemistry.

2. Fission Product Behavior during Electrorefining

The behavior of the fission products Se, Te, and Sb is of importance in the electrorefining process. Their behavior was therefore investigated in our laboratory-scale electrorefiner. The expectation was that these elements could form compounds that might be soluble in the salt phase. However, because these elements form strong intermetallic compounds with cadmium, they might remain in the cadmium pool at the bottom of the electrorefining vessel (see Fig. V-1). An additional complication is that the distribution of these elements between the cadmium and salt phases would likely change as the oxidation state of the electrorefiner is varied. Thus, to resolve this issue, three tests were conducted to establish the distribution of these fission products under normal operating conditions and with variations in the oxidation state of the electrorefiner (by addition of CdCl_2 to salt).

For each test, a metal ingot was prepared by heating mixtures of Se, Te, Sb, U, Pu, and Cd in an AlN crucible, and the resulting ingot was contacted with molten salt electrolyte for 12 to 19 days. Filtered salt samples were taken at different time intervals, and cuttings of the ingots were taken after the first and third test. (It was not possible to obtain a representative sample of the metal ingot after the second test.) Sample analyses were done with inductively coupled plasma/atomic emission spectroscopy (ICP/AES).

The analytical results are summarized in Table V-2. The identical values for Se, Te, and Sb for the salt samples taken at 15 to 19 days and after the second and third tests (increased

Table V-2. Analytical Results for Solubility Studies of Fission Products in Electrefining Process

Sample Type	Composition, ^{a,b} %				
	Pu	U	Se	Te	Sb
Salt after 15 days	0.093	0.017	<0.03	<0.03	<0.03
Salt after 16 days	0.105	0.031	<0.03	<0.03	<0.03
Salt after 19 days	0.139	0.064	<0.03	<0.03	<0.03
Metal ingot from 1st test	4.12	1.89	4.35	2.84	0.31
Salt after 2nd test ^c	0.369	0.085	<0.03	<0.03	<0.03
Salt after 3rd test ^d	0.493	0.185	<0.03	<0.03	<0.03
Metal ingot from 3rd test	1.57	0.896	2.27	1.73	1.02

^aAll are ICP/AES values.^bLess than sign indicates amounts below limit of detection.^cCadmium chloride (CdCl₂) added prior to test.^dAdditional CdCl₂ added prior to test.

oxidation conditions) indicate that equilibrium was reached, and that the solubility of these elements in the salt was low. The analytical results for the first product ingot indicate that essentially all of the added Se and Te remained in the metal ingot. The results for the metal ingot from the third test suggest that Se and Te were partially lost. It is possible that fission products escaped as volatile species, which condensed on the cooler part of the electrorefiner; more likely, however, these species were transported through the salt phase and were subsequently reduced by the large cadmium pool, which was not sampled. (The low antimony results for the first ingot compared to the third ingot are due to sampling error.) These results represent the first measurement of the behavior of these fission products in the electrorefiner and should be useful in helping to model the electrometallurgical process. These preliminary results indicate that Se, Te, and Sb behave like noble metals and are likely to be left in anode baskets when spent metal fuel is anodically dissolved.

3. Zeolite Experiments with Plutonium Salts

After the actinide chloride concentration is reduced in the electrorefiner salt (see Sec. V.A.1), the active metal fission products will be removed by ion exchange with zeolite A in a column, and the purified salt will be returned to the electrorefiner. The column contents then can be disposed of as a ceramic waste form. Since it will not always be desirable to reach extremely low levels of actinides, the electrolyte contacting the zeolite will also contact salt still containing plutonium. Because the uptake of plutonium by zeolite A was not known, we conducted a series of ten experiments in our laboratory-scale electrorefiner to measure this uptake. Five of these experiments were conducted using an electrorefiner salt which contained <1 wt% plutonium plus representative fission product elements, notably the rare earths. The next five were conducted with

plutonium concentrations varying from 3 to 19.1 wt%. For these tests, a special batch of salt (containing 20.6 wt% PuCl_3) was prepared.

The experimental procedure consisted of heating at $\sim 450^\circ\text{C}$ ($\sim 723\text{ K}$) weighed amounts of zeolite and plutonium-containing salt for either 24 or 72 h periods in the laboratory-scale electrorefiner. A porous nickel crucible was used to contain the zeolite and salt mixture. At the end of the heating period, the contents were removed, cooled to room temperature, and weighed. Mass balance checks indicated that some small weight losses were associated with each experiment, which could have been due to loss of moisture present in the starting zeolite material. Samples were taken of the zeolite embedded in the salt mixture and zeolite that had passed through the porous nickel crucible. Chemical analysis of these samples indicated that plutonium uptake by zeolite does occur, and that the uptake amount is substantial (up to 22 wt%). Thus, zeolite A appears to be a good candidate for removing plutonium from molten salts.

B. *Alternative Process Applications*

New projects were initiated to study the application of electrometallurgical technology to single-pass reactor fuel and the uranium-containing salt from the Molten Salt Reactor Experiment.

1. Single-Pass Reactor Fuel

Application of electrorefining to processing single-pass reactor (SPR) fuel is being investigated. This fuel consists of aluminum-clad uranium slugs bonded with an Al-Si braze. Decladding of this fuel was successfully tested with a mock fuel pin, composed of a brass cylinder in an aluminum can. The SPR fuel decladder works by drawing a cutting blade longitudinally along the surface of the SPR fuel element to remove the aluminum cladding. In the actual process, this step exposes the uranium and the Al-Si bond to the electrorefiner salt for anodic dissolution. This successful test with a mockup fuel pin was the first phase in development of the decladder device. The next phase will test the decladder with a uranium cylinder bonded to an aluminum can by a thin layer of Al-Si intermetallic braze. This test specimen has already been fabricated.

In the proposed treatment of SPR spent fuel, uranium will be separated from the aluminum cladding, TRU elements, and fission products. This low-level uranium would reduce the volume of high-level waste from the spent fuel and result in a significant savings in disposal costs. To test this concept, a uranium rod was placed inside an aluminum sheath to simulate the configuration of SPR fuel. This assembly was used as an anode in a small test cell, and a charge of 0.82 Ah was passed between this anode and a cathode at a controlled voltage of -0.150 V and temperature of 525°C . The mass of the aluminum sheath remained constant, and there was no visible evidence of corrosion. The mass of the uranium, however, decreased by 0.408 g. Based on the amount of charge passed, the theoretical mass loss was 0.540 g. The current density during this test was 60 to 80 mA/cm^2 . These results demonstrate that uranium can be selectively oxidized in the presence of aluminum at a reasonable current density and at a current efficiency of 75%. Testing of SPR fuel treatment will be continued in the engineering-scale electrorefiner. Some of the aluminum cladding will be removed from a uranium rod, and the uranium will be anodically dissolved with no dissolution of the remaining cladding.

2. Waste Salt from Molten Salt Reactor Experiment

a. Background

In the 1960s, Oak Ridge National Laboratory (ORNL) operated a reactor that used a uranium fluoride fuel that was dissolved in a mixture of molten fluoride salts. In the Molten Salt Reactor Experiment (MSRE), the initial charge loaded as fuel was ^{235}U , but this was later changed to ^{233}U . The reactor achieved criticality on June 1, 1965, and was operated until December 12, 1969. As designed, the reactor had a fuel salt containing the uranium and a flush salt that did not. At the end of the test, the fuel salt was drained, and the reactor vessel and piping were rinsed with the flush salt. Both fuel and flush salts were stored in three criticality-safe storage tanks. During most of the shutdown period, the salts in the storage tanks were kept molten, but in recent years, the salt has been stored as a solid.

Almost from the beginning, some migration of fissile materials, notably U as UF_6 , was detected. These volatile products were transported through the off-gas system for the storage tanks and collected in auxiliary charcoal beds, in which the carbon functions as a moderator. If this migration had been allowed to continue without some intervening action, a major criticality safety problem would eventually have arisen. Several measures were taken to stabilize the salt and reduce the uranium migration. Nonetheless, the radioactivity level within the containment building continued to increase. The level was sufficiently high that the offices in the containment building had to be evacuated. As a first step in disposing of the MSRE fuel salt, it is necessary to identify a suitable waste form, establish any processing needs, and develop a workable flowsheet for salt treatment. Oak Ridge asked ANL to develop a method for treating the MSRE fuel salt. We responded with a proposal that included conducting process development work and a cold (nonradioactive) demonstration.

b. Flowsheet Development

The basic elements of the proposed approach include receiving the salt in a sealed can inside a shipping cask container, removing the can from its container, and placing the can in an electrorefining vessel heated to $\sim 500\text{--}600^\circ\text{C}$ ($773\text{--}873\text{ K}$). Next, a solid lithium alloy electrode is placed inside this crucible, and the zirconium in the salt is collected by electrorefining with a solid cathode ($\sim 30\text{-cm}$ long). After the zirconium is removed from the electrorefining vessel, a bismuth cathode is inserted into the vessel. This cathode consists of a bismuth ingot (15-cm dia by 9-cm high) contained in a ceramic crucible. The cathode design is a "pounder," which is similar to that used with the liquid cadmium cathode (see Sec. V.A.1). This bismuth cathode is used for the collection of fission products (rare earths, alkali metals, and alkaline earths), uranium, TRU elements, and thorium and its daughters. The reaction vessel at the end of the processing is allowed to cool down, and the reaction crucible, which contains the original shipping can, is removed, sealed, and transferred into a cask for shipping. At this point, the processing is complete.

Two types of waste streams, metallic and salt, result from the proposed MSRE flowsheet, shown in Fig. V-2. The metallic waste streams are denoted by the letters B, E, F, I, and L. The uranium cathode product, E, will be pure ^{233}U and will be returned to the ^{233}U stockpile at

Fig. V-2. Flowsheet for Treating MSRE Fuel Salt
(TRU = transuranics, RE = rare earth fission products)

ORNL. Waste streams B, F, and I are essentially metals or bismuth alloys with noble metal fission products, zirconium, rare earths, cesium, barium, and thorium daughters. The last metal waste stream, L, contains a nitride bed that serves to scavenge Sr, Y, and the remaining Ba and Cs. This nitride bed can either be removed from the molten bismuth and converted to glass, or the entire metal/nitride bed can be converted to glass. The salt waste stream consists of a low-level salt waste (stream K) and a chloride salt containing TRU elements and rare earths (stream G). The latter chloride stream is identical to salt found in the process used to treat EBR-II fuel at ANL-West and will be treated by essentially the same process. The low-level fluoride salt will be converted into a ceramic waste form.

c. Preliminary Experiments with Liquid Bismuth Cathode

The proposed process for treatment of MSRE salt has an electrochemical step that recovers uranium and TRU elements from the fluoride melt by transport into a liquid bismuth cathode. To obtain experimental validation of this step in the process, we conducted 12 experiments (Table V-3) with liquid bismuth. These experiments were also done to gain information on the parameters that would affect the performance of the liquid bismuth cathode. We did this testing with our present laboratory-scale electrorefiner, which has a molten LiCl-KCl salt and contains UCl_3 and PuCl_3 and a large cadmium pool.

The general experimental procedure for these tests consisted of loading bismuth (or the product ingot from the previous test) into an AlN or BeO crucible, placing the crucible in the electrorefiner, conducting electrochemical operations for one or two days, removing the crucible from the electrorefiner at the end of testing, removing the product from the ceramic crucible, visually examining the recovered ingot, and obtaining samples for chemical analysis. This procedure was modified for the first and last tests, as no current was passed in those tests. The observations from these tests (Table V-3), as well as the analytical data, indicate the following:

1. A clean salt-metal separation was routinely obtained. Thus, we should be able to routinely obtain clean product ingots.
2. The experimental variables that affected the performance of the liquid cadmium cathode were found to be nearly the same for liquid bismuth.
3. The pounder operation is necessary if uranium loadings above saturation are needed.
4. The product ingots contained very low levels of plutonium and rare earth elements. Thus, a high degree of decontamination of uranium from these elements was achieved.
5. A very high loading of uranium in bismuth is possible. The B1-8 product ingot contained 15.4 wt% U. This high value may not be needed, but it is indicative of good cathode operations.

Table V-3. Results for Bismuth Cathode Experiments

Test Number	Purpose	Results
B1-1	To determine the compatibility of bismuth with AlN.	No attack of AlN.
B1-2	To load Bi with U above solubility limit.	Good product ingot obtained.
B1-3	To study the morphology of the product ingot when the axial gap ^a was reduced by 0.058 in. (0.147 cm).	Ingot appeared same as B1-2.
B1-4	To operate bismuth cathode without pounder.	Dendrites, material growing out of crucible.
B1-5	To test pounder in mixing motion only, i.e., no up-and-down motion.	Ingot appeared unaffected; U-Bi intermetallic formed as thin layer around periphery of crucible.
B1-6	To determine the effect of reducing radial gap ^b on product morphology.	Product morphology superior to that obtained with larger radial gap.
B1-7	To repeat B1-6, except with more uranium deposited.	Thin product layer on surface of ingot.
B1-8	To determine the effect of raising pounder speed from 35 to 67 rpm.	Ingot raised on periphery.
B1-9	To operate bismuth cathode using AlN crucible under conditions that were established to be near optimum with BeO crucible.	Similar to that obtained in B1-2.
B1-10	To determine the effect of increasing current from 0.75 to 1.0 A.	Similar to B1-8.
B1-11	Same as for B1-10, except current raised to 1.5 A.	Ingot raised on periphery more so than in B1-8.
B1-12	To determine if additional heating time would affect morphology of product ingot obtained in B1-11.	No shape change from that obtained in B1-11; the two ingot halves did not melt.

^aSeparation between the face of the pounder piston and the surface of the bismuth ingot.

^bSeparation between the cylindrical wall of pounder piston and the wall of the pounder crucible.

To demonstrate the viability of the proposed flowsheet for the cleanup of MSRE salt, we will have to modify our present laboratory-scale electrorefiner to work with a fluoride rather than chloride salt and with higher operating temperatures [600-700°C (873-973 K) vs. 500°C (773 K)]. Planned changes to the electrorefiner include using a larger diameter crucible (20 cm instead of 15 cm), Hastalloy 422 as construction material for the crucible, a new upper flange assembly, new anode baskets to contain the lithium alloy, and a catch basket that will be placed below the lithium anode. We are in the process of designing and procuring the needed hardware.

C. *Testing of Advanced Electrorefiner Concepts*

An effort is underway to develop an advanced electrorefiner having high throughput (>40 kg uranium per hour) and large batch size (>100 kg). The high throughput electrorefiner is proposed for treating large quantities of spent nuclear fuels, such as the N-reactor fuel from the Hanford site. During the past year, a high-throughput electrorefiner (HTER) was designed for laboratory-scale testing to process the granular uranium product from the lithium reduction step of the electrometallurgical treatment. This electrorefiner has been installed in a plutonium glovebox. Shakedown tests have been completed on the electrorefiner, the electrode insertion fixture, and the uranium-product compactor.

The anodic dissolution baskets for the electrorefiner are shown in Fig. V-3. Four baskets are attached to a common shaft, which is rotated to force electrolyte through the granular uranium bed in the baskets. After electrorefining, the uranium is separated from fission products and TRU elements in the feed. The baskets contain a stainless-steel screen (325 mesh) to retain fine particles in the granular feed and perforated steel plates to provide additional current collection in the bed. The cathode is a steel crucible with a salt drainage hole in the bottom of the crucible. The electrode assembly is shown in Fig. V-4. During electrorefining, uranium is electrodeposited on the walls of the cathode crucible, scraped off of the crucible by steel blades attached to the rotating anodic dissolution baskets, and collected in the bottom of the cathode crucible.

Fig. V-3.

Anodic Dissolution Baskets for Processing Product from Lithium Reduction Process

The initial anodic dissolution tests in the laboratory-scale HTER have been completed. Granular uranium (4.9 kg) collected in two earlier HTER tests in our engineering-scale electrorefiner was used as the feed in these laboratory-scale HTER tests. The density of the granular uranium from

Fig. V-4. Electrode Assembly for Processing Product from Lithium Reduction Process

the HTER tests was 4.1 g uranium per cubic centimeter, and the room-temperature packed density was 6.6 g/cm³. Chemical analysis of the uranium indicated that the bulk of the material contained about 6 wt% salt.

In a typical anodic dissolution run in the laboratory-scale HTER, the cell voltage was 0.15 V at 0.08 A/cm², and the coulombic efficiency was 94%. This performance meets the voltage, current density, and coulombic efficiency goals required of an HTER to treat the uranium product from the lithium-reduction metallurgical treatment. The tests of uranium anodic dissolution will be continued until 1 to 2 kg uranium is electrodeposited into the cathode crucible. Then, the anodic dissolution baskets will be replaced with the compactor to compact the uranium at about 400°C (673 K). A compacted product of greater than 10 g uranium per cubic centimeter is expected. This high density product will allow for a high throughput rate in the cathode processor.

D. *Waste Form Development*

A ceramic waste form (glass-bonded zeolite) and a metal waste form (stainless steel and zirconium) are being developed to contain the fission products and actinides from the electrometallurgical treatment of spent nuclear fuel. The ceramic form contains the fission products (rare earth, alkali and alkaline earth metals, halogens, and chalcogens) that accumulate in the electrorefiner salt. It is also the currently preferred stream for disposal of the TRU elements in the spent fuel. To make the ceramic waste form, the fission product and TRU ions are removed from the salt by ion exchange into a column of zeolite A, and the salt is returned to the electrorefiner. The zeolite column contents

are mixed with a low-melting glass binder and additional zeolite A; this additional zeolite immobilizes excess salt by occlusion into its crystal structure. The mixture is hot pressed to make a monolithic waste form.

The metal form contains the cladding hulls, zirconium, and noble metal fission products; these are all chemically unaffected by the electrorefining process. These constituents are melted together under a slag salt to make an actinide-free ingot that is highly durable and corrosion resistant. If desired, TRU elements can be placed in the metal waste rather than the ceramic waste. To do this, the TRU elements (and a large excess of uranium) are temporarily extracted from the electrorefiner salt into a liquid cadmium solution; "pyrocontactors" (centrifugal contactors designed to work at high temperatures) are used to effect the mixing and separation of the molten salt and liquid metal. The fission products are removed, as usual, from the salt. Next, the TRU elements are returned to the electrolyte salt by reoxidation using CdCl_2 oxidant in the salt phase, and the salt is returned to the electrorefiner. After sufficient TRU has built up in the salt, it can be removed as an alloy with uranium and some rare earth metals by electrotransport to a liquid cadmium cathode.

1. Waste Form Development Laboratory

- a. Facilities Upgrade

A new facility, the Waste Form Development Laboratory, has been built; it contains engineering-scale equipment for developing the processes needed for waste removal and waste form fabrication. The equipment is housed in three argon-atmosphere gloveboxes. One of the gloveboxes contains (1) a zeolite ion-exchange column to study removal of fission product ions from the process electrorefiner salt, (2) an apparatus to remove excess salt from the resulting zeolite material, and (3) a grinder to reduce the particle size of the column material before waste form fabrication is started. All related equipment (including dryers, blenders, and a hot isostatic press) has been installed in separate locations. The second glovebox holds a tilt-pour induction furnace for melting and casting samples of simulated metal waste. This furnace can melt up to 2.5 kg of waste form metals under a molten salt flux; to date, over 20 kg of simulated waste form alloys has been generated as large-scale ingots (~3 kg each). The third glovebox contains a four-stage, countercurrent-flow pyrocontactor, which will be used for extracting actinide and fission product constituents between molten salts and liquid cadmium alloys. This facility is currently undergoing shakedown testing.

- b. Process Equipment

Tests were undertaken in the Waste Form Development Laboratory to assess the performance of the equipment for pumping molten salt and cadmium, the four-stage pyrocontactor, and the ion-exchange column. Demonstrating the pumping of molten salt and cadmium and filtration of insoluble constituents is an essential step in waste extraction. In a successful series of nine tests at 500°C (773 K), molten LiCl-KCl and molten cadmium were pumped through sintered stainless steel or woven-wire mesh filters having either 10- or 35- μm pore sizes. In each test, flow and pressure data were obtained at several pump speeds. In these tests, a submerged centrifugal pump assembly could be positioned so that either salt or cadmium could be

pumped from a vessel, through the filter, and back into the vessel. The pump and filters operated more than 300 h at acceptable flow rates, 7 L/min for the salt and 8.5 L/min for the cadmium.

Pyrocontactors effect chemical reactions between solutes in molten salt and liquid cadmium by intensively mixing and then cleanly separating these streams. Previous work² carried out at ANL with a single-stage pyrocontactor used cerium as a stand-in for uranium, lanthanum for plutonium, and yttrium for rare earths, because of the similarity of the relative separation factors. These tests showed that it should be possible to use the pyrocontactor to separate the TRU elements from the rare earths in the electrorefiner spent salt; stage efficiencies of 90% were achieved at contactor speeds of 2700 rpm. A trend of increasing extraction efficiency with increasing contactor speed (between 2100 and 2700 rpm) was consistently seen.

During 1995, a four-stage pyrocontactor was designed, fabricated, and installed. The pyrocontactor unit has rotors of 4-cm dia in housings of 6.4-cm dia. The housings are drilled into a single block of steel; internal flow between stages is obtained via drilled passages. Molten metal from a feed tank is fed to the contactor through the housing of the first stage; it exits the block from the fourth stage, at the other end of the unit. Salt flows in the opposite direction. The four-stage unit was tested outside the glovebox in the Waste Form Development Laboratory; it ran for more than 130 h up to the maximum speed of 3300 rpm without vibrational or other problems. It was then installed in the glovebox and successfully tested without liquid at 500°C (773 K) for 16 h up to contactor speeds of 3300 rpm. Flow tests have been initiated and will be followed by extraction tests.

The ion-exchange column apparatus was built in the Waste Form Development Laboratory to determine the performance of a zeolite column under conditions expected in a large-scale facility. The column setup allows rapid interchange of columns of variable diameter to expedite operation at different temperatures and salt flow rates and to permit multiple reuse of salt batches. Two symmetric tanks supported on load cells serve as both feed and receiver tanks for the molten salt (see Fig. V-5). Interchangeable columns are connected to a transfer line by a threaded gasket connection; the transfer line is mounted on the feed tank by a freeze seal. The column is immersed in a gas-tight feed tank. Argon pressure forces salt upward through the column and transfer line to the receiver tank. Column effluent is collected through a sampling port above the column. Salt flow rates, which are monitored by changes in tank mass, load cell output, and thermocouple readings, are collected by a data acquisition system.

Initial runs established that the column system would operate at constant salt flow rates between 1.7 and 94 g/min and at temperatures between 425 and 500°C (698 and 773 K). We have also found that much of the residual salt remaining on the surface of the column beads can be removed as follows. Columns are detached from the transfer line and attached directly to an argon gas line, heated to 500°C (773 K), and then pressurized until gas breakthrough occurs. Salt is collected in a crucible located below the column. Initial tests of salt removal showed that the surface salt remaining on the zeolite can be reduced to less than 20 wt% of the total sample.

² J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, p. 95 (1995).

Because our present equilibrium column model does not describe dynamic operations, a model incorporating heat and mass transport, chemical kinetics, and equilibrium data is being developed to assist laboratory-scale testing as well as design of full-scale columns. This model is being verified with experimental column data.

Fig. V-5. Experimental Setup for Testing Zeolite Ion-Exchange Column

2. Development of the Ceramic Waste Form

In the project to develop the ceramic waste form, we have determined the solubilities of the active metal fission products in the molten salt and measured exchange factors for the distribution of fission products between the molten salt and zeolite. We also tested a dehydrator for zeolite A, which is extremely hydrophilic; a blender for mixing waste salt and dehydrated zeolite at high temperatures; and a hot isostatic press for fabricating the waste form of glass-bonded zeolite.

In electrometallurgical treatment, the active metal fission products must remain dissolved in the molten salt. The approximate solubility of several fission product chlorides in the molten LiCl-KCl salt at eutectic composition was determined as follows. Each fission product chloride was added to a separate batch of the eutectic salt at a 20:80 weight ratio. The mixture was heated to 450°C (725 K) and inspected. If solids were present, the supernatant was poured off and analyzed. The measured solubilities of all the individual fission products are given in Table V-4; all are significantly higher than is anticipated in the waste stream for the electrorefiner salt.

Table V-4. Results of 24-h Solubility Experiments of Various Components in Eutectic LiCl-KCl Salt at 450°C

Component	Melting Point, K (°C)	Solubility, ^a wt%	Equivalent Fraction
NaCl	1074 (801)	>20.3 ^b	0.194
KI	958 (685)	14.9	—
CsCl	919 (646)	>19.0	0.071
SrCl ₂	1147 (874)	>19.5	0.144
BaCl ₂	1235 (962)	>19.3	0.112
YCl ₃	994 (721)	15.0 ^c	0.128
LaCl ₃	1133 (860)	18.3	0.131
CeCl ₃	1090 (817)	19.1	0.137
PrCl ₃	1059 (786)	19.3	0.138
NdCl ₃	1033 (760)	>19.8	0.140

^aGreater sign indicates that no solids visible; solubility exceeds reported value.

^bWhen cooled slightly below 450°C, a solid precipitate appears.

^cThis solution had a melting point very close to 450°C.

The distribution of fission products between molten LiCl-KCl and pure zeolite A (powders) was measured as a function of fission product concentration (6-8 wt%) and temperature [400-512°C (673-785 K)]. The exchange reaction is described by

where M^{n+} represents a fission product ion, A^+ symbolizes an alkali metal ion (Li, K, or Na), and z and s denote the zeolite and salt phases, respectively. The exchange factor (EF) using lithium as the reference cation is defined by the following equation:

$$EF = \{M^{n+}(z)/M^{n+}(s)\} 1/n \cdot \{Li^+(s)/Li^+(z)\} \quad (2)$$

Exchange factors are analogous to equilibrium constants except that concentrations (expressed as mole fractions) are used in place of activities. Typical exchange factors calculated from the measured concentrations are tabulated in Table V-5. At very low fission product concentrations (<1 wt%), the

Table V-5. Exchange Factors of Fission Products vs. Lithium

Cation	Exchange Factor
Cs	5.2
Ba	1.6
Sr	1.5
Sm	2.5
Ce	2.9
La	3.3
Nd	2.5
Pr	2.4
Y	2

exchange factors for all fission product ions showed a marked increase; this effect is being investigated. The temperature dependence of the exchange factors was small, but a slight decrease with temperature was observed in the range 400 to 512°C (673 to 785 K).

Because zeolite A is extremely hydrophilic, it must be dehydrated before it can be contacted with molten salt. A dehydrator was built and operated to conduct this step. It consists of a cylindrical stainless steel vessel that can be sealed to isolate a bed of zeolite pellets or powder from ambient air. The vessel is heated in stepwise fashion to 527°C (800 K) in a resistance furnace; desorbed water is carried away in downward-flowing nitrogen gas. Zeolite is held at each temperature until the moisture content in the effluent nitrogen drops to inlet levels. Tests with the dehydrator demonstrate that zeolite can be fully dried in 48 h or, possibly, less.

The waste salt remaining on the surface of zeolite particles after ion exchange and bulk salt removal is incorporated into the crystal structure of additional zeolite. This is accomplished by blending anhydrous zeolite with the column contents at high temperatures in an axially rotating, double-cone blender. Simulated waste salt and dehydrated zeolite A have been blended at temperatures from 450 to 550°C (723 to 823 K) for 24 to 44 h, rotation speeds of 20 to 60 rpm, and total sample sizes of 100 to 400 g. Samples of the resulting blended zeolites were washed with water for one minute. The chloride content of the water was used as a measure of the quantity of free salt remaining on the blended zeolite. Relatively low concentrations of free chloride (<0.5 wt%) were obtained when the gross number of chloride ions per unit cell of zeolite was less than 8.5. Lower rotation speeds, lower salt-to-zeolite ratios, and higher temperatures appeared to lower the free chloride concentration in the blended zeolite.

A hot isostatic press has been obtained to fabricate the glass-bonded zeolite. It allows multiple samples to be run at up to 1500°C (1773 K) and 200 MPa (30×10^3 psi). The temperature gradient within its cylindrical hot zone (10-cm dia x 13-cm length) is less than 25°C. Samples of ceramic waste are prepared as follows. Hot-blended zeolite powders are mixed with glass frit in a glovebox. The mixture is cold-pressed in thin layers into cylindrical stainless steel cans until the cans are filled. Caps, which are welded to evacuation stems, are then welded onto the cans in air. The cans

are evacuated and heated to remove any residual gases and water, then the stem is crimped and welded. The sealed cans then undergo hot-isostatic pressing at temperatures near 700°C (973 K) and pressures near 170 MPa (25×10^3 psi). Samples of glass-bonded zeolite prepared with the hot isostatic press are being characterized by leach testing, and the physical and chemical characteristics of the resulting monolith are being measured. Compositions and pressing conditions are being systematically varied to determine optimum fabrication conditions.

Samples of glass-bonded zeolite cut from the interior of the sealed cans are routinely analyzed with scanning electron microscopy and energy dispersive X-ray spectroscopy. In analyses done to date, two distinct phases are visible: an amorphous glass phase and a cubic zeolite phase. The chloride is present in the zeolite phase, and the glass phase is rich in the glass constituents, e.g., Si and Ca. Aluminum is present in both phases but is more concentrated in the zeolite phase, as expected. These observations are evidence that the zeolite contains the salt, and that the glass acts as a binder or matrix material for the zeolite.

Because of operational limitations of our plutonium gloveboxes, a mechanical uniaxial press has been built for making plutonium-containing disposition forms that are similar to the ceramic waste form. Powdered mixtures of salt-loaded zeolite and glass frit are placed in a graphite die, the die and part of the press are heated in a glovebox well, and pressure is applied to the mixture with a worm gear-drive jack screw. The hot parts of the press are made of a high-strength Zr-Ti-Mo alloy. Temperatures up to 750°C (1023 K) and compressive forces up to 44 kN (10,000 lb) can be achieved. This waste form testing will be conducted in 1996.

3. Development of the Metal Waste Form

The metal waste form being developed for electrometallurgical treatment is a uniform stainless steel-zirconium alloy that is corrosion resistant. We are developing fabrication methods, studying the physical metallurgy, and evaluating the properties and performance of the waste form alloys. The first application of the electrometallurgical treatment will be to spent fuel from EBR-II; existing equipment at the Fuel Conditioning Facility of ANL-W will be modified to fabricate the metal waste form. A significant part of the metal-waste development effort at CMT is expended to guide this work.

The metal waste stream includes the cladding hulls, which constitute most of the waste, the noble metal fission products, and any zirconium from metal fuel alloys. The baseline compositions for the metal waste form are stainless steel-15 wt% zirconium (SS-15Zr) and Zircaloy-8 wt% stainless steel (Zr-8SS). The former is for stainless-steel-clad fuels, and the latter, zirconium-clad fuel. Each will also contain 1 to 5 wt% (depending on fuel burnup) of the abundant noble metal fission products (Ru, Rh, Pd, Tc, Mo, Zr, and Ag) and small amounts of other metals.

The metal waste stream is cast at 1600°C (1873 K) under a controlled atmosphere and a molten salt flux. Because the molten alloy contains zirconium, it is very reactive; an inert atmosphere and a stable material for containing the melt are required. Yttria (Y_2O_3) crucibles have been used, but the poor thermal shock resistance of yttria limits the furnace heating rate to less than $\sim 10^\circ\text{C}/\text{min}$. Alternative containment materials and processing techniques are being sought to overcome this limitation. We have found that crucible-melt interactions do not occur in the yttria

crucibles containing steel-rich melts, but zirconium-rich melts (>50 wt% Zr) result in minor dissolution of the yttria.

Small-scale (~20 g) alloy samples were generated with a range of zirconium compositions (5 to 92 wt% Zr) to simulate the SS-15Zr and Zr-8SS waste forms and off-normal alloy compositions. The alloy samples included noble metals. Molten samples were held at 1600°C (1873 K) for 1 to 2 h and solidified by cooling slowly. Then, they were sectioned, polished, and examined using a scanning electron microscope with energy dispersive X-ray analysis for quantitative composition analysis of individual phases. The samples had uniform microstructure and low porosity.

The stainless steel-rich alloys were found to contain ferritic and austenitic phases of stainless steel along with a brittle Laves intermetallic $\text{Zr}(\text{Fe}, \text{Cr}, \text{Ni})_{2+x}$. A eutectic exists at 15.1 wt% Zr in the Fe-Zr system; the baseline composition SS-15Zr has the eutectic microstructure (Fig. V-6). The fraction of $\text{Zr}(\text{Fe}, \text{Cr}, \text{Ni})_{2+x}$ in the alloy increased with zirconium concentration until, at ~40 wt% Zr, the alloy was completely intermetallic. Compositions between 40 and 84 wt% Zr contained only intermetallic phases; these compositions would be unacceptably brittle. Between 84 and 100 wt% Zr, the alloys contained increasing fractions of α -Zr solid solution. The baseline composition Zr-8SS showed a microstructure dominated by the primary α -Zr solid solution (Fig. V-7). This primary phase was surrounded by a complex eutectic structure containing the α -Zr solution and intermetallics, which were qualitatively identified as $\text{Zr}_2(\text{Fe}, \text{Ni})$ and $\text{Zr}(\text{Fe}, \text{Cr})_2$.

The noble metals Ru, Pd, Mo, and Ag were added to the SS-15Zr and Zr-8SS waste form samples. In addition, rhenium and technetium (^{99}Tc) were added in experiments carried out at ANL-West. The noble metal additions did not result in the formation of discrete phases indicative of fission product segregation. In the SS-15Zr alloy, some metals (i.e., Ru, Pd, and Ag) showed a preference for the intermetallic phase; others (e.g., Rh) showed a preference for the iron solution phases. The noble metal distribution has not yet been quantified for the Zr-8SS alloy.

Stainless steel-zirconium alloys containing actinide metals are being investigated for two reasons: (1) to understand the fate of actinide residues from the hulls if the salt flux should fail to remove them and (2) to evaluate incorporation of actinides into the metal waste form. Several small-scale samples of simulated waste form alloys (~30 g) containing U, Pu, and Np were placed in yttria crucibles and cast in an induction furnace. The compositions studied include SS-15Zr alloys with (in wt%) 0.5U-0.5Pu, 2U-2Pu, 6Pu, 10Pu, 6Pu-2Np, and 2Np; in addition, Zr-8SS alloys with 4, 7, and 10 wt% Pu were studied. The SS-15Zr alloys were generated using Type 316 SS, and the Zr-8SS alloys were generated using Type 304 SS.

The microstructures of the SS-15Zr alloys (Fig. V-8) are similar to the two-phase SS-15Zr eutectic structure, except for the presence of a third phase that is rich in actinides. This third phase is apparently an intermetallic that is miscible with the $\text{Zr}(\text{Fe}, \text{Cr}, \text{Ni})_2$ intermetallic, and its composition is essentially 33 at.% Fe-33 at.% Ni-20 at.% actinide (U, Pu, and/or Np) plus small amounts of Zr, Cr, and minor components. This phase was observed in all of the actinide-bearing SS-15Zr alloys, regardless of the actinide or group of actinides present; increasing the actinide

Fig. V-6. Backscattered Electron Image (500X) of the SS-15Zr Eutectic Structure. The dark phase is an iron solid solution, and the bright phase is the $\text{Zr}(\text{Fe}, \text{Cr}, \text{Ni})_{2+x}$ intermetallic.

content resulted in a higher volume fraction of this phase. The microstructure for the Zr-8SS-xPu alloys (Fig. V-9) resembles the nonactinide Zr-8SS alloy. Plutonium was observed in solution in the α -Zr matrix, but it also was found in higher concentrations at the α -phase boundaries. For the alloy compositions that were examined, increasing the amount of plutonium in the alloy increased the amounts of plutonium in the α -Zr matrix phase and at the α -phase boundaries. These results indicate that actinide metals are intimately entrained in the metal phases and do not segregate into discrete phases consisting of pure actinides. Future efforts will investigate the corrosion and leach behavior of the actinide-bearing metals.

Ingots of SS-15Zr and Zr-8SS were used to generate small- and large-scale samples (~20 g and ~3 kg, respectively) for testing and evaluation. Samples with various zirconium contents were machined and polished into disks (~1.6-cm dia) and tested using general and electrochemical corrosion methods in simulated J-13 well water that is representative of the groundwater at the Yucca Mountain site in Nevada.

Electrochemical corrosion tests were carried out at room temperature in simulated J-13 well water; the solution pH was varied from 2 to 10. The test method uses a corrosion cell with a potentiostat, and the cell current is measured vs. a controlled-potential scan over a small voltage range with respect to the measured corrosion potential. General immersion tests were carried out in sealed vessels that contained neutral J-13 solutions at 90°C (363 K) for extended durations up to

Fig. V-7. Backscattered Electron Image (100X) of the Zr-8SS Structure. The gray major phase is a zirconium solid solution, and the darker phases are intermetallics.

Fig. V-8. Backscattered Electron Image of SS-15Zr Alloy Containing 2 wt% U and 2 wt% Pu. The bright contrast phases are rich in U and Pu.

Fig. V-9. Backscattered Electron Image of Zr-8SS Alloy Containing 10 wt% Pu. The zirconium solution phase contains some plutonium, but the bright-contrast features indicate high plutonium contents at α -phase boundaries.

one year. Stainless steel (Types HT9, 304, and 316), zirconium, copper, low alloy steel, aluminum-bronze, and Incoloy 825 were tested along with the waste form alloys for comparison.

The electrochemical corrosion rate for both SS-15Zr and Zr-8SS alloys in neutral pH well water was approximately 0.5 to 0.8 μm per year [(4 to 6 $\text{g}/(\text{m}^2\cdot\text{yr})$]. This range is comparable or less than the measured rates for Types 316 and 304 stainless steel, zirconium metal, and Incoloy 825, and it is one to two orders of magnitude lower than the rates for copper, bronze, and low alloy steel. The corrosion rates are even lower in pH = 10 solution than neutral solution. At pH 2, the corrosion rates for Zr-8SS samples increased very slightly, and those for SS-15Zr increased by about an order of magnitude. The very acidic conditions at pH = 2 are not expected to occur naturally but serve only to accelerate corrosion rates. The electrochemical results indicate superior corrosion resistance for the waste form alloys. In the immersion tests, corrosion rates were at or below the resolution of the test sensitivity. More severe test solutions and alternative test methods are being considered.

Large-scale (~3 kg) SS-15Zr alloy castings were used to prepare mechanical test specimens. A tensile test was performed in air at 93°C with a deformation rate of 8×10^{-7} cm/s; these conditions were selected to enable future comparisons with tests designed to evaluate environmentally assisted corrosion. The tensile fracture stress of the SS-15Zr sample was measured to be

296 MPa (42.9×10^3 psi) with <1% elongation and reduction of area. Charpy impact tests were also performed on this alloy at 25°C, and the measured absorbed energy and normalized absorbed energy were 0.7 J and 0.8 J/cm², respectively. Intermetallic materials or composites containing intermetallics are commonly observed to fail under tension with very low ductility. However, they reportedly exhibit some ductility under compression. We intend to measure a complete set of thermophysical properties for the waste form alloys. These results, taken together, indicate that the cast SS-15Zr alloy has good strength but low ductility in tension compared to other metals (e.g., annealed Type 316 SS). Compared to other waste forms such as borosilicate glasses, the strength of the metal waste form is superior.

Future development activities for the metal waste form will continue to characterize the various alloy phases and evaluate the performance for SS-15Zr and Zr-8SS. Neutron diffraction and transmission electron microscopy methods will be used to advance the current understanding of the alloy phases, and the behavior of actinides and noble metals in the waste form alloys will be investigated further. Corrosion and mechanical testing will continue, and alternative performance evaluation methods will be investigated. The focus of all of these efforts will be on the SS-15Zr composition because this alloy will be generated during the first demonstration of the electrometallurgical process when EBR-II fuel is treated.

VI. TREATMENT OF SPENT OXIDE FUEL

Many different types of spent nuclear fuels are now in storage at several Department of Energy sites. Some of these spent fuels cannot be placed directly in a geological repository, without treatment, because of their chemical reactivity, the presence of hazardous materials, or difficulty of characterization. Electrometallurgical treatment (see Sec. V) of these spent fuels would convert this large variety of fuel types into well-characterized waste forms, and it would remove the chemical reactivity and hazardous material characteristics. An additional benefit would be separation of the uranium to a low-level waste stream, thus greatly reducing the volume of material destined for a geological repository.

The electrometallurgical treatment of spent oxide fuels requires that the oxides first be reduced to metals that can be processed in the electrorefiner. A lithium reduction process has been selected to convert the spent oxide fuels into metals.¹

In this process the spent oxide fuel is reduced by reaction with lithium at 650°C in the presence of molten LiCl. The Li₂O formed during the reduction process is soluble in the salt. The spent salt and lithium are recycled after the Li₂O is electrochemically reduced. The oxygen is liberated as either CO₂ at a carbon anode or as oxygen at an inert anode. The reduced metal components of the spent fuel are separated from the LiCl salt and introduced into an electrorefiner. The electrorefining step separates the uranium into a pure product. The uranium product may be enriched for recycle or converted to a suitable form for storage or disposal as low-level waste. The TRU elements can be recovered and alloyed with cladding material and combined with fission products to produce a leach-resistant and diversion-resistant form for ultimate disposal. Alternatively, the TRU elements can be converted, with the fission products, into a ceramic waste form.

Recent work has concentrated on developing an electrometallurgical process flowsheet for treating fuel debris from the accident involving the Three Mile Island-2 (TMI-2) reactor, improving the design of anodes used for electrowinning lithium oxide, and testing the electrometallurgical process steps in engineering-scale experiments (20-kg batches). Laboratory-scale experiments (0.5-kg batches) have also been done to help understand the rare-earth chemistry in the reduction salt.

A. *Process Chemistry and Flowsheet Development for TMI-2 Core Debris*

Prior to the accident (March 1979), the TMI-2 core consisted of 177 fuel assemblies, each of which was made up of a 15 x 15 array of fuel rods. Each fuel rod had UO₂ pellets stacked inside a Zircaloy-4 tube. Some of the fuel assemblies contained control rods in addition to the fuel. These control rods consisted of an Ag-In-Cd alloy clad with 304L stainless steel. Inconel spacer grids were located at intervals along the fuel assembly to prevent the fuel rods from contacting each other and

¹ J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, pp. 101-102 (1995).

to provide rigidity to the assembly. At the top and bottom of each assembly were end fittings made of Type 304 stainless steel.

A significant portion of the core was severely damaged in the accident. The upper portion of the core was essentially completely destroyed. The fuel rods in the central portion of the core melted together and formed a region consisting of a high-temperature ceramic melt containing separate uranium- and zirconium-rich phases of $(U,Zr)O_2$. This central region was bounded above by the upper crust and below by a metallic melt region (lower crust). The upper crust was formed when molten structural materials and control rod alloys flowed onto cracks in the solidified upper portion of the central ceramic melt. The lower crust was formed by molten metallic materials that relocated to the bottom of the core relatively early in the accident sequence; it contained intact fuel pellet stacks surrounded by a solidified metallic melt.

Four flowsheets have been developed for treating the TMI-2 debris. The first flowsheet is similar to one developed earlier for processing spent fuel from a light water reactor (LWR).¹ It is meant for use with fuel from the TMI-2 reactor that has remained intact. The second flowsheet has been developed for the mixed ceramic melt, $(U,Zr)O_2$, containing separate uranium- and zirconium-rich phases. The third and fourth flowsheets are intended to handle debris containing agglomerates of metallic and ceramic phases. The metallic phases contain both structural and control rod components (iron- and silver-rich phases). One flowsheet is for handling a charge that is mainly mixed $(U,Zr)O_2$ phase (90 wt%), while the other flowsheet deals with a charge that is predominantly metallic (90 wt%) in composition. These two flowsheets represent two extreme situations, and the real debris composition may lie anywhere in between these two extremes. In developing all four flowsheets, we made certain assumptions:

- (1) The burnup is assumed to be one-tenth that of the LWR fuel. Thus, the burnup for the TMI-2 fuel is assumed to be 0.33 wt%, while the burnup for the LWR fuel is 3.3 wt%. This effectively increases the amount of uranium and reduces the amount of fission products in the charge.
- (2) The cladding material is assumed to be oxidized in all cases, except for the portion of the fuel that is treated as being intact. All the components of the cladding material (Zr, Fe, and Sn) are assumed to be oxidized to ZrO_2 , Fe_2O_3 , and SnO_2 , respectively.
- (3) The elements from the structural and the control rod components are assumed to remain metallic, as observed in the upper and lower crust regions. The flowsheets developed for the TMI-2 rubble are similar to the flowsheet developed for the LWR fuel, except that a larger amount of reductant is required for the oxidized cladding, and the amount of noble metal stream is larger wherever structural elements are mixed with the fuel.

The characteristics of the TMI-2 core debris were reviewed to find a suitable simulated fuel that could be used in laboratory- and engineering-scale experiments. The TMI-2 debris characteristics were compared with those from earlier ANL core-melt experiments, which were designed to

determine the interactions that occur between molten reactor fuel and concrete.² This comparison has confirmed that the core-melt experiment debris will be a satisfactory substitute for the mixed $\text{UO}_2\text{-ZrO}_2$ phase in TMI-2 fuel. Future work will concentrate on demonstrating that the lithium reduction process can be applied to simulated TMI-2 debris.

B. *Laboratory-Scale Testing*

1. Electrolysis of Lithium Oxide

The initial step in the lithium process uses lithium metal to reduce the oxide fuel in molten salt. The Li_2O reduction product dissolves in the salt. To minimize waste, an electrochemical step is under development to recover the salt and lithium for recycle by converting the Li_2O back to lithium metal. Laboratory-scale experiments were performed during this period to investigate electrowinning of lithium metal from Li_2O in molten LiCl salt.

Anode performance is one of the key factors that has to be improved to successfully regenerate the reduction salt and lithium metal by electrowinning. In our earlier experiments testing a Pt-Rh anode, it had been observed that when tellurium was present in the electrolyte, a layer of compounds formed on the Pt-Rh anode surface and insulated the anode.³ Therefore, experiments were conducted to test the concept of employing a molybdenum getter electrode to remove tellurium from the electrolyte. These experiments were carried out in two stages. The first stage was a preliminary electrolysis to remove tellurium from the electrolyte by using a molybdenum rod as the anode. The electrolysis was conducted at a constant cell voltage of 1.6 V. This voltage was chosen because it lies between the decomposition potential of Li_2Te and the $\text{Li}_2\text{O-Mo}$ reaction potential. The final stage was the electrowinning of lithium metal from Li_2O . A Pt-Rh tube was employed as the anode, and the electrowinning was performed at a constant cell voltage of 3.0 V. The experimental results indicated that the concept of using a molybdenum sacrificial electrode to remove the tellurium has promise. The electrolysis was successfully brought to completion, and the current efficiency achieved was 81%. Further work on the electrowinning anode is reported in Sec. VI.B.2.

Two experiments were conducted to demonstrate the concept of direct UO_2 reduction with lithium electrowinning. This concept is illustrated in Fig. VI-1, which is a sketch of the cell setup employed in these experiments. The anode is a Pt-Rh tube, which is housed inside an MgO shroud that is open at the bottom. The cathode is a cylindrical basket made of stainless steel (SS) screen (325 mesh), with a SS support frame and SS tube (3.2-mm OD). The tube serves as a conductor and also as a helium-gas purge tube for the cell. The purpose of the helium purge is to dilute the oxygen concentration in the gas phase during electrolysis. The cell container is a high-density MgO crucible.

² J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1992*, Argonne National Laboratory Report ANL-93/17, p. 137 (1993).

³ J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, p. 107 (1995).

Fig. VI-1. Schematic of Experimental Cell for Uranium Oxide Reduction with Simultaneous Lithium Electrowinning

For the first experiment, the cell container was loaded with 429 g of LiCl salt and 8.75 g of Li_2O , and 100 g of UO_2 chips was loaded inside the basket cathode. The second experiment was similar except that only 55 g of UO_2 was used. During electrolysis, the lithium metal produced at the cathode reduced the UO_2 to uranium metal and re-created the lithium oxide:

The experiments were performed at 650°C and at a constant voltage of 3.0 V. The cell current was very stable during the entire period (approximately 30 h) of electrolysis. Post-electrolysis examination of the two cells showed that the SS basket cathode and conductor tube maintained their original condition. For the first experiment, in which 105% of the theoretical current was passed, some of the interiors of the uranium chips contained unreacted UO_2 . In the second experiment, in which 140% of the theoretical current was passed, the UO_2 chips contained in the cathode basket were completely reduced to uranium metal. This experimental result demonstrated that the concept of direct UO_2 reduction is workable.

2. Improved Anodes for Electrolysis of Lithium Oxide

Work on improvement of anodes for the electrochemical reduction of lithium oxide in a lithium chloride melt has focused on developing inert anode materials and improving the cell geometry for the platinum anode system. In laboratory- and engineering-scale cells tested to date, Pt-10% Rh electrodes have shown good stability. Performance (as measured by the production of lithium metal) in the laboratory-scale cells has also been good. Therefore, the primary objective in seeking new materials has been to reduce cost by eliminating the expensive Pt-Rh anode without seriously lowering performance. In the initial engineering-scale test, the performance with a platinum electrode was poor. Work was, therefore, focused on identifying the reason for the poor performance and correcting it. This problem developed into one of designing the electrode and cell geometry so that the desired fluid flow in the cell could be achieved.

The initial engineering-scale experiment (Fig. VI-2) used a cylindrical cell with a centrally located finned anode (6.4-cm high and 8.9-cm OD) inside a 43.2-cm dia cathode. A 10.5-cm ID shroud was intended to capture the oxygen released from the anode. A second shroud, 35.6-cm dia, was submerged about 5 cm into the salt to isolate the lithium evolved at the cathode. Unfortunately, this geometry did not produce lithium metal; the flow patterns that appear to have contributed to this problem are indicated in Fig. VI-2. Oxygen was liberated at the anode in the form of very small bubbles, which did not coalesce rapidly and which remained relatively stationary with

Fig. VI-2.

Anode Design Used in First Engineering-Scale Experiment for Electrowinning Li_2O

respect to the surrounding fluid. Consequently, the released oxygen did not rise to the surface of the salt. This oxygen may be thought of primarily as creating a homogeneous fluid with a lower density than the salt alone. When the current is initiated, the oxygen-salt mixture rises within the shroud;

after a short period the shroud becomes filled with the salt-oxygen mix, and the driving force for continued flow into the shroud is eliminated. Once this occurs, the additional oxygen produced flows outside the shroud by natural convection, and the oxygen reacts with the lithium in the salt near the cathode. This scenario was confirmed in a flow visualization test with a full-scale water electrolysis mockup, using Plexiglas® components and a 1 M KOH solution.

A new design was developed to correct this flow problem. In this geometry (Fig. VI-3), an upward flow of salt within the shroud is driven by the rising sparge gas. Holes in the inner shroud near the salt surface permit the salt to exit the inner shroud, flow downward between the shrouds, and thereby complete the flow loop. Oxygen from the anode is entrained by the flow, rises with the salt, and is largely removed from the salt in the turbulent salt surface. Tests and calculations for this new design confirmed the expected performance. In flow visualization tests, water was seeded with reflective particles and illuminated with a fan-shaped laser beam. These confirmed that the flow pattern produced by sparge gas formed as anticipated and also confirmed that the region outside the outer shroud could be made relatively quiescent by extending the outer shroud deeply in the salt. Water electrolysis testing was again done for the new conditions, and the flow velocities anticipated in the various regions of the system were calculated. An anode assembly was designed based on the results of the experiments and calculations.

Fig. VI-3.

Modified Anode Design Used in Second Engineering-Scale Experiment for Electrowinning Li_2O

Work has also progressed on identifying stable materials to replace the expensive Pt-Rh anode. Metal electrodes are precluded because of stability problems. Recent effort has focused on ceramic oxides because of the oxygen evolution at the anode surface. On the basis of experimental evidence and material properties, the primary candidates are lithium-doped NiO and Fe_3O_4 . Each is orders of magnitude more conductive than the salt and appears to be stable in the

anode environment. Cracking from thermal shock is a significant problem for all potential ceramic electrodes. It is of particular concern for this application because relatively frequent insertion and removal of the electrode from the molten salt will be required. A method of imparting a high degree of thermal shock resistance for the electrodes has been demonstrated. Approximately 10 wt% MgO incorporated into NiO resulted in a laboratory-scale electrode that could be removed from a furnace at 650°C and immediately quenched in water without apparent physical degradation. Both Fe_3O_4 and NiO anodes have been run in laboratory-scale cells. The Fe_3O_4 anodes were mechanically weak due to fabrication problems but appeared to be stable. The NiO suffered little or no attack in laboratory-scale testing. The emphasis is now on improved fabrication procedures for both candidate materials. For Fe_3O_4 this requires procedures for preventing oxidation or reduction during fabrication, and for both NiO and Fe_3O_4 , it requires development of an integral metal component for attachment of current leads. Effort will be focusing on developing a continuous metal sheath that will allow current-lead attachment and will provide a very durable component for in-cell handling.

3. Behavior of Rare-Earth Fission Products

In the electrometallurgical treatment of spent oxide fuels, it is important to understand the behavior of the fission products. A detailed study is underway to determine the behavior of rare-earth (RE) fission products in different processing conditions. First, it is important to determine the concentration of rare earths in the salt phase. This determination is complicated by three main factors: the rare earths do not all behave similarly; the sesquioxides, RE_2O_3 , are converted to the mixed oxides, LiREO_2 , under certain process conditions; and there is a strong mutual influence among the rare earths in solution in the salt phase. Several laboratory-scale experiments have been performed to address these factors.

Laboratory-scale experiments were performed by the equilibration of LiCl containing known concentrations of lithium and Li_2O with RE_2O_3 at 650°C. The rare earths chosen for this study included Nd, Ce, Eu, and Sm. Several experiments were conducted at various concentrations of Li_2O (0 to 8 wt%) in LiCl. After equilibration, filtered salt samples were analyzed for their rare-earth concentration by inductively coupled plasma/atomic emission spectrometry and for their Li_2O concentration by titration with 0.1 N HCl. At the end of the experiment, the insoluble rare-earth oxide phase was identified by X-ray diffraction. The analytical results were used to derive thermodynamic data for the mixed oxides. Models are being constructed to predict the behavior of the rare-earth fission products under various process conditions.

The results obtained so far indicate that Nd and Ce behave in a similar manner in that their concentration in the salt phase increases with increasing Li_2O concentration. On the other hand, Eu and Sm concentrations in the salt phase decrease with increasing Li_2O concentration in the salt. Most experiments were done under conditions where the salt was saturated in lithium. However, experiments were done in the absence of lithium, and the results showed that the concentrations of Eu and Sm in the salt phase are significantly reduced in the absence of lithium. This is illustrated for europium in Fig. VI-4, and a similar behavior is observed with samarium. It is consistent with the expectation that the dichlorides of Eu and Sm, formed in the presence of lithium, are the dominant

Fig. VI-4.

Europium Concentration in LiCl at 650°C in Presence (filled circles) and Absence (open circles, UR-122) of Lithium

soluble species for the Eu and Sm fission products. Mixed oxides, $LiREO_2$, were observed to form in all the cases when the Li_2O concentration in the salt phase was high enough, and this transition point (Li_2O concentration) for the change from the sesquioxide to the mixed oxide depends on the relative free energies of formation of the mixed oxide and the sesquioxide. Free energies of formation of $LiREO_2$ have been derived from the experimental measurements. The derived free energies of formation at 650°C are -101.445 kJ/mol for $LiNdO_2(c)$, -100.628 kJ/mol for $LiCeO_2(c)$, -995.8 kJ/mol for $LiEuO_2(c)$, and -103.365 kJ/mol for $LiSmO_2(c)$.

The only factor that remains to be investigated is the complex issue of the mutual influence of the rare earths in the salt phase. This will be part of a future study.

C. Engineering-Scale Demonstration

The objectives of the engineering-scale demonstration are to (1) provide proof that the individual process steps defined by the laboratory-scale experiments work at the 20-kg batch size and (2) obtain engineering information needed to further scale up the equipment and operations to larger plant sizes needed to process the DOE spent fuel in the time frame allocated and at the locations specified. The demonstration experiments are conducted in a large ($7.6 \times 2.4 \times 2.6$ m) argon-filled glovebox and a smaller ($2.4 \times 1.1 \times 2.6$ m) nitrogen-filled glovebox with an interconnecting transfer lock. A schematic of the gloveboxes is given in Fig. VI-5. Tests in these gloveboxes are underway to demonstrate the electrometallurgical process steps of reduction, electrowinning, casting, oxidation, drying, and retorting. The gloveboxes have the capability of storing the process materials between steps. The argon glovebox was completed in 1993, and the initial reduction demonstration (ES-1) was run with 4.4 kg of natural UO_2 -based simulated fuel. The reduction was based on the lithium process and employed a $LiCl$ - KCl salt at 500°C. The product was a very fine metal precipitate that was not easily consolidated into ingots or electrorefined. The spent salt from this experiment was not recovered, as is required to meet the waste minimization goal of

the process. During 1994 new process equipment was installed in the argon glovebox, and the nitrogen glovebox was completed.

Fig. VI-5. Engineering-Scale Process Glovebox (Plan View)

Two experiments were run in 1995. The first experiment (ES-2) combined the reduction of TRU-containing simulated fuel with the recovery of the spent salt and reductant by electrowinning. It was conducted at 650°C using a pure LiCl salt and 10 kg of simulated fuel to proof test the newly installed equipment and to verify the effectiveness of procedures and personnel training. The fuel reduction was successful, and the procedures and training were shown to be satisfactory. However, the electrowinning process step did not regenerate the spent salt and reductant because of design and material deficiencies in the anode that were not apparent during laboratory-scale testing. The second experiment run in 1995 was a test of a redesigned anode to regenerate the spent salt left from the unsuccessful first attempt.

The design of the ES-2 experiment differed from the earlier experiments in that the reduction process step used a stacked basket that held the simulated fuel immobile during the reduction. This basket concept was introduced to enhance the ability to easily transfer the reduced fuel from the reduction vessel to the next process in the flowsheet, electrorefining. This basket concept is in keeping with the present direction of development of large-scale electrorefiners.

The anode design in the ES-2 experiment also differed from the laboratory-scale tests. The laboratory-scale tests used Pt-10% Rh tubing (12.7-mm dia) for the anode, and the anode and cathode were usually contained in shrouds, which ducted the oxygen out of the crucible (anode) or confined the lithium produced to a localized volume (cathode). The ES-2 experiment used a star-shaped anode to enhance the effective surface area in an attempt to increase the evolution of oxygen. It also used an alumina shroud around the anode with the stainless steel crucible as the

cathode. During the ES-2 experiment, no oxygen was present in the anode off-gas stream, and upon post-test analysis of the anode shroud, significant quantities of the alumina were found to have eroded away and dissolved in the salt, probably as lithium aluminate. The reactants present in the process had been expected to react with the alumina, but chemical kinetics were thought to be slow because no problems had been observed during the laboratory-scale experiments.

Water electrolysis visualization and flow studies were done to determine other probable causes for the failure of the first engineering-scale anode, as described in Sec. VI.B.2. An electrowinning experiment, using the redesigned anode, did produce oxygen but much less than expected. In addition, the cylindrical Pt-Rh anode was severely corroded. Post-test analysis is not yet complete; however, further laboratory- and engineering-scale tests of the electrowinning process will be necessary to gain an understanding of the important design parameters involved in producing a workable anode.

Future engineering-scale tests will be used to demonstrate that flowsheet processes are viable for the DOE spent fuel inventory. The near-term emphasis will be on processing simulated TMI-2 core debris (Sec. VI.A).

VII. APPLIED PHYSICAL CHEMISTRY

The program in applied physical chemistry involves studies of the thermodynamic and transport properties of selected materials in environments simulating those of fission and fusion energy systems, as well as other technologically important systems.

A. *Thermophysical Property Studies of Metallic Nuclear Systems*

We are continuing to develop a consistent set of phase diagrams for key systems of importance to nuclear reactor technology and related waste and plutonium-handling issues. Presented below is the most recent in a series of studies involving the critical evaluation and thermodynamic optimization of binary and ternary subsystems of the Pu-U-Zr-Fe system at high temperatures. In this work, all available thermodynamic and phase equilibrium data for a system are collected and critically evaluated simultaneously to obtain one set of model equations for the Gibbs energies of all phases as functions of composition and temperature. From these equations, all of the thermodynamic properties and the phase diagram can be calculated. In this way, all the data are rendered self-consistent and consistent with thermodynamic principles. Discrepancies can often be resolved, and interpolations and extrapolations can be made, in a thermodynamically correct manner.

1. Binary System Calculations

Complete optimizations of the Pu-U, U-Zr, and Zr-Pu binary systems have already been presented.¹⁻³ Since these were published, new measurements of the liquidus and solidus of the Pu-U and Zr-Pu systems have become available. Accordingly, the liquid phases of these two systems were re-optimized in a collaborative project with Ecole Polytechnique, Montreal. Except for the liquid-phase properties and the liquidus and solidus in the Pu-U and Zr-Pu systems, these differ only very slightly from those reported previously.¹⁻³

The most significant changes from the previous work involved the Pu-U system. Recent measurements of the liquidus and solidus temperatures by Okamoto et al.⁴ using differential thermal analysis (DTA) show liquidus temperatures up to 40° lower than those reported by Ellinger et al.,⁵ upon which our earlier evaluation² was principally based. A datum of Kelman et al.⁶ is in good agreement with Okamoto et al.⁴ As discussed in the previous evaluation,² the width of the two-phase (solid + liquid) region depends upon the enthalpy of fusion of uranium. The controversy surrounding this value was resolved earlier in favor of the value 9.148 kJ/mol (2185 cal/mol). However, this resulted in the calculated two-phase region being significantly narrower than that reported by Ellinger et al.⁵ Nevertheless, the width of the two-phase region reported by Okamoto et al.⁴ and

¹ L. Leibowitz, R. A. Blomquist, and A. D. Pelton, *J. Nucl. Mater.* **167**, 76-81 (1989).

² L. Leibowitz, R. A. Blomquist, and A. D. Pelton, *J. Nucl. Mater.* **184**, 59-64 (1991).

³ P. K. Talley, A. D. Pelton, and L. Leibowitz, to be published in *J. Nucl. Mater.*

⁴ Y. Okamoto, A. Maeda, Y. Suzuki, and T. Ohmichi, *J. Alloys Compounds* **213/214**, 372-374 (1994).

⁵ F. H. Ellinger, R. O. Elliott, and E. M. Cramer, *J. Nucl. Mater.* **3**, 233 (1959).

⁶ L. R. Kelman, H. Savage, C. M. Walter, B. Blumenthal, R. J. Dunworth, and H. V. Rhude, in *Plutonium 1965*, Ed., A. E. Kay and M. B. Waldron, Chapman and Hall, London, pp. 458-484 (1967).

Kelman et al.⁶ is in excellent agreement with the calculations based on this enthalpy of fusion for uranium.

At uranium fractions below 0.4 in the Pu-U system, liquidus and solidus points measured by the Mound Laboratory⁷ lie at somewhat higher temperatures than the points of Okamoto et al. that were given preference. The present evaluation thus results in a small (liquid + η) region, whereas the earlier evaluation,² as well as the Pu-U diagram proposed by Ellinger et al.,⁵ showed no such region, although the (liquid + Γ) and (Γ + η) regions were calculated to approach within 2° of each other. However, within experimental error limits, the data of Ellinger et al.⁵ are consistent with the present interpretation. Work in this area will continue as new data become available.

2. Ternary System Calculations

The earlier calculation⁸ of the solidus and liquidus surfaces of the Pu-U-Zr ternary system has been revised to take account of additional experimental data and to render the optimization self-consistent with sub-solidus data which were not considered in the earlier evaluation. In collaboration with Ecole Polytechnique, Montreal, we have now optimized all available data on sub-solidus equilibria in the Pu-U-Zr system to obtain Gibbs energy expressions for all solid phases. From these expressions, the solvus surface and the solubilities in all solid ternary phases have been calculated.

The Gibbs energy of the ternary solution phases has been represented by means of the Kohler equation,⁹ which is based upon an extension of regular solution theory:

$$G = (X_{\text{Pu}}G_{\text{Pu}}^{\circ} + X_{\text{U}}G_{\text{U}}^{\circ} + X_{\text{Zr}}G_{\text{Zr}}^{\circ}) + RT (X_{\text{Pu}} \ln X_{\text{Pu}} + X_{\text{U}} \ln X_{\text{U}} + X_{\text{Zr}} \ln X_{\text{Zr}}) \quad (1)$$

$$+ (X_{\text{Pu}} + X_{\text{U}})^2 G_{\text{PuU}}^{\text{E}} + (X_{\text{U}} + X_{\text{Zr}})^2 G_{\text{UZr}}^{\text{E}} + (X_{\text{Zr}} + X_{\text{Pu}})^2 G_{\text{ZrPu}}^{\text{E}} + G_{\text{PuUZr}}^{\text{E}}$$

where X_i is the atom fraction of species i , G_i° is the free energy of species i , G_{AB}^{E} is the excess free energy from the A-B binary system, and $G_{\text{ABC}}^{\text{E}}$ is the excess free energy from the A-B-C ternary system.

In Eq. 1, the G_{AB}^{E} binary terms are evaluated not at the ternary composition point but in the A-B binary system at the same ratio $X_{\text{A}}/(X_{\text{A}} + X_{\text{B}})$ as at the ternary composition point. That is, X_{A} and X_{B} in the expressions for G_{AB}^{E} are replaced by $X_{\text{A}}/(X_{\text{A}} + X_{\text{B}})$ and $X_{\text{B}}/(X_{\text{A}} + X_{\text{B}})$, respectively. The G_{AB}^{E} terms are preceded by the factor $(X_{\text{A}} + X_{\text{B}})^2$, which represents the probability that a pair of neighboring atoms is either an A-A, a B-B, or an A-B pair. The Kohler equation thus

⁷ *Reactor Fuels and Materials Development Plutonium Research*, Mound Laboratory Report MLM-1346, -1402, -1445 (1967-1968).

⁸ L. Leibowitz, E. Veleckis, R. A. Blomquist, and A. D. Pelton, *J. Nucl. Mater.* **154**, 145-153 (1988).

⁹ F. Kohler, *Monats. Chem.* **91**, 738 (1960).

assumes that the Gibbs energy of forming two A-B bonds from an A-A and a B-B bond remains constant at constant $X_A/(X_A + X_B)$ ratio.

The ternary excess terms, G_{PuUZr}^E , vanish in all three binary systems (Pu-U, U-Zr, and Zr-Pu). In the present study, these were either set to zero or were given by a one-parameter expression $aX_{\text{Pu}}X_{\text{U}}X_{\text{Zr}}$, where a is a temperature-independent adjustable parameter chosen to best represent the available data for the ternary system.

For solutions in which the solubility of one component is limited, the G_i^0 terms and/or certain G_{AB}^E expressions in Eq. 1 were also found by fitting ternary data. For example, for the η phase in the Pu-U binary system, the calculated solubility of zirconium can be controlled through the terms G_{Zr}^0 , G_{UZr}^E , and G_{ZrPu}^E , which were chosen to give the best representation of the available ternary data.

All available phase equilibrium data in the Pu-U-Zr ternary system have been analyzed to obtain optimized equations for the Gibbs energies of all phases as functions of composition and temperature. Phase diagrams calculated from these optimized thermodynamic equations (see Fig. VII-1 for ternary phase diagrams at 873 and 923 K) agree with all reported data within experimental error limits. The calculated liquidus and solidus temperatures are estimated to be accurate to $\pm 25^\circ$ to $\pm 50^\circ$, and the calculated Γ -phase solvus temperatures (the point at which another phase first precipitates from the Γ -phase) have an estimated accuracy of $\pm 10^\circ$. The extent of ternary solubility in the other solid phases has been calculated as a function of temperature and is in agreement with the published data.^{7,10} The calculated phase diagram is believed to be the best presently available estimate of the Pu-U-Zr system.

3. Experimental Studies of Fe-Zr System

Because of disagreements among published phase diagrams for the Fe-Zr system, experimental studies have been undertaken following our previous work on a thermodynamic optimization of that system.¹¹ Studies involving differential thermal analysis and scanning electron microscopy of annealed and quenched samples have been performed. Clarification of some important regions of the Fe-Zr system is in progress. To date, we have verified the existence and extent of the Fe_2Zr - FeZr_2 , FeZr_2 - FeZr_3 , and FeZr_3 -Zr fields. However, a field supposedly existing just below the 1200 K eutectic that should be a FeZr_2 -Zr field has not been confirmed. This work is continuing to attempt to clarify the phase relations existing in this complex system. The previously calculated Fe-U-Zr ternary system may also require modification, depending on the results of our re-examination of this binary system.

¹⁰ D. R. O'Boyle and A. E. Dwight, in *Nuclear Metallurgy*, Vol. 17, *Plutonium 1970 and Other Actinides*, Ed., W. N. Miner, Chapman and Hall, London, p. 720 (1970).

¹¹ A. D. Pelton, L. Leibowitz, and R. A. Blomquist, *J. Nucl. Mater.* **201**, 218 (1993).

Fig. VII-1. Calculated Pu-U-Zr Phase Diagram at 873 K (a) and 923 K (b)

B. *Development of Synchrotron Analytical Capabilities*

The purpose of this work is to develop a micro-analytical facility that will allow simultaneous X-ray diffraction and X-ray fluorescence examination of materials on a microscopic scale. For this work, a dedicated beam line is being developed at the synchrotron radiation source at the Louisiana State University Center for Advanced Microstructures and Devices. This work will result in a unique facility for the microscopic X-ray examination of a wide range of technologically important systems.

A vast array of technologies face fundamental materials issues related to small-scale structures. The present work employs a synchrotron source to extract structural and compositional information from bonded materials that can lead to a better understanding of the processes involved. In contrast to scanning electron microscopy, synchrotron radiation sources can reveal both composition (via fluorescence) and structure (via absorption spectroscopy and diffraction), providing an ideal tool for studying materials and their interactions on a microscopic scale. For example, the kinetics and thermodynamics of material interactions can be studied by conducting experiments with isothermal diffusion couples. These experiments consist of bonding two materials under controlled conditions and examining the interdiffusion of the chemical elements. In such a study, a collimated or focused synchrotron X-ray beam can be translated in steps across the diffusion zone. At each step, diffraction patterns or fluorescence spectra can be collected to provide structure and composition profiles along the diffusion path.¹² Similar techniques can be applied to other interfaces of interest such as welds, brazes, and battery or fuel-cell connections.

The micro-analytical beamline is now capable of performing X-ray fluorescence studies by using a collimated beam of white X-rays. A unique four-circle goniometer with an X-Y-Z translation stage containing 1- μm stepping motors allows samples to be manipulated and scanned in many orientations. An intrinsic germanium detector for collecting characteristic X-rays from samples was designed with a snout that can be placed close to the sample to maximize collection efficiency. A special X-ray collimator was also designed to provide a thin line of X-rays either 50 μm , 20 μm , or 6 μm wide. This collimator is now being marketed for other synchrotron users.

The table and diffractometer motors that are used for sample alignment and positioning have been successfully tested remotely through an Alpha computer (Digital Equipment Corp.). Software provided by the University of Chicago allows "virtual motors" to be defined, so that several motors can be activated simultaneously. For example, a single command can pitch the table to a given angle by operating four motors at the same time. Software was also set up to collect X-ray spectra from three detectors and to analyze the results. A linear fluorescence scan was performed by collecting spectra as a copper and titanium sample was stepped through a collimated X-ray beam. The spectra were then analyzed to produce a qualitative profile of the copper and titanium concentrations in the sample. Quantitative fluorescence work will require that reference standards with known concentrations be used. Additional software will be needed to account for cross-absorption effects between elements. Development work is also needed for a monochromator that will allow X-ray

¹² M. C. Petri, L. Leibowitz, and P. Schilling, "Hard X-ray Microanalytical Beamline at the CAMD Synchrotron," in *X-ray Microbeam Technology and Applications*, Ed., W. Yun, Proc. of Soc. for Photo-optical Instrumentation Engineers, pp. 180-184 (1995).

diffraction measurements. In a collaboration with University of Chicago researchers, focusing optics will be designed to intensify the X-ray flux. These upgrades will allow X-ray diffractometry and X-ray absorption spectroscopy for structural analyses.

C. *Fusion Materials Studies*

A critical element in the development of a fusion reactor is the blanket for breeding tritium fuel. We are conducting experimental and calculational studies with the objective of determining the feasibility of using vanadium alloys as structural materials and lithium-containing ceramics (e.g., Li_2O , LiAlO_2 , Li_4SiO_4 , Li_2ZrO_3 , and Li_2TiO_3) as breeder materials.

1. Use of Vanadium Alloys with Ceramic Breeder Materials

Fusion energy is considered to be an attractive energy form because of its minimal environmental impact. To maintain this favorable status, every effort needs to be made to use low activation materials wherever possible. For example, of the several candidate lithium-containing ceramics being considered for use in the breeder blanket, Li_2O and Li_2TiO_3 are attractive choices because of their low activation. Also, other low activation materials, including vanadium alloys, are being considered for use as structural materials in the blanket. The suitability of vanadium alloys for containment of lithium ceramics is the subject of this study. Thermodynamic evaluations are being used to estimate the compatibility and stability of candidate ceramic breeder materials (Li_2O , Li_2TiO_3 , and Li_2ZrO_3) with vanadium and vanadium alloys. This thermodynamic evaluation will focus first on solid-solid interactions. As a tritium breeding blanket will use a purge gas for tritium recovery, gas-solid systems will also receive attention.

This thermodynamic evaluation focused on the oxidation of vanadium/vanadium alloy by lithium oxide, an undesirable reaction if vanadium were to be used as a structural material. The vanadium/oxygen phase diagram is quite complicated. The region of interest for this study is the α region, which exhibits an oxygen content well below that required for stoichiometric vanadium oxide. The chemistry of this region depends strongly on the oxygen potential and the kinetics of the dissolution of oxygen into the vanadium.

Equilibrium-type calculations were carried out for the $\text{Li}_2\text{O}/\text{V}$ system. The equilibrium constants were calculated to range from 10^{-7} to 10^{-11} for a typical blanket operating temperature regime (700-1000 K), indicating little potential for oxidation of vanadium. Similar calculations have been carried out for reactions resulting in the formation of V_2O_3 and V_2O_5 . These calculations show an even stronger resistance to formation of the vanadium oxide, with equilibrium constants in the range of 10^{-20} to 10^{-90} for a similar temperature regime.

The competitive reactions of various metal/metal oxide couples have been represented in an Ellingham diagram (see Fig. VII-2), wherein the oxygen potential for each couple is plotted against the temperature. This plot includes the elements Fe, Cr, V, Ti, Zr, and Li, which are all components in the candidate ceramics and structural materials. From a thermodynamic perspective, the diagram shows that Fe, V, and Cr are unable to reduce lithium oxide. Zirconium is able to reduce lithium oxide above 1300 K, while temperatures have to be increased above 1400 K before titanium

is able to reduce lithium oxide. This thermodynamic analysis suggests a very low probability for vanadium oxide formation under breeder blanket conditions.

The approach taken to evaluate the ternary lithium ceramics Li_2ZrO_3 and Li_2TiO_3 was to consider that these materials were composed of the binary oxides Li_2O and ZrO_2 and Li_2O and TiO_2 . This separation into binary components facilitates assessing whether either of the components making up the ternary ceramic may, in any fashion, interact with vanadium (alloy) to form a corrosion layer. As can be seen from the oxygen potential data for TiO_2 and ZrO_2 in Fig. VII-2, vanadium metal will not likely reduce either zirconium oxide or titanium oxide. Therefore, it appears safe to conclude that the lithium-containing ceramics are compatible with vanadium metal or vanadium alloy for the expected range of blanket operating temperatures.

Fig. VII-2.

Ellingham Diagram for Metal/Metal Oxide Couples at 450-1300 K. The y-axis plots $-G_f = RT \ln P_{\text{O}_2}$, where G_f is the "oxygen potential," R is the gas constant, T is temperature, and P_{O_2} is the oxygen partial pressure.

A possible problem may arise when these ceramics are placed in a neutron environment, where transmutation of lithium takes place. When tritium is released from the ceramic, it is believed that the tritium is likely to be released as a condensable "tritiated water" (T_2O), which may react with the lithium oxide to form LiOH (where H has been used instead of T):

The LiOH is soluble to a small extent in the lithium oxide, and a solid solution is thus likely to form. Also important to this evaluation is to estimate the expected partial pressure of tritiated water in an operating blanket. Such information can be used to determine the potential for formation of lithium tritoxide, LiOT(g). Because the tritoxide species can be very reactive, its behavior in this system must be thoroughly understood.

The SOLGAS computer code¹³ was used to carry out equilibrium calculations that would simulate the transmutation (i.e., neutron irradiation in a breeder blanket) of lithium to tritium for both the Li₂O and the Li₂ZrO₃ blankets. For the Li₂O blanket, we assumed that the LiOH (LiOT) was either in solid solution in the Li₂O or in the gas phase. The purge gas was assumed to be a mixture of He, H₂, and the oxygen-containing species formed by the liberation of oxygen resulting from the transmutation of lithium. This equilibrium calculation indicated that essentially all of the liberated oxygen ended up as VO; a very small amount of the oxygen formed H₂O, O₂, and LiOH(g); and a small amount of the LiOH was present in solid solution in the Li₂O. However, these "sinks" for oxygen were not very competitive with vanadium. For up to 2% transmutation of the lithium, only VO was formed. The higher oxides of vanadium and the lithium vanadate (LiVO₃) were not formed. The results for the Li₂ZrO₃ blanket were similar to those found for the Li₂O blanket; however, no solid solution of Li₂O and LiOH formed. Some of the liberated oxygen from the transmutation ended up as a separate ZrO₂ solid phase.

Our study assessing the compatibility between lithium-containing ceramics and vanadium alloys indicates that vanadium alloy has potential for use as a structural material in the design of ceramic breeder blankets for fusion reactors. There is no apparent compatibility problem between the ceramics and vanadium metal or vanadium alloys. However, compatibility problems may exist when small amounts of moisture are present in the system. The partial pressure of moisture generated during irradiation of lithium ceramics in a breeder blanket could be very close to that required thermodynamically for oxidation of vanadium to occur. However, there is still a paucity of data on the kinetics of vanadium oxidation. To resolve this issue, laboratory and in-reactor compatibility experiments need to be pursued.

2. Interactions of Water Vapor with Li₂ZrO₃

The interaction of water vapor with lithium-containing oxide ceramics is of interest because they are being considered for use in the tritium breeding blanket of a fusion reactor. The extent of interaction may affect the performance of the ceramic in two major areas, its physical integrity and the tritium inventory within the ceramic. Concern has been expressed that the reaction of water vapor with ceramic breeder material can form LiOH(g) and thereby enable transport of lithium from the breeding blanket region, affecting the breeding characteristics and mechanical strength of the blanket. In addition, the equilibrium between tritiated water in the gas phase and tritium in the ceramic breeder plays an important role in determining the tritium inventory in the ceramic.

¹³ G. Eriksson, *Chemica Scripta* 8, 100 (1975).

The interaction of water vapor with lithium oxide has been investigated by a number of workers.^{14,15} However, very little quantitative work has been performed to characterize the extent of reaction between water vapor and Li_2ZrO_3 . Our recent work in this area has included (1) thermodynamic calculations to determine whether breeder blanket transport of LiOH from Li_2ZrO_3 reacted with water vapor will be a problem and (2) measurement to determine whether the reaction between water vapor and Li_2ZrO_3 affects tritium inventory.

The thermodynamic calculations were carried out to determine the changes in Gibb's free energy for the reactions between water vapor and Li_2ZrO_3 to yield LiOH as a gas, liquid, or solid. The data for the free energy of formation for the respective reactants and products were obtained from Barin.¹⁶ For the condensed phases, solid LiOH was considered for temperatures below 744.3 K, while liquid LiOH was considered for temperatures above this point. Calculations for gaseous LiOH were performed over a wide temperature range.

The thermodynamic calculations indicated that the reaction to form LiOH(g) and ZrO_2 is highly unfavorable, with the free energy of formation ranging from +322 kJ at 600 K to +192 kJ at 1300 K. This translates into very low pressures of LiOH(g) over Li_2ZrO_3 . For moisture partial pressures of 10^{-5} atm (1 Pa), LiOH(g) pressures of less than 10^{-7} atm (10^{-2} Pa) at temperatures up to 1200 K were found. Even for moisture partial pressures as high as 10^{-4} atm (10 Pa), typical for some breeder blanket designs, LiOH(g) partial pressures less than 3×10^{-7} atm (3×10^{-2} Pa) at 1200 K were found. As a check on the LiOH(g) pressures obtained from these calculations, we also calculated the LiOH(g) pressure above Li_2ZrO_3 from reported $\text{Li}_2\text{O(g)}$ pressures and the equilibrium $\text{Li}_2\text{O(g)} + \text{H}_2\text{O(g)} = 2 \text{LiOH(g)}$. Both calculations indicate that the vapor pressure of LiOH(g) above Li_2ZrO_3 is extremely low, and that lithium transport via LiOH(g) vaporization should not be a problem when Li_2ZrO_3 is the breeder material.

The interaction of tritiated water vapor with Li_2ZrO_3 is also of interest due to the influence this reaction may have on the tritium inventory in such a material. Reaction of the Li_2ZrO_3 with HTO(g) or $\text{T}_2\text{O(g)}$ to form LiOT as a separate phase or in a solid solution would increase the tritium inventory. Adsorption of HTO or T_2O species on the Li_2ZrO_3 surface can also affect the tritium inventory. The extent of these reactions was investigated gravimetrically at temperatures of 473-923 K; water vapor was used as a substitute for HTO(g) . A sample of commercial Li_2ZrO_3 was placed in a platinum crucible suspended from a microbalance. The sample was heated to 1073 K under flowing helium for 5 h to remove any residual moisture from the sample. The furnace temperature was then lowered to the desired value under a flowing helium stream. After the sample had reached thermal equilibrium and the balance mass reading was steady, the gas was changed to $\text{He} + \text{H}_2\text{O}$ (H_2O concentrations were 202 ppm and 1000 ppm by volume). Changes in mass were followed over time to determine the weight gained by the sample. Also, mass loss was followed for the gas change from $\text{He} + \text{H}_2\text{O}$ to pure helium.

¹⁴ J. H. Norman and G. R. Hightower, *J. Nucl. Mater.* **122&123**, 913 (1984).

¹⁵ M. Tetenbaum, A. K. Fischer, and C. E. Johnson, *Fusion Technol.* **7**, 53 (1985).

¹⁶ I. Barin, *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft mbH, Weinheim, Germany (1993).

The results indicate that very little interaction occurred between water vapor and lithium zirconate, and the extent of interaction decreased with increasing temperature. It also appeared that the amount of water which reacted was proportional to the square root of the water pressure. Figure VII-3 shows the weight gain as the number of moles of H_2O reacted per mole of Li_2ZrO_3 normalized by the square root of the moisture partial pressure (in atmospheres). The mole fraction of water in the solid corresponding to this weight gain can be expressed as

$$X_{\text{H}_2\text{O}} = (1.76 \times 10^{-3}) P_{\text{H}_2\text{O}}^{0.5} e^{(906/T)} \quad (3)$$

The Li_2ZrO_3 weight gain generally occurred over a time period of 2-3 h; however, the experiments were continued for an additional 10-12 h, with no additional weight gain noticed.

Fig. VII-3.

Weight Gain as Function of Temperature for Water Vapor Reacted with Li_2ZrO_3 Samples ($X_{\text{H}_2\text{O}}$ = mole fraction of water; $P_{\text{H}_2\text{O}}$ = moisture partial pressure in atmospheres)

The decrease in the extent of the reaction with increasing temperature suggests that the Li_2ZrO_3 weight gain is due to moisture adsorption. The square-root dependence on the water partial pressure indicates dissociative chemisorption of the water molecule. The amount of surface coverage was estimated by assuming that the dissociatively chemisorbed water occupies the same volume as physisorbed water ($1.08 \times 10^{-9} \text{ m}^2/\text{molecule}$). The surface coverages were estimated to be in good agreement with those obtained by Kawamura et al.¹⁷ for samples with a similar specific surface area (our samples, $0.02 \text{ m}^2/\text{g}$; Kawamura et al., $0.06 \text{ m}^2/\text{g}$). These estimates indicate that the amount of reaction corresponds to less than a monolayer of surface coverage for the conditions investigated.

¹⁷ Y. Kawamura and M. Nishikawa, J. Nucl. Mater. **218**, 57 (1994).

Fig. VII-4. Measured and Calculated Weight Gain as Function of Temperature for Water Vapor Reacted with Li_2ZrO_3 (X_{LiOH} = mole fraction of LiOH; P_{H_2O} = moisture partial pressure in atmospheres)

Alternatively, the weight gain in these experiments may be due to formation of $LiOH(s)$ in the bulk Li_2ZrO_3 . Figure VII-4 compares the observed weight gain (expressed in terms of the mole fraction of LiOH which would form) with ideal solution calculations, which were based on the change in Gibb's free energy for the reaction $Li_2ZrO_3(s) + H_2O(g) = 2LiOH(l) + ZrO_2(s)$. The figure shows a much lower solubility than calculated from an ideal solution approximation. This indicates that the $LiOH/Li_2ZrO_3$ system is nonideal, with the activity coefficients for LiOH on the order of 100. This was not unexpected since LiOH in Li_2O also shows a large positive deviation from ideality, with activity coefficients for LiOH ranging from 20 to about 10,000 over the temperature range of interest for ceramic breeders.^{14,15} This leads to much lower solubility than predicted from an ideal solution calculation.

The low reactivity of $H_2O(g)$ with Li_2ZrO_3 suggests that the tritium inventory due to adsorption and/or solubility in Li_2ZrO_3 will be lower than the corresponding inventory for Li_2O . Of particular interest is the low temperature range, where precipitation of LiOH may lead to very large inventory in Li_2O . No hint of LiOH precipitation has been seen for Li_2ZrO_3 at temperatures down to 473 K. In sum, our results indicate that the thermodynamic stability of Li_2ZrO_3 makes it an excellent candidate for use in a tritium breeding blanket.

3. Modeling of Tritium Release from Lithium Oxide Surfaces

Lithium ceramics are being considered as tritium breeders for fusion technology. In numerous in-pile experiments, small amounts of hydrogen in the helium purge gas have been found to enhance the release of tritium from lithium ceramics. Despite this benefit, there are problems associated with tritium management via isotopic separation (due to the large hydrogen/tritium ratio) and tritium containment (arising from the presence of the reduced form of tritium and the potential permeation loss). To solve these problems, we need a better understanding of the mechanism through which hydrogen enhances tritium release. This knowledge would benefit the search for alternative "accelerator" materials for tritium release besides hydrogen. We have therefore developed a mechanistic model for the role of hydrogen in affecting tritium release. The model was derived from *ab initio* calculations concerning hydrogen chemisorption on Li_2O surfaces under typical breeder blanket conditions.

The *ab initio* calculations have provided insight into the experimental observation that tritium is released from Li_2O in the form of HT and HTO. Firstly, a bombardment of lithium ions by fast neutrons creates tritium in the form of T^+ . In this situation, there are several ways in which tritium could escape from the surface. Under normal conditions, a chemical species will be released from a solid surface in a molecular form, such as T_2 or T_2O . In the steady state and in the presence of irradiation with no hydrogen in the helium purge gas, the concentration of T^+ inside the solid is of the order of a few tens of parts per million.¹⁸⁻²² If the released form of tritium is T_2 or T_2O , the rate of release is proportional to the square of the tritium concentration in the lithium-based solid breeder material. The probability of forming T_2 or T_2O is therefore very small; consequently, the release rate is low. According to the present model the slow release of tritium in the absence of hydrogen is reaction-limited; that is, the process is limited by the difficulty of forming molecular species that require two tritium atoms. This slow tritium release in the absence of H_2 in the purge gas has been observed very extensively both in in-reactor tests and laboratory experiments.¹⁸⁻²²

The presence of H_2 (e.g., as an additive in the range of 0.1%-1%) in the purge gas stream provides a very different environment. The hydrogen is chemisorbed onto the lithium ceramic surfaces, forming OH^- and $\text{Li}^+\text{H}^-\text{Li}^+$ (as shown by the *ab initio* calculations). There are two possible reactions with the T^+ :

¹⁸ O. D. Slagle and G. W. Hollenberg, *Beatrix-II, Phase I: Data Summary*, Pacific Northwest Laboratory Report PNL-10279 (1995).

¹⁹ W. Dienst, D. Schild, and H. Werle, Kernforschungszentrum Karlsruhe Report KfK-5109 (1992).

²⁰ O. D. Slagle, T. Takahashi, F. D. Hobbs, K. Noda, D. L. Baldwin, G. W. Hollenberg, and R. A. Verrall, "Postirradiation Examination of BEATRIX-II, Phase I," to be published in *J. Nucl. Mater.*

²¹ H. Kwast, A. Kout, R. P. Muis, M. P. Stijkel, A. J. Flipot and J. D. Elen, *Fusion Eng. Des.* **8**, 359 (1989).

²² R. G. Clemmer, P. A. Finn, R. F. Malecha, B. Misra, M. C. Billone, D. L. Bowers, A. K. Fischer, L. R. Greenwood, R. F. Mattas, S.-W. Tam, R. B. Poeppe, G. T. Reedy, I. T. Dudley, F. F. Dyer, E. D. Clemmer, J. S. Watson, P. W. Fischer, J. R. Conlin, R. L. Childs, J. L. Scott, R. M. Arons, and A. E. Scandora, *The TRIO Experiment*, Argonne National Laboratory Report ANL-84/85 (1984).

or

In both reactions, the tritium release rate scales as the product of the surface coverage of the chemisorbed hydrogen and the tritium concentration. The hydrogen surface coverage is usually much larger than the tritium concentration. Therefore, the tritium release rate is proportional to the first power in the tritium concentration and not to its square, as is the case in the absence of hydrogen. As a consequence, the addition of hydrogen to the purge gas enhances the tritium release rate.

The present model suggests that relying on only the “intrinsic” impurity hydrogen level (which is present to the level of a few parts per million even in nominally “pure” helium), in contrast to adding hydrogen, is unlikely to be effective. In the former case the chemisorbed hydrogen surface coverage would be very low. The rates of HT and HTO formation would be no better, or even lower than, those of T_2 and T_2O . Hydrogen has to be added to a level substantially above the “normal” impurity level for it to be effective in enhancing tritium release. The present model also suggests that the tritium release rate cannot be enhanced by simply increasing the hydrogen partial pressure in the helium purge stream. In other words, there is a saturation effect. Our simulations indicate that a majority of the surface sites (i.e., the terrace sites) are not available for hydrogen chemisorption. Only a minority of sites (such as step ledges and point defects) are favorable. Once those sites are all occupied, further increases of the hydrogen partial pressure would not be useful. This effect has been observed experimentally, where hydrogen partial pressure beyond a few percent leads to no further significant enhancement of tritium release. No further work on this model is planned.

VIII. BASIC CHEMISTRY RESEARCH

Basic chemistry research is being pursued in three areas: (1) catalytic chemistry associated with molecular energy resources and precursor ceramic polymers, (2) materials chemistry of electrified metal/solution interfaces, molecular sieves, and diamond thin films, and (3) geochemical processes involved at mineral/fluid interfaces and in water/rock interactions occurring in active hydrothermal systems.

A. *Fluid Catalysis*

This program explores the catalytic reaction chemistry of small molecules that serve as precursors in many industrial processes. Precursors of interest include those of the C_1 chemical industry, e.g., CO, CO_2 , and CH_4 ; the ammonia synthesis precursors, H_2 and N_2 ; and the ceramic precursors, e.g., $(CH_3)_4Si$ and $(CH_3)_3B$. The efficient utilization of these molecules is potentially of great economic significance; however, in many cases the required conversion chemistry is difficult to achieve. We are exploring the conversion chemistry for several alternative strategies, including use of (1) phosphine-modified catalysts for the hydroformylation of olefins in supercritical fluids and (2) polyfluorophthalocyanine catalysts for hydrocarbon activation processes. Also, in a new initiative associated with development of a lithium-polymer battery (see Sec. I.A.3), ion transport mechanisms are being investigated by focusing the powerful *in situ* spectroscopic techniques previously developed in our catalysis research on near-electrode organometallic processes within the polymer electrolyte.

1. Catalytic Chemistry in Supercritical Fluids

More than 90% of all industrial processes involve the use of catalysts, and nearly half of these are homogeneous catalytic processes that use soluble catalysts dissolved in a fluid. Catalyst recovery and product separation are pervasive problems in industrial processes that utilize homogeneous catalysts, which are otherwise desirable because of their high reactivity, selectivity, and relative ease of modification for specific purposes. Use of supercritical fluids as the reaction medium is a potential solution to the problems with product separation and catalyst recovery, which are normally accomplished through energy-intensive distillations in conventional homogeneous catalytic processes. Supercritical fluids (CO_2 or H_2O) are also emerging as environmentally benign alternatives to the use, storage, and eventual disposal of organic solvents that are the mainstay of conventional catalytic processes. Compared with typical organic solvents, CO_2 is relatively more easily separated and less toxic. At approximately 4 cents per pound, CO_2 is the second least expensive industrial solvent; only water is less expensive. Our research into the catalytic chemistry of supercritical media could eventually lead to the conversion of some key industrial homogeneous catalytic processes to supercritical ones that are energy efficient and environmentally benign.

The largest scale industrial process for homogeneous catalysis is the oxo process for the hydroformylation of olefins. In this process, CO and H_2 are reacted with an olefin in the presence of a soluble catalyst to produce aldehydes and alcohols for use in detergents, plastics, and

agricultural products.¹ Our previous experiments with propylene hydroformylation in supercritical CO₂ using Co₂(CO)₈ as catalyst indicated that the catalyst works well in this medium, and that high selectivity to linear products is achieved.^{2,3} In the past year, our research was focused on use of *in situ* nuclear magnetic resonance (NMR) to study the hydroformylation process with phosphine-modified Co₂(CO)₈ catalysts. Phosphine ligands having differing σ-donor, π-acceptor, and steric properties can often be used to probe how conditions at the metal center affect the component steps of a catalytic reaction. An *in situ* NMR investigation of the phosphine-modified catalysts would not only result in the first definitive scrutiny of the component steps in these industrially important materials but would also settle, by some simple thermodynamic measurements, long-standing questions as to how phosphine substitution for carbonyl ligands on the cobalt catalyst affects the metal-metal, metal-carbon, and metal-hydrogen bonding in the cobalt carbonylphosphine complexes.

Currently, our efforts are concentrated on measuring the effects of increased CO pressures on the composition of cobalt species present in the catalytic solutions of the tributylphosphine-modified catalyst, [Bu₃PCo(CO)₃]₂. Potential reactions of CO with this catalyst at high pressures include CO addition to form a salt,

or phosphine displacement to form uncoordinated tributylphosphine,

As shown in Fig. VIII-1, ³¹P NMR spectra measured at CO pressures of 3.5-17.3 MPa prove that CO addition to produce the salt in Eq. 1 is the dominant reaction pathway. In this figure, the ³¹P signal for the catalyst, [Bu₃PCo(CO)₃]₂, decreases with increasing CO pressure, while a corresponding increase is observed in the ³¹P signal for the cationic product of Eq. 1, [(Bu₃P)₂Co(CO)₃]⁺. Since the salt produced via the reaction in Eq. 1 would be expected to be inert in hydroformylation catalysis, use of high CO pressures that encourage catalyst formation would appear to be counterproductive. Remarkably, at 100°C in 1,4-dioxane solution, most of the catalyst is converted to the salt at a relatively modest pressure, 17.3 MPa, as shown by the spectra in Fig. VIII-1. However, preliminary experiments at elevated temperatures (above ambient) indicate that the enthalpy change for the salt formation reaction is negative; hence, the equilibrium in Eq. 1 has a negative temperature coefficient. As a result, use of elevated temperature tends to counteract the effect of higher CO pressure.

¹ I. Kirshenbaum and E. J. Inchalik, "Oxo Process," in *Encyclopedia of Chemical Technology*, Third ed., Vol. 16, John Wiley & Sons, New York, pp. 637-653 (1981).

² J. W. Rathke, R. J. Klingler, and T. R. Krause, *Organometallics* **10**, 1350-1355 (1991).

³ J. W. Rathke and R. J. Klingler, U.S. Patent No. 5,198,589 (March 30, 1993).

Fig. VIII-1.

In Situ ^{31}P NMR Spectra of Modified Catalyst, $[\text{Bu}_3\text{PCo}(\text{CO})_3]_2$, at Varied CO Pressure and 100°C in 1,4-Dioxane Solution

The results reported here clearly establish Eq. 1 as an important equilibrium process in the hydroformylation system using phosphine-modified catalysts. In future efforts, we will complete our work on determining the thermodynamics for Eq. 1 and investigate the effects of solvent polarity on the salt formation process.

2. Hydrocarbon Activation Chemistry

Catalytic functionalization of unactivated hydrocarbons remains a great challenge to organometallic chemists. The report by Sherry and Wayland⁴ that mononuclear (TMP)Rh (where TMP^{2-} = dianion of α , β , γ , δ -tetramesitylporphyrin) reacts with CH_4 reversibly under mild conditions has greatly promoted interest in hydrocarbon activation by radical metal complexes. We have also shown that $[(\text{R}_8\text{Pc})\text{Rh}]_2$ (where R_8Pc^{2-} = dianion of 1,4,8,11,15,18,22,25-octakis-*n*-pentylphthalocyanine) activates hydrocarbons reversibly, *via* the Rh(II) radical complex $(\text{R}_8\text{Pc})\text{Rh}$ generated by homolysis of $[(\text{R}_8\text{Pc})\text{Rh}]_2$.^{5,6} Our investigation of the chemistry of Rh(II) radical complexes has continued.

The reaction of $[(\text{R}_8\text{Pc})\text{RhH}]_2$ (designated as compound 1) with trimethylphosphine in toluene- d_8 at -40°C leads to immediate formation of the six-coordinated hydride complex $(\text{R}_8\text{Pc})(\text{PMe}_3)\text{RhH}$ (compound 2) in 91% yield, as revealed by the two doublets for the hydride resonance at -20.810 ppm in the NMR spectra. The remaining 9% yield is the six-coordinated Rh(II) complex $(\text{R}_8\text{Pc})(\text{PMe}_3)_2\text{Rh}$ (compound 3), which has been isolated in a separate experiment and characterized by chemical analyses and by ^1H NMR spectra. At -40°C , compound 2 is quite stable

⁴ A. E. Sherry and B. B. Wayland, *J. Am. Chem. Soc.* **112**, 1259 (1990).

⁵ M. J. Chen and J. W. Rathke, *Organometallics* **13**, 4875 (1994).

⁶ M. J. Chen and J. W. Rathke, *J. Chem. Soc., Chem. Commun.*, 308 (1992).

in the presence of PMe_3 ; however, compound 2 and PMe_3 react at higher temperatures to produce compound 3 and H_2 :

Figure VIII-2 shows the spectral change in the high field region, which indicates the successive conversion of compound 1 to 2 and 3.

If compound 2 is warmed up from -40°C to ambient temperature in the absence of PMe_3 , compound 3 and $[(\text{R}_8\text{Pc})\text{Rh}]_2 \cdot \text{PMe}_3$ (compound 4) are produced in equal moles; H_2 is also liberated. This reaction may be depicted by

Compounds 3 and 4 are also generated by the reaction of PMe_3 with the Rh-Rh bonded dimer $[(\text{R}_8\text{Pc})\text{Rh}]_2$ (compound 5). As a matter of fact, compound 5 may be titrated with PMe_3 to produce compound 4, which reacts with additional PMe_3 to give compound 3:

The compound 3 generated from the reaction of compound 1 or 5 with PMe_3 is stable indefinitely under an inert atmosphere. It is most likely that compound 3 is a ligand-centered "18+ δ complex,"⁷⁻⁹ in which δ indicates the fraction of the unpaired electronic charge that is delocalized onto the metal. The strong delocalization of the unpaired electron onto a ligand orbital is manifested by the large upfield shift of the ^1H NMR for the aromatic H's of compound 3 (see Fig. VIII-2). Our failure to produce the analogous $(\text{R}_8\text{Pc})(\text{pyr})_2\text{Rh}$ by the reaction of pyridine with compound 1 or 5 must be due to the weaker Rh-pyr bond.

In another study, we found that $[(\text{CF}_3)_8\text{Pc}](\text{MeO})\text{Rh}$ and $[(\text{CF}_3)_8\text{Pc}](\text{MeO})(\text{PMe}_3)\text{Rh}$ were reduced by NaBH_4 in MeOH-d_4 to give the five-coordinated $[(\text{CF}_3)_8\text{Pc}](\text{MeOH-d}_1)\text{Rh}$ and the six-coordinated $[(\text{CF}_3)_8\text{Pc}](\text{MeOH-d}_1)(\text{PMe}_3)\text{Rh}$, respectively. These fluorinated Pc-Rh(III) and

⁷ W. E. Geiger, *Acc. Chem. Res.* **28**, 351 (1995).

⁸ D. R. Tyler, *Acc. Chem. Res.* **24**, 325 (1991).

⁹ D. Astruc, *Acc. Chem. Res.* **24**, 36 (1991).

Fig. VIII-2. Plots of ^1H NMR Spectral Change in the High-Field Region in Reaction of $[(\text{R}_8\text{Pc})\text{RhH}]_2$ with PMe_3

Pc-Rh(II) complexes are being examined for their catalytic activities in hydrocarbon activation. We are also extending our studies to include fluorinated Pc-Fe and Pc-Mn complexes as catalysts for hydrocarbon activation.

3. Ion Transport Properties Determined by *In Situ* NMR Spectroscopic Imaging

Nuclear magnetic resonance spectroscopy is one of the most powerful tools available for the determination of chemical structure and reaction dynamics. Yet, it has not been widely used to study electrochemical systems because the concentration profiles within the diffusion layer, the electric double layer, and the electrode-electrolyte interface are not uniform. Furthermore, all of these latter areas of electrochemical interest have very small volumes in comparison to the bulk electrolyte. In contrast, conventional NMR methods work best on identifying the major components in homogeneous samples. Magnetic resonance imaging (MRI) adds the ability to map the spin density of a target nucleus. However, the distance resolution of standard MRI methods is gained at the cost of sacrificing all chemical structure and reaction dynamics information. Consequently, traditional NMR and MRI methods are not well suited to study near-electrode chemistry. Indeed, the primary use of NMR spectroscopy for electrochemical systems has been for the *ex situ* analysis of complex electrolyte materials, such as polymers. Notably, NMR spectroscopy is one of the best

methods to measure ionic mobility. It can distinguish between motion in the amorphous and crystalline phases that often coexist in polymer-electrolyte systems.

We have discovered a new analytical technique that better bridges the disciplines of NMR spectroscopy and electrochemistry. The method under development provides high-resolution NMR spectra as a function of distance from the working electrode. Furthermore, the distance resolution of this NMR imaging method is close to the micron scale, which is sufficient to resolve most of the details that are of interest to electrochemical problems. Significantly, all of the NMR chemical shift, coupling constant, and relaxation time information are retained in this new electrochemical-NMR imaging technique.

The electrochemical-NMR imaging technique employs a modification of the toroid cavity detector that we initially developed for *in situ* NMR work on fluid catalysis at high pressure and temperature.¹⁰⁻¹³ The central conductor of the cavity detector (Fig. VIII-3) functions both as the electrochemical working electrode and as the central wire in the NMR detector circuit. Distances are measured radially with respect to the working electrode. Currently, the cell is being used to investigate the mechanism(s) of lithium ion transport in lithium-polymer electrolyte batteries. Lithium ion mobility is macroscopically characterized by the lithium-ion diffusion coefficient, the overall ionic conductivity, and the fraction of the ionic current that is carried by the lithium ion (its transference number). Because the lithium-ion transference number is the least well documented of these three factors, it is a primary focus of our NMR imaging work.

Fig. VIII-3.

Schematic of Electrochemical-NMR Imaging Device

¹⁰ J. W. Rathke, J. Magn. Reson. **85**, 150-155 (1989).

¹¹ R. J. Klingler and J. W. Rathke, Prog. Inorg. Chem. **39**, 131-180 (1991).

¹² K. Woelk, J. W. Rathke, and R. J. Klingler, J. Magn. Reson. A **109**, 137 (1994).

¹³ K. Woelk, J. W. Rathke, and R. J. Klingler, J. Magn. Reson. A **105**, 113 (1993).

In past studies, the lithium-ion transference numbers have been measured by the traditional Hittorf method, in which the amount of the electrolyte that is depleted directly adjacent to the electrodes is measured after the passage of a known quantity of charge through the cell. This has been done by mechanically dissecting the polymer-electrolyte cells with a razor blade so that the lithium content in the various regions of the polymer electrolyte can be chemically determined.¹⁴ This tedious mechanical procedure has limited the number of polymers that have been investigated by the Hittorf method.

Significantly, our electrochemical-NMR imaging technique is ideally suited for the rapid, nondestructive measurement of the ion concentration profiles in the electrolyte depletion area adjacent to electrodes. The results in Fig. VIII-4 illustrate the triflate (CF_3SO_3) concentration as a function of distance from the center of the working electrode both before and after 0.5 C of charge is passed through a sample of $\text{CF}_3\text{SO}_3\text{Li}$ in polyethylene oxide. The triflate concentration was measured using ^{19}F NMR spectroscopy. We found that the electrolyte is depleted over a range of approximately 0.5 mm after 5 μmol of lithium is electroplated onto the working electrode. The results in Fig. VIII-4 demonstrate that the NMR imaging technique has ample sensitivity and distance resolution to directly measure electrolyte depletion zones adjacent to the electrode. These measurements can then be used to calculate lithium-ion transference numbers.

Fig. VIII-4.

Ion Migration in $\text{CF}_3\text{SO}_3\text{Li}$ /Polyethylene Oxide. Initial concentration profile of the lithium triflate (dashed curve), concentration profile after 0.5 C of charge (solid curve), and the difference (dotted curve). Shaded region indicates radius of the electrode.

In addition to transference numbers, our electrochemical-NMR imaging cell will be used to better define the lithium-ion diffusion coefficients in lithium battery systems. The diffusion coefficients will be measured by two NMR techniques. The first technique will employ the salt depletion zones as depicted in Fig. VIII-4. Thus, it should be possible to monitor the electrolyte as it diffuses back toward the electrode by imaging the salt depletion zone after various time intervals. The second method of measuring diffusion coefficients will employ another new NMR technique. The essence of the technique is the use of the rf field gradient (B_1) in the toroid cavity NMR cell to "spin label" the sample as a function of distance from the working electrode before the image data are collected. Spin labels are frequently used in NMR spectroscopy to follow chemical reactions. Thus, it is possible to follow the rate at which spin-labeled nuclei move from an initial focus compound to other compounds by chemical reaction pathways. In the current application, a spin

¹⁴ P. G. Bruce, M. T. Hardgrave, and C. V. Vincent, *Solid State Ionics* **53-56**, 1087 (1992).

label is being used to follow diffusion. Therefore, the spin labeling is done on the basis of different regions of space and not on different chemical shift environments. For example, if a sample is spin labeled with a longitudinal magnetization grid along the distance axis, then the resultant NMR intensity of the subsequent image will oscillate with the frequency of the initial magnetization grid. The results in Fig. VIII-5 illustrate this effect in an electrochemical-NMR cell that was homogeneously filled with a sample of chloroform. These oscillations in the NMR signal intensity decrease with time due to diffusion as the sample labeled with excess α spin (maxima in Fig. VIII-5) mixes with the sample labeled with excess β spin (minima in Fig. VIII-5). Quantitative analysis of the oscillations in Fig. VIII-5 provides a measure of the self-diffusion coefficient.

Fig. VIII-5. Image from ^1H NMR Spectroscopy of z-Magnetization Grid in Sample of Chloroform

Future effort will focus on using the electrochemical-NMR imaging cell to more closely analyze the chemical composition of the components in the lithium-polymer electrolyte battery. The lithium foil anodes, as well as the lithium-polymer electrolyte interface, will be investigated by a combination of ^7Li , ^1H , ^{13}C , and ^{17}O NMR spectroscopy. The resulting NMR chemical shift information should be useful to probe the chemical composition and other factors that influence the growth of films at the electrode-electrolyte interface. In addition, the NMR spectral properties of the polymer electrolyte will be probed as a function of distance across the lithium-ion concentration gradient established in a working electrochemical cell. This information will be used to search for specific ion-polymer interactions during the ion transport. Finally, the factors that influence dendrite formation on the lithium anodes will be probed in a working secondary battery by imaging the surface with ^7Li NMR spectroscopy.

B. *Materials Chemistry*

The materials chemistry program encompasses fundamental research on the characterization of electrochemical metal/solution interfaces under conditions that are relevant to corrosion science and to electrochemical devices, the development of first-principle methods for computing molecular energies, and the study of materials properties by advanced computational methods.

1. Electrochemical and Corrosion Studies

Electrochemical processes occurring in aqueous media are key steps in many established and emerging energy-related technologies. Two such technologies, high-performance batteries for electric vehicles and large-scale fuel cells for primary electric power generation, are on the verge of commercialization. Moreover, photoelectrochemical energy production and chemical processing (e.g., water splitting) are also at an advanced stage of development, and corrosion is an electrochemical process that cuts across practically all energy technologies. The goal of this research effort is to provide (1) experimental information on the structure and dynamics of metal/solution and metal oxide/solution interfaces as a function of temperature and solution chemistry and (2) theoretical models against which the experimental results can be tested. The research program that we have established to reach this goal employs *in situ* surface-sensitive synchrotron radiation methods, transient and steady-state electrochemical techniques, and theoretical modeling based on a combination of molecular dynamics and molecular orbital methods.

a. Synchrotron and Spectroelectrochemical Studies

The purpose of this activity is to elucidate the relationship between the structure of metal/solution interfaces and the mechanisms of interfacial reactions in various solutions. Synchrotron X-ray scattering (specular and diffuse), X-ray absorption spectroscopy, and far infrared spectroscopy techniques are employed for *in situ* determinations of the structure of the electrode surface and the metal/solution interface region, as well as the composition of corrosion films on metals. Electrochemical techniques, such as dc polarization, ac impedance, and cyclic potentiodynamic scanning, are used to determine the rates and mechanisms of the interfacial processes involved in the corrosion of metals.

In situ synchrotron far infrared spectroscopy is being used to study surface films formed on a copper electrode in 0.1 M NaOH solution. At -0.05 V vs. a standard calomel electrode, spectral bands at 1110 and 630 cm^{-1} were observed (Fig. VIII-6), which are characteristic of Cu_2O .^{15,16} At 0.30 V, a broad band was found at $\sim 410\text{ cm}^{-1}$, which is significantly lower than the literature value of 515 cm^{-1} for bulk CuO .¹⁷ This shift may reflect the difference between a hydrated thin film and fairly crystalline bulk material. We also believe that the band is likely to be a superposition of bands due to CuO and $\text{Cu}(\text{OH})_2$, which is also present in the film. Future

¹⁵ G. W. Poling, J. Electrochem. Soc. **116**, 958 (1969).

¹⁶ M. O'Keeffe, J. Chem. Phys. **39**, 1789 (1963).

¹⁷ S. H. Narang, V. B. Kartha, and N. D. Patel, Physica C **204**, 8 (1992).

Fig. VIII-6.

In Situ Synchrotron IR spectrum of Copper in 0.1 *M* NaOH solution at -0.05 V (vs. standard calomel electrode)

measurements will endeavor to confirm this hypothesis. This work is being done in collaboration with the University of Auckland (New Zealand) and the University of Poitiers (France).

In situ synchrotron X-ray absorption spectroscopy is also being used to determine the structure and composition of the anodic corrosion films on nickel in alkaline solution. The problem is of great interest from the standpoint of developing advanced nickel-based batteries and electrochromic devices. During the past year, thin films (50 to 250 Å) of nickel were vacuum deposited on a chromium overlayer on mica sheets, which were then used as electrodes in 5 *M* KOH. These films were anodically polarized and cycled in the appropriate potential regions to form Ni^{2+} and Ni^{3+} oxides (including hydroxides). *In situ* spectra were simultaneously obtained using X-ray absorption spectroscopy (extended X-ray absorption fine structure and X-ray absorption near edge) with fluorescence detection. Preliminary results indicate the formation of $\text{Ni}(\text{OH})_2$ and NiOOH , depending on the potential. The data are now being analyzed to obtain bond lengths and coordination numbers. This work is being done in collaboration with the Naval Surface Warfare Center, Carderock Division.

Synchrotron X-ray scattering (specular and diffuse) studies are being conducted to examine the morphology of electrodeposited metals. The problem is analogous to that of electrochemically induced pitting, which was reported previously.¹⁸ Pits formed on copper in 0.01 *M* NaHCO_3 solution showed a distinct correlation in their average separation. In contrast, our initial results showed that bulk crystallization of copper on a copper substrate in CuSO_4 acidic solution proceeds randomly, with no correlation in the microcrystal separation. The same appears to be true for the deposition of silver on platinum from acidified nitrate solution. Further study of the early stages of nucleation and growth of the electrodeposit is planned. This work is being undertaken in collaboration with workers in ANL's Advanced Photon Source and Materials Science Divisions.

¹⁸ J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, pp. 133-134 (1995).

b. Electrode Structure and Kinetics

This research concentrates on understanding (1) the kinetic aspects and atomistic mechanism of heterogeneous charge-transfer reactions in aqueous solutions at a wide range of temperatures (25 to 300°C) and (2) the atomic level structure of electrified interfaces that strongly influence the dynamics of these reactions. The electrode kinetic measurements of this study are carried out with relaxation techniques, such as galvanostatic, coulstatic, or potentiostatic pulse transients, ac-impedance measurements, and rotating-disk-electrode technique, and the resulting data are evaluated by computerized methods. The interfacial structural studies use synchrotron X-ray surface scattering measurements. Heterogeneous charge-transfer reactions are the essential chemical reactions in many energy-related technologies, such as high power-density and energy-density batteries for electrical vehicles and large-scale fuel cells for primary electrical power generation. They are also involved in corrosion of these and other electrochemical processes cutting across practically all energy technologies. Clearly, a fundamental understanding of the dynamics of these reactions could result in improvements in many energy technologies.

This year, we continued our kinetic studies of the $\text{Cu}^{2+}/\text{Cu}^0$ electrode reaction, which is an important cathodic reaction occurring during stress corrosion cracking in light water nuclear reactors. The mechanism for this corrosion is poorly understood. The reaction consists of two consecutive electron-transfer steps followed by the incorporation of the copper adatom into the metal lattice. Earlier, we determined that the reaction rate is controlled by the $\text{Cu}^{2+}/\text{Cu}^+$ charge transfer step, and that this reaction is strongly catalyzed by traces of chloride ions in the solution.¹⁹ We have begun high-temperature/high-pressure (HTHP) kinetic measurements under conditions when the chloride catalytic effect is negligible. A thermodynamic calculation of the $\text{Cu}/\text{Cu}^+/\text{Cu}^{2+}$ equilibrium in the temperature range of 25 to 300°C was performed, and the results were used to modify our HTHP measuring system in order to achieve the above equilibrium. Initial HTHP measurements indicated that the rate of the $\text{Cu}^{2+}/\text{Cu}^+$ charge-transfer reaction increased about a hundred fold between 25 and 200°C, with the transfer coefficient seemingly independent of temperature. Indications are that we can also measure this reaction rate on a gold (rather than copper) electrode surface; this will make the comparison with theoretical predictions much easier. This work is carried out in close coordination with the theoretical modeling effort described in Sec. VIII.B.1.c.

In a collaborative effort with the Synchrotron Studies Group in the ANL Materials Science Division, we continued the use of synchrotron X-ray techniques in probing the structure of electrified interfaces buried under or within condensed phases. A synchrotron X-ray-scattering study of incipient pore formation in luminescent silicon layers was completed during the past year. It is widely recognized that porous silicon, and porous semiconductors in general, are potentially very important materials for future industrial applications because of their luminescence at visible frequencies. We prepared porous silicon samples by anodic dissolution of single-crystal silicon (p+ type) in aqueous/alcoholic hydrogen fluoride. *In situ* measurements of the porous layer were then performed in our transmission X-ray/electrochemistry cell. The structure of pores near the liquid/porous silicon interface was determined from X-ray reflectivity and diffuse-scattering

¹⁹ J. J. Laidler et al., *Chemical Technology Division Annual Technical Report, 1994*, Argonne National Laboratory Report ANL-95/24, pp. 134-135 (1995).

measurements. We found a funnel-shaped (tapered) interfacial layer, followed by a layer of uniform porosity with relatively straight circular pores and increased branching with depth. For our conditions, the porosity was around 50%, and the pore diameter was 50 to 70 Å. These and future results will be used to establish the validity of competing theoretical models of pore growth.

c. Theoretical Studies of Electrode Reactions

The $\text{Cu}^{2+}/\text{Cu}^0$ electron transfer reaction is very important in stress corrosion cracking in nuclear reactors. In a theoretical study, we recently reported on how chloride anions catalyze electron transfer in the copper deposition reaction in aqueous solutions.²⁰ In this work, it was found that any increase in electronic coupling for the inner-shell reaction (chloride bridge) compared to the outer-shell reaction (water-water bridge) is due to a shorter copper-copper distance rather than intrinsic chemical effects. In the past year, we have investigated the effect of other anions, including fluorine and bromine, on the electronic coupling in the $\text{Cu}^{2+}/\text{Cu}^0$ electron-transfer reaction. We found that the electronic couplings for bromine- and fluorine-bridged reactions are similar to those of the water-water bridged reaction. Hence, as in the case of the chloride anion, any catalytic effect of the fluoride or bromide anions because of increased electronic coupling results from a structural difference in the two types of reactions, such as a closer approach of the donor and acceptor in the inner-shell (anion bridge) electron transfer reaction. In future work we will include a model for an electrode surface in our computations and compare the results to experimental studies of anion catalysis at the electrode/electrolyte interface.

2. Theoretical Studies of Materials

The goal of this work is to develop new quantum mechanical methods and apply them, along with previously established ones, to the study of zeolites, thin diamond films, and molecular clusters. One of the methods that has been developed, Gaussian-2 (G2) theory,²¹ is now being widely used in universities and industry for the accurate calculation of thermochemical data. The method is based on *ab initio* molecular orbital theory and was initially designed to calculate accurate thermochemical data for molecules containing first- and second-row atoms. Since its introduction, G2 theory has been applied to numerous species for which experimental data are lacking or uncertain.

a. Gaussian-2 Theory Development

During this reporting period, G2 theory has been extended to the elements Ga through Kr of the third row in the periodic table. Basis sets compatible with those used in G2 theory for molecules containing first-row and second-row elements have been derived. Spin-orbit corrections for atoms and molecules having spatially degenerate states are explicitly included in the G2-calculated energies. The average absolute deviation from experiment for 40 test reactions involving species containing Ga-Kr atoms is 1.37 kcal/mol, which is only slightly higher than the deviation determined for the G2 treatment of first- and second-row elements. In contrast to the

²⁰ Z. Nagy, J. P. Blaudeau, N. C. Hung, L. A. Curtiss, and D. J. Zurawski, *J. Electrochem. Soc.* **142**, L87 (1995).

²¹ L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).

situation for first- and second-row elements, inclusion of spin-orbit effects is very important in attaining accurate energies for molecules containing third-row atoms. Without spin-orbit effects, the average absolute deviation is 2.36 kcal/mol. In future work, G2 theory will be applied to molecules with third-row atoms and to clusters for which experimental data are not reliable or unavailable. In addition, alternative methods for assessing residual basis set errors will be investigated for molecules of third-row atoms.

b. Molecular Sieve Materials

Zeolites are solid acid catalysts that are widely used in the petrochemical industry for hydrocarbon cracking. Proton transfer from the Brønsted acid site to an adsorbed molecule is assumed to be the key step in reactions in zeolites not only involving hydrocarbons, but also involving other molecules such as ammonia, water, and methanol. Our previous computational study on water adsorption in the zeolite ZSM-5 (ZH) based on large clusters suggests that the structure resulting from proton (H) transfer to an adsorbed water molecule ($Z \dots \text{HOH}_2^+$) exists only as a transition state for proton movement from one acid site to another.²² This transition state is about 5 kcal/mol higher in energy than the minimum for the adsorbed H_2O molecule. While the proton transfer structure is a transition state when only *one* H_2O molecule interacts with the Brønsted acid site, we have calculated that the addition of a *second* H_2O molecule to the *first* H_2O molecule stabilizes the proton transfer structure, making it a local minimum in the potential energy surface. This structure is shown schematically in Fig. VIII-7. Calculated vibrational frequencies of the resulting equilibrium ion-pair structure, $Z \dots \text{H}(\text{OH}_2)_2^+$, show significant changes from those of the neutral structure with no proton transfer to the adsorbed water molecule. These changes are consistent with experimental IR spectra²³ at pressures above 10^{-2} mbar (1 Pa). The theoretical methods used in this study of H_2O adsorption will be employed in studies of mechanisms for hydrocarbon cracking and NO_x reduction in zeolites.

Fig. VIII-7.

Structure of Ion-Pair Complex $Z \dots \text{H}(\text{OH}_2)_2^+$ Resulting from Proton Transfer to Water Dimer from an Acid Site in Zeolite ZSM-5

²² L. A. Curtiss, L. E. Iton, and S. A. Zygmunt, "Computational Studies of Brønsted Acid Sites in Zeolites," Proc. of 1995 Simulation Multiconference, Society for Computer Simulation, San Diego, CA, April 9-13, 1995, pp. 111-115 (1995).

²³ A. Jentys, G. Warecka, M. Derewinski, and J. Lercher, J. Phys. Chem. **93**, 4837 (1989).

c. Diamond Thin Films

Rapid growth of thin films of diamonds has been observed in experiments involving chemical vapor deposition following fragmentation of C_{60} ("buckyball") in a microwave discharge.²⁴ We have carried out a theoretical study of the potential energy surface for addition of C_2 to a diamond (110) surface using diamond-like clusters of 18 and 46 carbon atoms terminated by hydrogens. The purpose was to help explain the reaction mechanism for diamond thin-film growth from buckyball precursors. By use of molecular orbital calculations, the addition of a C_2 to a hydrogen-terminated diamond (110) surface was found to be very favorable, with energy lowerings of about 200 kcal per mole of C_2 . Unlike diamond growth with other species, this addition does not require abstraction of hydrogen atoms from the surface. The barriers for addition of C_2 to the (110) surface were determined to be small (<10 kcal/mol). Adjacent C_2 moieties on the (110) surface, adsorbed in ethylene-like arrangements, can be connected via a radical mechanism involving initiation by hydrogen atom addition to the double bond of one ethylene-like group. The results suggest that there is little or no energy barrier for this reaction. A path also exists for linking adjacent surface ethylene-like species directly, without the assistance of hydrogen addition. The barrier for this process is also small and corresponds to the linking of the first two ethylene-like units to form a singly bonded diradical structure. The results of this theoretical study are consistent with diamond growth from buckyball precursors in the absence of hydrogen in the feed gas.²⁴ In future work, we will investigate growth mechanisms on (100) and (111) diamond surfaces and compare the results to those obtained for the (110) surface.

C. Geochemistry

The geochemistry research program in CMT is currently focused on experimental studies of the chemical processes occurring at mineral-fluid interfaces. The approach is to observe reacting mineral surfaces *in situ* by use of synchrotron X-ray radiation. Reactions occurring at mineral-water interfaces play a crucial role in geochemical transport processes. Traditionally, atomic-scale structural information concerning these processes has been inferred from chemical measurements made in systems where powders are reacted with fluids. In these studies, the initial condition of the surface is unknown, crystallographic control is lacking, reactive surface area is difficult to determine, and product characterization may be extremely tedious if not impossible. We have applied synchrotron X-ray scattering techniques in response to the need for high-resolution atomic-scale structural information regarding processes at the mineral-water interface. To understand these processes, we need to study solid-liquid interface phenomena that occur at mineral-water interfaces, including dissolution and precipitation, adsorption, heterogeneous nucleation, epitaxial growth, recrystallization, solid-solution formation, oxidation-reduction, and the formation of an electric double layer.

Here we present some results of X-ray standing wave measurements made at mineral-water interfaces. The objective of these measurements is to provide atomic-scale information on the structure of metal adsorbates at mineral-fluid interfaces. Such information is crucial for understanding contaminant transport in groundwater aquifers, but as yet may only be inferred indirectly from

²⁴ D. M. Gruen, S. Liu, A. R. Krauss, and X. Pan, J. Appl. Phys. **75**, 1758 (1994).

other data. Specifically, we have applied the X-ray standing wave technique²⁵ to determine the location of adsorbed lead atoms relative to the (104) lattice plane of calcite. In an earlier publication,²⁶ we presented results from an experiment in which lead was adsorbed from an aqueous solution onto the (104) cleavage surface of calcite, and then the solution was removed from the surface with a jet of helium gas prior to making the X-ray standing wave measurements *ex situ* in a flowing helium atmosphere. We found that approximately 5% of a monolayer of lead was adsorbed onto the calcite surface, and that this lead occupied the same position as calcium relative to the (104) lattice plane. Since that time, we have developed the capabilities to make these measurements relative to lattice planes other than the (104) plane and to make them *in situ* in the presence of a thin film of aqueous fluid at the calcite surface. The former uses a conventional four-circle diffractometer, while the latter also uses a new type of sample cell.

During 1995, we performed experiments comparing the results of X-ray standing wave measurements of adsorbed lead, made both *in situ* and *ex situ*, on the same samples, and measurements made *ex situ* relative to lattice planes other than (104). These experiments used a pH = 9 solution that was approximately calcite-saturated and contained about 20 mg/L lead. Most of the lead in this solution was complexed with ethylenediaminetetraacetic acid, and about 0.05 mg/L lead was present as Pb^{2+} or PbOH^+ ions that are available for adsorption to the calcite surface. This uncomplexed concentration of lead is representative of naturally occurring concentrations in groundwaters. Coverage of the lead on calcite was estimated from measurements of a lead-implanted silicon mirror having a known lead concentration.

The results of the X-ray standing wave measurements were as follows: (1) about 5-17% of a monolayer equivalent of lead was adsorbed from the solution onto the calcite surface, (2) the amount adsorbed was independent of time from 5 to 93 h of reaction; (3) the lead occupied calcium sites, (4) the coverage and ordering of the lead were about the same for *in situ* and *ex situ* measurements, and (5) the adsorbed lead was stable in both aqueous solution and flowing helium for the duration of the X-ray standing wave measurements (up to about 96 h).

These results are significant because they represent the first atomic-scale information for lead adsorbed on calcite and demonstrate that *in situ* and *ex situ* measurements yield the same results for this mineral-water system. Because of the large ionic radius of lead relative to calcium, we did not expect lead to be preferentially incorporated into calcite. However, these results show that lead is preferentially adsorbed to the calcite surface from aqueous solution. This lead is apparently chemisorbed to calcite, and we infer that it is exchanged for calcium in the surface layer of calcite. Further work is planned using X-ray standing wave techniques to examine the structure of other metal adsorbates at the calcite-water interface.

²⁵ P. Cowan, J. Golovchenko, and M. Robbins, Phys. Rev. Lett. **22**, 703 (1980).

²⁶ Y. Qian, N. C. Sturchio, R. Chiarello, P. Lyman, T. Lee, and M. Bedzyk, Science **265**, 1555-1557 (1994).

IX. ANALYTICAL CHEMISTRY LABORATORY

A. *Introduction*

The Analytical Chemistry Laboratory is a full-cost-recovery service center, with the primary mission of providing chemical analysis and related technical support to solve research problems of our clients—Argonne National Laboratory, the Department of Energy, and others. The ACL also does research and development in analytical chemistry and its applications. In carrying out this mission, the ACL handles a wide range of analytical problems. Although some routine or standard analyses are done, many Argonne programs generate unique problems that require significant development of methods and adaption of techniques to obtain useful analytical data.

The ACL is administratively within CMT, its principal ANL client, but provides support for many of the technical divisions and programs at ANL. The ACL has four technical groups—Chemical Analysis, Instrumental Analysis, Organic Analysis, and Environmental Analysis—which together include about 45 technical staff members. Talents and interests of staff members cross group lines, as do many projects that the ACL undertakes.

The Chemical Analysis Group uses wet-chemical and instrumental methods for elemental, compositional, and isotopic determinations in solid, liquid, and gaseous samples and provides specialized analytical services. The Instrumental Analysis Group uses nuclear counting techniques to determine the radiochemical constituents in a wide range of sample types, from environmental samples with low radioactivity to samples with high radioactivity that require containment. Other types of determinations use X-ray diffraction and X-ray fluorescence of solids. The Organic Analysis Group uses a number of complementary techniques to separate organic compounds and measure them at trace levels. Samples that can be analyzed include complex organic mixtures and compounds, environmental soils and waters, potentially hazardous wastes, and drugs. The Environmental Analysis Group analyzes environmental, hazardous-waste, and coal samples for the inorganic constituents.

New ACL capabilities established in 1995 include an X-ray diffractometer system, a Fourier transform infrared (FTIR) spectrometer for use with an infrared microscope, a microwave sample preparation system for inorganic determinations, a detector for an existing ion chromatograph, a Fourier transform Raman system, and an automated sample changer for the X-ray diffractometer. In addition, the control system for our thermal ionization mass spectrometer was upgraded.

B. *Technical Highlights*

The ACL provides analytical chemistry support to CMT, other ANL divisions and programs, other DOE sites, DOE's Chicago Operations Office, and DOE Headquarters. In addition, ACL conducts research and development programs funded by DOE and other sponsors. Selected

accomplishments for 1995 are summarized here. In addition, the ACL did analytical work on many other projects, which are described in more detail elsewhere.¹

1. Electrometallurgical Treatment Applications

In 1995, the ACL continued to provide analytical support for various projects involving electrometallurgical treatment of spent nuclear fuels (see Sections V and VI). These projects included further development of electrorefiner applications and oxide fuel treatment, investigations of the behavior of elements not previously studied in electrorefiners, and experiments on the feasibility of using zeolites as the basis for waste forms with a high plutonium content.

Cations, including U and Pu, are determined by using an inductively coupled plasma/atomic emission spectrometer (ICP/AES) that has been configured to analyze radioactive solutions. The mass spectrometric isotopic dilution technique is used whenever higher precision and accuracy than attainable with ICP/AES are required. X-ray diffraction is frequently used to identify chemical components.

Examples of work supported by the ACL were tests performed to understand the behavior of elements such as Se, Te, and Sb in the electrorefiner process. Analytical results indicate that in the electrorefiner these elements behave like noble metals. Also, studies were undertaken to determine whether plutonium could be incorporated at high levels in zeolite, which could then be used as a waste form. Analytical data showed that when zeolite is exposed to PuCl_3 in electrolytic salt (LiCl-KCl), substantial amounts of plutonium can be contained within the zeolite.

2. Development of a Continuous Emission Monitor for Thermal Treatment Systems

The objective of this project, which is a collaboration with the Energy Systems Division, is to develop a continuous emission monitor based on FTIR technology. This on-stream device will monitor stack gases for volatile organic and selected inorganic compounds.

The primary benefit of an on-stream monitor for stack effluent is the near real-time determination of the performance of the thermal treatment systems being monitored. On-stream analysis of the stack effluent would satisfy the requirements of the Clean Air Act of 1990 and address public concern about incinerator safety. Another benefit is that such a monitor eliminates the need for the expensive techniques currently employed to characterize the effluent, such as use of a volatile organic sampling train followed by gas chromatography/mass spectrometry (GC/MS) in the laboratory. In addition to cost considerations, the techniques required under current procedures provide a one-time analysis only.

Development of the monitor has progressed in three focus areas. The first is technical development in instrument optimization, automation software, sampling, and advanced data analysis. The second is obtaining regulatory approval by the Environmental Protection Agency (EPA), and

¹ D. W. Green et al., *Analytical Chemistry Progress Report for FY 1995*, Argonne National Laboratory Report ANL/ACL-95-5 (December 1995).

the third is commercialization of the instrument. At the successful completion of this project, all data would comply with EPA requirements, and the instrument would be packaged as a complete unit.

Instrument development has largely been completed. A commercially viable instrument that consists of three transportable modules has been constructed and successfully tested. Data analysis is currently being improved with time-domain and Fourier-domain methods that use peak width to mathematically separate components with overlapping bands. This two-domain approach will enhance the system's ability to detect substances that have overlapping absorbances and allow us to digitally filter system noise. We submitted a procedure (described in Sec. IX.B.3) to EPA in October 1994 and to the American Society for Testing and Materials in April 1995. At this stage, data generated with our system will be accepted by the EPA Office of Air Quality Planning and Standards. In October 1994, a Cooperative Research and Development Agreement (CRADA) to commercialize the system was completed with Clean Air Engineering and Martin Marietta Energy Systems, the operators of DOE's Toxic Substances Control Act incinerator at the K-25 site in Oak Ridge, TN.

3. Characterization of Products from Automobile Shredder Fluff Recycling

About 225 kg (25%) of every junked car that is processed by automobile shredders to recover ferrous metal scrap is made up of a mixture of plastics, glass, fibers, and foam. This mixture is referred to as "fluff" and represents a substantial waste stream from the automobile shredder industry. At present, shredder fluff is sent to landfills. Researchers in ANL's Energy Systems Division have developed and are testing technologies to segregate and recover the plastic and foam fluff components for recycling. They are also exploring alternatives to landfill disposal for residues ("fines") that are collected during segregation of the recyclable materials.

The ACL is providing chemical analyses to help characterize the various product streams from these processes, including oils, recovered plastics and foams, and the shredder fines. We use an FTIR microscope to examine plastics recovered by solvent extraction of shredder residues. With this technique, selectivity of the extraction and purity of the products are assessed by comparing spectra for polyvinylchloride and acrylonitrilebutadienestyrene polymer standards with spectra from reconstituted plastics produced by solvent extraction. Other analytical methods are applied to determine specific contaminants in the foams, oils, and fines. Heavy metals and polychlorinated biphenyls (PCBs) are common contaminants in the shredder fluff as a result of their presence in automotive components and fluids (e.g., lead from batteries, mercury from mercury switches, PCBs from capacitors or hydraulic fluids). After suitable treatment of samples to bring the metals into solution, all metals except mercury are determined by ICP/AES. Mercury is determined by cold vapor atomic absorption (CVAA) spectrophotometry. The PCBs are extracted with an appropriate solvent and measured by gas chromatography. We also determine the total chlorine content of many samples by a procedure that employs oxygen-bomb combustion and ion chromatography to measure the chlorine as chloride.

These and other analysis tools were used to provide the Energy Systems Division with (1) data on the effectiveness of a new process that removes metals and oil contaminants from the polyurethane foams generated from the shredder fluff and (2) a comprehensive characterization of shredder fines to determine their suitability for use as a raw material in the manufacture of cement.

4. Support for High-Temperature Superconductor Development

The ACL continued to provide extensive analytical support to high-temperature superconductivity programs in ANL's Energy Technology and Chemical Technology Divisions. Much of this work involves analysis of starting materials, process samples, and products related to fabrication, as well as characterization studies on various ceramic compositions, including $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and lead-doped bismuth/strontium/calcium/copper oxides. Our measurements include determining elemental composition by ICP/AES or classical methods, anions by ion chromatography, carbon with a LECOTM analyzer, and phase composition by X-ray powder diffraction. We also use an iodometric titration method to determine excess valence of the metals in a given ceramic (e.g., Cu^{3+}), which is related to the oxygen stoichiometry of the compound. Through these and related activities, the teamwork among chemists, ceramists, and analysts is helping to move the technology of superconducting ceramics toward practical applications.

5. Integrated Performance Evaluation Program

In collaboration with DOE's Radiological and Environmental Sciences Laboratory and the Environmental Measurements Laboratory, the ACL is developing and implementing a comprehensive Integrated Performance Evaluation Program (IPEP) for DOE's Office of Environmental Management (EM). The program is managed by EM's Analytical Services Division and is designed to provide information on the quality of radiological and nonradiological analytical data being produced by all laboratories that provide DOE with data on environmental restoration and waste management samples. The Interagency Agreement between ANL and EPA's Region V establishing IPEP as a pseudo-EPA Region was renewed for 1995. This Interagency Agreement allows the IPEP to nominate laboratories performing analyses for EM into the Water Supply and Water Pollution programs sponsored by the National Exposure Research Laboratory (Cincinnati, OH), and to access relevant information about laboratories from these programs. Historical and current data from these programs are now routinely transferred electronically from the EPA data base at Research Triangle Park, NC, to the IPEP data base at ANL. Contract Laboratory Program (CLP) data for government-owned, contractor-operated laboratories are being entered into the IPEP data base by double hand-keying to make them available for electronic generation of reports. The IPEP is routinely transferring current EML Quality Assessment Program data via modem to its data base. These data have been used to develop a performance-based statistical assessment and scoring scheme to address EM criteria.

Pilot studies for the production of IPEP reports are being conducted with both the Idaho National Engineering Laboratory Sample Management Office and the DOE Albuquerque Operations Office Field Sample Management Program. These pilot studies are designed to provide IPEP developers with an opportunity to test the feasibility of the proposed operating mechanisms and to allow report users to have direct input about the report formats, technical content, and other needs during the developmental stage.

6. Determination of Platinum in Inner-Ear Fluid of Guinea Pigs

The concurrent use of the antitumor drug cisplatin [*cis*-dichlorodiamineplatinum(II)] and the antibiotic gentamycin is known to cause inner-ear damage in humans (usually cancer patients

with unspecified bacterial infections). Researchers at Loyola University Medical Center are examining the mechanisms by which this damage occurs. In the Loyola study, a large group of Duncan Hartley guinea pigs was placed on a cisplatin/gentamycin dosing protocol. After an appropriate post-dose delay ranging from 0 to 21 days, subjects were anesthetized, and samples of inner-ear fluid (perilymph) and inner-ear bone (cochlea) were drawn. The subjects were then sacrificed for additional postmortem examination.

After sampling, the cochlea was examined for damage, and the gentamycin content in the perilymph was determined. However, Loyola did not have the analytical technology necessary to determine the cisplatin content in the perilymph, as the samples were very small (less than 10 μL) and the expected platinum concentrations were quite low (less than 100 ng/mL). Therefore, the perilymph samples were sent to the ACL, where they were prepared for ICP/MS analysis. Preparation involved digestion of the samples in aqua regia and dilution to a manageable volume (5 mL). The prepared samples were introduced into the ICP/MS instrument by using ultrasonic nebulization.

Instrument detection limits for platinum were on the order of 0.3 pg/mL, and all of the samples were found to contain detectable quantities of platinum. As expected, the platinum content in the perilymph samples (which is a direct indicator of cisplatin content) was strongly correlated with the delay between dose administration and sampling; i.e., longer delays yielded lower platinum concentrations. Furthermore, as expected, the platinum concentration in perilymph samples drawn from the right and left ears agreed to within several percent. Further analysis of the samples using ICP/MS and the technique of standard additions indicated that the initial data obtained by ICP/MS were accurate to within several percent for all but the lowest platinum concentrations. These data indicate that the platinum measurements are reasonably accurate and thus may be used by the Loyola team as they attempt to understand the mechanism for cochlea damage.

7. Radon Remediation

A researcher in ANL's Reactor Analysis Division has observed that oil can remove radon and other noble gases from air. Under a project sponsored by DOE and EPA, an apparatus containing an oil-based liquid for continuous, low-cost removal of radon is under development. Such a device is needed because radon is present in many homes and public buildings, sometimes at unsafe levels. Natural radon accounts for about two-thirds of the annual radiation exposure received by individuals worldwide.

In support of this project, the ACL tested a wide variety of oils for their ability to remove radon from air. Among the best were corn, soybean, and mineral oil. Other oils tested included olive, safflower, peanut, and walnut oil and various types of motor oil. Corn oil was selected for use in a prototype radon-removal system, and very good results—up to 95% removal efficiency—were obtained with this small-scale model. The final design of the radon removal apparatus has not yet been determined. Additional work is needed to develop a method for removing the accumulated radon from the oil, so the oil can be reused continuously.

8. Development of "Smart" Chemical Sensors

Current ACL research efforts in chemometrics (the use of mathematics, statistics, and formal numerical methods for analysis of chemical data) are focused on the development of a software workbench for designing automated monitoring algorithms for spectroscopic, chromatographic, electrochemical, and radiochemical sensors of interest to DOE. The objective of this work is to produce "smart" chemical sensors. The term "smart" is used to imply that the sensor can (1) interpret multivariate data in real time; (2) perform data reduction and decision making; (3) communicate processed results to an end user, process control loop, or data fusion system; and (4) alter system operation based upon certain detection results. Smart sensors have obvious advantages for both invasive and noninvasive monitoring scenarios. We have designed unique signal processing algorithms that combine digital filtering, pattern recognition, and multivariate calibration methods to provide enhanced qualitative and quantitative data analysis. These algorithms are initially developed using software; however, final versions of the algorithms can be implemented in hardware by encoding the algorithm onto a small digital signal processing board, which would become an integral part of the sensor electronics. Although the software workbench for designing these algorithms is still in the development phase, novel algorithms have been successfully generated for (1) qualitative processing of data from a passive FTIR sensor used for remote monitoring of chemical emissions and (2) quantitative processing of data from an extractive FTIR system used for continuous monitoring of incinerator emissions. In 1996, we will also begin development of qualitative and quantitative algorithms for infrared monitoring of the plasma hearth system at ANL-West. The plasma hearth is a prototype thermal system for treating mixed organic and radioactive wastes. Smart sensor algorithms have also been designed for automated analysis of multispectral image data and recognition of naval ships.

9. Performance Demonstration Program for the WIPP

The Waste Isolation Pilot Plant (WIPP) is a DOE installation consisting of large interconnecting cavities hollowed out of a salt vein approximately 600 m underground in the vicinity of Carlsbad, NM. It was prepared approximately five years ago to be used as a test repository for the disposal of transuranic (TRU) waste resulting from defense-related processing of nuclear materials. Wastes to be shipped to the site must first be characterized to identify the presence of any hazardous materials in the waste in addition to the radioactivity. One waste form present in relative abundance that requires characterization is semisolid waste sludge. The WIPP Transuranic Waste Characterization Program of the Carlsbad Area Office of DOE has established a performance demonstration program (PDP) for laboratories that will participate in the analysis of sludge to be shipped to the WIPP site. The ACL was given the task of preparing, verifying, and distributing samples for the PDP.

The PDP was designed to qualify those laboratories planning to supply analytical data that will be used to characterize solidified TRU waste destined for the WIPP site. Three organizations were chosen to participate in the PDP: Oak Ridge National Laboratory, Los Alamos National Laboratory, and Rocky Flats Plant.

The sample material that was prepared for Cycle 1 of the PDP was synthetic wastewater sludge. The synthetic sludge was prepared by the ACL to simulate Type I waste, which

is defined as cemented or dewatered sludge precipitated from aqueous waste treatment processes. The ACL prepared both cemented and uncemented forms of this sludge type.

The TRU Waste Characterization Quality Assurance Program Plan lists both inorganic and organic analytes required for characterization of waste prior to shipment to the WIPP site. The list includes both inorganic and organic analytes. The organic PDP samples were more challenging to prepare than the inorganic PDP samples because some of the organic analytes are unstable in the highly alkaline sludge matrix, and some analytes are very volatile; so the potential for analyte loss is high. The reproducibility and accuracy of the spiking procedures were extensively tested. In addition, holding-time studies were conducted for up to 14 days after initial sample preparation to track the stability of organic constituents and the loss of volatile organic compounds (VOCs) expected to occur over time.

The PDP samples were prepared to cover the analytes of concern to the program and their expected concentration ranges. Approximately 250 bottles of PDP samples were shipped in July 1995. Results of the participating laboratories' analyses have been sent to Lockheed Martin Idaho Technologies Co. and are currently to be scored according to guidelines from the Carlsbad Area Office. Results of the scoring are not yet available.

10. Holding-Time Study of Volatile Organic Compounds in WIPP Sample Canisters

Before radioactive wastes can be transported from various DOE sites for burial at the WIPP repository near Carlsbad, NM, they must be analyzed to determine whether they pose a chemical hazard in addition to the radioactivity hazard. Measurements must be made to determine the gaseous compounds in the void spaces (headspace) of the waste. Target analytes for these measurements include 29 VOCs that are listed as hazardous under the Resource Conservation and Recovery Act (RCRA). At the sites where the waste is stored, headspace gas samples are drawn and analyzed. In following this procedure, it is important that no change in composition occur when the gas is drawn into the shipping container and held for subsequent analysis. A study has been completed in which gas samples drawn at a waste storage site were held for an extended period, and measurements were made to determine any change of composition with time.

Nine of the most frequently occurring RCRA-listed hazardous organic compounds were present in, or added to, the actual field samples. The concentrations of the analytes were repeatedly measured by use of gas chromatography with mass spectrometric detection. Nine sets of measurements were made, spanning a period of approximately 900 days. For each measurement set, five replicates were obtained by withdrawing aliquots from a diluted portion of the field sample. The measured values for the individual analytes over time were fitted with a straight line by using regression analysis. The fitted lines had slopes between +9.5 and -6.2% change in composition per year. To assess the significance of the slopes, the fits were evaluated in terms of the scatter of the data points around the values predicted by the fit. For the analytes studied, the fitted lines with finite slopes were not significantly better models of the data according to the statistical F- and t-tests than the assumption of zero slope, which corresponds to no change of composition with time.

The conclusion of this work is that there is no technical basis for the present WIPP requirement to measure field samples within 28 days to avoid the effects of changes in gaseous

composition within the canisters. In fact, the allowable holding time could well be extended to several months if the extension would improve the efficiency of sampling and analytical operations.

11. Validation of Mercury Determination Methods for WIPP Program

In a collaborative effort under the WIPP Transuranic Waste Characterization Program, the ACL participated in a study led by Oak Ridge National Laboratory to validate alternative methods for determining mercury in wastes composed of soils, sludges, sediments, and oils. This study was intended to demonstrate equivalence between the conventional EPA method (SW-846 Method 7471, which specifies aqua regia digestion in a water bath, subsequent additions of several reagents, and measurement by CVAA) and two alternatives: (1) a newer method that replaces water-bath digestion with a microwave-assisted acid digestion based on EPA Method 3051 and (2) neutron activation analysis. If the alternative methods could be shown to be equivalent to Method 7471, they would be submitted for inclusion in the DOE Methods Compendium. They would then be considered acceptable for use in analyzing waste for mercury to determine the waste's conformance to the acceptance criteria established for the WIPP. For its part in the study, the ACL helped select reference materials suitable for testing each method and performed measurements on each reference material with the neutron activation method and the method based on microwave-assisted acid digestion.

For the validation measurements, five portions of each of four different reference materials were digested by both the water-bath procedure and the microwave oven procedure, and each digestate was analyzed in triplicate by CVAA. With the materials used (sediment, fly ash, sewer sludge, and oil), both methods gave excellent recovery of mercury over a range of concentrations from 0.16 to 100 mg/kg. The microwave procedure has several advantages: it uses fewer reagents, is faster, results in lower blanks, and is likely to be less susceptible to contamination. Data from the ACL measurements were submitted to Oak Ridge within the specified schedule so that they could decide whether to use the microwave method or other methods later in 1995 for analysis of sludge wastes in support of the WIPP project.

12. Method Development for WIPP Program

As part of the characterization of waste to be shipped to WIPP, the determination of seven special VOCs in solidified waste is required. These special VOCs are polar and water soluble, properties that prevent them from being determined by traditional purge-and-trap methods.

The ACL has developed an aqueous extraction method to analyze WIPP Type I sludge waste for the seven special VOCs. This extraction method involves addition of a known volume of water to a sludge sample, followed by vigorous agitation to extract the VOCs. The sample is then centrifuged for several minutes to separate the sediment. This separation is followed by direct injection of an aliquot of the water extract into a gas chromatograph equipped with a flame ionization detector.

This aqueous extraction technique was chosen because of its compatibility with polar VOCs, its simplicity, and its time-saving ability. Any time saved in sample preparation reduces the cost of analysis and reduces analyst exposure to radioactive samples. The ACL has validated the

performance of this method by meeting all of the WIPP quality assurance objectives for method detection limits, precision, and accuracy. This validated method was used to verify the polar VOC concentrations in samples for the performance demonstration program involving WIPP Cycle I solidified waste.

13. Analytical Procedures for Waste Minimization and Pollution Prevention

The waste generated by the analytical procedures used for characterization of waste is a significant source of new DOE waste. Success in reducing the waste volume and corresponding costs of handling this waste would significantly decrease the overall cost of characterization. We are studying the performance of waste-minimizing analytical procedures in three areas: microanalysis using flow injection nebulization, reduction of the solvent volume required for dissolution of waste samples for radiochemical analysis, and alternative sample preparation for analysis of organic constituents in waste samples. We have completed our comparison of nebulization techniques for ICP spectrometry. With continuous pneumatic nebulization as the baseline technology, we have concluded that flow injection/direct injection nebulization will reduce waste and analysis time with little or no compromise in analytical figures of merit. Significant reductions in waste volume from radiological analysis have been achieved by preparing samples with a high-pressure microwave system. In addition, we have demonstrated that alternative, nontoxic solvents can be used for preparation of samples for radiological analyses without compromising extraction efficiency. Recoveries using microwave-assisted extraction of semivolatile organic compounds (SVOCs) from soil, sediment, and sludge compare well with those using traditional extraction techniques. Solvent usage, and thus waste produced, is decreased by an order of magnitude with microwave-assisted extraction.

We are also investigating methods for analyzing high-efficiency particulate air (HEPA) filters, which provide the final stage of containment on many exhaust systems in DOE facilities by preventing the escape of chemical and radioactive materials entrained in the exhausted air. Before used HEPA filters can be accepted for disposal, they must be tested for the presence of regulated contaminants. One of these tests is U.S. EPA SW-846 Method 8270 for the determination of SVOCs. This test is especially important for HEPA filters because dioctylphthalate, a regulated SVOC, has historically been used to test and certify each filter's efficiency.

We studied supercritical fluid extraction using carbon dioxide fluid as an alternative method for removing SVOCs from HEPA filters. Traditional extraction methods for removing SVOCs require up to 300 mL of hazardous solvents and produce significant amounts of secondary waste. By contrast, SFE uses only small amounts of solvent for analyte trapping.

Recoveries obtained with SFE were compared to those obtained with Soxhlet, automated Soxhlet (Soxtec) and sonication (currently the ACL standard method) extractions. The traditional methods required 75 mL (Soxtec and sonication) or 300 mL (Soxhlet) of extraction solvent, whereas the SFE method required only 10-15 mL of collection solvent. In terms of average recoveries, the SFE method (70%) compared favorably with sonication extraction (74%) and with Soxtec extraction (63%). Soxhlet extraction yielded an average recovery of 83%.

Although SFE extraction yields of SVOCs from HEPA filters are somewhat lower than Soxhlet yields, SFE decreases solvent usage and waste production by more than an order of magnitude and decreases extraction times by more than a factor of 20. Addition of supercritical fluid modifiers will likely increase SFE yields, making them comparable to those obtained with Soxhlet extraction.

14. Orphan Waste Work Projects

Many ANL facilities have "orphan" waste materials that remain from programs that are no longer funded, have unknown origins, or have inadequate documentation. Funding made available through ANL's Environmental Management Operations (EMO) Division has provided many of these facilities with the opportunity to undertake work projects directed at accumulating, characterizing, and documenting these so-called "orphan wastes" so that they may be properly disposed of. In support of these work projects, the ACL is conducting chemical and radiological analyses to provide the composition and hazards-classification data needed by treatment/storage/disposal facilities that will ultimately process the wastes. Working closely with EMO to ensure that information and procedural requirements of the appropriate treatment/storage/disposal facility are satisfied, ACL staff have prepared detailed sampling and analysis plans for some projects, have fielded sampling teams to collect appropriate representative samples, and have collaborated with EMO staff in interpreting the analysis results for waste handling.

Through its orphan waste work projects, EMO has helped ANL divisions dispose of tens of thousands of kilograms of waste materials. The difficulty and expense of orphan waste disposal have brought home to many ANL divisions the need for timely and complete records on stored materials and prompt disposal of materials that are no longer needed.

15. Characterization of Used HEPA Filters for Disposal

For a number of years, used HEPA filters removed from laboratory exhaust systems at ANL had accumulated in the EMO Division because no facility could be found that would accept them for disposal. In 1993, EMO determined that these used filters would be accepted for disposal at DOE's Hanford Reservation if they could be shown to meet the relevant waste acceptance criteria. Procedures were proposed by EMO for repackaging and composite sampling of the used HEPA filters, and the ACL established an analysis methodology for evaluating the composite samples against the Hanford criteria.

Over a period of one and a half years, EMO repackaged and sampled 102 bins of these stored filters and submitted the composite samples from each bin to the ACL for analysis. During 1995, data from the last batches of filters were reported to EMO. Overall, approximately 80 bins were found to meet the Hanford acceptance criteria and were shipped by EMO to Hanford for disposal. These shipments substantially reduced the historical waste inventory at ANL. Now, new HEPA waste is characterized as it is generated so that it does not accumulate.

In the characterization process, each HEPA composite is homogenized (by manual cutting) and then analyzed for metals, semivolatile organics, PCBs, and radionuclides. Samples

shown to contain high concentrations of heavy metals are also subjected to the Toxicity Characterization Leaching Procedure to determine whether the metals they contain exceed regulatory standards for mobility under landfill conditions. Early batches of samples were also screened for pH, cyanide, sulfide, and inorganic anions, but these tests were discontinued when a clear pattern of negative results was established to Hanford's satisfaction. This has been a very successful collaborative effort between ACL and EMO, with considerable benefit to many ANL operations.

16. Methods for Determining Metals in Waste Oil

Many ANL programs depend on vacuum pumps, hydraulic systems, or machines that contain oil, which needs changing and, ultimately, disposal. To dispose of oil properly, one must first determine whether it is contaminated with hazardous metals (e.g., As, Ba, Cd, Cr, Hg, Pb, Se, Ag) and/or radionuclides. Because commonly used methods for measuring these contaminants perform best with aqueous samples, we studied two methods for decomposing oils to provide a single aqueous solution that could be used in all the hazardous metal determinations. For this project, elemental measurements were done by using graphite furnace atomic absorption, cold vapor atomic absorption, or ICP/AES.

The two preparation techniques evaluated were (1) combustion of the oil with oxygen in a sealed pressure vessel and (2) decomposition/digestion of the oil with acid and microwave-energy heating in a closed vessel. The microwave digestion procedure proved more effective in recovering most metals (>90% recovery for every metal tested).

Following the microwave decomposition, the results obtained for all 20 hazardous metals measured in this project (Al, As, B, Ba, Ca, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Mo, Ni, Pb, Se, Ag, Ti, V, and Zn) were within $\pm 10\%$ of the certified values. Because no oil standard is available with certified quantities of radionuclides, we were not able to evaluate the radiological measurements. However, we are confident that these measurements can be done reliably on a portion of the solution prepared by microwave digestion. Having this method available will help the ACL to provide ANL programs with reliable, cost-effective characterization of waste oil.

17. Separation of Mercury from Americium for Radioactive Waste Analysis

Analysis of waste solutions to provide proper hazards classification for disposal often requires determination of toxic metals, including mercury, in the waste. The ACL is able to measure most of the toxic metals in the presence of substantial amounts of radioactivity (using our "hot" ICP/AES), but our facilities for measuring mercury are more limited. Therefore, when we were asked to characterize a group of strongly acidic waste solutions containing as much as 10^8 dpm/mL ^{241}Am (in support of efforts by ANL's Environmental Management Operations Division to dispose of historical waste), we needed a means for removing the radioactive americium without affecting the reliability of the mercury measurement.

We determined that this separation could be achieved through column chromatography with Diphonix resin (Eichrom Industries, Darien, IL). With dissolved waste solution having a concentration of 2 M in hydrochloric acid, the Diphonix resin shows quantitative retention of americium but virtually no retention of mercury. By merely diluting a portion of each waste solution

to obtain the 2 M acid concentration and passing the diluted sample through the Diphonix column, we obtained an eluate that contained no detectable alpha activity. By spiking a few solutions with a known amount of mercury, we also demonstrated high recovery (>90%) of mercury in the column eluate. This separation technique will allow the ACL to use existing facilities to determine mercury in many types of americium-contaminated waste solutions. It might also be useful for the analysis of other types of mixed waste because it should be possible to adapt the technique for use in separating mercury not only from americium but also other radioactive actinide elements.

18. National Acid Precipitation Assessment Program

The National Acid Precipitation Assessment Program (NAPAP) was initiated in the early 1980s with the goal of quantifying the extent to which air pollution, including acid deposition, accelerates the weathering of materials used in the construction of cultural resources. Materials of particular interest are marble and limestone because they are widely used in exterior structures and monuments and because the calcium carbonate stones are especially sensitive to acid attack. In one NAPAP subprogram at ANL, limestone and marble briquettes are exposed to a variety of atmospheric conditions at a number of sites throughout the country. The weathered briquettes are brought to ANL for sampling and analysis to determine the surface chemistry and mineralogical changes in the test stones. In support of this program over the past few years, the ACL has analyzed hundreds of specimens for anions (F^- , Cl^- , NO_3^- , SO_4^{2-}) by ion chromatography and a smaller number for metal cations by ICP/AES. Cation concentrations changed little following exposure at the test sites. However, sulfate and nitrate concentrations were substantially elevated in some samples. These results have provided a quantitative measure of attack by atmospheric sulfur and nitrogen oxides. This year, the ACL performed anion measurements on 256 specimens.

19. Determination of Reaction Products from Molten Sodium and Chlorinated Hydrocarbons

Researchers in the Reactor Engineering Division at ANL performed a series of preliminary experiments to study the reaction between molten sodium and chlorinated hydrocarbons. This reaction might provide a means for treating waste solvents to destroy such compounds. The ACL assisted in this study by analyzing samples of argon cover gas from the reaction vessel to identify products of the reaction. Each argon sample was analyzed by gas mass spectrometry to determine the permanent gases (H_2 , N_2 , CO_2 , etc.) and light hydrocarbons (methane through propane). The argon samples were also analyzed by GC/MS to measure VOCs. These measurements demonstrated that H_2 and CH_4 were major products, although trace amounts of many VOCs (up to 32 compounds in one test) also formed. Evidence for residual chlorinated hydrocarbons was found in only one test.

The ACL also analyzed a black slag material that was found on top of the sodium bed after the tests were completed. This material was reacted with water under a flowing helium stream, and the evolved gases were collected for analysis. Acetylene present among these gases provided a measure of reactive carbides in the slag. The slag also evolved trace amounts of other VOCs and contained a substantial amount of elemental carbon. The data provided by the ACL will help the Reactor Engineering team determine whether further investigation of the proposed waste-treatment process is warranted.

20. Dissolution Process for Low-Enriched Uranium Metal Targets

The radioisotope ^{99}Mo is the precursor to $^{99\text{m}}\text{Tc}$, which is an important nuclide in diagnostic nuclear medicine. At present, ^{99}Mo is produced by neutron irradiation of highly enriched uranium (HEU) oxide targets, which are subsequently processed to recover the ^{99}Mo product. Under the aegis of the Reduced Enrichment for Research and Test Reactors program at Argonne, work is underway to develop a low-enriched uranium (LEU) metal foil target to replace the HEU oxide target (Sec. IV.D). However, new procedures are needed to recover ^{99}Mo from the LEU targets. The ACL has been assisting in this research by analyzing dissolver solutions to determine reactants and reaction products and by conducting experiments to determine the types and quantities of gases that are released during the dissolution reaction.

Information on the consumption of nitrate ion during the dissolution is being obtained by applying ion chromatography to acid solutions in which varying amounts of uranium metal were dissolved. Acid consumption during the dissolution is being evaluated by titration of the "free acid" remaining in the same solutions. This procedure employs fluoride ion as a complexant to prevent reaction between uranium species and the hydroxide titrant. Gas evolution during the dissolution process is being studied with a specially designed vacuum manifold, which allows pressure changes accompanying the dissolution to be measured and also allows samples of the evolved gases to be acquired for analysis by gas mass spectrometry or other means. The combination of data from these various measurements is expected to help guide selection of an appropriate acid mixture for effective dissolution of the LEU metal targets and to aid design of a dissolver vessel. Results obtained so far have been quite interesting in that they show the dissolution reaction to be fairly complex, with a number of variables affecting the reaction rate and product distribution in unexpected ways.

21. Transition Metal Speciation in Textile Mill Wastewater

Under the new Stream Quality Standards enforced by EPA, certain metals discharged into receiving streams from industrial facilities will be sharply curtailed. This reduction is especially significant to the U.S. textile industry because many of the important dyes used in textile processing are "premetallized"; i.e., the dye molecules contain Cu, Cr, or Co as part of the chromophore. With support from the AMTEXTM partnership (a CRADA-based initiative between DOE and the textile industry), the ACL is developing analytical procedures that will be used to characterize the lability of these metals as they appear in textile mill wastewater. In these procedures, cationic metal species are isolated by using ion-exchange chromatography, and organically bound metals are isolated by using columns of nonionic polymer resins. The isolated metals are stripped from the columns and determined by ICP emission spectroscopy. For quality assurance, the sum of the speciated metal concentrations is compared to the total metal concentration, which is determined separately. The data on metal speciation (categorized by lability of the metal) will be used to assess the bioavailability and environmental impact of the metals present in the wastewater. These data will also provide the information necessary to formulate an effective process by which toxic species can be removed from the wastewater.

22. Automated Target Recognition Using Multispectral Images

A state-of-the-art algorithm was developed in the ACL to achieve automated, accurate, and rapid target recognition regardless of the orientation and size of the target objects. This algorithm was designed to identify naval ships in multispectral imaging data. The Airborne Multisensor Pod System was established through DOE's Office of Nonproliferation and National Security to develop a new generation of technology for airborne data collection, integration, and analysis. Our work demonstrates that multiple images from several spectral bands can be combined and used simultaneously to produce results that could not be obtained from a single-band image. The power of this approach is fully realized by combining multispectral image preprocessing techniques with a novel artificial neural network, adaptive resonance theory (ART2A), for pattern recognition. The ART2A network can create new classes *dynamically*, thus providing a way to identify both new types of targets and anomalous observations. Because of the simplicity of the ART2A algorithm, it is computationally rapid and could be used for on-line data processing. It is also important to note that the pattern recognition results show that the algorithm can distinguish moving from nonmoving ships. By combining innovative preprocessing procedures with a state-of-the-art pattern recognition method, this work represents a highly effective technique for automated, accurate identification of targets in multispectral images.

23. Project in Support of Counternarcotics Efforts

The ACL continued to provide analytical support to a collaborative program between ANL's Technology Development Division and the Office of the National Drug Control Policy. In 1995, 287 U.S. currency bills from 13 locations in the suburbs of Chicago were each treated with methanol extractant and analyzed by GC/MS for the presence of cocaine. We obtained a five-point calibration curve using 1 μ L injections of calibration standards consisting of cocaine at concentrations of 10, 40, 80, 120, and 160 μ g/mL. For every 12 h of data acquisition on the GC/MS, a 40-ng or 80-ng standard was analyzed. Cocaine was identified by retention time and mass spectrum. The external standard method was used for quantification of cocaine in the sample extracts.

The bills for GC/MS analysis were acquired at five types of locations: banks, family restaurants, high schools, public places, and places where liquor/gambling exists. The experimental results indicated that 220 of the bills analyzed, or approximately 78%, were contaminated with cocaine, ranging from trace level (less than 1 μ g) to about 1.0 mg on a single bill.

Ion mobility spectrometry (IMS) was used to screen the bills prior to sample extraction. Of the 220 contaminated bills, only 37 had shown an IMS response. An additional nine samples with nondetectable or trace cocaine contamination had elicited positive results from the IMS. cursory examination of analytical data seemed to indicate no discernible one-to-one correspondence between cocaine concentration and IMS response. However, when all samples with positive IMS hits were sorted by currency age and the GC/MS results were plotted, a more revealing pattern emerged. All new bills that had IMS hits had negligible cocaine concentration, while all very old bills with IMS hits had significant levels of cocaine concentration. One explanation of these observations might be that cocaine in bills is cumulative and dependent on the surface morphology of the bills. In very old bills, the protective coating either wore thin or was cracked. Cocaine particles falling into cracks in older bills would then become trapped and accumulate in the crevices. To verify

whether IMS hits indicate more recent contamination, IMS data for bills from specific locations were checked. It was found that 40% of the bills from a gambling casino and 50% of the bills from a grocery store had positive IMS hits. In contrast, bills from family restaurants and schools had relatively low cocaine contamination, as determined by both IMS and GC/MS.

24. Chromatographic Optimization for the GC/MS Analysis of Semivolatile Organic Compounds

The ACL performs many analyses to determine SVOCs according to EPA methods. The GC/MS analysis techniques required by these methods involve instrument run times on the order of 50-60 min per sample. In addition, instrument check and continuing calibration samples must be analyzed during each 12-h period. Our objective was to improve the efficiency of our semivolatile analyses by reducing the run times for the splitless-injection GC/MS technique for environmental and mixed-waste samples.

The determination of base/neutral/acid components under SW-846 Method 8270 involves the separation, detection, and quantitation of 92 analytes, 6 surrogate standards, and 6 internal standards. There are nine pairs of compounds that have similar mass spectra and tend to be particularly difficult to separate chromatographically. Any new chromatographic method must be able to achieve reasonable resolution between these pairs of compounds. The standard GC column is a 5% phenyl-substituted methyl silicone (J&W DB-5). A new chromatographic method was developed that makes use of a DB-5 column having a length of 30 m, diameter of 0.25 mm, and a film thickness of 0.5 μ m. We were able to reduce the GC/MS run time from 58 to 34 min, a savings of over 40%. This improvement allows us to analyze approximately 15 samples in 12 h, compared to approximately 10 samples using the previously established method. In all nine pairs of problem compounds, the resolution is such that there is at least an 85% valley between the two peaks, a difference adequate for compound quantitation.

25. Development of Solid-Phase Extraction Disks for Radiochemical Analyses

Disk solid-phase extraction technology has been proven to be highly effective for sample preparation in the analysis of organic compounds, wastewaters, and other aqueous samples. Through a CRADA, the 3M Co. and ANL are expanding the 3M Empore™ technology to address sample preparation and recovery of radionuclides from aqueous samples, i.e., surface, ground, and drinking waters. Disk technology significantly improves sample throughput while reducing secondary waste and disposal costs. Sample processing and procedures for counting source preparation may be condensed into a single step, thereby significantly improving laboratory efficiency. Sample preparation takes as little as 20 min for a 1-L sample. Moreover, many of the hazardous chemicals associated with traditional procedures are eliminated. Disks have been developed that demonstrate high selectivity and great affinity for important radionuclides, including ^{99}Tc , $^{89/90}\text{Sr}$, and $^{226/228}\text{Ra}$. The ACL, in collaboration with ANL's Environmental Research Division, is evaluating the performance of these disks and developing appropriate analytical procedures. Methods for determining ^{99}Tc and $^{89/90}\text{Sr}$ have been submitted for inclusion in a DOE report on methods for evaluating environmental and waste management samples.

26. Analysis of Samples from Process to Recycle Aluminum Salt Cake

When aluminum is recycled, it is melted in the presence of an alkali-metal-chloride flux, which serves to extract impurities from the molten scrap metal. The spent flux, after it solidifies, is referred to as "salt cake." Composed of salt, aluminum metal, and oxide residues, the salt cake represents a substantial waste stream in the aluminum recycling industry, which is seeking ways to eliminate the environmental and economic disadvantages associated with disposing of salt cake waste. Researchers in ANL's Energy Systems Division are working with the Aluminum Recycling Association to develop cost-effective processes for treating salt cake to recover the salt cake constituents, recycle the aluminum and salt fractions, and convert the oxide-residue fraction to high-value-added products.

The ACL has been assisting in this research by analyzing samples from a pilot-scale test of a process that converts the oxide residues into fiber insulation products. Materials from various stages of the process have been analyzed to determine elemental composition, leachable salt content, free-metal content, and phase composition. Data from these analyses are being used to assess the effectiveness of individual process steps (e.g., removal of the salt fraction from the oxides) and to evaluate the roles of minor elements and compounds in causing difficulties that have been encountered with the process. By providing expertise in compositional analysis of refractory materials (dissolution and analysis by atomic emission or ion chromatography), X-ray diffraction, and gas-generation methods (free metals by hydrogen evolution), the ACL is working with the Energy Systems Division team to enhance the viability of the aluminum recycling industry and the environmental and economic benefits associated with it.

27. Determination of Arsenic Species in Soil Samples from the Rocky Mountain Arsenal

In 1995, the ACL continued a collaborative research effort with ANL's Energy Systems Division and the U.S. Army at the Rocky Mountain Arsenal. As part of this research effort, we developed a method to distinguish among arsenic(III), arsenic(V), and organoarsenic compounds in soil samples. This method will be used to support studies being conducted at Rocky Mountain Arsenal on the use of thermal desorption to remove chemical warfare agents and pesticides from soil. The approach chosen was a combination of high-performance liquid chromatography and ICP/MS. This permits separation of the arsenic species, followed by sensitive detection of arsenic. This project draws upon the ACL's experience in soil extractions, chromatographic separations, and atomic spectroscopy.

X. ADDENDUM.**CHEMICAL TECHNOLOGY DIVISION
PUBLICATIONS—1995**

The Division's publications and oral presentations for 1995 were entered into a bibliographic data base. The pages that follow are a printout of this information sorted into six categories: (1) journal articles, books, and book chapters, (2) patents, (3) ANL progress and topical reports, as well as contributions to reports published by organizations other than ANL, (4) abstracts and papers published in proceedings of conferences, symposia, workshops, etc., (5) oral presentations at scientific meetings and seminars not referenced in the fourth category, and (6) papers accepted for publication but not yet published.

Chemical Technology Division Publications—1995

A. Journal Articles, Books, and Book Chapters

The Investigation of Cerium as a Cathodic Inhibitor for Aluminum-Copper Alloys

A. J. Aldykiewicz, H. S. Isaacs, and A. J. Davenport
J. Electrochem. Soc. **142**(10), 3342–3350 (1995)

Modeling of Growing Oxide Film: The Iron/Iron Oxide System

V. S. Battaglia and J. Newman
J. Electrochem. Soc. **142**(5), 1423–1430 (1995)

Determination of Decontamination Factors of Radioactive Liquid Waste Streams Using Neutron Activation Analysis

S. E. Betts, S. Landsberger, D. B. Chamberlain, and G. F. Vandegrift
Radioactive Waste Manage. Environ. Restor. **20**, 49–59 (1995)

The Inorganic Chemistry of Wood Combustion for Power Production

M. Blander, K. W. Ragland, R. L. Cole, J. A. Libera, and A. D. Pelton
Biomass Bioenergy **8**(1), 29–38 (1995)

Leaching Dynamics Studies of Municipal Solid Waste Incinerator Ash

B. A. Buchholz and S. Landsberger
J. Air & Waste Manage. Assoc. **45**, 579–590 (1995)

Uranium-Contaminated Soils: Ultramicrotomy and Electron Beam Analysis

E. C. Buck, N. L. Dietz, and J. K. Bates
Microsc. Res. Tech. **31**, 174–181 (1995)

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W. F. Calaway, R. C. Wiens, D. S. Burnett, M. J. Pellin, and D. M. Gruen
J. Vac. Sci. Technol. A **13**, 1310–1315 (1995)

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Separations of f-Elements, Eds., K. L. Nash and G. R. Choppin, Plenum Press, NY, pp. 225–240 (1995)

Extraction of Technetium from Simulated Hanford Tank Wastes

D. J. Chaiko, Y. Vojta, and M. Takeuchi
Sep. Sci. Technol. **30**(7–9), 1123–1137 (1995)

The Calcite (1014) Cleavage Surface in Water: Early Results of a Crystal Truncation Rod Study

R. P. Chiarello and N. C. Sturchio
Geochim. Cosmochim. Acta **59**(21), 4557–4561 (1995)

A Quantitative Method Using FT-IR to Detect Explosives and Selected Semivolatiles in Soil Samples

M. Clapper, J. C. Demirgian, and G. Robitaille

Spectroscopy 10(7), 45-49 (1995)

Determination of Long-Lived Actinides in Soil Leachates by Inductively Coupled Plasma-Mass Spectrometry

J. S. Crain, L. L. Smith, J. S. Yaeger, and J. A. Alvarado

J. Radioanal. Nucl. Chem. 194(1), 133-139 (1995)

Energies of C_2H_5O and $C_2H_5O^+$ Isomers

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J. Chem. Phys. 102(8), 3292-3300 (1995)

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L. A. Curtiss, M. P. McGrath, J. P. Blaudeau, N. E. Davis, R. C. Binning, and L. Radom

J. Chem. Phys. 103(14), 6104-6113 (1995)

Superexchange Pathway Calculation of Electronic Coupling through Cyclohexane Spacers

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L. A. Curtiss and K. Raghavachari

Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy: Understanding Chemical Reactivity, Ed., S. R. Langhoff, Kluwer Academic Press, The Netherlands, pp. 139-171 (1995)

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J. Hazard. Mater. 41, 351-358 (1995)

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J. K. Fink and L. Leibowitz

J. Nucl. Mater. 226, 44-50 (1995)

Meyer-Neldel Rule for Liquid Semiconductors

J. A. Fortner, V. G. Karpov, and M.-L. Saboungi

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Managing the Modern Laboratory, Vol. 1, No. 3, pp. 83-87 (1995)

Getting Results from Individual Goal Setting

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Managing the Modern Laboratory, Vol. 1, No. 1, pp. 17-23 (1995)

Lithium/Iron Sulfide Batteries

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 Chapter 39 in *Handbook of Batteries*, Second Edition, Ed., D. Linden, McGraw-Hill Book Co. (1995)

Safety Characteristics of Lithium Alloy/Metal Sulfide Batteries

G. L. Henriksen, D. R. Vissers, and A. A. Chilenskas
 J. Power Sources **54**, 134-137 (1995)

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A Theoretical Study of the Energetics of Insertion of Dicarbon (C_2) and Vinylidene into Methane C-H Bonds

D. A. Horner, L. A. Curtiss, and D. M. Gruen
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^{129}Xe MAS Spectra of Xenon in Zeolite NaA. Direct Observation of Mixed Clusters of Co-Absorbed Species

A. K. Jameson, C. J. Jameson, A. C. de Dios, E. Oldfield, R. E. Gerald, and G. Turner
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C. J. Jameson, A. K. Jameson, R. E. Gerald, and H. M. Lim
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J. Nucl. Sci. Technol. **32**(1), 68-74 (1995)

Performance of Ceramic Breeder Materials in the SIBELIUS Experiment

J. P. Kopasz, C. E. Johnson, and D. L. Baldwin

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Z. Mao and J. C. Demirgian

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C. A. Melendres, B. Beden, and G. A. Bowmaker
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- Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations
R. W. Morrow and J. S. Crain, Editors
Applications of Inductively Coupled Plasma-Mass Spectrometry to Radionuclide Determinations, American Society for Testing and Materials, STP-1291, Philadelphia, PA (1995)
- Chloride Ion Catalysis of the Copper Deposition Reaction
Z. Nagy, J. P. Blaudeau, N. C. Hung, L. A. Curtiss, and D. J. Zurawski
J. Electrochem. Soc. **142**(6), L87-L89 (1995)
- Radiolytic Effects on the *In Situ* Investigation of Buried Interfaces with Synchrotron X-ray Techniques
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Evaluation of Bond Energies to Chemical Accuracy by Quantum Chemical Techniques

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Evaluation of a Field Portable X-ray Fluorescence Spectrometer for the Determination of Lead Contamination in Soil

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A Neutron Scattering Study of Poly(ethylene glycol) in Electrolyte Solutions

P. Thiagarajan, D. J. Chaiko, and R. P. Hjelm

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J. Magn. Reson. A **115**(1), 106-115 (1995)

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B. Patents

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I. Bloom and K. L. Ley

Patent No. 5,453,331, issued September 26, 1995

Method for Extracting Metals from Aqueous Waste Streams for Long Term Storage

D. J. Chaiko

Patent No. 5,395,532, issued March 7, 1995

Aqueous Biphasic Extraction Process with pH and Particle Control

D. J. Chaiko and R. Mensah-Biney

Patent No. 5,411,149, issued May 2, 1995

Synthesis of Highly Phase Pure BSCCO Superconductors

S. E. Dorris, R. B. Poeppel, B. C. Prorok, M. T. Lanagan, and V. A. Maroni

Patent No. 5,468,566, issued November 21, 1995

Method of Removal of Heavy Metal from Molten Salt in IFR Fuel Pyroprocessing

E. C. Gay

Patent No. 5,454,914, issued October 3, 1995

Corrosion Resistant Ceramic Materials

T. D. Kaun

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Feedthrough Apparatus

T. D. Kaun

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Electrorefiner

W. E. Miller and Z. Tomczuk

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Development of a Catalytic Methanol Partial Oxidation Reformer for Light-Duty Fuel Cell Vehicles

S. Ahmed, R. Kumar, and M. Krumpelt

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J. H. Aldstadt, J. M. Kuo, L. L. Smith, and M. D. Erickson

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D. A. Bass

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D. A. Bass

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D. A. Bass, J. S. Yaeger, J. S. Crain, J. T. Kiely, K. J. Parish, M. J. Gowdy, and G. B. Mohrman

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D. A. Bass, J. S. Yaeger, K. J. Parish, J. S. Crain, J. T. Kiely, M. J. Gowdy, and G. B. Mohrman

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J. K. Bates and A. J. G. Ellison

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J. K. Bates, A. J. G. Ellison, J. W. Emery, and J. C. Hoh

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M. Blander

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J. P. Blaudeau, L. A. Curtiss, Z. Nagy, N. C. Hung, and D. J. Zurawski

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Evaluation of Radioactivity Removal Procedures

A. S. Boparai, M. A. Gritters, Y. Tsai, and L. L. Smith

Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 5-10, 1995

Waste Minimization via Preparative Scale High Performance Gel Permeation Chromatography

A. S. Boparai, K. J. Parish, S. D. Kent, Y. Tsai, and D. A. Joe

Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 5-10, 1995

Fuel Cell Technology Development

C. Borroni-Bird, S. Swathirajan, R. Sims, and J. F. Miller

Presented at the National Research Council Review of the Research Program of the Partnership for a New Generation of Vehicles (PNGV), Dearborn, MI, August 27-31, 1995

Processing of LEU Targets for ^{99}Mo Production—Dissolution of U_3Si_2 Targets by Alkaline Hydrogen Peroxide

B. A. Buchholz and G. F. Vandegrift

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), Paris, France, September 18-21, 1995

The Nature of Uranium Contamination at Fernald, Ohio

E. C. Buck, N. R. Brown, and N. C. Dietz

Presented at the Emerging Technologies in Hazardous Waste Management VII Symp., Am. Chem. Soc., Atlanta, GA, September 17-20, 1995

The Nature of Contaminant Uranium Phases at Fernald

E. C. Buck, N. L. Dietz, and R. J. Abitz

Presented at the Emerging Technologies in Hazardous Waste Management VII Symp., Am. Chem. Soc., Atlanta, GA, September 17-20, 1995

Characterization of Uranium- and Plutonium-Contaminated Soils by Electron Microscopy

E. C. Buck, N. L. Dietz, J. A. Fortner, J. K. Bates, and N. R. Brown

Presented at the Waste Management '95 Conf., Tucson, AZ, February 26-March 2, 1995

Trace Analysis Using Lasers and Ion Beams

W. F. Calaway

Presented at Beloit College, Department of Chemistry, Beloit, WI, April 21, 1995

Yield and Distribution of Atoms and Molecules from Calcium Metal during Ar^+ Ion Bombardment

W. F. Calaway

Presented at the Fall Meeting of the Illinois Chapter of the American Vacuum Society, Argonne National Laboratory, September 14, 1995

An Integrated, Chemometrics-Based Approach to Creating "Smart" Chemical Sensors: A Necessary Step Towards Multisensor Data Fusion

S. E. Carpenter

Presented at the Ninth Int. Forum on Process Analytical Chemistry in Conjunction with the Third Int. Conf. on On-Site Analysis, Houston, TX, January 22-25, 1995

A Comparative Study of PLS-Based Techniques for Quantifying Methane in Stack Gas Emissions

S. E. Carpenter, J. C. Demirgian, and A. R. Demlow

Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 5-10, 1995

Expansion on Reduction of Calcium Doped Lanthanum Chromite

J. D. Carter, P. V. Hendriksen and M. Mogensen

Presented at the EPRI/GRI Fuel Cell Workshop on Fuel Cell Technology Research and Development, Irvine, CA, April 4-5, 1995

Portable Concentrator for Processing Plutonium-Contaminated Solutions

D. B. Chamberlain, C. J. Conner, and D. G. Wygmans

Presented at the Facility Transitioning, Decommissioning, and Final Disposition Focus Area Mid-Year Review, Gaithersburg, MD, May 2-4, 1995

TRUEX Processing of Plutonium Analytical Solutions at Argonne National Laboratory

D. B. Chamberlain, C. J. Conner, D. G. Wygmans, J. C. Hutter, R. A. Leonard, and G. F. Vandegrift

Presented at the Ninth Symp. on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 22-26, 1995

Metallophthalocyanine Radicals in Catalysis

M. J. Chen and J. W. Rathke

Presented at the Catalysis Club of Chicago, Spring Symp., Argonne, IL, May 9, 1995

Persistent Rh(II) Phthalocyanine Radicals

M. J. Chen and J. W. Rathke

Presented at the Int. Chemical Congress of Pacific Basin Societies, Honolulu, HI, December 17-22, 1995

X-ray Scattering at Mineral-Water Interfaces

R. P. Chiarello

Presented at the Brookhaven National Laboratory National Synchrotron Light Source Annual User's Meeting, Upton, NY, May 8, 1995

X-ray Scattering at Mineral-Water Interfaces

R. P. Chiarello

Presented at the Am. Phys. Soc. Meeting, Pittsburgh, PA, March 1995

X-ray Scattering at Mineral-Water Interfaces

R. P. Chiarello

Presented at the University of Washington, Department of Physics, Seattle, WA, April 14, 1995

X-ray Scattering at Mineral-Water Interfaces

R. P. Chiarello

Presented at Stanford University, Department of Material Science, Menlo Park, CA,
March 21, 1995**X-ray Scattering at Mineral-Water Interfaces**

R. P. Chiarello

Presented at the X-ray Physics Gordon Conf., Plymouth, NH, July 31–August 4, 1995

X-ray Scattering at Mineral-Water Interfaces

R. P. Chiarello

Presented at the Argonne National Laboratory Material Science Division Seminar, Argonne,
IL, April 5, 1995**Determination of Naturally-Occurring Actinides and their Progeny in Fresh Water Using Inductively Coupled Plasma-Mass Spectrometry and Batch Separation**

J. S. Crain, J. A. Alvarado, J. T. Kiely, L. L. Smith, J. S. Yaeger, and F. G. Smith

Presented at the 209th Am. Chem. Soc. National Meeting, Anaheim, CA, April 2–6, 1995

Actinides at the Crossroads: ICP-MS or Alpha Spectrometry?

J. S. Crain, L. L. Smith, F. P. Smith, J. T. Kiely, D. G. Graczyk, and J. A. Alvarado

Presented at the Fourth Annual Meeting of the Council on Ionizing Radiation Measurements
and Standards, Gaithersburg, MD, November 28–30, 1995**Chloride Ion Catalysis of the Copper Deposition Reaction**

L. A. Curtiss, J. P. Blaudeau, Z. Nagy, N. C. Hung, and D. J. Zurawski

Presented at the Annual DOE/BES Corrosion Contractors' Meeting, University Park, PA,
September 14–15, 1995***Ab Initio* Calculations of Structures, Energies, and Dynamics of Zintl Molecules**

L. A. Curtiss, C. Cramer, and M.-L. Saboungi

Presented at the Ninth Int. Conf. on Liquid and Amorphous Metals, Chicago, IL,
August 27–September 1, 1995**Theoretical Studies of Reaction Mechanisms for Growth of Diamond Surfaces from Buckyball Precursors**

L. A. Curtiss, D. A. Horner, P. Redfern, and D. M. Gruen

Presented at the Int. Chemical Congress of Pacific Basin Societies, Symp. on Computational
Quantum Chemistry: A Viable Partner to Experiment in Chemical Research, Honolulu, HI,
December 17–22, 1995**Detection of Emission Sources Using Passive-Remote Fourier Transform Infrared Spectroscopy**

J. C. Demirgian, S. M. Macha, S. M. Darby, and J. Ditillo

Presented at the Fourth Int. Symp. on Field Screening Methods for Hazardous Wastes and
Toxic Chemicals, Las Vegas, NV, February 22–25, 1995**A Continuous Emission Monitor for Incinerators: Advanced Field Test Results**

J. C. Demirgian, Z. Mao, and C. J. Chapo

Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and
Applied Spectroscopy, New Orleans, LA, March 5–10, 1995

Development of Low-Level Radioactive Waste Disposal Capacity in the United States—Progress or Stalemate?

J. S. Devgun and G. S. Larson

Presented at the Fifth Int. Conf. of Radioactive Waste Management and Environmental Remediation, ICEM '95, Berlin, Germany, September 3–9, 1995

Processing of LEU Targets for ^{99}Mo Production—Dissolution of Metal Foil Targets by Alkaline Hydrogen Peroxide

D. Dong, G. F. Vandegrift, S. Amini, J. B. Hersubeno, H. Nasution, and Y. Nampira

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), Paris, France, September 18–21, 1995

Electrode Development for a Low Temperature Direct Methanol Solid Oxide Fuel Cell

R. Doshi and M. Krumpelt

Presented at the 187th Electrochem. Soc. Meeting on Direct Electrochemical Oxidation Reactions of Methanol, Reno, NV, May 21–26, 1995

Ceramics in Electrochemical Devices

R. Doshi, M. Krumpelt, R. Kumar, T. W. Kueper, and J. D. Carter

Presented at the Ceramic Industry Manufacturing Exposition, Pittsburgh, PA, October 12–13, 1995

Status of Plutonium Ceramic Immobilization Processes and Waste Forms

B. B. Ebbinghaus, R. A. Vankonynenburg, E. R. Vance, A. Jostons, R. G. Anthony, C. V. Philip, and D. J. Wronkiewicz

Presented at the Plutonium Vittrification/Immobilization Workshop, Washington, DC, August 22–24, 1995

The Release of Technetium from Defense Waste Processing Facility Glasses

W. L. Ebert, S. F. Wolf, and J. K. Bates

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27–December 1, 1995

Collaborative Study to Validate Procedure for the Determination of Strontium-89/Strontium-90 in Water

M. A. Edgell, M. D. Erickson, S. Hedayat, P. C. Lindahl, A. E. Scandora, L. L. Smith, W. E. Streets, and G. Su

Presented at the 36th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10–12, 1995

Cost Effective Methods for Environmental Radionuclides

M. D. Erickson, J. H. Aldstadt, J. S. Alvarado, J. S. Crain, K. A. Orlandini, and L. L. Smith

Presented at the Seventh National Technology Information Exchange (TIE) Workshop, Cincinnati, OH, April 18–20, 1995

Environmental Radioanalytical Methods Development

M. D. Erickson, J. H. Aldstadt, J. S. Alvarado, J. S. Crain, K. A. Orlandini, and L. L. Smith

Presented at the 36th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10–12, 1995

Faster, Cheaper Radioanalytical Methods

M. D. Erickson, J. H. Aldstadt, J. S. Alvarado, J. S. Crain, K. A. Orlandini, and L. L. Smith

Presented at the Waste Management '95 Conf., Tucson, AZ, February 26–March 2, 1995

Methods for Environmental Radionuclides

M. D. Erickson, J. H. Aldstadt, J. S. Alvarado, J. S. Crain, K. A. Orlandini, and L. L. Smith
Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 5-10, 1995

Faster, Cheaper, and Pollution-Preventing Analytical Methods for Environmental Radionuclides

M. D. Erickson, J. H. Aldstadt, J. S. Alvarado, J. S. Crain, K. A. Orlandini, and L. L. Smith
Presented at the 41st Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Boston, MA, November 12-16, 1995

Glass Durability Evaluation Using Product Consistency, Single-Pass Flow-Through, and Vapor Hydration Tests

X. Feng, D. K. Peeler, B. P. McGrail, P. Hrma, M. J. Schweiger, H. Li, A. J. Bakel, and W. L. Ebert
Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 1, 1995

X-ray Off-Specular Reflectivity Studies of Electrochemical Pitting of Copper Surfaces in Sodium Bicarbonate Solution

Y. P. Feng, S. K. Sinha, C. A. Melendres, and D. D. Lee
Presented at the Fourth Int. Conf. on Surface X-ray and Neutron Scattering, Lake Geneva, WI, June 26-30, 1995

Spinel Anodes for Lithium-Ion Batteries

E. Ferg, R. J. Gummow, A. de Kock, and M. M. Thackeray
Presented at the Ninth Int. Battery Association Symp., Cape Town, South Africa, March 20-22, 1995

The Behavior of Spent Fuel during Unsaturated Testing at 90°C

P. A. Finn, J. C. Hoh, S. F. Wolf, J. W. Emery, E. C. Buck, D. J. Wronkiewicz, S. A. Slater, and J. K. Bates
Presented at the Spent Fuel Workshop, Uberlingen, Germany, September 18-20, 1995

The Release of Cesium and the Actinides from Spent Fuel under Unsaturated Conditions

P. A. Finn, J. C. Hoh, S. F. Wolf, S. A. Slater, and J. K. Bates
Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 1, 1995

The Release of Uranium, Plutonium, Cesium, Strontium, Technetium, and Iodine from Spent Fuel under Unsaturated Conditions

P. A. Finn, J. C. Hoh, S. F. Wolf, S. A. Slater, and J. K. Bates
Presented at the Fifth Int. Conf. on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere, MIGRATION '95, Saint-Malo, France, September 10-15, 1995

Long-Term Results from Unsaturated Durability Testing of Actinide-Doped DWPF and WVDP Glasses

J. A. Fortner and J. K. Bates
Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 1, 1995

- Disposition of Plutonium and Cerium in Waste Forms Determined by Electron Energy Loss Spectroscopy
J. A. Fortner, E. C. Buck, and J. K. Bates
Presented at the 29th Annual Meeting of the Microbeam Analysis Soc., Breckenridge, CO,
August 6-11, 1995
- Analytical Electron Microscopy of Alteration Phases from Nuclear Waste Glasses
J. A. Fortner, E. C. Buck, N. L. Dietz, and J. K. Bates
Presented at the Ninth Int. Conf. on Liquid and Amorphous Metals, Chicago, IL,
August 27-September 1, 1995
- Disposition of Plutonium and Cerium in Realistic Glass-Crystalline Composite Waste Forms
J. A. Fortner, E. C. Buck, J. W. Richardson, D. J. Wronkiewicz, and J. K. Bates
Presented at the Am. Crystall. Assoc. Annual Meeting, Montreal, Canada, July 23-28, 1995
- The Meyer-Neldel Rule in Semiconductors at High Temperatures
J. A. Fortner, M.-L. Saboungi, and V. G. Karpov
Presented at the Fall Meeting of the Materials Research Soc., Boston, MA,
November 27-December 1, 1995
- Feedback Revision Request Process
A. A. Frigo
Presented at the Ninth Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc.,
Minneapolis, MN, July 19-22, 1995
- A Glovebox Design Checklist
A. A. Frigo
Presented at the Ninth Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc.,
Minneapolis, MN, July 19-22, 1995
- Plant-Scale Anodic Dissolution of Unirradiated N-Reactor Fuel
E. C. Gay, W. E. Miller, and J. J. Laidler
Presented at the GLOBAL '95 Int. Conf. on Evaluation of Emerging Nuclear Fuel Cycle
Systems, Versailles, France, September 11-14, 1995
- Separation of Uranium from Zircaloy Clad N-Reactor Fuel in a High Throughput Electrorefiner
E. C. Gay, W. E. Miller, and J. J. Laidler
Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995
- Visualization of Second-Rank Tensors: Electronic Shielding. The Computational and Visual Geometry
Seminar Series
R. E. Gerald
Presented to the Department of Mathematics, University of Wisconsin, Madison, WI,
May 10, 1995
- Visualization of Second-Rank Tensors: Electronic Shielding
R. E. Gerald
Presented at the 37th Rocky Mountain Conf. on Analytical Chemistry, Denver, CO,
July 23-28, 1995
- Radial Distribution of $^7\text{Li}^+$ Ions in Polyethylene Oxide in a Cylindrical Cavity Imager
R. E. Gerald, J. W. Rathke, and R. J. Klingler
Presented at the 37th Rocky Mountain Conf. on Analytical Chemistry, Denver, CO,
July 23-28, 1995

Secondary Phase Formation and the Microstructural Evolution of the Surface Layer during Vapor Phase Alteration of the French SON 68 Nuclear Waste Glass at 200°C

W. L. Gong, R. C. Ewing, L. M. Wang, E. Vernaz, J. K. Bates, and W. L. Ebert

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA,
November 27–December 1, 1995

Determination of Free Energies of Formation of Mixed Oxides between Li_2O and RE_2O_3 (RE-Ce, Nd, Eu, Sm) in LiCl Melts

K. Gourishankar, G. K. Johnson, and I. Johnson

Presented at the 50th Calorimetry Conf., National Institute of Standards and Technology,
Gaithersburg, MD, July 23–28, 1995

One Hundred and One Ways to Obtain Precise but Inaccurate Numbers by Thermal Ionization Mass Spectrometry

J. W. Gramlich

Presented at the University of Michigan, Ann Arbor, MI, July 13, 1995

Reflections on the DAM Mission

D. W. Green

Presented at the 13th DOE Analytical Lab Managers Meeting, Las Vegas, NV, October 2–5,
1995

Some Areas of Potential Growth for Chemists

D. W. Green

Presented at the 210th Am. Chem. Soc. National Meeting and Exposition Program on
Chemistry and the National Agenda: Future Employment Opportunities in the Chemical
Sciences, Chicago, IL, August 20–24, 1995

New Analytical Methods to Minimize Secondary Waste

D. W. Green, L. L. Smith, J. S. Crain, A. S. Boparai, J. T. Kiely, J. S. Yaeger, and J. B. Schilling

Presented at the Laboratory Safety and Environmental Management Conf., Baltimore, MD,
June 27–29, 1995

Microstructure of CVD Diamond Films Grown from Fullerene Precursors

D. M. Gruen, J. S. Luo, C. D. Zuiker, and A. R. Krauss

Presented at the 187th Electrochem. Soc. Meeting, Reno, NV, May 21–26, 1995

Environmental Control Processes Using Plasmas

J. Harkness and T. R. Krause

Presented at the Workshop on the Treatment of Gaseous Emissions via Plasma Technology:
Present and Future Needs, National Institute of Standards and Technology, Gaithersburg,
MD, March 19–21, 1995

IPEP Laboratory Performance Evaluation Reports for Management of DOE EM Programs

J. E. Hensley, P. C. Lindahl, W. E. Streets, D. A. Bass, S. W. Warren, and W. R. Newberry

Presented at the DOE ER '95 Environmental Restoration Conf., Denver, CO, August 13–17,
1995

Microwave-Extraction of Polynuclear Aromatic Hydrocarbons from Coal Ash Samples

E. Y. Hwang and K. R. Vanderveen

Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and
Applied Spectroscopy, New Orleans, LA, March 5–10, 1995

Thermodynamic Considerations for the Use of Vanadium Alloys with Ceramic Breeder Materials

C. E. Johnson, I. Johnson, and J. P. Kopasz

Presented at the Fourth Int. Workshop on Ceramic Breeder Blanket Interactions, Kyoto, Japan, October 9-11, 1995

Characteristics of Lithium Ceramics Irradiated in the FUBRIB/BEATRIX Experiment

C. E. Johnson, L. A. Neimark, and D. L. Bowers

Presented at the Fourth Int. Workshop on Ceramic Breeder Blanket Interactions, Kyoto, Japan, October 9-11, 1995

Preparation and Characterization of α -MnO₂ for Rechargeable Lithium Batteries

C. S. Johnson, D. W. Dees, M. F. Mansuetto, M. M. Thackeray, D. R. Vissers, D. Argyriou, C.-K. Loong, and L. Christensen

Presented at the Int. Battery Association Meeting, Chicago, IL, October 7-8, 1995

Iron Corrosion Inhibition by the Carbonate System in Oxygenated Water, A Mechanistic Study

D. A. Johnson, R. V. Davis, S.-H. Shim, L. J. Simpson, and C. A. Melendres

Presented at the Eighth European Symp. on Corrosion Inhibitors, Fararra, Italy, March 1995

The Calorimetry Conference and Argonne National Laboratory, Fifty Years of Collaboration

G. K. Johnson

Presented at the 50th Calorimetry Conf., National Institute of Standards and Technology, Gaithersburg, MD, July 23-28, 1995

High Temperature Treatment of Oxide Spent Fuels and Residues

G. K. Johnson, R. D. Pierce, C. C. McPheeters, and K. Gourishankar

Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995

Infrastructure Impact of PNGV Technologies

L. Johnson, J. F. Miller, and G. Fenske

Presented at the National Research Council Review of the Research Program of the Partnership for a New Generation of Vehicles (PNGV), Dearborn, MI, August 27-31, 1995

Determination of the Sorption Capacity of Europium onto Ferromagnetic Microparticles Coated with CMPO

M. D. Kaminski, L. Nuñez, S. Landsberger, and G. F. Vandegrift

Presented at the Ninth Symp. on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 22-26, 1995

Script for Argonne Lithium Process Video

E. J. Karell

Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995

Engineering-Scale Demonstration of Oxide Spent Fuel Treatment: Part II—Test Results

E. J. Karell, T. P. Mulcahey, G. K. Johnson, C. C. McPheeters, R. E. Everhart, R. G. Palm, R. D. Pierce, J. L. Smith, M. A. Vest, and D. W. Warren

Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995

Toxic Combustion Byproducts: Generation, Containment, Separation, Cleansing for Hazardous, Mixed and Transuranic Waste Processing

W. Kephart, K. Eger, and M. K. Clemens

Presented at the Fourth Int. Congress on Toxic Combustion Byproducts, Berkeley, CA, June 5-7, 1995

Flow Injection-Direct Injection Nebulization (FI-DIN) for High Efficiency Sample Introduction and Waste Minimization in ICP-MS

J. T. Kiely and J. S. Crain

Presented at the 36th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1995

Radium Separation and Measurement Using EmporeTM Radium Rad Disks

R. M. Kinney, R. T. Shannon, L. L. Smith, K. M. Hoffmann, and D. C. Seely

Presented at the 41st Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Workshop on Innovative Radiochemical Analyses through the Use of EmporeTM Rad Disks with AnaligTM, Boston, MA, November 12-16, 1995

High-Pressure NMR Studies in Supercritical Media

R. J. Klingler, J. W. Rathke, and K. W. Kramarz

Presented at the Catalysis Club of Chicago Spring Symp., Argonne, IL, May 9, 1995

Investigation of the Interactions of H₂O_(g) with Li₂ZrO₃

J. P. Kopasz and C. E. Johnson

Presented at the Fourth Int. Workshop on Ceramic Breeder Blanket Interactions, Kyoto, Japan, October 9-11, 1995

ANL's Proposed SOFC Research for FY 96 and FY 97

M. Krumpelt and R. Doshi

Presented to Westinghouse Corporation, Churchill, PA, June 6, 1995

Overview of Fuel Cell Power Sources for Vehicles

M. Krumpelt and R. Kumar

Presented at the Symp. on Electrochemical Power Sources for Electric Vehicles, AIChE Annual Meeting, Miami Beach, FL, November 12-17, 1995

Sealant Materials for Solid Oxide Fuel Cells

T. W. Kueper, M. Krumpelt, and J. H. Meiser

Presented at the Fuel Cells '95 Review Meeting, Morgantown Energy Technology Center, Morgantown, WV, August 9-10, 1995

Development of a Catalytic Partial Oxidation Reformer for Methanol Used in Fuel Cell Transportation Systems

R. Kumar and S. Ahmed

Presented at the Fuel Cells for Transportation TOPTEC Meeting, Santa Fe, NM, March 28-29, 1995

Modeling the Methanol Steam Reformer

R. Kumar, H. K. Geyer, R. K. Ahluwalia, and M. Krumpelt

Presented at the Int. Energy Agency Annex IV Annual Meeting, Ottawa, Ontario, Canada, October 5-6, 1995

Electrochemical Processing of Spent Nuclear Fuel

J. J. Laidler

Presented at the GLOBAL '95 Int. Conf. on Evaluation of Emerging Nuclear Fuel Cycle Systems, Versailles, France, September 11-14, 1995

Use of Spent Fuel Treatment Technology for Plutonium Immobilization

J. J. Laidler, J. P. Ackerman, and C. C. McPheeters

Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995

Implementation of Waste Minimization of a Complex R&D Site

R. E. Lang, J. R. Thuot, and J. S. Devgun

Presented at the Waste Management '95 Conf., Tucson, AZ, February 26-March 2, 1995

Polymers, Ceramics, and Nuclear Energy

R. A. Leonard

Presented at the Dept. of Chemical Engineering Seminar, University of Cincinnati, Cincinnati, OH, October 19, 1995

Centrifugal Contactors for Laboratory-Scale Solvent Extraction Tests

R. A. Leonard, D. B. Chamberlain, and C. J. Conner

Presented at the Ninth Symp. on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 22-26, 1995

The Sorption Properties of Zeolite A for +1, +2, and +3 Ions in Molten LiCl-KCl Salt

M. A. Lewis, J. C. Hutter, and J. P. Ackerman

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 1, 1995

DOE's Integrated Performance Evaluation Program (IPEP) Laboratory Performance Reports for Sample Management Offices

P. C. Lindahl

Presented at the Sample and Data Management Workshop, Richland, WA, May 23-24, 1995

Laboratory Performance Evaluation Reports for Management

P. C. Lindahl, J. E. Hensley, D. A. Bass, P. L. Johnson, J. J. Marr, W. E. Streets, S. W. Warren, and W. R. Newberry

Presented at the Sixth Int. Environmental Quality and Waste Management Conf., Denver, CO, April 17-20, 1995

Development of the Integrated Performance Evaluation Program (IPEP) for the Department of Energy's Office of Environmental Management

P. C. Lindahl, W. E. Streets, D. A. Bass, J. E. Hensley, W. R. Newberry, and M. H. Carter

Presented at the Seventh National Technology Information Exchange (TIE) Workshop, Cincinnati, OH, April 18-20, 1995

IPEP—The Integrated Performance Evaluation Program for the Department of Energy's Office of Environmental Management

P. C. Lindahl, W. E. Streets, D. A. Bass, P. L. Johnson, J. J. Marr, A. E. Scandora, J. E. Hensley, K. J. Parish, W. R. Newberry, and M. H. Carter

Presented at the 37th Rocky Mountain Conf. on Analytical Chemistry, Denver, CO, July 23-28, 1995

IPEP: The Integrated Performance Evaluation Program for the Department of Energy's Office of Environmental Management

P. C. Lindahl, W. E. Streets, D. A. Bass, P. L. Johnson, J. J. Marr, A. E. Scandora, K. J. Parish, J. E. Hensley, W. R. Newberry, and M. H. Carter

Presented at the DOE ER '95 Environmental Restoration Conf., Denver, CO, August 13-17, 1995

Pilot Implementation Studies of the DOE's Office of Environmental Management's Integrated Performance Evaluation Program (IPEP)

P. C. Lindahl, W. E. Streets, W. R. Newberry, M. H. Carter, J. Connolly, C. Watkins, J. Fisk, and E. Baugher

Presented at the 36th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10-12, 1995

The Department of Energy's Integrated Performance Evaluation Program (IPEP): Pilot Studies for Implementation

P. C. Lindahl, W. E. Streets, W. R. Newberry, M. H. Carter, C. Watkins, J. Connolly, J. Fisk, and E. Baugher

Presented at the 41st Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Boston, MA, November 12-16, 1995

Glovebox Window Seal Test

R. F. Malecha, D. E. Preuss, and S. G. Wiedmeyer

Presented at the Ninth Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc., Minneapolis, MN, July 19-22, 1995

Analysis of Carbon Species in High Temperature Superconducting Ceramics Using the BIO-RAD FTS-185

V. A. Maroni

Presented at the BIO-RAD 1995 FT-IR User's Meeting, Cambridge, MA, June 20-22, 1995

Silver-Sheathed Bi(Pb)-2223 Composite Conductors: What's Going on during Thermomechanical Processing?

V. A. Maroni, N. Merchant, S. E. Dorris, and J. S. Luo

Presented at the Materials Science Division Seminar, Materials Science and Chemical Technology Division, Argonne National Laboratory, April 26, 1995

Silver-Sheathed Bi(Pb)-2223 Composite Conductors: What's Going on during Thermomechanical Processing?

V. A. Maroni, N. Merchant, S. E. Dorris, and J. S. Luo

Presented at the 124th Annual Meeting and Exhibition of the Minerals, Metals, and Materials Soc., Las Vegas, NV, February 21-25, 1995

The Application of Imaging Raman Microscopy to High Temperature Superconducting Ceramics

V. A. Maroni, K. Wu, and A. K. Fischer

Presented at the Federation of Analytical Chemistry and Spectroscopy Meeting, Cincinnati, OH, October 18, 1995

Trace Analysis of Calcium Impurities in Silicon

A. H. Marshall, D. R. Spiegel, and W. F. Calaway

Presented at the Texas Section of the Am. Phys. Soc., Lubbock, TX, October 27-28, 1995

Vitrification as a Low-Level Radioactive Mixed Waste Treatment Technology at Argonne National Laboratory

J. J. Mazer and H. J. No

Presented at the Third Biennial Mixed Symp., Am. Soc. Mech. Eng., Temple University, Baltimore, MD, August 7-11, 1995

Vitrification of Low-Level Radioactive Mixed Waste at Argonne National Laboratory

J. J. Mazer, S. D. Rosine, and H. J. No

Presented at Waste Management '95 Conf., Tucson, AZ, February 26-March 2, 1995

Alloy Waste Forms for the Disposal of Low TRU Metal Wastes from Spent Nuclear Fuel Treatment

S. M. McDeavitt, D. P. Abraham, and J. Y. Park

Presented at the Fall Meeting of the Minerals, Metals, and Materials Soc., Physical Metallurgy and Materials, Cleveland, OH, October 29-November 2, 1995

A Zirconium Metal Alloy for the Immobilization of Surplus Fissile Materials

S. M. McDeavitt, T. R. Johnson, R. P. Jacqmin, R. N. Hill, and D. D. Keiser

Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995

X-ray Diffuse Scattering for the *In-Situ* Study of Electrochemically Induced Pitting on Metal Surfaces

C. A. Melendres

Presented at the Gordon Conf. on Electrochemistry, Ventura, CA, January 16-20, 1995

In-Situ Laser Raman and Infrared Spectroscopic Studies of Anodic Corrosion Films on Metals

C. A. Melendres

Presented at the Fall Meeting of the Minerals, Metals, and Materials Soc., Cleveland, OH, October 29-November 2, 1995

Phase Evolution and Microstructure Development in Mono- and Multifilamentary Ag/Bi-2223 Composite Conductors: A Comparison

N. Merchant, V. A. Maroni, W. L. Carter, and E. Podtburg

Presented at the Spring Meeting of the Materials Research Soc., San Francisco, CA, April 17-21, 1995

Objectives for Breakout Working Groups

J. F. Miller

Presented at the Partnership for a New Generation of Vehicles (PNGV) Workshop on Fuel Processing for Proton Exchange Membrane (PEM) Fuel Cells, Dearborn, MI, October 24, 1995

PNGV Overview—A Technical Roadmap

J. F. Miller

Presented at the Interagency Advanced Power Group Meeting, Cleveland, OH, May 25, 1995

Potential of Solid Oxide Fuel Cells for Transportation

J. F. Miller

Presented at the Society of Automotive Engineers TOPTEC Meeting, Santa Fe, NM, March 28-29, 1995

Engineering-Scale Demonstration of Oxide Spent Fuel Treatment: Part I— Operations

T. P. Mulcahey, E. J. Karell, G. K. Johnson, C. C. McPheeters, R. E. Everhart, R. G. Palm, R. D. Pierce, J. L. Smith, M. A. Vest, and D. W. Warren

Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995

Radiolytic Effects in the Use of Synchrotron X-ray Techniques with Aqueous Solutions

Z. Nagy and H. You

Presented at the 210th Am. Chem. Soc. National Meeting and Exposition Program, Chicago, IL, August 20-24, 1995

Radiolytic Effects on the Investigation of Buried Interfaces with X-ray Scattering

Z. Nagy and H. You

Presented at the Fourth Int. Conf. on Surface X-ray and Neutron Scattering, Lake Geneva, WI, June 26-30, 1995

Radiolytic Effects on the Investigation of Electrode/Solution Interfaces with X-rays

Z. Nagy and H. You

Presented at the Gordon Research Conf. on Electrochemistry, Ventura, CA, January 15-20, 1995

Fuel Cell Systems for First Lunar Outpost - Reactant Storage Option

P. A. Nelson

Presented at the Fourth Space Electrochemical Research and Technology (SERT) Conf., NASA Lewis Research Center, Cleveland, OH, May 2-3, 1995

Application of Single-Ion Activity Coefficients to Determine Solvent Extraction Mechanism for Components of High Level Nuclear Waste

L. Nuñez, and G. F. Vandegrift

Presented at the Ninth Symp. on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 22-26, 1995

Ultratrace Analysis Using Laser Ablation and Laser Postionization

M. J. Pellin and W. F. Calaway

Presented at the OE/LASE '95 Conf., Advanced Optical Methods for Ultrasensitive Detection, San Jose, CA, February 4-10, 1995

Femtosecond Laser Postionization of Sputtered and Laser Desorbed Atoms

M. J. Pellin, K. R. Lykke, and W. F. Calaway

Presented at the Fourth Workshop on Postionization Techniques in Surface Analysis (PITSA4), Rust Burgenland, Austria, April 23-27, 1995

Supercritical Hydroformylations

J. W. Rathke and R. J. Klingler

Presented at the 209th Am. Chem. Soc. National Meeting, Division of Industrial and Engineering Chemistry, Anaheim, CA, April 2-6, 1995

Holding Time Study of Volatile Organic Compounds in SUMMA Canisters

G. T. Reedy, D. V. Applegate, M. A. Gritters, S. E. Carpenter, and A. S. Boparai

Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 5-10, 1995

Spectroscopy of Plutonium-Organic Complexes

M. K. Richmann and D. T. Reed

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 1, 1995

Progress in Carbonate Fuel Cells

M. F. Roche, M. Krumpelt, I. Bloom, H. K. Geyer, J. E. Indacochea, S. A. Johnson,
M. T. Lanagan, and S. H. D. Lee

Presented at the Fuel Cells '95 Review Meeting, Morgantown Energy Technology Center,
Morgantown, WV, August 9-10, 1995

The Use of Diphonix Ion Exchange Resin as a Preconcentration Step for the Actinides and Lanthanides in Analytical Applications

A. N. Rollins, A. Thakker, M. J. Gula, M. J. Fern, E. P. Horwitz, R. Chiarizia, H. Diamond,
L. L. Smith, and S. Maxwell

Presented at the 209th Am. Chem. Soc. National Meeting, Anaheim, CA, April 2-6, 1995

Reactions of Mn_2O_3 with Acid: Synthesis and Electrochemical Characterization of α - MnO_2

M. H. Rossouw, D. C. Liles, and M. M. Thackeray

Presented at the Ninth Int. Battery Association Symp., Cape Town, South Africa,
March 20-22, 1995

DOE's IPEP on the Infobahn—Electronic Dissemination of Assessments from Multiple Performance Evaluation Programs

A. E. Scandora, P. L. Johnson, W. E. Streets, P. L. Vignola, D. A. Bass, P. C. Lindahl,
W. R. Newberry, and M. H. Carter

Presented at the 210th Am. Chem. Soc. National Meeting and Exposition Program,
Division of Computers in Chemistry, Chicago, IL, August 20-24, 1995

Extraction of Semivolatile Organic Pollutants from HEPA Filters Using Supercritical Carbon Dioxide

J. B. Schilling

Presented at the 36th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology,
Gatlinburg, TN, October 10-12, 1995

Microwave-Assisted Extraction of Semivolatile Organic Pollutants from Soil

J. B. Schilling and C. M. Newcomb

Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and
Applied Spectroscopy, New Orleans, LA, March 5-10, 1995

Ab Initio Hartree-Fock Calculation of Dimeric Iron(III) Chloride

G. Scholz and L. A. Curtiss

Presented at the Molecular Quantum Mechanics and Applications Conf., Cambridge,
England, September 3-7, 1995

Thermal Desorption of Agent Simulant-Spiked Soil Rocky Mountain Arsenal

L. M. Shem, H. J. O'Neill, D. A. Bass, D. E. O'Reilly, and M. Besmer

Presented at the 10th Annual Conf. on Contaminated Soils, Analysis, Fate, Environmental
and Public Health Effects and Remediation, University of Massachusetts at Amherst,
Amherst, MA, October 23-26, 1995

Thermal Desorption Screening of Agent-Simulant-Spiked Soil from Rocky Mountain Arsenal

L. M. Shem, H. J. O'Neill, D. A. Bass, D. E. O'Reilly, and M. Besmer

Presented at the Scientific Conf. on Chemical and Biological Defense Research, Aberdeen
Proving Ground, MD, November 14-17, 1995

Optimization of Magnetite Carrier Precipitation Process for Transuranic Waste Reduction

S. A. Slater, D. B. Chamberlain, S. A. Aase, B. D. Babcock, C. J. Conner, J. Sedlet, and G. F. Vandegrift

Presented at the Ninth Symp. on Separation Science and Technology for Energy Applications, Gatlinburg, TN, October 22–26, 1995

Materials Issues in USABC-Sponsored Battery Technologies

J. A. Smaga

Presented at the Capital Metals and Materials Forum in Electric Vehicle Battery Technology, Washington, DC, January 18, 1995

Innovative Radiochemical Analyses through the Use of Empore™ Disk Technology

L. L. Smith, K. A. Orlandini, J. A. Alvarado, M. D. Erickson, K. M. Hoffmann, D. C. Seely, and R. T. Shannon

Presented at the 36th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10–12, 1995

Application of Empore™ Disk Technology to Environmental Radiochemical Analysis

L. L. Smith, K. A. Orlandini, J. A. Alvarado, K. M. Hoffmann, D. C. Seely, and R. T. Shannon

Presented at the 41st Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Boston, MA, November 12–16, 1995

An Evaluation of Empore™ Strontium Rad Disks

L. L. Smith, K. A. Orlandini, J. S. Alvarado, M. D. Erickson, K. M. Hoffmann, D. C. Seely, and R. T. Shannon

Presented at the 41st Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Workshop on Innovative Radiochemical Analyses through the Use of Empore™ Rad Disks with Analig™, Boston, MA, November 12–16, 1995

Application of Selective Membrane Technology to Environmental Radiochemical Analysis: ⁹⁰Sr and ⁹⁹Tc

L. L. Smith, K. A. Orlandini, M. D. Erickson, G. L. Goken, T. A. Dirksen, K. M. Hoffmann, and D. C. Seely

Presented at the 46th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 5–10, 1995

Development and Processing of LEU Targets for ⁹⁹Mo Production—Overview of the ANL Program

J. L. Snelgrove, G. L. Hofman, T. C. Wiecek, C. T. Wu, G. F. Vandegrift, S. Aase, B. A. Buchholz, D. J. Dong, R. A. Leonard, B. Srinivasan, D. Wu, A. Supto, and Z. Aliluddin

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), Paris, France, September 18–21, 1995

Processing of LEU Targets for ⁹⁹Mo Production—Dissolution of Metal Foils by Nitric-Acid/Sulfuric-Acid Mixtures

B. Srinivasan, R. A. Leonard, S. B. Aase, G. F. Vandegrift, A. A. Rauf, H. Lubis, A. Hardi, S. Amini, and Y. Nampira

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), Paris, France, September 18–21, 1995

Designing Electrodes for Lithium-Ion Batteries

M. M. Thackeray

Presented at the Ninth Int. Battery Association Symp., Cape Town, South Africa, March 20–22, 1995; and Northwestern University, Chicago, IL, May 24, 1995

Insertion Electrodes for Lithium-Ion Batteries

M. M. Thackeray

Presented at the Electrochem. Soc. Meeting, Ann Arbor, MI, October 24, 1995

Structural Stability of $\text{Li}_x\text{Mn}_2\text{O}_4$ (Spinel) and Li_xCoO_2 (Layered) Insertion Electrodes

M. M. Thackeray, M. F. Mansuetto, D. W. Dees, and D. R. Vissers

Presented at the Int. Battery Association Meeting, Chicago, IL, October 7-8, 1995

Electrochemical Processing Using Cadmium Electrodes

Z. Tomczuk

Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995

Cocaine Contamination on Currency

S. Ulvick, J. Cui, T. Kunz, J. C. Demirgian, E. Y. Hwang, B. S. Tani, C. Roche, C. Su, and S. Rigdon

Presented at the Tactical Technologies and Wide Area Surveillance Int. Symp., Nashua, NH, October 23-27, 1995

ANL/U of I/BATAN Studies of the Cintichem Process and its Conversion to LEU

G. F. Vandegrift, R. A. Leonard, B. Srinivasan, D. Wu, and S. Landsberger

Presented at Sandia National Laboratory, Albuquerque, NM, November 6, 1995

TRUEX Processing of Idaho Sodium-Bearing Wastes: Treatment of the Extraction Behaviors of Mercury and Zirconium in the Generic TRUEX Model

G. F. Vandegrift, C. J. Mertz, and M. C. Regalbuto

Presented at the 19th Actinide Separations Conf., Monterey, CA, June 12-15, 1995

The Development of a Bench-Scale Metal Distillation Furnace

M. A. Vest, J. L. Smith, and R. D. Pierce

Presented at the Am. Nucl. Soc. Meeting on Computer-Based Human Support Systems: Technology, Methods, and Future, Philadelphia, PA, June 25-29, 1995

Radionuclide Content of Simulated and Fully Radioactive SRL Waste Glasses: Comparison of Results from ICP-MS, Gamma Spectrometry, and Alpha Spectrometry

S. F. Wolf and J. K. Bates

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 1, 1995

An Evaluation of Glass-Crystal Composites for the Disposal of Nuclear and Hazardous Waste Materials

D. J. Wronkiewicz, T. DiSanto, S. F. Wolf, E. C. Buck, N. L. Dietz, and X. Feng

Presented at the Waste Management '95 Conf., Tucson, AZ, February 26-March 2, 1995

Apatite- and Monazite-Bearing Glass-Crystal Composites for the Immobilization of Low-Level Nuclear and Hazardous Wastes

D. J. Wronkiewicz, S. F. Wolf, and T. S. DiSanto

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 1, 1995

Processing of LEU Targets for ^{99}Mo Production—Testing and Modification of the Cintichem Process

D. Wu, S. Landsberger, B. A. Buchholz, and G. F. Vandegrift

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors (RERTR), Paris, France, September 18-21, 1995

Application of Neutron Activation Analysis in a Fission Molybdenum Separation Study

D. Wu, S. Landsberger, and G. F. Vandegrift

Presented at the Ninth Int. Conf. on Modern Trends in Activation Analysis, Seoul, Korea,
September 24-30, 1995

Compositions and Spatial Distributions of Second Phases in Bi-Pb-Sr-Ca-Cu-O Powders as Determined by Imaging Raman Microscopy

K. Wu, A. K. Fischer, and V. A. Maroni

Presented at the Spring Meeting of the Materials Research Soc., San Francisco, CA,
April 17-21, 1995

Place Exchange during Surface Oxidation of Platinum

H. You and Z. Nagy

Presented at the Cornell University CHESS User's Meeting, Ithaca, New York, June 20-21,
1995

Proton Transfer via Adsorption of Water in Zeolites

S. A. Zygmunt, L. A. Curtiss, and L. E. Iton

Presented at the 210th Am. Chem. Soc. National Meeting and Exposition Program,
Chicago, IL, August 20-24, 1995

A Computational Study of H₂O Adsorption in H-ZSM-5

S. A. Zygmunt, M. Erhardt, L. A. Curtiss, and L. E. Iton

Presented at the Int. Zeolite Symp., Quebec, Canada, October 10-20, 1995

F. Papers Accepted for Publication

Microstructure and Phase Identification in Type 304 Stainless Steel-Zirconium Alloys

D. P. Abraham, S. M. McDeavitt, and J. Y. Park

To be published in Metall. Trans.

Determination of Uranium by Flow Injection Inductively Coupled Plasma Mass Spectrometry

J. H. Aldstadt, J. K. Kuo, L. L. Smith, and M. D. Erickson

To be published in Anal. Chim. Acta

Microwave Dissolution of Plant Tissue and the Subsequent Determination of Trace Lanthanide and Actinide Elements by Inductively Coupled Plasma-Mass Spectrometry

J. S. Alvarado, T. J. Neal, L. L. Smith, and M. D. Erickson

To be published in Anal. Chim. Acta

Radiolysis and Hydrolysis of Magnetically Assisted Chemical Separation Particles

B. A. Buchholz, L. Nuñez, and G. F. Vandegrift

To be published in Sep. Sci. Technol.

Contaminant Uranium Phases and Leaching at the Fernald Site in Ohio

E. C. Buck, N. R. Brown, and N. L. Dietz

To be published in Environ. Sci. Technol.

Hydrido(1,4,8,11,15,18,22,25-octa-*n*-pentylphthalocyaninato)-rhodium Dimers: Single-Crystal X-ray Structure and the Isomerization of the Four Isomers

M. J. Chen, L. Nuñez, J. W. Rathke, and R. D. Rogers

To be published in Organomet.

Phthalocyanines in Hydrocarbon Activation

M. J. Chen and J. W. Rathke

Book Chapter to be published in Volume 4 of *Phthalocyanines: Properties and Applications*, Eds., A. B. P. Lever and C. C. Leznoff, VCH Publishers, Inc., New York

Removal of CO₂ in Closed Loop Off-Gas Treatment Systems

M. K. Clemens, P. A. Nelson, and W. M. Swift

To be published in J. Environ. Sci. Health, Special Edition on Toxic and Hazardous Substance Control

Applications of ICP Mass Spectrometry in Environmental Radiochemistry

J. S. Crain

To be published in Spectrosc.

Electrokinetic Study of Kraft Lignin

D. Dong and A. L. Fricke

To be published in Tappi J.

Investigation of Pulping Effect on Pulp Yield and the Lignin Content of Black Liquor with a Central Composite Kraft Pulping Design

D. Dong and A. L. Fricke

To be published in Holzforschung.

Kinetics of Dissolution of Uranium Metal Foil with Alkaline Hydrogen Peroxide

D. Dong and G. F. Vandegrift

To be published in Nucl. Sci. Eng.

A Glovebox Design Checklist

A. A. Frigo

To be published in Release 2 of *Guideline for Gloveboxes*, Am. Glovebox Soc., Santa Rosa, CA

Avoidance of Suspect/Counterfeit Products

A. A. Frigo and R. B. Smith

To be published in Release 2 of *Guideline for Gloveboxes*, Am. Glovebox Soc., Santa Rosa, CA

Secondary Waste Minimization in Analytical Methods

D. W. Green, L. L. Smith, J. S. Crain, A. S. Boparai, J. T. Kiely, J. S. Yaeger, and J. B. Schilling

To be published in Am. Environ. Lab.

Sulfide Ceramics in Molten-Salt Electrolyte Batteries

T. D. Kaun, M. C. Hash, and D. R. Simon

To be published in Ceram. Trans.

Glove Protection for Extended Periods of Non-Use

R. F. Malecha and A. A. Frigo

To be published in Release 2 of *Guideline for Gloveboxes*, Am. Glovebox Soc., Santa Rosa, CA

Test Requirements for Gloveboxes

R. F. Malecha, A. A. Frigo, and J. L. Bailey

To be published in Release 2 of *Guideline for Gloveboxes*, Am. Glovebox Soc., Santa Rosa, CA

Pollution Prevention and Waste Minimization

L. Nuñez

Chapter to be published in *Industrial Waste Stream Generation, Reduction, and Treatment*, Eds., I. Tasker, L. I. Middleman, M. Lee, and L. Nuñez, INTELECOM, Pasadena, CA

Waste from the Consumer-Related Industries

L. Nuñez

Chapter to be published in *Industrial Waste Stream Generation, Reduction, and Treatment*, Eds., I. Tasker, L. I. Middleman, M. Lee, and L. Nuñez, INTELECOM, Pasadena, CA

Waste from the Hazardous Waste Clean-Up Industry

L. Nuñez

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Waste from the Meat Packing Industries

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Waste from the Metal Production Industry

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Waste from the Mining Industries

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Waste from the Petroleum Industry

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Waste from the Plating, Finishing, and Circuit Board Industries

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Eds., I. Tasker, L. I. Middleman, M. Lee, and L. Nuñez, INTELECOM, Pasadena, CA

Waste from the Textile Industry

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Chapter to be published in *Industrial Waste Stream Generation, Reduction, and Treatment*,
Eds., I. Tasker, L. I. Middleman, M. Lee, and L. Nuñez, INTELECOM, Pasadena, CA

Actinide Separation of High-Level Waste Using Solvent Extractants on Magnetic Microparticles

L. Nuñez, M. D. Kaminski, B. A. Buchholz, S. B. Aase, N. R. Brown, and G. F. Vandegrift

To be published in *Sep. Sci. Technol.*

Production of Sodalite Waste Forms by Addition of Glass

C. Pereira

To be published in *Ceram. Trans.*

Surface Enhanced Raman Spectroelectrochemical Studies of the Corrosion Films on Iron in Aqueous Carbonate Solutions

L. J. Simpson and C. A. Melendres

To be published in *J. Electrochem. Soc.*

Temperature Dependence of the Surface Enhanced Raman Spectroelectrochemistry of Iron in Aqueous Solutions

L. J. Simpson and C. A. Melendres

To be published in *J. Electrochim. Acta*

Hydrothermal Outflow Plume of the Beppu Hydrothermal System at Yufuin, Japan

N. C. Sturchio, S. Ohsawa, Y. Sano, G. B. Arehart, K. Kitaoka, and Y. Yusa

To be published in *Geothermics*

Composition and Origin of Thermal Waters in the Gulf of Suez Area, Egypt

N. C. Sturchio, M. Sultan, G. B. Arehart, Y. Sano, Y. Abo Kamar, and M. Sayed

To be published in *Appl. Geochem.*

Waste from the Medical Industries

I. Tasker and L. Nuñez

Chapter to be published in *Industrial Waste Stream Generation, Reduction, and Treatment*,
Eds., I. Tasker, L. I. Middleman, M. Lee, and L. Nuñez, INTELECOM, Pasadena, CA

The Thermal Stability of Lithium-Manganese-Oxide Spinel Phases

M. M. Thackeray, M. F. Mansuetto, D. W. Dees, and D. R. Vissers

To be published in *Mater. Res. Bull.*

Physical and Chemical Characterization of Heavy Metal Contaminated Soils in Support of Remedial Design

V. C. Tidwell, D. E. Morris, J. C. Cunnane, and S. Y. Lee

To be published in *Remed. J.*, John Wiley & Sons

Electrical Design for a Glovebox

R. L. Tollner

To be published in *Guideline for Gloveboxes*, Release 2, Am. Glovebox Soc.

A New Quality Control Test for Biological and Recombinant Products

B. Y. Zaslavsky and D. J. Chaiko

To be published in *Validation Practices for Biotechnology Products*, American Society for Testing and Materials, ASTM STP 1260, Ed., J. K. Shillenn, Philadelphia, PA

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