ANL-95/24

Chemical Technology Division

Annual Technical Report

1994

Cover Description

1. Device used in electrometallurgical treatment of spent nuclear fuel.
2. Lithium-polymer cell developed in collaborative effort involving CMT, Hydro-Quebec, and 3M Corp.
3. Testing of silver-sheathed wire prepared with high-temperature superconducting materials.
4. Evaporator technology being investigated for concentrating radioactive product and waste streams.
5. Laser photoacoustic spectroscopy used in studying actinide speciation in groundwater-relevant systems.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Argonne National Laboratory, with facilities in the states of Illinois and Idaho, is owned by the United States Government, and operated by The University of Chicago under the provisions of a contract with the Department of Energy.

Printed in the United States of America

This report has been reproduced from the best available copy.

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831
Prices available from (615) 576-8401,
FTS 626-8401

Available to the public from the
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Disclaimer

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Distribution Category:
General Energy Research (UC-400)
General, Miscellaneous, and Progress
Reports (Nuclear) (UC-500)

ANL-95/24

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, IL 60439

CHEMICAL TECHNOLOGY DIVISION

ANNUAL TECHNICAL REPORT

1994

J. J. Laidler	Division Director
K. M. Myles	Associate Division Director
D. W. Green	Associate Division Director
C. C. McPheeters	Acting Associate Division Director

June 1995

Previous reports in this series

ANL-94/15	January-December 1993
ANL-93/17	January-December 1992
ANL-92/15	January-December 1991
ANL-91/18	January-December 1990

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

for

1
2
3
4

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	1
I. ELECTROCHEMICAL TECHNOLOGY	14
A. Battery Research and Development	14
1. U.S. Advanced Battery Consortium	14
2. Bipolar Lithium/Iron Sulfide System	14
3. Lithium-Polymer Electrolyte System	16
4. Sodium/Nickel Chloride System	17
B. Analysis and Diagnostics Laboratory	21
C. Fuel Cell Research and Development	22
1. Solid Oxide Fuel Cells	22
2. Molten Carbonate Fuel Cells	28
3. Polymer Electrolyte Fuel Cell	32
4. Fuel Reformer Technology	33
5. Technical Management	36
II. FOSSIL ENERGY RESEARCH	38
A. Alkali Vapor/Aerosol in Exhaust Gases of Pressurized Fluidized-Bed Combustor	38
B. Alkali Emission in Flue Gases of Atmospheric, Circulating Fluidized-Bed Combustor	38
III. HAZARDOUS WASTE RESEARCH	40
A. Aqueous Biphasic Separation Process	40
1. Actinide Recovery from Solid Wastes	40
2. Treatment of Uranium-Contaminated Soils	41
3. Partitioning System for Waste Pretreatment	42
4. Biocatalytic Destruction of Nitrate and Nitrite	44
B. Actinide Speciation in Groundwater	45
C. Studies for Waste Isolation Pilot Plant	48
1. Radiolytic Effects	48
2. Gas Generation Rates	49
D. Chemically Bonded Phosphate Waste Forms	50

TABLE OF CONTENTS (contd)

	<u>Page</u>
E. Environmental Management Program Office	51
1. Minimum Additive Waste Stabilization Project	51
2. Hazardous Substance Research Centers	52
3. In-Situ Remediation Integrated Program	53
IV. NUCLEAR WASTE PROGRAMS	54
A. Preparation of Review Documents	54
B. Testing of High-Level Waste Glasses	54
1. Static Tests of Savannah River Glass	55
2. Drip Tests of Savannah River Glass	56
3. Testing of West Valley Glasses	58
4. Use of Analytical Electron Microscopy to Analyze Glasses and Spent Fuel	59
5. Immobilization of Plutonium Glass	60
C. Testing of Spent Fuel	60
1. Unsaturated Tests with UO ₂ Samples	60
2. Unsaturated Tests with Spent Fuel Samples	61
D. Vitrification of Low-Level Waste	63
1. Development of Low-Level Glass Waste Forms	63
2. Development and Testing of Glass-Crystal Composite Waste Forms ..	65
3. Testing of Glass Waste Forms for Low-Level Waste	66
E. Characterization of Contaminated Soils and Residues	67
V. SEPARATION SCIENCE AND TECHNOLOGY	68
A. Development of Solvent Extraction Processes	68
1. Improvements to Generic TRUEX Model	68
2. Validation of the Generic TRUEX Model	69
3. Technical Support	71
4. Flowsheet Demonstrations	72
5. Centrifugal Contactor Development	74
B. Development of Separation Technologies for Radioactive and Hazardous Wastes	74
1. Magnetically Assisted Chemical Separation	74
2. Advanced Evaporator Technology	77
3. Decontamination and Decommissioning	78
4. Closed-Loop Off-Gas System	79

TABLE OF CONTENTS (contd)

	<u>Page</u>
C. Technical Support to Argonne's Waste Management	80
1. Mixed-Waste Treatment	80
2. Upgrade for Evaporator/Concentrator	81
3. Transuranic-Waste Treatment	82
D. Production of ⁹⁹ Mo from Low-Enriched Uranium	82
1. Processing of Uranium Foil Target	83
2. Processing of U ₃ Si ₂ Target	84
VI. ELECTROMETALLURGICAL TECHNOLOGY	86
A. Process Development Studies	86
1. Development of Liquid Cadmium Cathode	86
2. Process-Monitoring Instrumentation	88
B. Tests with Engineering-Scale Electrefiner	90
1. Drawdown Operations	91
2. Production of Low Salt Deposits	92
3. Testing of Advanced Electrefiner Concepts	93
C. Electrefiner Waste Treatment Processes	94
1. Salt Extraction	95
2. Salt/Cadmium Filtration	96
3. Demonstration of Engineering-Scale Process	97
D. Development of High-Level Waste Form	97
1. Mineral Waste Form	97
2. Metal Waste Form	100
VII. ACTINIDE RECOVERY	101
A. Process Chemistry and Flowsheet Development	101
B. Laboratory-Scale Testing	103
1. Process Demonstration	103
2. Behavior of Rare Earth Fission Products	105
3. Electrolysis of Lithium Oxide	107
4. Development of Laboratory-Scale Retort	108
C. Engineering-Scale Demonstration	109
VIII. APPLIED PHYSICAL CHEMISTRY	111

TABLE OF CONTENTS (contd)

	<u>Page</u>
A. Thermophysical Property Studies of Metallic Nuclear Fuel	111
B. Development of Synchrotron Analytical Capabilities	112
C. Fusion-Related Research	115
1. Tritium Release from Ceramic Breeders	115
2. Desorption of Hydrogen from Lithium Oxide	117
3. Dissociative Hydrogen Adsorption on Lithium Oxide	120
IX. BASIC CHEMISTRY RESEARCH	123
A. Fluid Catalysis	123
1. Catalytic Chemistry in Supercritical Fluids	123
2. High-Resolution Detector for Studying Ceramic Precursor and Other Chemistry	126
3. Hydrocarbon Activation Chemistry	129
B. Materials Chemistry	131
1. Studies of High-T _c Superconducting Materials	131
2. Electrochemical and Corrosion Studies	133
3. Theoretical Studies of Materials	137
4. Enhanced Metallurgical Processes	141
C. Geochemistry	142
1. Trace Elements in Calcite	142
2. Heteroepitaxial Nucleation and Growth of Otavite on Calcite	143
X. ANALYTICAL CHEMISTRY LABORATORY	146
A. Introduction	146
B. Technical Highlights	147
1. Engineering Studies of Electrometallurgical Treatment of Spent Nuclear Fuels	147
2. Analytical Certification of Special Reference Materials	147
3. Thermal Treatment Systems for Organic Effluents	148
4. Characterization of Used HEPA Filters for Disposal	149
5. Development of "Smart" Chemical Sensors	149
6. Development of the Integrated Performance Evaluation Program	150
7. Analytical Procedures for Waste Minimization and Pollution Prevention	150
8. Gross α/β Analysis of Environmental and Mixed-Waste Samples	151
9. Microwave-Assisted Extraction of Semivolatile Organic Compounds from Soil	152

TABLE OF CONTENTS (contd)

	<u>Page</u>
10. Characterization of Products and Residues from Automobile Shredder "Fluff" Recycling	152
11. Analysis of Highly Acidic Mixed Waste	153
12. Determination of Arsenic Species in Soil Samples from the Rocky Mountain Arsenal	153
13. Stand-off Detection	154
14. Analysis of Soil Samples for Special Volatile Organics	154
15. Transition Metal Speciation in Textile Mill Wastewater	154
16. Determination of Uranium in Dissolver Solutions for Production of ⁹⁹ Mo from Low-Enrichment Uranium	155
17. Determination of Volatile Organic Compounds in Headspace for WIPP Project	155
18. Development of an Analytical Scheme to Determine Actinides in Soil	155
19. Methods for Determining Metals in Waste Oil	156
20. Support for High-Temperature Superconductor Development	156
21. Orphan Waste Disposal	157
22. Facility Closure	158
23. Wastewater Treatability Studies	158
24. Measurement of Calcium Isotope Ratios in Canine Blood Serum	159
 XI. ADDENDUM. CHEMICAL TECHNOLOGY DIVISION PUBLICATIONS -- 1994	 160

**CHEMICAL TECHNOLOGY DIVISION
ANNUAL TECHNICAL REPORT
1994**

ABSTRACT

Highlights of the Chemical Technology (CMT) Division's activities during 1994 are presented. In this period, CMT conducted research and development in the following areas: (1) electrochemical technology, including advanced batteries and fuel cells; (2) technology for fluidized-bed combustion; (3) methods for treatment of hazardous waste and mixed hazardous/radioactive waste; (4) the reaction of nuclear waste glass and spent fuel under conditions expected for an unsaturated repository; (5) processes for separating and recovering transuranic elements from waste streams, concentrating radioactive waste streams with advanced evaporator technology, and producing ^{99}Mo from low-enriched uranium for medical applications; (6) electrometallurgical treatment of the many different types of spent nuclear fuel in storage at Department of Energy sites; and (8) 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 superconducting oxides, electrified metal/solution interfaces, molecular sieve structures, and impurities in scrap copper and steel; and the geochemical processes involved in mineral/fluid interfaces and 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 use of fuel cells for transportation applications.

The support that the CMT Electrochemical Technology Program receives from the U.S. Advanced Battery Consortium (USABC) continues to grow. 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 is 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 continuing effort with SAFT America to develop a bipolar battery that will meet the long-term goals of the USABC (performance of 300 Wh/L and 600 W/L, life of >1000 cycles, cost of <\$100/kWh). This battery system has a molten salt electrolyte and operates at temperatures above 400°C. During 1994, activities in CMT included developing sealant materials with higher strength and lower cost, conducting diagnostic tests to identify cell components that limit overall performance, and upgrading test facilities to better evaluate full-size cells under simulated driving profiles.

Under a newly awarded CRADA (January 1994), CMT is working with 3M Corp. and Hydro-Quebec to develop lithium-polymer batteries for the USABC. These batteries show considerable promise for meeting the demanding performance requirements of electric vehicles and operate at low temperature (typically 60°C). They are assembled from lithium-polymer sandwiches that are less than a hundredth of an inch in thickness. The battery's flexible, multilaminate structure makes possible very high power and energy.

Work also continued on development of the Na/NiCl₂ cell. In 1992, we had significantly improved the power characteristics of the positive electrode, which had limited the performance of the Na/NiCl₂ cell. During 1994, this improved performance was demonstrated in over 1300 cycles of testing with sealed cells (4-12 Ah capacity). This substantial performance improvement was achieved by the use of additives and a modified morphology in the Ni/NiCl₂ electrode. This battery system has an exceptionally wide and safe operational temperature range, 150-400°C.

The Analysis and Diagnostics Laboratory in CMT includes a test laboratory to conduct battery evaluations under simulated application conditions. During 1993, performance and life evaluations were conducted for nickel/metal hydride, sodium/sulfur, 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.

Three advanced fuel cells are under development at CMT: the solid oxide, molten carbonate, and polymer electrolyte fuel cells. The first two systems are targeted for utility applications, and the third for transportation vehicles.

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 have identified a glass-ceramic sealant that appears to have the desired properties. Conductivity testing and long-term compatibility testing (up to 4000 h) with cell components have confirmed the promise of this composite material.

Efforts are also underway to develop materials for use in a solid oxide fuel cell that operates at lower temperatures (450-800°C). Several alternative materials that show promise for this application are being studied: metallic bond layers between pre-sintered stack components, a commercially available low-expansion metal for the interconnect material, a ceria-based electrolyte, and a bismuth aluminate electrolyte. Preliminary results are reported.

In molten carbonate fuel cells, the present NiO cathodes have dissolution/precipitation problems that limit cell lifetime under pressurized operating conditions, and we are searching 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 performance equivalent to that of the state-of-the-art NiO cathode. In other work, 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, and corrosion resistance tests were started on the Type 316 stainless-steel components used in the molten carbonate fuel cell.

Research has been continued on the polymer electrolyte fuel cell, which operates at lower temperature (<100°C) than the molten carbonate or solid oxide fuel cells. Two methods of fabricating polymer electrolyte fuel cells are being evaluated: impregnating the polymer electrolyte into the electrodes and mixing the polymer directly with the platinum catalyst used in the anode. We are comparing the performance of cells fabricated by these methods and possessing different flow channel configurations.

The low temperature fuel cells being developed for transportation applications 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 40% hydrogen.

In another effort, we are managing contracts by industrial firms developing fuel cell systems for transportation applications. The contractors include General Motors Corp., Ford Motor Co., Pentastar Electronics, Inc., Arthur D. Little, and H-Power Corp.

2. *Fossil Energy Research*

Among clean coal technologies being supported by DOE are pressurized fluidized-bed combustion/gas-turbine combined cycle (PFBC/GTCC) systems and integrated gasification combined cycle systems. The presence of alkalis (Na and K) in the exhaust from the PFBC of coal can lead to unacceptable corrosion of turbine blade materials. The Chemical Technology Division has developed an analytical activated-bauxite sorber bed (AASB) technique for the control and measurement of alkali vapors in PFBC exhaust. During the past year, CMT

researchers have designed and fabricated AASB instruments for measuring the alkalis in the flue gas of the PFBC Demonstration Plant in Kitakyushu City, Japan, and an atmospheric, circulating fluidized-bed combustor of Ahlstrom Pyropower, Inc. The alkali measurement in the PFBC Demonstration Plant is planned for 1995. The test results from the Ahlstrom combustor will be used in assessing the emissions from pressurized, circulating fluidized-bed combustion.

3. *Hazardous 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 separation processes for solid waste treatment, soil remediation, high-level liquid waste treatment, and industrial waste treatment. For the treatment of solid radioactive wastes, we are investigating the wet grinding of radioactive solids to a particle size of 1 μm , followed by aqueous biphasic extraction to maximize plutonium recovery and minimize waste volume. The biphasic system combines aqueous solutions of polymers [e.g., polyethylene glycol (PEG)] with aqueous salt solutions $[(\text{NH}_4)_2\text{SO}_4, \text{Na}_2\text{SO}_4, \text{or } \text{Na}_2\text{CO}_3]$. Promising results have been attained in test-tube-scale extraction studies using actual plutonium residues (incinerator ash and ash heels, metallurgical residues, and LECO crucibles). Also, in test-tube-scale experiments with uranium-contaminated soil, the best extraction results were obtained with PEG (molecular weight of 1500) and Na_2CO_3 aqueous salt at 35°C. We have installed a pilot-scale column to test aqueous biphasic extraction with uranium-contaminated soils. In preliminary tests, the uranium concentration in the soil was reduced from 471 mg/kg to about 78 mg/kg. Further improvements are being sought.

Aqueous biphasic systems are also being developed for the selective extraction of long-lived radionuclides (such as ^{99}Tc and ^{129}I) from alkaline liquid waste. These systems are generated by adding PEGs and polypropylene glycols (PPGs) to electrolyte solutions with high ionic strength. It was found that extraction of TcO_4^- from simulated tank waste supernatants by PPGs is rapid, and extraction selectivities are significantly improved over those obtained with PEGs. Also under investigation is the biocatalytic destruction of nitrate in mixed-waste streams by use of aqueous biphasic separation.

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, inorganic substrates, and metal cations. One study involved examining the interactions of the plutonium-nitrilotriacetic acid (NTA) complex with the *chelatorbacter* microbe, a known degrader of the NTA complexant (associated with DOE plutonium processing). Results showed that NTA degradation primarily forms CO_2 , the rate of CO_2 formation decreased with increased plutonium concentration (0, 10^{-7} , and 10^{-5} M), and the presence of plutonium lowered the survivability of the microbe. Studies are also underway to determine the effects of gamma radiation on the *halobium* microbe (being considered for use in bioremediation of DOE sites), and the speciation of Pu(IV) in the presence of phosphate species in aqueous solutions. In the latter, we found that colloidal forms of the plutonium-phosphate species predominated in aqueous solutions with pH > 4.

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 storage facility. Our investigations focused on the alpha particle degradation of WIPP-specific plastic and rubber materials in a hydrogen/carbon dioxide environment; hydrogen and carbon dioxide are gaseous products generated from microbial and corrosion processes in WIPP. We found that the predominant radiolytic products, other than hydrogen and carbon dioxide, were a wide variety of volatile organic compounds. Yields of the volatile organics were low enough that their generation will not likely be a problem in WIPP.

A project has been initiated to evaluate the suitability of phosphate inorganic binders for solidification and stabilization of mixed wastes that are not amenable to, or compatible with, thermal processes. During the past year, small samples of magnesium and zirconium phosphate waste forms containing surrogate waste materials (at loadings up to 70 wt%) were subjected to standard leaching tests. The leaching results indicated that the phosphate matrix was effective in stabilizing the hazardous metal components of the waste, even at high waste loading.

The Environmental Management Program Office in CMT is assisting DOE in maintaining a national program of applied R&D in environmental restoration and waste management. Effort in the past year focused on providing technical and management support to the Minimum Additive Waste Stabilization Program, the Hazardous Substance Research Center Program, and the In-Situ Remediation Integrated Program.

4. *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.

During the past several years, the literature regarding the corrosion characteristics of borosilicate glasses developed worldwide for high-level waste disposal has been reviewed to evaluate the state of understanding of the glass corrosion process and the effect of testing parameters [e.g., temperature, glass composition, radiation, glass surface area to leachant volume (SA/V)] on glass corrosion. The findings have been summarized in a draft document entitled *High-Level Nuclear Waste Borosilicate Glass: A Compendium of Characteristics*.

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. In one such series, long-term tests are underway with radioactive sludge-based and simulated nuclear waste glasses having three compositions (SRL 131, 165, and 200). In tests up to 980 days at SA/V ratios 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 SA/V ratio of 20,000 m⁻¹, the simulated glass leached faster than the radioactive counterpart (up to a factor

of 1000 difference within 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.

In another series, static leach tests at SA/V ratios of 10 to 20,000 m⁻¹ have been in progress for up to 1400 days using SRL glasses. The predominant effect of the SA/V ratio was that, for the high SA/V ratios (≥ 2000 m⁻¹), leachate solutions with high concentrations of dissolved glass components were generated sooner.

A series of drip tests following the Unsaturated Test Method has been in progress for 2.5 years with 200-type radioactive glass. This glass was used as-cast or was aged by reacting the glass in a water vapor environment before testing. Significant differences were observed for the two kinds of glass: the solution pH for the aged glass was higher than that for the as-cast glass (above 11 vs. about 8); leachates from the aged glass had significantly higher concentrations of cations (mainly Li, Na, and B), anions (SO₄²⁻, PO₄³⁻, and Cl⁻), and organic carbon; the plutonium release from the aged glass was several orders of magnitude greater than from the as-cast glass; and the percentage of actinides dissolved in solution was >75% for the aged glass tests and >90% for the as-cast glass tests. Tests are also in progress to assess the performance of glasses representative of the West Valley Demonstration Project and glasses containing significant amounts of plutonium (>1%).

In addition to glass studies, long-term tests with unirradiated UO₂ pellets and simulated spent fuel are in progress to determine radionuclide release rates when these materials are exposed to repository-relevant conditions. Results from drip tests with UO₂ pellets and EJ-13 well water for 2 to 9 years indicated an order of magnitude decrease in the uranium release rate compared with the initial 1- to 2-year period. This decrease is thought to result from the formation of a dense surface mat of uranyl silicate phases that have entrapped particulate material in the UO₂ pellet surface. Tests have also been ongoing for 2 years with two types of spent fuel (ATM-103 and ATM-106) under drip conditions. These results indicate that the spent fuel matrix is reacting to form more stable mineral phases, analogous to the alteration products of unirradiated UO₂. A small fraction of the actinides are being released to the leachate, where they appear as dissolved species, colloids, and precipitated materials on the test vessel walls.

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, soils, industrial spent catalysts, and incinerator residues. Vitrified waste forms which require a minimum amount of additives are being developed to lower treatment and disposal costs. 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.

5. *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, GTM improvements included better models for calculating the distribution ratios of several species (Zr, F, Cs, Na, and Ca) and the addition of 38 new species to the model for calculating speciation. The GTM was also used to better understand problems encountered by Power Reactor and Nuclear Fuel Development Corp. (PNC) of Japan in demonstration of the TRUEX process at the Tokai Works Chemical Processing Facility. In addition, the TRUEX process has been selected as the reference treatment for the high-level waste being stored at Idaho National Engineering Laboratory (INEL), and flowsheets are being designed for removing actinides from sodium-bearing waste and dissolved calcine at INEL's Idaho Chemical Processing Plant.

An effort was begun to demonstrate new flowsheets being developed by the ANL Chemistry Division for the cleanup of nuclear waste. These flowsheets are for the TRUEX-SREX process, which combines the TRUEX and SREX (strontium extraction) processes; the SREX-NEPEX process, which combines the SREX and NEPEX (neptunium-plutonium extraction) processes; and the SREX process by itself. In multistage minicontactor (2-cm rotor dia) tests, both the TRUEX-SREX and SREX-NEPEX processes exhibited major problems that had not been evident in earlier batch tests. For each process, areas were identified where further development efforts are required. However, test results did show that the SREX process works.

Magnetically assisted chemical separation (MACS) processes are being developed for removing contaminants (^{137}Cs , ^{90}Sr , transuranics) from waste solutions. The MACS process combines the selective and efficient separation afforded by chemical sorption with the high physical separation afforded by magnetic recovery of ferromagnetic beads. Studies during 1994 involved designing a fluidized-bed system for laboratory-scale testing of the MACS process. In a series of experiments with MACS particles and simulated waste solutions, the results indicated that the MACS particles were quite effective in separating Am and Pu from the waste but only marginally effective for cesium separation.

Accomplishments in our other programs to develop separation technologies for radioactive and hazardous wastes included the following. First, an evaporator/concentrator system was designed for removing the significant amount of water that will likely be added to nuclear waste solution in underground storage tanks during retrieval operations at the DOE Hanford site. Second, a method was developed for the *in situ* decontamination of equipment in defense production plants. Third, a facility is being built for testing a CMT-developed process that will prevent the direct release of toxic off-gases during incineration of hazardous and mixed radioactive wastes. In initial tests, the facility's 250,000 Btu/h (75 kW thermal) combustor was operated in an open loop to demonstrate the removal of combustion-product CO_2 in a fluidized bed of lime, and particulates were removed with hot gas candle filters.

A large effort this past year was devoted to providing support for ANL Waste Management Operations. Our duties included testing a mixed-waste treatment facility designed by CMT staff; assisting in the installation, testing, and operation of evaporators and concentrators for treating ANL waste waters; and designing a treatment facility for liquid transuranic waste.

Finally, we have renewed our effort in determining the feasibility of substituting low-enriched uranium (LEU) for the high-enriched uranium currently used in the production of ^{99}Mo for medical applications. Two LEU target materials are being studied: uranium-metal foil and uranium silicide (U_3Si_2). Because of the difficulty in dissolving irradiated U_3Si_2 , we are also focusing our efforts on the use of uranium foil targets for ^{99}Mo producers whose target processing begins with basic dissolution. The use of sodium hydroxide with hydrogen peroxide appears very promising as a means of dissolving a target in less than an hour. The foil will also eliminate the problems in later processing caused by the presence of silicate. The metal foil target, its acid dissolution, and the processing we have developed for it will be demonstrated in 1995 in Indonesia.

6. *Electrometallurgical Technology*

The CMT Division is developing an electrometallurgical treatment for spent nuclear fuels. The process uses electrorefining to isolate pure uranium and a uranium-transuranic (TRU) mixture containing some rare earth 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 mineral, the other metal), which have very low actinide contents and 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.

Development of the electrometallurgical treatment is proceeding at both laboratory and engineering scales. Laboratory experiments to develop a high-efficiency cathode for collection of TRU elements have been conducted with plutonium and other elements. In 40 electrorefining experiments with a reciprocating "pounder" cathode design, up to 60 g of heavy metal was collected per experiment. Average collection efficiency was more than 97%, except in off-design experiments where large amounts of uranium were incorporated. The composition of the electrolyte salt used in the electrorefiner is critical because this salt controls the cathode (cadmium) product composition; voltammetric techniques are thus being developed to allow monitoring of electrolyte composition with little or no delay for obtaining analytical results.

In electrometallurgical treatment 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 to the mineral waste form. 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; this reduces actinide chlorides from the electrolyte and deposits the resulting actinide metal on the cathode. Tests in an engineering-scale electrorefiner showed that uranium chloride concentrations could be reduced to 0.1 wt% without removing significant quantities of rare earth chlorides; further reduction to <0.01 wt% (99.9% uranium removal) was possible by removing approximately 13% of the rare earths along with the uranium.

The engineering-scale electrorefiner was also used to develop conditions for depositing a uranium product having low salt content (1-5 wt% vs. 10-15 wt% for the normal

deposits). These conditions will be incorporated in advanced electrorefiners having high throughput (>40 kg uranium per hour) and large batch size (>100 kg). The high-throughput electrorefiner will be particularly useful for treating large amounts of spent nuclear fuels, such as the blanket from Experimental Breeder Reactor-II and, especially, the N-reactor fuel from the Hanford site. Six tests were carried out with unirradiated N-reactor fuel to determine conditions suitable for high-throughput electrorefining, and a conceptual electrorefiner design was developed. In this design, a 3-metric-ton batch of fuel is electrorefined at about 40 kg uranium per hour in a vessel whose diameter and height are both 1.5 m.

Also during this period, experimental studies have been carried out on the use of a "pyrocontactor" (a centrifugal contactor designed for operation at 500°C) for high-speed treatment of the spent electrolyte salt, and on equipment for the pumping and filtration of salt and cadmium. Multiple-stage pyrocontactors having countercurrent flow allow complete removal of TRU actinides and nearly complete uranium removal from the salt in very short times with negligible fission product carryover. This leaves the salt poised for removal of the fission product to make a waste form having TRU contents much less than 10 ppm. The first test series with a single-stage pyrocontactor using cadmium and salt working fluids at 500°C gave smooth, repeatable operation and high efficiencies (90% at 2700 rpm). A four-stage pyrocontactor will replace the single-stage unit shortly. A centrifugal pump and filter were also developed and tested during this reporting period; methods for measuring flow were developed using this assembly, and successful filtration of salt and cadmium was demonstrated.

Mineral and metal waste forms are being developed for handling the waste streams from the electrometallurgical treatment. A new Waste Form Development Laboratory is being built for this effort. It will house engineering-scale waste removal and waste form preparation equipment in three large, negative-pressure gloveboxes. Laboratory-scale studies to date have shown that glass-bonded zeolite and sodalite are both viable candidates for the mineral waste form. Metal waste form work has focused on an alloy composed only of the stainless steel, zirconium, and noble metal fission product components intrinsic to the spent fuel. This waste form appears very attractive and has the lowest possible volume.

7. *Actinide Recovery*

A lithium-based pyrochemical process has been developed to separate the actinides from spent nuclear fuel to enhance waste management and disposal. This process is applicable to oxide fuels, as well as non-oxide fuels with appropriate head-end treatment. The lithium process was selected as the reference process from among several options. In this process the oxide spent fuel is reduced by reaction with lithium at 650°C in the presence of molten LiCl. The Li_2O formed during the reduction process is soluble in the salt. The spent salt and lithium are recycled after the Li_2O is electrochemically reduced. The oxygen is liberated as either CO_2 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 phase and introduced into an electrorefiner. The electrorefining step separates the uranium and TRU elements into two products. The uranium product may be enriched for recycle or converted to a suitable form for storage or disposal. The TRU product can be alloyed with cladding material and combined with fission products to produce a leach resistant and diversion resistant form for ultimate disposal.

The lithium process has been demonstrated at the laboratory scale using 0.5 kg of simulated fuel. The simulated fuel contained PuO_2 , NpO_2 , and AmO_2 , as well as UO_2 and selected fission products. The steps demonstrated were reduction, electrotransport of uranium, and melting of the uranium dendrites. The uranium product contained only minimal amounts of the TRUs and no detectable fission products. The TRU elements were found, as expected, in the electrolysis salt. Material balances were adequate for the elements charged to the process, and the results of the demonstration confirm the feasibility of the process. It was observed in trial reduction experiments that a much larger concentration of the rare earth elements was in solution in the reduction salt than was expected. Laboratory experiments are being conducted to measure the solubility of the rare earth oxides in $\text{LiCl-Li}_2\text{O-Li}$.

The reduction salt used in the lithium process must be recycled to minimize the process wastes. This requires removal of the Li_2O from the salt by electrowinning. Several anode materials have been evaluated for this process. Good electrowinning performance was achieved with a graphite electrode, which liberates the oxygen as CO_2 . However, the salt always contained some carbon, which would be undesirable in the recycled salt. Three inert oxygen anodes (Pt-10 wt% Rh, Fe_3O_4 , and LiFeO_2/Cu) have been evaluated. The copper in the LiFeO_2/Cu cermet was attacked during the electrochemical process, but the LiFeO_2 appeared to be unaffected. The best results were obtained with the Pt-10 wt% Rh anode; however, it reacts with the fission product tellurium to form an insulation layer on the anode. Both the Pt-Rh and Fe_3O_4 anodes are attacked by lithium and must be removed from the system when the circuit is open.

Engineering-scale tests are planned to demonstrate the feasibility of each step of the processes developed in the laboratory. The test equipment is sized to handle up to 20-kg batch sizes of simulated fuel. Gloveboxes and test equipment have been designed and fabricated, and installation and checkout are in progress. It is anticipated that this facility will be ready for experiments in early 1995.

8. *Applied Physical Chemistry*

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

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 to the study of the Fe-U-Zr system. Excess Gibbs energies in the liquid and solid phases of the Fe-U-Zr system were calculated by substituting the values of the three binary systems (Zr-U, Fe-U, and Fe-Zr) into either the Kohler equation or the Toop equation. Phase diagrams were derived for the Fe-U-Zr system for two limiting cases: (1) the compounds were assumed to have no mutual solubility, and (2) they were assumed to be completely miscible in an ideal solid solution. The two phase diagrams showed relatively little difference, except near the $\text{Fe}_2\text{U-Fe}_2\text{Zr}$ join. A few liquidus measurements in the vicinity of the $\text{Fe}_2\text{U-Fe}_2\text{Zr}$ join are planned. In related work, we have demonstrated the feasibility of examining fuel/cladding interfaces at the microscopic scale by use of synchrotron radiation sources. The compositional

and structural information obtained by such an analysis could help in understanding and predicting intermetallic compound formation, local melting, and fuel redistribution. Significant progress has also been made in designing and constructing a white-beam facility for X-ray fluorescence work.

A critical element in the development of the fusion reactor is the blanket for breeding tritium fuel. Studies are underway with the objective of determining the feasibility of using lithium-containing ceramics as breeder material. During this period, experiments were conducted to determine the tritium release characteristics from the candidate ceramic breeders and beryllium neutron multiplier used in the SIBELIUS experiment--a CMT/European collaborative effort designed to assess the compatibility of beryllium/lithium compacts in a neutron environment. The tested ceramics are Li_2ZrO_3 , Li_2O , Li_4SiO_4 , and LiAlO_2 . The test results indicated that intimate contact between beryllium and the lithium ceramics has no detrimental effects on the performance of the ceramics, chemical interactions between the ceramics and the beryllium also are negligible, and the tritium inventories for all the tested ceramics should cause no safety problems.

Lithium oxide is one of the leading candidates for use as a tritium breeding material in a fusion reactor. Tritium release is particularly facile when the purge gas (argon or helium) contains hydrogen, typically 0.1%. To gain information about the species present on the surface and their relationship to tritium desorption, we are investigating hydrogen and deuterium adsorption and desorption by using a combination of temperature programmed desorption (TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). From the shape and position of the desorption peak in the TPD spectra, information was obtained about the energetics of the desorption process. The DRIFTS study provided information on the identity and form of the species that is desorbing from the surface. We are also studying the process of hydrogen adsorption onto lithium oxide surfaces by using *ab initio* Hartree-Fock calculations and a slab model.

9. Basic Chemistry Research

Fluid Catalysis. This program uses an array of *in situ* spectroscopic and kinetic techniques to investigate the chemistry of precursor molecules that serve as raw materials for many industrial processes. Precursors of interest include those of the C_1 chemical industry, e.g., CH_4 , CO , CO_2 , and CH_3OH ; the ammonia synthesis precursors, N_2 and H_2 ; and the ceramic precursors, e.g., $(\text{CH}_3)_4\text{Si}$, $(\text{CH}_3)_3\text{B}$, and $\text{Al}_2(\text{CH}_3)_6$. Current activities include studies of (1) catalytic chemistry in supercritical fluids, (2) catalytic and ceramic precursor processes associated with the production of advanced materials, (3) catalytic processes for the selective functionalization of hydrocarbons.

Phosphine-modified cobalt hydroformylation catalysis was invented by the Shell Chemical Co. to produce agricultural chemicals, industrial solvents, and detergents from olefinic feedstocks. Our own interest in phosphine-modified cobalt catalysts stems from our recent research on the conventional oxo catalyst, which would benefit from comparable data on the phosphine-modified systems. During the past year, we have shown that carbon monoxide addition is far more important than carbon monoxide displacement of phosphine when the tributyl-

phosphine modified Shell-type catalyst is subjected to the high pressures and temperatures that are used in this important commercial process.

In recent research in the ceramic precursor area, we have invented the toroid cavity imager and the toroid cavity detector. Both devices show great promise in providing structural information for the characterization of advanced materials and for identifying and characterizing materials chemistry processes at elevated temperatures and pressures. We have developed some new 180° pulse sequences that nearly quantitatively compensate for the rf field gradient within the torus and extend its capabilities to the many types of nuclear magnetic resonance experiments that require accurate 180° pulses.

Research in the hydrocarbon activation area 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. During the past year, we reported the X-ray structure for the first hydrido metallophthalocyanine complex. The new species is a product of the reaction of CH_4 with a reactive rhodium phthalocyanine catalyst.

Materials Chemistry. The Division's materials chemistry program has continued to explore the thermodynamic properties of ceramic superconductors with high critical temperatures. Recently completed measurements using electromotive force methods have defined the temperature-oxygen pressure domains for stability of the $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{CaCu}_2\text{O}_y$ (Bi-2212) phase. Lead-doped Bi-2212 ($x = 0.4$) was found to exhibit a broader single phase range than the lead-free version ($x = 0$).

Electrochemical and corrosion research has continued to emphasize the coupling of experiment with first-principle theoretical calculations. Experimental observation has indicated that the rate of the $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ electron transfer reaction is accelerated by some types of anionic impurities. This finding has been explained by calculations which show that anions, like Cl^- , influence the reaction by controlling the internuclear distance between charge transfer centers. The integration of interfacial electrochemistry with synchrotron radiation techniques has continued to produce many important insights about corrosion processes. The oxidation states of nickel in a variety of higher valency nickel oxide phases (e.g., NiOOH , NiO_2 , Ni_3O_4) have been characterized; diffuse X-ray scattering has been used to monitor the onset of pitting corrosion on copper surfaces; and solution radiolysis effects as a function of X-ray beam intensity have been examined and elucidated in preparation for work at the Advanced Photon Source (under construction at ANL).

Theoretical studies of materials have focused on the further development of Gaussian-2 theory to improve its accuracy and to extend it to high atomic number elements. Gaussian-2 theory has been used successfully to examine the energetics of silicon clusters, the local structure around Brønsted acid sites in zeolites, and the stability of the types of carbonium ions that play a role in molecular sieve catalysis.

Two related projects involving the enhancement of established metallurgical processes are examining novel molten-salt extraction methods for (1) the removal of copper from

scrap steel and (2) the removal of lead from scrap copper and brass. In both cases, the extraction methods have produced ten-fold reductions in the concentration of the tramp element (i.e., copper or lead).

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 were performed at the National Synchrotron Light Source. In one study, the X-ray standing waves generated by dynamical Bragg diffraction were used to directly measure lattice locations of trace elements within and at the surface of a calcite single crystal that was cleaved along the (10 $\bar{1}$ 4) plane and reacted with a dilute aqueous lead solution. In another study, a new and accurate approach was demonstrated for measuring *in situ* precipitation and growth mechanisms in mineral-water systems. In this demonstration, X-ray reflectivity and diffraction were used to characterize an otavite overgrowth during its precipitation from aqueous solution onto the calcite cleavage surface.

10. *Analytical Chemistry Laboratory*

The Analytical Chemistry Laboratory (ACL) is administratively within CMT, the 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 processes for treating spent nuclear fuel; development of a Fourier transform infrared spectrometer for continuously monitoring the organic effluents of waste incinerators; characterization of used laboratory exhaust filters for disposal; development of automated methods for real-time analysis of chemical sensor data from environmental samples; development and implementation of a comprehensive program to provide DOE with information on data quality from laboratories analyzing environmental and waste samples; development of methods for reducing the secondary waste and turnaround time for analyses of environmental and mixed-waste samples; characterization of products from recycling of automobile shredder "fluff"; development of a method for analyzing highly acidic, radioactive samples; determination of arsenic species in soil samples from the Rocky Mountain Arsenal; research in support of a U.S. Army program on stand-off detection of chemical plumes; analyses of environmental samples (water, soils, sediments, filters, etc.) and waste samples for ANL and other DOE sites; development of analytical procedures that will be used to characterize the lability of transition metals in textile mill wastewater; determination of uranium in dissolver solutions for production of ^{99}Mo from low-enriched uranium; development of analytical methods in support of the Waste Isolation Pilot Plant; development of improved methods for determining actinides in contaminated soils and metal contaminants in waste oil; analyses in support of the development of high-temperature superconductors; and measurements for a study of metabolic uptake and incorporation of calcium isotope into bone.

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. To date, in-house battery R&D has focused on three advanced technologies: lithium/iron disulfide, lithium-polymer, and sodium/nickel chloride. 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 (EPRI). In 1994, CMT continued its advanced battery R&D activities under two Cooperative Research And Development Agreements (CRADAs) with the USABC, and initiated R&D activities under a new CRADA (24 months) with 3M Corp. and Hydro-Quebec. The ongoing CRADAs involve two 38-month projects. One of the projects incorporates the independent evaluation of advanced batteries in CMT's Analysis and Diagnostics Laboratory and technical support to the USABC's Technical Advisory Committee (see Sec. I.B). The other ongoing 38-month project and the new 24-month project 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.) The ongoing project is to work with SAFT America to develop bipolar Li-Al/FeS₂ batteries (Sec. I.A.2), while the new project (awarded in January 1994) is to work with 3M and Hydro-Quebec to develop lithium-polymer batteries (Sec. I.A.3).

2. Bipolar Lithium/Iron Sulfide System

Under a 38-month CRADA, CMT researchers are working with SAFT America on the development of the bipolar lithium/iron sulfide battery system. The basic design for this

system is shown in Fig. I-1.¹ It employs disk-shaped cells, assembled into a series-connected stack in which adjacent cells share a common current collector, denoted the bipolar plate. The cells employ lithium-alloy anodes, dense FeS_2 cathodes, LiCl-LiBr-KBr molten salt electrolyte,

Fig. I-1.

Exploded View of Li-Alloy/ FeS_2 Bipolar Stack

and MgO powder separators. Cells are sealed around their periphery by using a chalcogenide-based material for ceramic-to-metal seals. Final assembly is accomplished with metal-to-metal peripheral welds. Cells are operated in the temperature range of $375\text{--}450^\circ\text{C}$ to maintain the electrolyte molten. Cylindrical bipolar stacks will be housed inside thermal modules engineered to maintain acceptable operating temperature (see Fig. I-2). Vacuum multifoil thermal modules are being developed to achieve low thermal losses in lightweight, low-volume packages.

Fig. I-2. Cutaway View of Thermally Controlled Module for Bipolar Lithium/Sulfide Battery

¹ G. L. Henriksen and D. R. Vissers, "Lithium-Aluminum/Iron Sulfide Batteries," *J. Power Sources* **51**, 115-128 (1994).

During 1994, ANL continued to refine baseline cell components, conduct diagnostic tests, and upgrade test facilities. The component refinement efforts were directed toward developing metal-to-ceramic seals with higher strength and lower cost and further increasing cell performance. The diagnostic tests were used to identify cell component contributions to limitations of the overall cell performance and thereby formulate the best approaches for enhancing performance. The upgraded test facilities include capability to evaluate full-size engineering cells under simulated driving profiles, e.g., the Dynamic Stress Test (DST) and other test regimes specified by the USABC.

3. Lithium-Polymer Electrolyte System

As mentioned earlier, the lithium-polymer electrolyte battery for electric-vehicle applications is being developed under a CRADA with 3M and Hydro-Quebec. The lithium-polymer battery is a lightweight, high-energy system that can operate at low temperatures (typically 60°C). With a polymer electrolyte, the 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.

Rechargeable lithium-polymer batteries with either metallic lithium or lithium carbon as the anode use transition metal oxides as the cathode, for example, oxides of vanadium, manganese, cobalt, or nickel. 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 insertion electrodes made of transition metal oxide are, in general, not tolerant to overcharge or overdischarge. It is, therefore, critically important to 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.

Under the CRADA with 3M and Hydro-Quebec, Argonne provides technical support related to all aspects of battery development, including cell and battery testing, post-test diagnostic analysis, electrochemical modeling, and electrode evaluation and optimization.

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 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 battery 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 of this task is to precisely determine the factors affecting the electrochemical performance of cells.

Electrochemical modeling studies of lithium-polymer 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.

Materials development within the lithium-polymer battery project is focused on the synthesis and characterization of metal oxide electrodes that offer superior electrochemical behavior to state-of-the-art materials. Attention is being paid to processing conditions, chemical composition, and structure. Structural analyses of electrode materials at various states of charge and discharge are undertaken with neutron-diffraction data from ANL's Intense Pulse 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 importantly, clues about how to modify the structures to enhance their electrochemical properties.

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 the ANL and Hydro-Quebec 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.

4. Sodium/Nickel Chloride System

The objective of this research is to (1) generate the scientific and technical base needed for development of sodium/nickel chloride (Na/NiCl_2) batteries for electric-vehicle propulsion and (2) transfer the technology to industry.

Of the possible metals for the positive electrode, nickel offers the technically most promising choice. The high voltage (2.58 V at 300°C) and the high theoretical specific energy (790 Wh/kg) make a cell with a nickel-containing positive electrode especially attractive. The cell system can be represented as

The cell uses a solid β -alumina electrolyte that conducts sodium ions. Moreover, NaAlCl_4 is added to the porous Ni/NiCl_2 positive electrode to transport sodium ions from the surface of the β -alumina electrolyte to the reaction sites at the interior of the electrode. The NaAlCl_4 and sodium are molten at the operational temperature of the cell (typically, $\sim 300^\circ\text{C}$), but the NiCl_2 of the positive electrode is solid.

In the past, cell performance was limited because NiCl_2 is sparingly soluble in the chloroaluminate electrolyte and forms a poorly conducting layer on the nickel electrode during charge. This layer hinders capacity uptake during charge and limits power during discharge.² As reported earlier,^{3,4} we overcame these problems by developing a new type of Ni/NiCl_2 electrode, termed the "ANL-92 electrode." This positive electrode contains chemical additives (NaBr , NaI , and S) and has a dual-porosity morphology produced by a sintering process.

The excellent performance of the ANL-92 electrode has been verified by electrochemical measurements in engineering research cells⁵ and sealed tubular Na/NiCl_2 cells. The sealed cells (4-12 Ah capacity) were built by two industrial partners (Eagle-Picher Industries and Hughes Aircraft) according to our composition and design recommendations. Projections based on performance measurements in the research cells indicated that this system can be developed to a high-performance battery that meets the requirements of electric-vehicle propulsion.^{6,7}

In the reporting period, we have completed the performance testing of the sealed cells. The tests verified the good performance of the ANL-92 electrode and the viability of our cell designs. Furthermore, the 1300 cycles achieved by one of the sealed cells demonstrated the robustness of the Na/NiCl_2 system. In addition, the long cycle-life combined with the measured

² L. Redey and D. R. Vissers, "Investigations of Ni/NiCl_2 Electrodes in Basic Chloroaluminate Melt," Extended Abstracts, Electrochem. Soc. Meeting, October 15-20, 1989, Hollywood, FL, Vol. 89-2, p. 143 (1989).

³ L. Redey, J. Prakash, D. R. Vissers, and K. M. Myles, "Development of Na/NiCl_2 Cells," Proc. of the IEEE 32nd Power Sources Symp., Cherry Hill, NJ, June 22-28, 1992, p. 343 (1992).

⁴ J. Prakash, L. Redey, R. Skocypiec, and D. R. Vissers, "High-Performance Nickel Chloride Electrode Studies," Extended Abstracts, Electrochem. Soc. Meeting, Toronto, Canada, October 11-16, 1992, Vol. 92-2, p. 108 (1992).

⁵ L. Redey, "Characterization of Active Materials and Electrodes for Battery R&D," Proc. of 179th Electrochem. Soc. Meeting, Washington, DC, May 5-10, 1991, Vol. 91-6, p. 127 (1991).

⁶ L. Redey, "Dynamic-Performance Measurements of Battery Cells for Electric Vehicle and Other Applications," Proc. of 180th Electrochem. Soc. Meeting, Phoenix, AZ, October 13-18, 1991, Vol. 91-10, p. 38 (1991).

⁷ L. Redey, T. Rauworth, J. Prakash, and D. R. Vissers, "Electric-Vehicle Battery Performance Projections from Research Cell Measurements," Presented at 184th Electrochem. Soc. Meeting, New Orleans, LA, October 10-15, 1993.

good performance has proved that the chemical environment of the ANL-92 electrode does not pose corrosion problems with the current collectors and seal materials.

The performance-improving effects of our chemical additives were compared in two sealed cells with an "inside Ni/NiCl₂ electrode" configuration, one fabricated with and the other without additives. Figure I-3 shows Ragone plots of these cells at 300 and 360°C. In these tests, the standard dynamic load profile (DST) was used instead of constant-power discharge.⁶ The greatly improved power and energy of the cell with additives at both temperatures are due to the additives decreasing the area-specific impedance of the nickel electrode.

Fig. I-3. Ragone Diagram of Sealed Na/NiCl₂ Cells with Inside Positive Electrode at 300 and 360°C. Also shown is engineering research cell with outside positive electrode at 300°C. The symbol W* represents power at the highest power level of the Dynamic Stress Test.

Measurements in engineering research cells (unsealed) indicated that the same amount of nickel produces higher energy and power if the Ni/NiCl₂ electrode is outside the β"-alumina tube as opposed to inside. As Fig. I-3 shows, about 1.0 Wh/g Ni specific energy was measured for the outside configuration at 300°C. Moreover, almost as high a specific energy was measured for a sealed cell with the outside configuration in high-rate discharges (not shown in Fig. I-3). This cell had 31.0 g Ni in the positive electrode and produced 27.6 Wh in a 10-A discharge; this is equivalent to a specific energy of 0.89 Wh/g Ni.

In addition to the performance measurements, we completed several other experiments that provided information about electrode processes, such as the effect of iodide additive and overcharge and overdischarge.

The iodine additive was studied in a sealed cell that was equipped with a special isothermal pressure sensor. We concluded from these experiments that NaI additive increases the performance of the Ni/NiCl₂ electrode by two different mechanisms. The first mechanism is dominant at potentials lower than the potential for iodine evolution (2.8 V vs. Na). The I⁻ ions help to develop a NiCl₂ layer in an electrode with a higher capacity and lower impedance compared with an additive-free electrode. This very favorable effect is probably due to a doping mechanism, which is also affected by the different solubilities of NiCl₂ and NiI₂.⁸ The second mechanism occurs when the cell is cycled through the iodine-evolution potential range (2.8-3.1 V). The iodine evolution, however, does not produce high pressure in a sealed cell. From Fig. I-4, it is evident that only a minimal gas pressure (~10 kPa) develops even during a very severe overcharge.⁹ This experiment proves that NaI is a safe additive in sealed cells. The low pressure increase is explained by the formation of highly soluble iodine species. In turn, the high concentration enhances diffusion of the iodine species in the liquid chloroaluminate to new reaction sites and, thus, improves the kinetics of the electrode.

Fig. I-4.

Overpressure in Sealed Na/NiCl₂ Cell with NaI Additive during Overcharge, Open Circuit, and 3-h Discharge. Overcharge done with C₄/0.2 current (in amperes) to 4.4 V, where C₄ is the Ah capacity for a 4-h discharge, and 0.2 is in hours.

From the performance measurements with engineering research cells and sealed cells and other investigations as well, we have concluded that the Na/NiCl₂ cell system has numerous, previously overlooked, advantages. First, this system has an exceptionally wide and safe operational temperature range, 150-400°C, which is the most advantageous temperature range for dynamic high-power applications such as an electric car. No other battery system has such

⁸ L. Redey, C. Rose, and R. Lowrey, "Solubility of NiCl₂ in Sodium-Chloroaluminate Melts," Extended Abstracts, Electrochem. Soc. Meeting, Toronto, Canada, October 11-16, 1992, Vol. 92-2, p. 116 (1992).

⁹ L. Redey, J. Prakash, A. Scheglov, D. R. Vissers, and J. DeGruson, "Performance Enhancement of Na/NiCl₂ Cells by Iodine," Extended Abstracts, Electrochem. Soc. Meeting, Miami Beach, FL, October 9-13, 1994, pp. 218-219 (1994).

a temperature range. This 250°C-wide temperature range makes the battery construction simple and inexpensive because the need for peripheral components, such as a narrow-range temperature control, is minimized. Second, in this battery, three times more energy per weight of nickel can be stored than in the other nickel battery systems under development. The Ni/Cd, Ni/metal hydride, Ni/H₂, Ni/Zn, Ni/Fe cells all require about 6.3 kg nickel per kWh; in contrast, the Na/NiCl₂ cell requires less than 2 kg nickel per kWh. (These numbers include weight of nickel in the electrodes, current collector, and other cell hardware.) This advantage arises from the high cell voltage (2.6 V) and the excellent performance of the new electrode. Third, the Na/NiCl₂ cell can be hermetically sealed. Because of the sealed construction and easy recycling of used batteries, this system is environmentally safe. Fourth, it has a great degree of overcharge or overdischarge tolerance and long cycle life. The cells fail by short circuit and produce a very low resistance path for the battery current. Finally, mass-produced Na/NiCl₂ batteries would be relatively inexpensive because their manufacturing requires only abundant and cheap raw materials, such as NaCl, AlCl₃, Al₂O₃, and a form of already mass-produced nickel.

B. *Analysis and Diagnostics Laboratory*

The Analysis and Diagnostics Laboratory was established in CMT 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 the DOE, EPRI, USABC, 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.

Under a CRADA with the USABC initiated in 1992, performance and life evaluations continue to be performed on two electric-vehicle battery systems: (1) nickel/metal hydride (Ni/MH) cells and multi-cell modules from Ovonic Battery Co., manufactured under a contract with the USABC, and (2) a Na/S multi-cell module from Silent Power Ltd. (England), fabricated as part of the DOE ETX-II Program. In early 1994, ANL activities under this CRADA were expanded to include evaluation of a full-size electric-vehicle battery from Ovonic Battery. Testing of the Ovonic deliverables is continuing. Evaluation of the Silent Power deliverables has been completed. The results of these tests will be released by the USABC at a later date.

Two advanced lead-acid battery systems are being evaluated by ANL for EPRI. One battery, manufactured by GNB Industrial Battery Co., is a lead-acid design for deep discharge applications. The second technology is a quasi-bipolar, lead-acid design from Electrosorce, Inc. These evaluations are continuing, and the performance and life data on both systems will be available in mid-1995.

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 CMT and Ovonic.

Besides battery testing and analysis, we support 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. The objectives of the Tiger Team are to discuss and resolve issues regarding testing terminology, methodology, and reporting. We are also participating in various battery readiness review meetings for the USABC. These meetings are conducted prior to the initiation of unique battery tests to verify proper test planning, instrumentation, and data acquisition.

In 1995, performance and life evaluations, as well as post-test analyses, will be continued on cells, modules, and batteries for the USABC and EPRI. We will also continue to support the USABC by having representatives on the Technical Advisory Committee and its various working groups.

C. *Fuel Cell Research and Development*

The CMT Division continues to conduct R&D on the solid oxide fuel cell (SOFC) and the molten carbonate fuel cell (MCFC), which are targeted for utility applications, and on the polymer electrolyte fuel cell (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. In the low-temperature fuel cell (PEFC), only hydrogen can be used directly, and hydrocarbons need to be reformed in separate reforming reactors. Even in the high-temperature fuel cells (SOFC and MCFC), at least part of the reforming must be done external to the fuel cell.

1. Solid Oxide Fuel Cells

The present SOFC design 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 cell operating temperature is 800-1000°C. Recent research in SOFCs has focused on developing materials for lower temperature operation (400-800°C) and on improving the stability of the materials for high-temperature operation (1000°C). Currently, our SOFC program includes research on alternative materials and fabrication methods for electronically insulating sealants, metal interconnects and bond layers, and electrolyte and electrode materials.

a. Sealants

The objective of this effort is to develop insulating materials for sealing the edges and gas-supply and exhaust manifolds in solid oxide fuel cells and stacks. These sealants must be compatible with the fuel cell materials under the aggressive operating conditions in the fuel cell. In addition to forming a good bond, the sealants must have a coefficient of thermal expansion that closely matches coefficients of the SOFC and manifold materials. Since

all of these materials do not have identical coefficients of thermal expansion, the sealant must possess a degree of compliance to tolerate the thermal expansion mismatches without unduly stressing the fuel cell stack or manifold components.

Our previous work¹⁰ on a glass-ceramic sealant for high-temperature application has demonstrated that it has excellent characteristics for bonding to the SOFC components, has a thermal expansion coefficient properly matched to the SOFC materials, and has a low permeation constant for oxygen diffusion (making it a good separator for the fuel and oxidant gases). In addition, the sealant was found to have the correct viscosity range to allow some thermal expansion mismatches in the SOFC stack.

We have continued the development of this family of sealing materials. Additional characterization of the glass-ceramic sealant included conductivity testing and some long-term compatibility testing. Four-point conductivity measurements were taken on bars of the sealant over a range of temperatures and oxygen partial pressures. At a given temperature, the conductivity was found to be independent of oxygen partial pressure (from 10^{-19} to 0.21 atm), indicating no electronic contribution to the conductivity. The purely ionic conductivity was quite low (ranging from 3×10^{-5} S/cm at 800°C to 2×10^{-3} S/cm at 1000°C) so that the sealant should be suitable for insulating applications such as the manifold seal.

Long-term compatibility testing (up to 400 h) revealed limited interactions with some of the SOFC components. In an effort to minimize the thicknesses of the reaction layers, the sealant composition was modified to stabilize the reacting components. Modified versions of the sealant were successful in reducing interaction zones, for example, from 30 to 6 μm at the electrolyte interface and from 10 to 3 μm at the anode interface.

Modified compositions which were successful in improving the long-term chemical stability of the glass-ceramic sealant were then characterized for thermomechanical behavior. The objective was to determine if the altered compositions had changed the thermal expansion behavior or the temperature dependence of the viscosity. We found that modified versions of the glass-ceramic material had basically unchanged thermal expansion coefficients. Viscosities, however, were changed for compositions that significantly altered the volume fraction of crystalline material. Compositions that were optimized for chemical and mechanical behavior were used for further study, including long-term testing in a reducing atmosphere. This work is in progress.

In addition, progress was made on the scaleup of sealant production, and some commercial testing was performed. Sem-Com, Inc. (Toledo, OH), was contracted to prepare a large quantity of the sealant material. Half-scale equipment was used to prepare 9 kg of glass-ceramic material. This material has been sent to fuel cell manufacturers for evaluation in their stacking applications. Preliminary results have been favorable, with mechanical properties greatly improved over previous glass sealants.

¹⁰ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 24-26 (1994).

b. Bond Layer and Interconnect

In the planar SOFC design, the assembly of separately fired layers simplifies cell fabrication and avoids the restraints of co-sintering. However, several other design issues need to be addressed if improved stacks operating at temperatures below 1000°C are to be fabricated. We are investigating fabrication techniques for joining separately fired bond layers and a candidate metal interconnect (an alternative to the strontium-doped lanthanum chromite) that shows promise for the lower temperature operation.

Ceramic powders generally will give poor bond layers between pre-sintered stack components, because the shrinkage which takes place only in the bond layer during sintering will cause cracks. In this research, metals are being used in the bond-layer fabrication process to improve the conductivity, and the use of dense foils is being explored to reduce bond layer shrinkage. Such a design also gives the opportunity to apply the sealant as a thin, dense, fiber-like gasket during the initial assembly of the stack. This would eliminate the earlier problems of slurry application and high porosity after firing.

Research has been conducted on silver-containing alloy systems, including silver-based braze pastes and foils. Our experiments showed that a metallic bond layer has distinct advantages over previously used ceramic slurries. Bonds were made between anode/electrolyte/cathode trilayers and both ceramic and metal interconnect materials. No measurable electronic resistance could be attributed to these bond layers, and their mechanical properties were excellent (the bonds tended to hold in situations where ceramic bond layers had previously fractured). Metallic bonds were also tested in combination with edge seals formed from compression-bonded glass fibers (materials developed in our sealant development program) and again had excellent electrical and mechanical properties. Work is also underway on evaluating bonding conditions between 800 and 1000°C in varied atmospheres.

Metals can be used for the interconnect in intermediate-temperature (800°C) fuel cells, but their oxidation behavior and high thermal expansion both require attention. We have identified a commercially available low-expansion metal which may be suitable for the SOFC application. The candidate metal has a listed corrosion rate that is slightly greater than would be required if cells are to be operated for sufficient lifetimes at 800°C. However, the corrosion resistance requirements for metal interconnects depend on the location within the fuel cell; requirements will generally be strictest on the air side of the fuel cell and for electrical contact areas. In this research, we determined the behavior of our candidate metal for the conditions of each functional area in an intermediate-temperature SOFC.

The candidate metal appears to have adequately matched thermal expansion to survive thermal cycling with stack components. The measured thermal expansion coefficient of $10.4 \times 10^{-6}/^{\circ}\text{C}$ is slightly lower than the values for the zirconia electrolyte and electrode materials. Bonds formed with platinum paste and with glass sealants survived thermal cycling to 800°C without fracture. Other tested metals, which had expansions of about $17 \times 10^{-6}/^{\circ}\text{C}$, were found to de-bond when subjected to similar tests. After these tests, no measurable electrical resistance could be attributed to the formation of a corrosion layer on the platinized surfaces. Thus, the formation of an oxide layer may not be a problem in areas where a metallic bond layer

has been applied. Oxide formation on other surfaces of the interconnect (such as within the flow channels) should not affect the electrical performance of the stack.

The other critical area of the interconnect surface where corrosion may be a problem is the sealing area around the edges of the stack. Glass sealants were found to react to some extent with corrosion products of the candidate interconnect material. When thin (200 μm diameter) fibers of glass were used as the seal material, the reaction tended to prevent good compression bonds from forming; in some cases complete de-bonding of the layers occurred. However, thicker glass fibers yielded better seals. The improvement was probably the result of better compressibility of the greater volume of glass and a greater extent of spreading over the metal surface, which distributed any stresses more evenly.

While it appears that both critical areas of the interconnect surface may be adequately protected from corrosion by the materials to which they are joined, work is also being conducted on possible coating methods for corrosion resistance, which would be applied before the stack is assembled. Initial experiments are being conducted with both sol-gel film formation and electrophoretic deposition to produce coatings of zirconia or yttria.

c. Ceria-Based Electrolyte

The purpose of this effort is to develop technology for the operation of SOFCs at 400 to 500°C. At these low temperatures, the stack sealing problem would be eased, interfacial stabilities would be improved, less expensive materials could be used for some components, and the technology would be much more attractive for transportation applications. Two main obstacles to such a reduction in the operating temperature are the electrolyte resistance and the electrode overpotentials, both of which would be too large if the conventional materials were used at these temperatures. We are investigating a ceria-gadolinia electrolyte with high conductivity and seeking to improve the electrode material composition and morphology to increase the overpotentials to a reasonable level. Effort this past year focused on the ceria-based electrolyte.

The low-temperature concept that we are investigating is for the planar design, although it could be used in any of the other configurations such as the present tubular design. The design also differs from the high-temperature version in terms of fuel composition. Our calculations indicate that the ceria-based electrolyte will be an ionic conductor at 450°C and an oxygen partial pressure of 2.7×10^{-30} atm. Increasing the temperature or decreasing the oxygen partial pressure will induce some electronic conductivity in the ceria-based electrolyte. Based on the temperature and oxygen pressure limitations, a suitable fuel is methanol, which can be used without external reforming to hydrogen.

Both the sintering temperature and the conductivity of ceria-based materials depend on the starting powders used. Commercially available powders require sintering temperatures as high as 1800°C and can give materials with high resistivities (450 $\Omega\text{-cm}$ at 450°C). The high sintering temperature is also a drawback for thin-electrolyte technology, which usually requires sintering of the electrolyte while in contact with an electrode support material. Most electrode materials could not tolerate such temperatures.

We carried out a conductivity study of ceria-based materials prepared by different methods. Calcium, gadolinium, samarium, praseodymium, and barium were used as doping agents. Samples were prepared for each of these dopants by mixing the component oxides and sintering at 1500°C for 6 h. In addition, several of these compositions were prepared by the Pechini method and the glycine-nitrate process. The gadolinia- and samaria-doped samples exhibited the highest conductivities, and the highest conductivity occurred for gadolinia-doped ceria prepared by the glycine-nitrate process. The ionic transference number (fraction of the total conductivity due to ionic transport) was also found to be a function of the preparation method and to increase with increasing sample density and conductivity in all cases.

Work is also being conducted on thin electrolyte fabrication by tape casting and on electrode application methods to these tapes. Electrodes applied by screen printing, slurry coating, and spraying are being tested for electrochemical performance.

d. Bismuth Aluminate Electrolyte

Bismuth aluminate is another promising material for the electrolyte in a low-temperature SOFC. Among solid oxide materials, the δ - Bi_2O_3 phase exhibits the highest reported oxygen ion conductivity at temperatures from 730 to 825°C.¹¹⁻¹³ A number of Bi_2O_3 -containing phases also have exceptionally high ionic conductivities above 500°C. However, these materials exhibit poor stability at very low oxygen partial pressures, precluding them for use as the electrolyte in a solid oxide fuel cell. Combining bismuth oxide with a thermodynamically very stable oxide, such as alumina, is being explored as a method to obtain a stable electrolyte material that would also be a good oxygen ion conductor.

Polycrystalline samples of the orthorhombic compound $\text{Bi}_2\text{Al}_4\text{O}_9$ were produced by the glycine-nitrate combustion method, followed by leaching of a secondary bismuth-rich phase in dilute acetic acid. The samples were more stable than δ - Bi_2O_3 with respect to oxygen partial pressure and temperature. The electrical properties of these polycrystalline $\text{Bi}_2\text{Al}_4\text{O}_9$ samples are being investigated to determine whether or not the material would be suitable for use as an SOFC electrolyte.

Figures I-5 and -6 show the dependence of lattice conductivity on temperature and oxygen partial pressure. Preliminary analysis of the curves in Fig. I-5 yielded activation energies for lattice conductivity ranging from 1.1 eV at low temperature and high oxygen partial pressure to 2.1 eV at high temperature and low oxygen partial pressure. At low temperature (600°C), the conductivity remains nearly constant with respect to oxygen partial pressure (see Fig. I-6). At higher temperatures, the conductivity increases with decreasing oxygen partial pressure. These results indicate that the candidate material is an ionic conductor at low temperature and high oxygen partial pressure, while it is an n-type electronic conductor at high temperature and low oxygen partial pressure, with mixed conduction in intermediate conditions.

¹¹ A. R. Von Hippel, Ed., *Dielectric Materials and Applications*, John Wiley & Sons, New York (1954).

¹² T. Esaka, T. Mangahara, and H. Iwahara, *Solid State Ionics* 36, 129 (1989).

¹³ T. Takahashi, T. Esaka, and H. Iwahara, *J. Appl. Electrochem.* 7, 303 (1977).

Fig. I-5. Arrhenius Plots of Lattice Conductivity for $\text{Bi}_2\text{Al}_4\text{O}_9$ at Three Oxygen Partial Pressures and Temperatures of 600-800°C

As shown in Fig. I-6, lattice conductivities range from 7×10^{-8} S/cm at 600°C to 9×10^{-6} S/cm at 800°C. These values are much too low for use in solid oxide fuel cells (target of ~ 0.05 S/cm at 600-800°C). The low values are probably due to the low charge carrier concentration in these undoped materials. However, since the activation energies for conduction are similar to those of zirconia (the present electrolyte material), suitable conductivities may be obtained for optimally doped materials. Impurity content analysis and microscopic characterization are planned for this material. Doping optimization studies will then be performed on the fully characterized material.

Fig. I-6. Dependence of Lattice Conductivity of $\text{Bi}_2\text{Al}_4\text{O}_9$ on Isothermal Oxygen Pressure and Temperature

2. Molten Carbonate Fuel Cells

The present molten carbonate fuel cell (MCFC) comprises a porous (chromium-stabilized) nickel anode, a porous nickel oxide cathode, a liquid electrolyte of lithium and potassium carbonates retained by a ceramic matrix of LiAlO_2 , and appropriate metal separators. The operating temperature is 650°C . Our MCFC program is engaged in efforts to (1) develop alternative cathodes that will extend the lifetime of pressurized fuel cells, (2) develop a simpler design based on a multiply manifolded concept that has the potential for significantly increased power density, and (3) improve the corrosion resistance for the Type 316 stainless-steel components employed in the fuel cell, such as the cell interconnects, aluminized seals, and gas-distribution channels. The goals of these efforts are extended life, improved 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 of nickel to the Ni-Cr anode, particularly in pressurized MCFCs. The transport mechanism is dissolution of NiO and migration of Ni^{2+} to the anode through the molten alkali-carbonate electrolyte (e.g., 70 mol% Li_2CO_3 -30 mol% K_2CO_3), followed by its deposition there as metallic nickel.¹⁴ The NiO solubility and, consequently, the Ni^{2+} transport rate increases with increasing CO_2 pressure in the cathode gas. We have been developing lithium ferrate (LiFeO_2) and lithium cobaltate (LiCoO_2) cathodes, which exhibit lower rates of transport than the NiO cathode. They are, therefore, expected to have a longer life in MCFCs, especially in cells operated at high pressures (3-10 atm). These two new cathodes originated in early work at ANL.¹⁵ The LiCoO_2 cathode is also being developed in the Netherlands.¹⁶

Double doping was found to decrease the resistivity of LiFeO_2 from 300 to $0.3\ \Omega\cdot\text{cm}$ at 650°C . This decreased resistivity produced a LiFeO_2 cathode capable of high power density in MCFCs. Both the doubly doped LiFeO_2 cathode and the LiCoO_2 cathode (which has a resistivity of $1\ \Omega\cdot\text{cm}$ at 650°C) now exhibit performance equivalent to that of the lithiated NiO cathode, as shown in Fig. I-7. In 1995, the cathode studies will focus on determination of the relative lifetimes of the NiO, LiCoO_2 , and LiFeO_2 cathodes.

¹⁴ W. M. Vogel, L. J. Bregoli, H. R. Kung, and S. W. Smith, "Stability of NiO Cathodes in Molten Carbonate Fuel Cells," Proc. of 166th Electrochem. Soc. Meeting, Vol. 84-12, New Orleans, LA, October 7-12, 1984, pp. 443-451 (1984).

¹⁵ 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).

¹⁶ L. Plomp, E. F. Sitters, J. B. J. Veldhuis, R. C. Makkus, and S. B. van der Molen, "Performance and Dissolution of Molten Carbonate Fuel Cell Cathodes," Proc. of Third Int. Symp. on Carbonate Fuel Cell Technology, 183rd Electrochem. Soc. Meeting, Honolulu, HI, May 16-21, 1993, Vol. 93-3, pp. 171-185 (1993).

Fig. I-7. Potential vs. Current Density of Doubly Doped LiFeO₂ and LiCoO₂ in Air-CO₂ Cathode Gas at 1 atm. (Performance range for NiO cathode shown for comparison.)

b. Multiply Manifoldd Fuel Cells

The previous annual report¹⁷ described the initial studies of a multiply manifolded MCFC concept.¹⁸ This new 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, a two-dimensional model was developed that relied on first principles and employed overpotential relationships reported by Wilemski et al.¹⁹ The model permitted a detailed calculation of MCFC properties for a wide variety of flow configurations. Recently, the model has been applied to optimizing the multiply manifolded MCFC and to increasing its power density.

For example, a modeling study was conducted in which pressure drops in the anode and cathode gas, anode and cathode utilizations, and areas of the gas inlet and outlet manifolds were held constant as the number of inlet and outlet manifolds in the MCFC was increased. This study showed that the multiply manifolded MCFC would significantly reduce the stack height and cell temperature gradients. These factors were decreased by 37% and 48%, respectively, when a four-by-four array of 625 cm² cells was substituted for each 1 m² cell in the conventional MCFC stack. This study also showed that arrays much larger than a four-by-four

¹⁷ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 30-31 (1994).

¹⁸ G. B. Kirby Meacham, "Multiple Manifold Fuel Cell," U.S. Patent No. 5,268,241 (December 7, 1993).

¹⁹ 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).

array of 625 cm² cells (e.g., a ten-by-ten array of 100 cm² cells) would provide little additional benefit in reducing stack height and cell temperature gradients.

Another modeling study compared the performance of multiply manifolded MCFCs having four different types of flow (corner, cross, co-flow, and counter) of the anode and cathode gases in 25 x 25 cm fuel cells employing 70% air and 30% carbon dioxide at 1 atm as their cathode gas. The four types of flow are depicted in Fig. I-8. Table I-1 shows some results from these calculations. For the same average temperature, the current density and power were, respectively, about 50% and 20% higher for co-flow than for counter flow, which yielded the lowest current and power of the four types of flow (counter flow is being employed by commercial developers). Both corner flow and cross flow yielded intermediate levels of current and power. This modeling study is being used to guide our development of MCFCs with high power density.

Fig. I-8. Types of Flow Modeled for Multiply Manifolded Design of Molten Carbonate Fuel Cell

Flow visualization experiments were employed to confirm and extend the modeling studies. In these experiments, ammonia-saturated air was injected at selected points near the MCFC gas inlet of a plastic mock-up (25 x 25 cm) of the multiply manifolded MCFC, and the gas flow was visualized on an ammonia-sensitive paper that had been placed in the gas flow channels. The flow pattern depended on the length-to-width ratio of the manifolding and the design of the gas flow channels. These flow visualization studies, in conjunction with computer modeling, showed that the corner-flow characteristics of the multiply manifolded MCFC could be converted to counter, cross, or co-flow as desired by suitable modification of the gas flow channels. Thus, the multiply manifolded MCFC provides a high degree of design flexibility. As noted previously, it also yields a higher power density and lower temperature gradients than other designs.

Testing has been completed with six corner-flow MCFCs (10 x 10 cm) having flat metal current collectors employing dimpled Ni-Cr anodes and NiO cathodes to form

Table I-1. Calculated Results for Effects of Different Types of Flow in Anode and Cathode Gases of Molten Carbonate Fuel Cell

Flow Type	Temp., °C	Potential, V	Current Density, A/m ²	Specific Power, W/m ²
Counter	637	0.880	798	702
Corner	637	0.850	1016	864
Cross	637	0.852	1037	883
Co-flow	637	0.832	1193	992
Counter	673	0.709	2819	1998
Corner	673	0.643	3199	2057
Cross	673	0.643	3168	2037
Co-flow	673	0.555	4294	2387

the gas flow channels. The performance has been as good as that of previous MCFCs having conventional designs, which employed expensive corrugated metal parts to form the gas flow channels and current collectors. Thus, many of the concepts in the original patent,¹⁸ including a simpler cell design having a significantly lower cost than conventional designs, have now been demonstrated. Larger cells (625 cm²) incorporating co-flow of the anode and cathode gases are now being fabricated to confirm the high power density predicted by the modeling studies.

The multiply-manifolded MCFC design has yet to be assessed in our cell tests of LiFeO₂ and LiCoO₂ cathodes, but we have already demonstrated high power density in an MCFC having a conventional design and employing the doubly doped LiFeO₂ cathode. This small MCFC (5 x 5 cm) was operated for about 1200 h at a current density of 3200 A/m², which is twice the current density usually employed in MCFCs. The cathode gas simulated operation with an air-carbon dioxide mixture at about 5 atm. The cell voltage, initially 0.72 V, declined to 0.64 V toward the end of the test because of increased resistance. The increased resistance, probably associated with corrosion of the Type 316 stainless-steel current collectors of the MCFC, appears to be the main impediment to extended operation at high current density. Various solutions to this problem are being investigated (Sec. I.C.2.c).

c. Pitting Corrosion of Type 316 Stainless-Steel Components

Pitting corrosion affects nearly all metals, including aluminum and its alloys. Its occurrence in MCFCs has not been previously investigated. The stainless-steel components of the MCFC include the cell interconnects, the gas-distribution channels, and the aluminized wet seals. Of particular interest in this study is pitting corrosion of the aluminized Type 316 stainless steel in the wet-seal areas of the MCFC. These wet seals, which are formed between aluminized Type 316 stainless-steel surfaces and the electrolyte, are used at the periphery of the MCFC and around the gas manifolds that deliver fuel and oxidant to the MCFC

anode and cathode, respectively. Their purpose is to contain the anode and cathode gases within the MCFC.

The corrosion of Type 316 stainless steel is known to be most severe on the anode side of the MCFC. It is particularly severe in areas exposed to exhaust anode gas (CO_2 with a high concentration of H_2O and a low concentration of H_2). To minimize this corrosion, the Type 316 stainless-steel current collector is protected by nickel plating. In addition, the Type 316 stainless steel around the seal areas at the MCFC periphery and around the gas manifolds within the MCFC is protected by some form of aluminizing process that can provide protection for at least 10,000 h of operation.

Using potentiostatic and static immersion techniques, we have found severe pitting corrosion of Type 316 stainless steel exposed to a combination of exhaust anode gas and molten $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ electrolyte. In the potentiostatic measurements, severe pitting corrosion was found at potentials ranging from -1000 to -550 mV (vs. $\text{O}_2\text{-CO}_2$ reference electrode). The pitting corrosion was detected by removing the overlying duplex corrosion layer and examining the steel substrate. It was most severe in the gas-electrolyte-steel interface, but was also seen in the electrolyte-steel interface at more cathodic potentials, above -750 mV (vs. an $\text{O}_2\text{-CO}_2$ reference electrode). Aluminized Type 316 stainless-steel coupons have been received from a commercial supplier; these coupons will be annealed and will then be subjected to potentiostatic- and static-immersion corrosion tests to determine their pitting-potential ranges in molten carbonate electrolytes. This study of the pitting corrosion characteristics of the Type 316 stainless steel is expected to lead to an increased MCFC life.

3. Polymer Electrolyte Fuel Cell

The goal of this program is to advance the technology of power systems based on PEFCs. As part of this program we are evaluating the performance of membrane/electrode assemblies (MEAs) fabricated by different techniques and operated under varying conditions. A polymer electrolyte fuel cell typically consists of a carbon-cloth gas diffusion anode with carbon-supported platinum catalyst for the oxidation of the hydrogen fuel, an identical cathode for reduction of oxygen, and a polymer membrane electrolyte for transport of hydrogen ions from the anode to the cathode. The polymer electrolyte or "ionomer" is impregnated into the electrodes (impregnation technique) or mixed directly with the platinum catalyst during fabrication (ink technique) to extend the area where reactant, catalyst, and electrolyte come together. Oxygen and hydrogen gas are supplied to the cathode and anode, respectively, through flow channels machined into graphite block supports. During this report period, the performance of MEAs fabricated by the impregnation and ink techniques and with different flow channel configurations was compared.

The performance of MEAs fabricated by the impregnation technique was tested for serpentine and waffle gas flow channels. The performance is illustrated in Fig. I-9, which shows the measured cell voltage as a function of current drawn from the fuel cell (polarization

Fig. I-9. Polarization Curves of Polymer Electrolyte Fuel Cells Fabricated by Impregnation Technique with Different Configurations of Gas Flow Channels. Literature values from Ref. 20.

curves). Also shown for comparison is a polarization curve taken from the literature²⁰ for an MEA fabricated by the same technique and tested with serpentine gas flow. These polarization curves show that, at current densities above 0.1 A/cm², the serpentine gas flow yields higher cell voltages than the waffle gas flow. The curves also show that the former slightly exceeds the performance reported in the literature.²⁰

Figure I-10 compares the polarization curves for MEAs fabricated by the impregnation and ink techniques. The polarization curves for these two MEAs differ only in the current density region above 1.3 A/cm², where the transfer of hydrogen and oxygen to the catalyst sites limits cell performance. The lower cell voltage in this region indicates that the ink technique allows somewhat better access of reactants to catalyst sites. Efforts are underway to develop a procedure which incorporates the best features of these fabrication techniques with the goal of optimizing PEFC performance and reducing the overall cost.

4. Fuel Reformer Technology

The objective of this work is to develop the catalyzed partial-oxidation reforming process for the production of hydrogen from alcohols for low-temperature fuel cells being developed for the transportation application, such as the PEFC and the PAFC. Fuel processors in transportation applications need to be simple and compact and to possess rapid startup and load-following capabilities.

²⁰ E. A. Ticianelli, C. R. Derouin, A. Redondo, and B. Srinivasan, J. Electrochem. Soc. **135**, 2209-2214 (1988).

Fig. I-10. Polarization Curves of Polymer Electrolyte Fuel Cells Fabricated by Impregnation and Ink Techniques

The partial oxidation of methanol takes place according to the following reaction (unbalanced),

The carbon monoxide is subsequently reacted with water, in a water-gas shift reactor, to produce additional hydrogen,

The amount of oxygen introduced per mole of methanol (oxygen-to-methanol molar ratio) is an important variable for this process since it determines the distribution between CO and CO₂ produced by Eq. 1, as well as the thermal effects of the reaction. For example, at an oxygen-to-methanol ratio of 0.5, all the carbon in the methanol is converted to CO₂, and the reaction releases 155 kJ of heat. On the other hand, at an oxygen-to-methanol ratio of 0.25, empirically, the product contains equal amounts of CO and CO₂, and the reaction is only mildly exothermic, with 13 kJ of heat release per mole of methanol. Reducing the oxygen-to-methanol ratio also reduces the nitrogen concentration in the reformat and yields a higher hydrogen concentration.

The partial oxidation reformer can meet the requirements of transportation fuel cells because it is easy to start up and permits direct liquid feed and thereby eliminates the need for a separate vaporizer. The process does not require any indirect heat exchange and, therefore, can be designed as a simple adiabatic reactor, which can be compact and lightweight. Such a reactor is dynamically responsive to load changes.

A bench-top [10 kW(e)] methanol reformer based on partial oxidation has been built and is being tested. In this reformer, liquid methanol is sprayed in as a fine mist at the top

and is mixed in and carried down with oxidation air. The mixture first passes through an electrically heated igniter coil. The igniter generates sufficient heat to vaporize some methanol and raise the mixture temperature so that the reaction can continue in the catalyst section that follows. The catalyst is copper zinc oxide (in the oxidized form) supported on a ceramic honeycomb. The product gas is analyzed by on-line analyzers for H_2 , CO , and CO_2 , as well as by a gas chromatograph for these and other chemical species.

Testing of the reformer has shown that the reactor starts up rapidly. Figure I-11 shows a typical startup, with curves for temperature (T_2 , measured below the igniter section), as well as concentrations of carbon dioxide and hydrogen. The temperature increased rapidly and reached 400°C in less than a minute after start of methanol injection. The first trace of hydrogen was detected 23 s after the methanol flow was started, and increased to over 15% within 1 min.

Fig. I-11. Reactor Temperature and Product Gas Composition during Startup

Figure I-12 shows the product distributions obtained during steady-state operations, as a function of the fuel processing rate. The data indicate no significant effect of the methanol feed rate on the product distribution. The reactor produced a gas stream containing 36-40% hydrogen, 16-18% carbon monoxide, and 7-9% carbon dioxide (on a dry basis). The methane content in the product gas (not shown in the figure) was less than 0.5%. This measured composition corresponds to 51-54% hydrogen obtainable after the water-gas shift conversion.

These tests have demonstrated that the partial-oxidation reformer can provide rapid startup and a reformat containing over 40% hydrogen at the reformer exit. A water-gas shift converter is being installed downstream of the reformer to verify that the final reformat stream will indeed contain the expected 51-54% hydrogen. Testing of the reformer for responses during transient operations is planned.

Fig. I-12. Product Gas Distributions as Function of Methanol Feed Rate

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 and involves preparing work statements, evaluating proposals, and conducting progress reviews. Major ongoing projects managed by CMT include DOE contracts with General Motors, Ford, Chrysler, and component suppliers.

The Electrochemical Technology Program manages a DOE contract with General Motors for development of a methanol-fueled PEFC for automotive applications. In 1994, DOE awarded a 30-month follow-on contract for General Motors to continue a project with the goal of building and testing a complete 60-kW propulsion system.

The Electrochemical Technology Program also manages two contracts awarded by DOE in 1994 to teams headed by Ford Motor and Pentastar Electronics, Inc. (a Chrysler company). The goal is to develop PEFC propulsion systems for passenger cars fueled directly by hydrogen carried on the vehicle. Under the 30-month contracts, Ford and Chrysler will each carry out: (1) conceptual design of a passenger vehicle powered by a PEFC system, (2) R&D of on-board hydrogen storage technologies, and (3) fabrication and testing of a 30-kW propulsion system.

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 1994, H-Power Corp., the prime contractor, fabricated the first U.S.-built bus powered by a fuel cell. The bus has a capacity of 25 passengers and meets all applicable standards for transit buses, including wheelchair lifts and air conditioning. A 50-kW phosphoric acid fuel cell supplies all

the vehicle's energy needs. The fuel cell operates on methanol fuel at over 40% fuel efficiency. The bus has carbon monoxide and nitrogen oxide emission 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 30-month DOE contract (co-funded by the State of Illinois) with Arthur D. Little, Inc., to develop a prototype ethanol fuel reformer. During 1994, Arthur D. Little built a bench-scale partial oxidation reformer in which ethanol is converted to hydrogen and carbon dioxide. In future phases of the program, the fuel processor will be evaluated with a 25-kW phosphoric acid fuel cell system and, eventually, will be tested in one of DOE's fuel cell vehicles, likely a transit bus.

In other related activities, we assisted DOE in preparing a solicitation for a cooperative program to demonstrate that fuel cell propulsion systems applied to locomotives can meet or exceed conventional diesel locomotive performance, with dramatically reduced environmental emissions and increased efficiency. Development contracts with industry will be awarded by DOE in 1995; Phase I, an 18-month effort, is expected to involve one or two contracting teams led by locomotive manufacturers and lead to the development of a preliminary design for a test locomotive powered by a 1-MW (1350 hp) fuel cell and the conceptual design of a commercial locomotive powered by a 2.25 to 4.5 MW (3000 to 6000 hp) fuel cell. The Electrochemical Technology Program also prepared a solicitation for a new DOE program which is intended to lead to significant cost reductions and improved performance in fuel cell technology for transportation applications.

II. FOSSIL ENERGY RESEARCH

Coal is the most abundant fuel for electricity generation in the United States. Clean coal technologies aim to efficiently use coal and minimize the environmental impacts of combustion. Among clean coal technologies being supported by DOE are pressurized fluidized-bed combustion (PFBC)/gas-turbine combined-cycle systems and integrated gasification combined-cycle systems. In both of these technologies, the high-temperature, high-pressure gas stream expands through a gas turbine to recover thermal energy for improved efficiency. The entrained particulates and alkalis in this gas stream must be removed to protect the gas turbine from erosion and hot corrosion and to meet the Environmental Protection Agency's New Source Performance Standards for particulate emission.

We have developed a method, called the analytical activated-bauxite sorber bed (AASB) technique, for controlling and measuring alkali vapors in the PFBC flue gas.¹ During the past year, we have designed and fabricated AASB instruments for measuring the alkalis in the flue gas of the PFBC demonstration plant in Kitakyushu City, Japan, and an atmospheric, circulating fluidized-bed combustor of Ahlstrom Pyropower, Inc. (San Diego, CA).

A. *Alkali Vapor/Aerosol in Exhaust Gases of Pressurized Fluidized-Bed Combustor*

At the request of Electric Power Development Co. and Ishikawajima-Harima Heavy Industries Co. in Japan, we were contracted to measure the alkali vapor/aerosol in the exhaust gases downstream of a hot-gas filter assembly at the Wakamatsu PFBC Demonstration Plant [71MW(e)] in Kitakyushu City, Japan. The plant is the first utility-scale PFBC to operate in the combined-cycle mode in Japan.

During 1994, we accomplished the following: (1) the design, fabrication, and testing of an AASB pressure vessel to interface with the Wakamatsu PFBC exhaust duct, (2) the design, fabrication, and testing of two downstream gas-conditioning and flow-control trains for use with the AASB pressure vessel, (3) shipment of this equipment, as well as activated-bauxite sorbent, to the Wakamatsu PFBC Demonstration Plant, and (4) documentation of our measurement procedure. During 1995, we will provide technical assistance in conducting the on-site alkali measurement and in analyzing the test results.

B. *Alkali Emission in Flue Gases of Atmospheric, Circulating Fluidized-Bed Combustor*

At the request of Ahlstrom Pyropower, we were also contracted to use our AASB technique to measure the alkali vapor/aerosol concentration in the flue gas from an atmospheric, circulating fluidized-bed combustor fabricated by Ahlstrom Pyropower. This work was performed as a subcontract to Ahlstrom Pyropower's contract with the Illinois Clean Coal Institute (ICCI).

¹ M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, pp. 44-46 (1988).

In this work, we designed, fabricated, and installed (1) an AASB vessel to interface with the flue gas exhaust duct and (2) a downstream gas-conditioning and flow-control train for use with the AASB vessel. The objective of the AASB measurements is to obtain a data base on alkali-vapor concentration in the flue gas from atmospheric, circulating fluidized-bed combustion. The results from this work will be used in assessing alkali emission in pressurized, circulating fluidized-bed combustion.

In Phase I of this work, three Illinois No. 6 coals (Rend Lake mine, Crown II mine, and Arch mine) were selected by Ahlstrom Pyropower. Each coal was combusted at an average bed temperature of 871°C, and the AASB measurements were conducted for a steady-state, on-stream duration of 76-81 h. The time-averaged concentration of vapor-phase sodium in the flue gas was determined to be 49, 47, and 44 ppb (by weight) for the Rend Lake, Crown II, and Arch coals, respectively. The vapor-phase potassium concentration was determined to be negligible for all three coals. These alkali-vapor concentrations are similar to those measured in PFBC² and are about two times greater than the industrial gas-turbine specification limit (24 ppb) for total alkalis in the combustion gas entering a gas turbine. We concluded that the alkali vapor content may have to be controlled if Illinois coals are to be burned in gas-turbine combined-cycle systems employing circulating PFBC.

In Phase II of this work, we tested two in-bed getter materials (emathlite and kaolin) for the control of alkali emission in the combustion of Illinois Rend Lake coal. These getters have been shown to be very effective for capturing alkali vapors in the simulated flue gas from coal combustion^{3,4} and gasification.⁵ The time-averaged sodium-vapor concentration in the flue gas from the atmospheric, circulating fluidized-bed combustor was measured to be 19 ± 3 ppbW for emathlite and 23 ± 4 ppbW for kaolin. These values are approximately 50% lower than the 49 ± 5 ppbW obtained in a similar test under the same conditions but without getter material. It is recommended to further optimize operating conditions that influence in-bed alkali gettering. Among these conditions are the getter particle size and the weight ratio of coal to getter. Studies to investigate other getters, such as activated bauxite and diatomaceous earth, are also recommended.

² S. H. D. Lee, F. G. Teats, W. M. Swift, and D. D. Banerjee, *Combust. Sci. Technol.* **86**, 327-336 (1992).

³ S. H. D. Lee and I. Johnson, *J. Inst. Energy* **63**, 203-210 (1990).

⁴ M. Uberoi, W. A. Punjak, and F. Shadman, *Prog. Energy Combust. Sci.* **16**, 205-211 (1990).

⁵ D. M. Bachuchin, M. A. Alvin, E. A. Dezubay, and P. R. Mulik, *A Study of High Temperature Removal of Alkali in a Pressurized Gasification System*, Department of Energy Report DOE-MC-20050-226, Westinghouse Research and Development Center, Pittsburgh, PA (1986).

III. HAZARDOUS WASTE RESEARCH

Over 40 years of nuclear-defense production and other activities at DOE sites such as the Hanford site, Oak Ridge National Laboratory, and Savannah River Laboratory have produced a massive quantity of hazardous and mixed hazardous/radioactive waste. This waste contains radionuclides, heavy metals, organic compounds, and many other regulated hazardous compounds. It is in a variety of forms, including soils, solid radioactive waste, supernatant liquids, slurries, salt cakes, and sludges. One of the current missions of DOE is the cleanup of these wastes. It is anticipated that this mission will last over 30 years and will cost hundreds of billions of dollars. To help accomplish this mission, we are participating in a variety of projects aimed at developing new or improved technologies for treating and disposing of this waste. We are also experimentally investigating actinide speciation in groundwater-relevant systems and radiolytic gas generation from transuranic-containing waste buried underground.

A. *Aqueous Biphasic Separation Process*

The aqueous biphasic separation (ABS) process is a new and highly adaptable separation technique that can be used in a wide range of applications, such as treatment of solid nuclear wastes, contaminated soils, wastewater, and mineral ores. The biphasic systems that we have been working with combine aqueous solutions of polymeric materials such as polyethylene glycol (PEG) and salt solutions such as Na_2SO_4 . We are evaluating several possible applications for this process, as well as conducting fundamental studies of solution microstructure in biphasic systems.

1. Actinide Recovery from Solid Wastes

The ABS process is being evaluated for possible application to the treatment of solid radioactive wastes. The goal is to recover the majority of the actinides in a concentrate that is only 1-5% of the initial waste volume. This project has three primary tasks: (1) residue characterization, (2) fundamental studies of solution chemistry pertaining to biphasic formation, and (3) tests of actinide separations.

During 1994, we characterized several different plutonium-containing residues. The samples included incinerator ash and ash heels from the Rocky Flats Plant and Los Alamos National Laboratory, SSC (sand, slag, and crucible) metallurgical residues from DOE's Hanford Site, and LECO crucibles from Savannah River Laboratory. Earlier studies indicated that plutonium was present in the residues in particulate form, and that some of the plutonium phases were encased inside larger aluminosilicate particles.¹ Interestingly, this morphology was observed in both the ash and ash heel samples. The characterization studies just completed involved grinding the residues to average particle sizes of 1 μm or less. The objective was to evaluate the potential for using ultrafine grinding to liberate the plutonium from the residue matrix. The grinding procedure also enabled us to generate samples that could be thin sectioned and examined by transmission electron microscopy. Common plutonium phases (found in all of the ash/heel

¹ D. J. Chaiko, R. Mensah-Biney, C. J. Mertz, and A. W. Rollins, Sep. Sci. Technol. **28**, 765 (1993).

samples) were determined to be PuO_2 , non-stoichiometric PuO_{2-x} , and $\text{Pu}_2\text{O}_{3+x}$. In addition, an unidentified, crystalline Pu-Si-Ti phase was observed in the Rocky Flats ash. Furthermore, glass phases appeared in the ash samples that contained low concentrations of plutonium.

In 1994, studies were completed on the solution microstructure of PEG in electrolyte solutions under static and shearing conditions. In collaboration with the ANL Intense Pulsed Neutron Source and Los Alamos National Laboratory, we carried out small angle neutron scattering of various PEG/salt solutions. In solution and in the presence of salts that do not promote biphasic formation (e.g., NaNO_3), PEG was found to behave like a random coil with no evidence of aggregation. However, in the presence of biphasic-forming salts (e.g., Na_2SO_4 or Na_2CO_3), extensive aggregation took place, and the aggregate size increased with increasing salt concentration until a discontinuity appeared at the point of biphasic formation. Once in the biphasic regime, the polymer returned to the random coil structure observed in the absence of salt.

Under moderate shear conditions (e.g., $20\text{--}38\text{ s}^{-1}$), PEG formed supra-molecular aggregates in the presence of salt. This suggests that shearing can change the polymer activity and would explain the progressive reductions in solute partition coefficients as a function of time when the biphasic system is subjected to intensive mixing over a period of 1-20 min.

Actinide extraction tests are underway with plutonium-containing residues in a 1-m-high Karr column. The plutonium residues were prepared by wet grinding to an average particle size of $1\text{ }\mu\text{m}$ or less. A $\text{PEG}/(\text{NH}_4)_2\text{SO}_4$ biphasic system was used with chlorophosphonazo III as the phase transfer agent ($2 \times 10^{-4}\text{ M}$). This agent is used to selectively transfer the plutonium from the salt-rich phase to the PEG-rich phase, leaving the non-plutonium phases behind in the salt-rich solution. To estimate separation efficiencies, we will determine the mass ratios between plutonium and various elements in the column effluents (Si, Al, and a number of transition metals), and these results will be compared with the corresponding data for the starting materials. The analysis of the column effluents is not complete, and separation factors are yet to be determined.

2. Treatment of Uranium-Contaminated Soils

The primary objective of this project is to develop an ABS process for removing ultrafine uranium particles from contaminated soil. Our decontamination target is a residual uranium concentration of 50 mg/kg , or less, in the clean soil. The contaminated soil samples used in this work were provided by DOE's Fernald Environmental Management Project. Because of high levels ($>80\%$) of silt and clay, this soil is not directly amenable to treatment by conventional soil washing techniques. A number of uranium(IV)- and (VI)-bearing phases have been identified in the Fernald soil. Some of these phases are extremely refractory and are present as discrete particles with sizes in the micron and submicron range.

In test-tube-scale studies, we examined a number of PEG/salt systems. These systems included sodium and potassium carbonate, sodium hexametaphosphate, and sodium sulfate, as well as two different PEG molecular weights (PEG-1500 and -3400). We found that the most suitable system, in terms of phase separation capabilities and partitioning selectivity,

was PEG-1500/ Na_2CO_3 at temperatures above 35°C. Under these conditions, a uranium concentrate was recovered in the salt-rich phase that contained only 1-2 wt% of the soil feed.

During 1994, extraction studies were initiated with a pilot-scale Karr column (2.54-cm ID and 3.6-m height). The column is operated with the less-viscous, salt-rich phase as the continuous phase. During the extraction, the clean soil partitions to the PEG-rich phase, while the uranium contaminants partition selectively to the salt-rich phase. Therefore, to minimize the amount of mass transfer during soil decontamination, the soil feed is dispersed in the PEG phase. Column capacity can be dramatically increased by suspending high concentrations (30-35 wt%) of soil (particle size of <150 μm) in the PEG phase, effectively making the PEG the more-dense phase. Column tests have confirmed that varying the concentration of solids from 1 to 35 wt% has no effect on column performance or mass transfer rates.

In preliminary tests using the pilot-scale Karr column, the uranium concentration in the Fernald soil was reduced from 471 mg/kg to approximately 78 mg/kg. However, examination of the clean soil by electron microscopy indicated that some of the uranium particulates still remained in the cleaned soil. We believe that adsorbed humic acids are acting as phase transfer agents and are responsible for partitioning some of the uranium particulates into the PEG phase. This surface activation mechanism also explains the recovery of crystalline silicates, like quartz, in the PEG phase. Ways to selectively alter the surface chemistry of the uranium phases for improved recovery of uranium particulates in the salt phase are being investigated.

In addition to improved uranium recovery and column throughput, work is proceeding on optimizing the downstream processing of column effluents. Because of the high clay content of the Fernald soil, solid/liquid separation is expected to dominate capital equipment and processing costs. To minimize the size of filtration equipment, we are exploring the use of flocculants for enhancing the rate of solid/liquid separation. Since most of the soil is recovered from the PEG-rich phase, our initial studies were focused on this process stream. Our concern is that high PEG concentrations in that effluent stream will interfere with flocculant adsorption onto the soil particles. Several polymeric flocculants (Nalco 7871, 7877, and 9857; Magniflor 1956C and 1555C) have been tested. In the absence of any flocculant, the settling rate of the soil was only 0.026 m/h. The settling rate was little improved by the majority of the flocculants; however, the Nalco 7877 flocculant produced the highest settling rate observed, 2.04 m/h.

During 1995, optimization of uranium extraction column throughput and column effluent treatment will be continued. In addition, a detailed design flowsheet will be prepared, and a preliminary economic analysis will be performed.

3. Partitioning System for Waste Pretreatment

We are developing an ABS system for pretreating supernatant solutions from underground storage tanks at Hanford. The primary objective is to remove long-lived radio-nuclides, such as ^{99}Tc , from alkaline solutions. The ABS system is generated by adding polyethylene glycols (PEGs) or polypropylene glycols (PPGs) to electrolyte solutions with high ionic strength.

In 1993, we evaluated the ability of PEGs to selectively extract pertechnetate (TcO_4^-) from simulated supernatants.² During 1994, work was centered on improved extraction selectivity and back-extraction efficiency. In working toward this goal, we have found that PPG-based biphasic systems offer certain advantages over PEG-based systems. The PPGs are good candidates for biphasic separations because of their lower water solubility, which reduces polymer losses through dissolution into the aqueous waste stream. Extraction of TcO_4^- from simulated tank waste supernatants by PPGs is rapid, and extraction selectivities are significantly improved over those obtained with PEGs.

Partition coefficients for TcO_4^- between PPG and tank waste simulants were determined to be in the 75-95 range, while those for many tank waste constituents [e.g., $\text{Al}(\text{OH})_4^-$, PO_4^{3-} , SO_4^{2-} , and F^-] are below 10^{-3} . The single-stage separation factors (ratio of partition coefficients) for separating TcO_4^- from various ions are given in Table III-1.

Table III-1. Separation Factors Obtained for Pertechnetate
Extracted from Tank Waste Simulant by
Polypropylene Glycol (molecular weight of 424)
at 25°C

Ionic Species	Separation Factor
NO_3^-	1049
NO_2^-	2297
CO_3^{2-}	3148
Na^+	2576
$\text{Al}(\text{OH})_x^{3-x}$	10,500

The separation of TcO_4^- from NO_3^- has traditionally been difficult. With PPGs of various molecular weights (e.g., 400-1000), single-stage separation factors greater than 1000 between pertechnetate and $\text{NO}_3^-/\text{NO}_2^-$ have been achieved (Table III-1). Additionally, secondary waste production is minimized because deionized water can be used to strip TcO_4^- from the loaded polymer phase when using PPGs with high molecular weights (e.g., PPG-1000).

We have developed a proprietary process that will back-extract ionic species from PPGs and PEGs and will eliminate the need for using high-ionic-strength salt solutions to maintain the biphasic system. This process will be used as the basis for designing polymer-based systems that will extract technetium from high-ionic-strength nitrate solutions without producing significant secondary waste.

² J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 46-47 (1994).

4. Biocatalytic Destruction of Nitrate and Nitrite

The presence of high nitrate and nitrite concentrations in many DOE mixed-waste streams complicates decisions regarding final waste forms and disposal options. We are thus developing a pretreatment process for destroying nitrate and nitrite in aqueous waste streams. The process combines immobilized enzyme technology with aqueous biphasic separation. The ABS process is used to selectively partition nitrate and nitrite from other constituents, such as hydroxide and phosphate, present in the waste streams and to provide a low-ionic-strength environment (glycol/aqueous phase), which will inhibit denaturing of the enzymes. After separation, the nitrate/nitrite-bearing stream is moved past an electrode surface covered by reductase enzymes. Immobilizing the enzymes onto the surface of an electrode confines these enzymes to the glycol-rich phase of the biphasic system while maintaining their high specific activity. An electron transfer agent, which shuttles electrons from the electrode to the enzyme, is also immobilized on the electrode surface.

The enzymes catalyze the reduction of nitrate to elemental nitrogen (N_2) and water. The overall reaction proceeds through a series of reduction intermediates:

Each reaction is catalyzed by the appropriate reductase, namely, nitrate, nitrite, and nitrous oxide reductase. The overall reduction reaction is

During the past year, our research was focused on the initial step in the reduction process, i.e., the reduction of nitrate to nitrite (reaction 1).

The reductase and electron transfer agent are immobilized by using a modification of the procedure developed by Willner et al.³ In our procedure, a thin polymeric film of thiophene-3-acetic acid is electroplated onto the surface of a gold electrode. This film provides an "anchor" to which the enzymes are chemically bonded. The electroplating is conducted over a sweep voltage range of +0.0 to +1.7 V (vs. Ag^+/Ag) and uses a plating solution consisting of 0.10 M thiophene-3-acetic acid in acetonitrile. The sulfur atom in thiophene-3-acetic acid bonds

³ I. Willner, E. Katz, N. Lapidot, and P. Bauerle, *Biochem. Bioeng.* **29**, 29-45 (1992).

to the gold surface, which allows the acetic acid (carboxylic) group to remain chemically available to the enzymes.

An important aspect in selecting the electron transfer agent is that the redox potential be such that it operate at a potential above -0.828 V, which is the potential at which water is reduced to generate hydrogen gas. Based on the work of Shu and Wrighton,⁴ we chose an N,N'-dimethyl-4,4'-bipyridinium(I) complex as the electron transfer agent. This bipyridinium complex can be coupled to thiophene-3-propyl bromide to yield a 1-methyl-1'-(3-thiophene-3-yl)-propyl-4,4'-bipyridinium complex, which can be electrochemically polymerized onto the surface of a gold electrode to yield a conducting 2-5 thiophene polymer. A cyclic voltammetry study of the electrode-bound polymer indicated an oxidation wave at 0.6 V and two-successive reduction waves, -0.6 V and 1.1 V. The bipyridinium complex is relatively mobile and can easily come within the required distance necessary to transfer an electron to the enzyme.

We also evaluated the activity of two nitrate reductase enzymes: a ferrocytochrome form from *Escherichia coli* (EC 1.9.6.1) and a NAD[P]H form (reduced nicotinamide adenine dinucleotide phosphate) from *Aspergillus* (EC 1.6.6.2). In preliminary screening tests, the EC 1.9.6.1 was found to be an order of magnitude more active than the EC 1.6.6.2. In addition, the bonded enzymes appeared to retain their activity over an extended period, with little evidence of denaturing.

Currently, we are proceeding toward a demonstration of this process to reduce nitrate to nitrite in a surrogate DOE waste stream. Upon completion of this demonstration, procedures will be developed for immobilizing both the nitrite and nitrous oxide reductase along with the nitrate reductase. Then, we will demonstrate the reduction of nitrate and nitrite to elemental nitrogen and water.

B. 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 sites. Emphasis is on factors that affect mobilization/immobilization of plutonium species. Expected results of this work will establish the key factors concerning the chemistry of plutonium-organic mixtures in the presence of microbes, inorganic substrates, and metal cations. During 1994, work focused on (1) interactions of the plutonium-nitritotriacetic acid (NTA) complex with the *chelatorbacter* microbe, (2) effects of gamma radiation on the *halobium* microbe, and (3) the speciation of Pu(VI) in the presence of phosphate. This work involves collaborations with Pacific Northwest Laboratory, Brookhaven National Laboratory, and Lawrence Berkeley Laboratory.

We are investigating the Pu(IV)-NTA complex because NTA is a complexant associated with DOE plutonium processing. The Pu(IV)-NTA complex formed at near-neutral pH (6 to 8) is stable over a period of months. In the presence of the *chelatorbacter* microbe, a known NTA

⁴ C.-F. Shu and M. S. Wrighton, *Electrochemical Surface Science: Molecular Phenomena at Electrode Surfaces*, Ed., M. P. Soriaga, Advances in Chemistry Series, Am. Chem. Soc., Washington, DC, No. 378, pp. 408-430 (1988).

degrader, it is expected that the NTA will be metabolized, destabilizing the Pu(IV)-NTA complex and forming plutonium polymers. We prepared the Pu(IV)-NTA complex by adding NTA to a Pu(III)-containing aqueous solution at $\text{pH} < 4.0$ to suppress hydrolysis of Pu(IV). Owing to a combination of radiolysis, reaction with the NTA, and air oxidation, the Pu(III) is oxidized to Pu(IV) and, in the presence of NTA, forms a stable complex. This complex was then added to a 0.01 M PIPES [1,4-piperazinebis(ethane-sulfonic acid)] buffer solution and adjusted to $\text{pH} = 6.2 \pm 0.1$, which is at the lower end of the pH range suitable for microbial growth. Spectrometry was used to establish the stability of the complex. Subsequent to this, the solution was diluted to vary the relative plutonium concentration from 10^{-5} to 10^{-9} M . After this dilution, the *chelatobacter* microbe suspended in 0.01 M PIPES was added to the solution. Both the gas and liquid were monitored as a function of time to track the biodegradation process and establish the fate of the Pu(IV)-NTA complex.

Degradation of NTA results primarily in CO_2 formation. We monitored CO_2 formation by gas chromatographic measurements of the gas phase above the Pu-NTA-microbial system. The results are shown in Fig. III-1. Initially, the presence of plutonium did not significantly affect CO_2 formation. After $\sim 50 \text{ h}$, however, the rate of CO_2 formation was found to be lower with increased plutonium.

Fig. III-1. Cumulative Moles of CO_2 Generated in Solution with and without Pu(IV)-NTA Complex

The fate of the Pu(IV)-NTA complex in the microbial system was also established. After degradation of the NTA, absorption spectra (detection limits $>1\%$) did not show any evidence of the complex. Although total plutonium concentrations in solution were lowered slightly, up to 80% of the plutonium became associated with the microbial fraction (as determined by filtration with $0.2 \mu\text{m}$ filters and centrifugation). These results are shown in Fig. III-2. The mechanism by which the plutonium becomes associated with the microbe is still under investigation.

Fig. III-2. Relative Plutonium Content as Function of Time in Pu-NTA-Microbial System

The presence of plutonium lowered the survivability of the microbe. Survivability was measured by stirring the microbial sample, taking known aliquots of the sample, inoculating Agar plates with an NTA growth medium, and counting the number of colonies that grew. The presence of plutonium had a significant detrimental effect on the survivability of the microbe, leading to <1% survivability at the highest plutonium concentrations evaluated (10^{-5} M).

In the second area of work, the radiation tolerance of the *halobium* microbe, which is a halophile being considered for use in bioremediation of DOE sites, was evaluated by exposing microbial solutions to gamma radiation and measuring the survival of the microbe by bioassay. The survivability curve as a function of absorbed dose is shown in Fig. III-3. The radiation tolerance of the microbe was established to be ~ 1 Mrad. This supports the conclusion that, when plutonium alone is the source of ionizing radiation, only radiation resulting from the uptake of plutonium leads to irradiation damage.

Lastly, a study is underway to establish the speciation, bulk solubility, and spectroscopy of plutonium-phosphate species in aqueous solutions (pH = 2-10) at 25°C. Phosphate is being investigated because it is frequently present in groundwaters and is an important nutrient for microbes. We found that, at pH > 4, colloidal forms of the plutonium-phosphate species predominated. These species, when suspended in solution, have narrow absorption bands in the 800-875 nm spectroscopic regime.

Future plans are to extend the Pu-NTA-microbial study to investigate biotic transformation, expand our work to include plutonium-ethylenediaminetetraacetic acid (EDTA) complexes and EDTA degraders, and investigate cation competition with plutonium.

Fig. III-3. Survivability Curve for *Halobium* as Function of Absorbed Dose

C. *Studies for Waste Isolation Pilot Plant*

1. Radiolytic Effects

Studies are continuing to evaluate the effects of ionizing radiation on gas production in environments similar to those expected in the Waste Isolation Pilot Plant (WIPP). This work is part of an overall effort, coordinated through Sandia National Laboratories, to help evaluate the long-term performance of WIPP for the disposal of defense-related transuranic (TRU) waste. Ionizing radiation will be present in WIPP primarily as alpha particles from the radioactive decay of TRU species. The objective of the ANL effort is to evaluate the potential effects of alpha particle interaction with WIPP wastes and the anticipated WIPP environment. Such interactions are important in assessing the long-term performance of WIPP.

Recent work has concentrated on the alpha particle degradation of WIPP-specific plastic and rubber materials in a hydrogen/carbon dioxide environment. These tests were analogous to past tests conducted in both an air and nitrogen atmosphere.⁵ Hydrogen and carbon dioxide are gaseous products generated from microbial and corrosion processes in WIPP. This atmosphere is most relevant to that expected in WIPP over long times.

The alpha particle irradiations were performed with gold-plated foils containing 6 mCi ²⁴¹Am as the alpha particle source. Four WIPP-relevant materials were investigated: two rubbers (neoprene and hypalon) and two plastics (polyvinylchloride and polyethylene). The plastic is typical of materials used to package TRU waste at Rocky Flats Plant, and the rubber is typical of glove materials used in glovebox and radioactive waste cleanup. The plastic/rubber materials

⁵ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 52-54 (1994).

were irradiated for three months in a hydrogen/carbon dioxide environment at 30°C and at a surface dose rate of 2×10^5 rad/h. Periodically, gas samples were taken and analyzed by gas chromatography or gas chromatography/mass spectrometry to determine gas composition and radiolytic yield.

The predominant radiolytic products, other than hydrogen and carbon dioxide, were a wide variety of volatile organic compounds (VOCs). For neoprene and hypalon, the radiolytic yields were low (typically $\ll 0.1$ molecule/100 eV). The concentrations of VOCs usually did not increase linearly with absorbed dose. The VOC yields for polyethylene were slightly higher than those observed for the two rubber materials, but also did not increase linearly with absorbed dose. The highest VOC yields were observed for polyvinylchloride, with the concentration of most radiolytic products increasing linearly with absorbed dose. Final VOC concentrations for all four materials were in the parts per million range after three months of exposure (Table III-2), corresponding to yields that are <0.1 molecule/100 eV. Our results indicate that VOC gas generation due to direct degradation of the plastic and rubber materials investigated will not likely be a problem in WIPP. This is consistent with past observations for experiments performed in the air and nitrogen atmosphere.⁵

Table III-2. Concentration of Volatile Organic Compounds in the Final Gas Phase of the Alpha Particle Irradiation of WIPP Plastic/Rubber Materials (3-month duration)

Organic Class of Compound	Concentration, ppm			
	Polyethylene	Polyvinylchloride	Neoprene	Hypalon
Alkane	69	595	ND	ND
Alkene	ND ^a	79	ND	ND
Ketone	99	88	43	42
Alcohol	14	120	5.4	0.8
Aldehyde	3.5	69	3.7	ND
Benzyl	ND	3.3	ND	0.3
Halogenated Hydrocarbon	ND	88	1.4	7.7

^aND = not detected.

In addition to studies to establish VOC production, 3- and 6-month irradiations of the same four materials were performed to establish the effect of alpha particles on the biodegradability of the materials. Bioassays of these materials are planned in collaboration with Brookhaven National Laboratory.

2. Gas Generation Rates

A new program was initiated during 1994 to investigate gas generation under conditions relevant to WIPP. This work is part of a collaborative effort with Brookhaven National

Laboratory and Pacific Northwest Laboratory, coordinated through Sandia National Laboratories. The objective of the planned work is to establish net gas generation rates when radiolytic, corrosion, and microbial mechanisms are combined. These data will help establish the key factors needed to evaluate the long-term performance of WIPP.

The test matrix is not yet defined but will likely consist of experiments that include unsaturated conditions, saturated conditions in Brine A, ^{239}Pu concentrations up to 10^{-4} M, WIPP-relevant waste materials (cellulose, plastic, rubber, and metal), and halophilic microbes typically found at the WIPP site. Various combinations of these components will be placed in 2-L vessels, sealed, over-pressured with nitrogen gas, and monitored for pressure buildup and gas generation. The test vessels will contain glass or Teflon liners, which our developmental tests had shown to undergo less interaction with plutonium species than polyethylene, Hastelloy C-276, or iron. Thirty experiments are planned (20 radioactive and 10 nonradioactive). All experiments will be performed at 30°C.

D. *Chemically Bonded Phosphate Waste Forms*

We are participating in a project to evaluate the suitability of phosphate inorganic binders for solidification and stabilization of mixed wastes that are not amenable to, or compatible with, thermal processes. Phosphate binders are attractive for such wastes because the waste forms involved can be formed at ambient temperatures. The phosphate binding phases solidify the waste and stabilize waste components (e.g., heavy metals and actinides) by incorporating them into the binding phases and encapsulating them in the solidified matrix. The phosphate matrix is thought to be effective in stabilizing such contaminants by suppressing their dissolution as a result of the very low solubility of heavy metal phosphates. The durability of phosphate mineral phases (e.g., monazite and apatite minerals) in natural environments and the affinity of such phases to incorporate uranium, thorium, and rare earth elements attest to the potentially attractive properties of phosphate binders as waste form materials.

This project is a cooperative effort between the Energy Technology (ET) and CMT Divisions. The ET Division has developed processes for incorporating surrogate (including ash, salt, and cement formulations) and real mixed wastes into monolithic samples by using magnesium and zirconium phosphate binders. The CMT effort has focused on testing the performance of waste samples.

During 1994, samples of magnesium and zirconium phosphate waste forms containing surrogate waste materials (at loadings up to 70 wt%) were subjected to two standard leaching tests: the Toxicity Characteristic Leaching Procedure (TCLP)⁶ and Method ANSI/ANS-16.1.⁷ Figure III-4 illustrates the TCLP results for the surrogate materials. It shows that the TCLP

⁶ U.S. Environmental Protection Agency, "Toxicity Characteristic Leaching Procedure," in *Test Methods for Evaluating Solid Waste*, Method 1311, SW-846, U.S. Environmental Protection Agency, Washington, DC (1992).

⁷ American Nuclear Society, "American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure," Method ANSI/ANS-16.1-1986, American Nuclear Society, LaGrange Park, IL (1986).

Fig. III-4. Results from Leach Testing of Mg-Na Phosphate with Ash Loadings up to 70 wt%. The EPA limits included for comparison.

extract concentrations in the untreated ash waste greatly exceed the Environmental Protection Agency (EPA) limits. However, the phosphate stabilized forms, with ash waste loadings up to 70 wt%, give TCLP extract concentrations much lower than the EPA limits. In sum, the leaching results indicate that the phosphate matrix is effective in stabilizing the hazardous metal components of the waste even at high waste loading. Our future efforts will concentrate on testing the performance of these waste forms with real wastes and scaling up of the waste-form production processes.

E. *Environmental Management Program Office*

This office is assisting DOE in maintaining a national program of applied R&D in environmental restoration and waste management. Effort in the past year focused on providing technical and management support to the Minimum Additive Waste Stabilization (MAWS) Project, the Hazardous Substance Research Center (HSRC) Program, and the In-Situ Remediation Integrated Program (ISRIP).

1. Minimum Additive Waste Stabilization Project

The objective of this project is to demonstrate the MAWS process at the Fernald site. This process involves the treatment and blending of multiple waste streams (initially Pit-5 sludges, spent ion-exchange resins, and contaminated fractions from soil washing). Blending these streams in the optimum proportions maximizes overall volume reduction of the final waste form and minimizes additives that would otherwise be necessary for the vitrification process. Vitrification is the center of the MAWS technology, which is applicable for a large variety of DOE wastes, such as soils, tank wastes, sludge, ashes, asbestos, and transite. Preliminary surveys have indicated that DOE sites at Hanford, Savannah River, Rocky Flats, Oak Ridge, and Fernald are potential users of this technology. Also participating in this project is the Vitreous State

Laboratory of the Catholic University of America and Lockheed Environmental Services and Technology.

We support the MAWS Project in several areas: (1) contract administration and monitoring, (2) evaluation of waste form performance and test development, and (3) evaluation of the efficacy of extending the desirable vitrified waste forms to include glassy slag for waste streams with high metal content. Key accomplishments in the MAWS Project include the following:

- A 300 kg/day MAWS demonstration system has been installed at the Fernald site. A fluoride composition surrogate formulated to approximate actual Mg-F_2 -containing sludges was successfully tested in a 72-h run. The melter, feed, and off-gas systems performed within specifications, and the glass-making machine ran well for approximately 2.5 h.
- Uranium-contaminated soils have been successfully vitrified in the 300 kg/day melter. The initial test ran continuously for four days and treated 3633 L of contaminated-soil feed, producing approximately 60 kg of glass gems.
- A soil washing unit was installed and demonstrated by Lockheed Environmental. With this unit, the uranium concentration in 76 m³ of contaminated soil was reduced to levels as low as 20 pCi/g, from an initial average of 600 pCi/g.

2. Hazardous Substance Research Centers

The HSRC Program is co-funded by DOE and the EPA. The Environmental Management Program Office in CMT continues to provide technical and management support to five HSRCs. Each center covers two federal EPA regions. Each center is located at a main participant university but consists of a consortium of several universities in the region. These centers are the Northeast HSRC, Great Lakes and Mid-Atlantic HSRC, South/Southwest HSRC, the Great Plains/Rocky Mountain HSRC, and the Western Region HSRC. Currently, 23 universities participate in the program. The basic mission of the HSRCs is to study all aspects of the management of hazardous substances and waste. Most of the research is focused on developing characterization and remediation technologies for hazardous waste sites.

During 1994, the Environmental Management Program Office prepared HSRC Project Notebooks for DOE. These notebooks describe the scope of work for the individual research projects and update research progress at the centers. Argonne panels also reviewed over 100 research proposals for the HSRC Program. Based on recommendations from these reviews, DOE has selected additional projects for funding in 1995.

During 1994, nine of 21 DOE co-funded HSRC projects were completed. Examples of successful technologies developed through the program include use of pneumatic fracturing for removing VOCs from clay, siltstone, and sandstone formations; a field-applicable gas chromatography/mass spectrometry instrument for characterizing contaminated sites; and an *in situ* bioremediation method for microbial degradation of contaminants. Two other technologies

also show promise: an electrochemical sensor for heavy metals in groundwater and use of nano-scale metal oxides for destruction of hazardous substances.

In demonstrations at several sites, the use of pneumatic fracturing improved removal of trichloroethylene by a factor of six over remediation efforts in the pre-fracture environment. Continuing projects involve the following: use of a ^{222}Ra method for locating non-aqueous liquids in the subsurface, modeling of contaminant plumes in the subsurface, use of electric purging of heavy metal from soil, use of a ceramic matrix for immobilizing heavy metals, and development of hollow-fiber membranes for metal recovery in waste.

3. In-Situ Remediation Integrated Program

The objective of this task is to assist DOE's Environmental Management Office of Technology Development in the execution of the Integrated Program for Development of In-Situ Remediation Technologies. We maintain an informational interface with program contractors to allow the collection, analysis, and dissemination of technical, cost, and schedule information. Activities include the following:

- Technical evaluation/review of emerging and maturing *in situ* environmental restoration technologies from all sectors--academia, industry, and the national laboratories.
- Review of R&D information from program contractors and integration with DOE needs assessments.
- Management of technical review panels and technical consultants.

IV. NUCLEAR WASTE PROGRAMS

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 samples 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. Our work to characterize the radioactive phases in contaminated soil and other materials is continuing.

A. *Preparation of Review Documents*

In this effort, we are compiling and interpreting data that address the effects of several important parameters on the reactions between glass and repository groundwater. During this year, *High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics*¹ was published. It is a distillation of worldwide information regarding the characteristics of glass and glass reactivity and includes an objective interpretation of how glass can be expected to perform under repository conditions. The key conclusion is that glass is likely to perform acceptably in the final repository system, but that certain conditions will accelerate glass reaction and should be avoided during storage and disposal (e.g., high temperature and rapidly flowing water). The material presented in the Compendium will be expanded upon in a series of critical reviews and data reports. During 1994, reports were completed on glass reaction modeling and the effects of radiation, glass composition, and the ratio of glass surface area to water volume (SA/V) on glass reaction.

B. *Testing of High-Level Waste Glasses*

Projects have been ongoing for several years to support DOE in efforts to qualify vitrified high-level wastes for geologic disposal. The work has been aimed primarily at the glass compositions that are likely to be produced at the Savannah River Site in the Defense Waste Processing Facility and in the West Valley Demonstration Project. The major goal is information on the reaction of the glass waste forms with groundwater that can be used to predict their long-term performance in an unsaturated repository, i.e., a relatively dry, porous rock structure above the water table.

¹ J. K. Bates et al., *High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics*, Volumes 1-3, U. S. Department of Energy, Office of Waste Management, DOE-EM-0177 (March 1994).

1. Static Tests of Savannah River Glass

Long-term static tests are underway to compare the reaction of fully radioactive glasses with simulated (nonradioactive) waste glasses (SRL 165, SRL 131, and SRL 200). The fully radioactive glasses were obtained from Westinghouse Savannah River Co. In static leach tests at 90°C and SA/V ratios of 340 and 2000 m⁻¹ up to 980 days, the leach rates of glass matrix elements (such as boron, a benchmark for glass corrosion) showed only small differences between radioactive and simulated waste glasses. The small differences in reactivity among these glasses are not large enough to alter the order of durability for the different compositions (SRL 165 > 131 > 200), nor to change the controlling glass dissolution processes. Also, the small differences can be explained if the controlling reaction process and leachate pH's are taken into account. However, in static tests at an SA/V ratio of 20,000 m⁻¹, the simulated SRL 200 glass leached during a one-year period 1000 times faster than the corresponding radioactive glass. The accelerated reaction with this simulated glass is associated with the formation of crystalline phases, such as clinoptilolite (and/or potassium feldspar), and a rapid rise in pH. The radiation field generated by the fully radioactive glass reduces the solution pH, which, in turn, may retard the onset of the increased reaction rate. This result suggests that the fully radioactive 200 glass, if the lower pH in the leachate can be sustained in a repository, may be substantially more durable than the simulated glass. The radionuclides are generally contained in the alteration phases that form on the glass surface; as a result, the radionuclide releases are at least 100 times slower than the boron release for all glass compositions at all SA/V values tested.

Another series of static leach tests is being conducted with other SRL glasses to assess how the SA/V ratio affects the rate and mechanism of glass corrosion. Tests have been completed at 90°C for periods between 3 and 1400 days at SA/V ratios of 10, 340, 2000, and 20,000 m⁻¹. The predominant effect of the SA/V ratio was the extent to which corrosion products are diluted in the leachate. At all SA/V ratios, glass corrosion results in the rapid formation of smectite clay at the outer surface of the glass, which does not impede the corrosion rate of the glass surface beneath this clay layer. In tests at high SA/V ratios (2000 and 20,000 m⁻¹), higher silicic acid concentrations are attained initially, and this lowers the initial glass corrosion rates; however, leachate solutions with high concentrations of dissolved glass components are generated sooner. This initial period is thus followed by the precipitation of secondary crystal phases, which causes an increased corrosion rate.

Beyond a description of the mechanism and rate of glass matrix corrosion, the behavior of individual radionuclides must be known to assess the performance of a waste form and a waste disposal system. While much is known about the chemistries of various radionuclides in aqueous solutions, little is known regarding the effects of glass corrosion on the potential disposition of radionuclides in a geologic repository. Static tests were conducted using glasses doped with Tc, U, Np, Pu, and Am to measure their disposition at SA/V ratios from 10 to 20,000 m⁻¹ and at different stages of the corrosion process. The following conclusions were reached:

- Technetium is usually released stoichiometrically with boron and is not retained by secondary phases under most test conditions.

- The dispositions and solubilities of actinide elements are sensitive to the SA/V ratio.
- Actinides are associated with suspended and colloidal material formed by corrosion products in the leachate. They may increase the amount of actinides transported with groundwater.
- The amount of suspended material in the leachate depends on the SA/V ratio and the reaction time.
- The amount of actinide materials available for transport is affected by both their solubilities and the stabilities of the suspended phases with which they are associated.

The results from all our static tests have led to a description of the corrosion mechanism of DWPF reference glasses that accounts for interactions among the glass, the leachate solution, and the secondary phases. This information is being used to quantify the behavior of these glasses in the initial, interim, and long-term stages of corrosion. By conducting a suite of static leach tests at different SA/V ratios, one can characterize the corrosion behavior of high-level waste glasses for use in performance assessments of any disposal site.

2. Drip Tests of Savannah River Glass

In drip tests, water is slowly dripped on a sample supported above the leachate in a test vessel at 90°C. Results from analyses of the glass and leachate are used to determine the reaction progress of glass under conditions that are likely to exist at Yucca Mountain, the potential repository site. A series of drip tests (designated N2) is being performed with EJ-13 well water (representative of Yucca Mountain site) and SRL 165 glass that has been doped with transuranic elements (Np, Pu, and Am) and with Tc. During the tests, the leachates are monitored for the release of glass components, such as B and Li, and for radionuclides. Boron and lithium indicate the extent of glass reaction, and the radionuclides provide information on the release of transuranic elements. Interactions between the glass and the 304L stainless steel supports holding the glass are also investigated. The tests have been ongoing for more than 8 years. The leachate and glass were last sampled in December 1993, after an interval of 190 weeks without sampling. The test results showed that interaction between the glass and the metal supports is producing iron silicate particles, which are released into the solution. Also, the glass is reacting such that the alteration layer, which retains most of the Pu and Am, is not firmly attached to the glass. Thus, these actinides are released from the glass as particulates suspended in solution.

Drip tests with fully radioactive SRL 200 glass (as-cast and pre-aged by reacting the glass in a water vapor environment before testing) have been in progress for nearly 2.5 years. A modified drip test procedure is used to investigate the effects of both the glass and metal component aging and thereby make the results more relevant to the anticipated environment for the unsaturated repository. Aging alters the physical state of both the glass and metal components and is due to hydration by warm, humid air. The results of the solution analyses are available for

the first two test periods (30 and 60 weeks) and indicate several significant differences in the reaction and subsequent solution composition for the aged and as-cast glass.

First, the solution pH values for the aged glass tests are consistently in the 11.0 to 11.5 range, while the as-cast glass tests have pH values of about 8.

Second, major glass cations, such as Li, B, Na, and Si, were detected in leachates from aged glass at levels several hundred times greater than those from as-cast glass. This difference suggests that not all of the major elements are incorporated into stable alteration products as the glass forms a hydrated layer during the aging process. Thus, these elements are readily rinsed from the surface during initial contact with liquid water.

Third, anion release results show perhaps the most striking and significant difference in the solution chemistries between the two test types. Anion concentrations in starting glasses are generally not reported because they are minor components (<0.1 wt %) and have been thought to have little effect on glass reactivity when present at these levels. However, the potential for anions to complex radionuclides² adds significance to their concentrations in the leachates. The concentrations of SO_4^{2-} , Cl^- , and HPO_4^{2-} in the leachates from the aged-glass tests were in the 200 to 10,000 ppm range, which is significantly larger than the 2 to 25 ppm range in the starting EJ-13 water and in the leachates from the as-cast glass tests.

Fourth, a marked difference was found in the organic carbon content between the test types. The increase in organic carbon in the aged-glass leachates is due to increased concentrations of formate (CHO_2^-) and oxalate ($\text{C}_2\text{O}_4^{2-}$). Both species are known to complex actinides in solution² and have the potential for affecting the solubility of the transuranics in solution.

Finally, the actinide content in the leachates for both test types has "truly" dissolved and particulate fractions. (The truly dissolved fraction passes through a final filter with a pore size of $50 \text{ \AA}$.) Greater than 90% of the transuranic elements in the as-cast glass leachates was in the particulate fraction, while more than 75% of the actinides in the aged glass leachates was truly dissolved. Also, the release of plutonium from the aged glass was several orders of magnitude greater than that from the as-cast glass, and a higher fraction of the released plutonium was dissolved.

Although analyses of the drip test data are not complete, several trends have been established. For the tests done with as-cast glasses, the glass/water reaction results in layers and secondary phases that form on the glass surface and are released during contact with slowly dripping water. The reaction products depend on the starting glass composition, and for the most part, retain Pu and Am within their structure and remain suspended in solution during testing. For aged glass, the initial release of radionuclides to solution differs strikingly from as-cast glass. Possibly because of the high anionic content of the water that is released from the aged glass/metal assembly, most transuranic elements released are dissolved at concentrations greater than observed with as-cast glasses. The initial reaction represents a release of radioactivity that

² J. I. Kim et al., Mater. Res. Soc. Symp. 44, 359-368 (1985).

depends on the extent of glass aging before liquid water contact. Whether this initial reaction represents a pulsed release that is only a perturbation in the total release is unknown at this time, but this behavior will be better understood as the tests continue.

3. Testing of West Valley Glasses

The West Valley Demonstration Project will produce glass containing high-level wastes generated during the reprocessing of commercial nuclear fuels at West Valley, New York. We are conducting static and vapor hydration (saturated steam) tests on a nonradioactive target composition, West Valley Reference 6 (WV6) glass. A fully radioactive West Valley glass will be tested when it becomes available.

The results from the static tests indicate that the WV6 glass is as durable as other reference high-level waste glasses, such as the SRL Environmental Assessment (EA) glass. The vapor hydration tests of the WV6 glass formed a variety of secondary phases as it corroded, including zeolites, phosphates, and uranium silicates. Whether they retain radioactive elements besides uranium or not will be determined during testing of the radioactive glass.

Drip tests (N3 series) similar to the N2 series described in Sec. IV.B.2 are being conducted with a simulated West Valley reference glass, ATM-10,³ that had been doped with Np, Pu, Am, and Tc. Leachates from the tests, which have been in progress since 1987, were removed twice during this year and analyzed. Of all the waste glass elements, the fractional releases of B and Li through 340 weeks of exposure are the greatest, followed closely by neptunium. Uranium, plutonium, and americium have fractional releases an order of magnitude (or more) lower than neptunium. This finding strongly suggests incorporation of the actinides into secondary phases or sorption onto the glass or stainless steel support. Figure IV-1 shows the cumulative solution mass of Np, Pu, and Am from three tests of the ATM-10 glass through the July 1994 samplings. We also found that the transuranics, plus thorium and uranium, may be incorporated into crystalline mineral phases, a likely candidate being brockite, a calcium-thorium-phosphate phase.

Another objective of the N3 tests is to identify the solid products formed by the glass reaction, the interactions between the glass and the 304L stainless steel supports, and the distribution of radionuclides between the glass and steel. Optical microscopy indicated increased quantities of clay and other secondary phases on both the glass and stainless steel supports with increasing test duration. The bottom of the glass was more likely to display substantial evidence of interaction with the stainless steel support than the top; likewise, the stainless steel at the glass bottom displayed more evidence of corrosion than the top. Rust deposits appeared in the area of welded support posts used in the test assembly. This finding is consistent with increased sensitization of the stainless steel in the weld area.

³ G. D. Maupin, W. M. Bowen, and J. L. Daniel, *Fabrication and Characterization of MCC Approved Testing Material--ATM-10 Glass*, Pacific Northwest Laboratory Report PNL-5577-10 (1990).

Fig. IV-1.

Cumulative Solution Masses of Transuranic Elements from Three Drip Tests with ATM-10 Glass

Embedded in the surface clay layer were particles, sometimes exceeding 200 nm in length, of a separate phase, having a composition consistent with brockite. The typical size of the observed brockite particles increased with the test duration. Small brockite particles, often 50 nm or less, were found on all test surfaces examined. These findings suggest continuous nucleation and growth of this phase.

A thorium phase containing substantial iron and titanium was observed within voids or pits in the glass and, to a lesser extent, on the surface between the glass and clay. It is probably related to the "amorphous" group minerals davidite $[(\text{Fe,Ce,U})_2(\text{Ti,Fe})_5\text{O}_{12}]$ or thorutite $[(\text{Th,U,Ca})\text{Ti}_2\text{O}_6]$. Like the brockite, the thorutite-like phase is more abundant on samples that have been reacted for long time periods.

These results will provide important input for use in modeling the durability of West Valley glass waste forms.

4. Use of Analytical Electron Microscopy to Analyze Glasses and Spent Fuel

Techniques continue to be developed for using analytical electron microscopy (AEM) to examine secondary alteration phases that are formed on the leached surfaces of waste glass and spent fuel, and that are present as colloids in the leachates of fully radioactive and simulated nuclear waste forms. The AEM is used for the analyses reported above and in Sec. IV.C, and consists of transmission electron microscopy (TEM) combined with X-ray energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Structural identifications are accomplished by using electron diffraction, either selected area electron diffraction or convergent beam electron diffraction.

Colloid examinations are being performed on samples collected by wicking the leachate through filters with an alcohol onto a "holey" carbon grid. Analysis of colloids present

in the leachate has permitted not only identification of colloidal phases but also insight into how colloidal particles are formed in the leachate.^{4,6}

New facilities have been set up for preparing TEM samples by methods other than ultramicrotomy. These methods have been used in other related glass testing efforts to provide new information on the microstructure of waste materials.

5. Immobilization of Plutonium Glass

A large amount (up to 50 tons) of plutonium will potentially become surplus as nuclear weapons are dismantled. The Department of Energy is considering several methods for improving safety during interim storage, decreasing the likelihood that the plutonium would be diverted back into the nuclear arsenal, and facilitating ultimate disposal. One method is to immobilize the plutonium in a glass matrix that could, if necessary, be placed in a geologic repository. Because no information is available on the long-term durability of a glass containing significant amounts (>1%) of plutonium, a series of glass corrosion tests has been started. Several glass formulations have been prepared, corresponding to SRL 202 glass containing 2 and 7 wt% PuO₂, and 2% PuO₂ plus 1.3% Gd₂O₃. Gadolinium is added to mitigate criticality problems during preparation, storage, and ultimate disposal. Initial results from these tests will be presented in the next report in this series.

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 the Yucca Mountain site. This multiple barrier system will be designed to limit the radionuclide release from the spent fuel, which is irradiated UO₂ in Zircaloy tubes. Long-term tests with both spent fuel and unirradiated UO₂ at 90°C and drip rates (EJ-13 water) of 0.075 and 0.75 mL every 3.5 days are in progress to determine the behavior and radionuclide release characteristics of spent fuel under the unsaturated conditions expected at the Yucca Mountain site.

1. Unsaturated Tests with UO₂ Samples

Unsaturated drip tests with unirradiated UO₂ pellets have been in progress for nine years. The tests were initiated to determine the feasibility of using the unsaturated drip test with spent fuel. While reactions with UO₂ are not completely analogous to spent fuel behavior, the reaction processes and the formation of secondary alteration products should be similar, because spent fuel is more than 95% UO₂.

⁴ J. K. Bates, J. P. Bradley, A. Teetsov, C. R. Bradley, and M. Buchholtz ten Brink, *Science* **256**, 649-651 (1992).

⁵ E. C. Buck, J. K. Bates, J. C. Cunnane, W. L. Ebert, X. Feng, and D. J. Wronkiewicz, *Mater. Res. Soc. Symp. Proc.* **294**, 199-206 (1993).

⁶ X. Feng, J. K. Bates, E. C. Buck, C. R. Bradley, and M. Gong, *Nucl. Technol.* **104**, 193-206 (1993).

The rate of uranium release from UO_2 samples in the 1- to 2-yr interval was high, ranging up to $14 \text{ mg}/(\text{m}^2 \cdot \text{days})$. Most of this release was attributed to the spallation of UO_2 granules. In the 2- to 9-yr interval, the rate decreased to an average of approximately 0.10 to $0.30 \text{ mg}/(\text{m}^2 \cdot \text{days})$. This decrease is thought to result from the formation of a dense surface mat of uranyl silicate phases on the glass that entrapped spalled particulate material.

Filtered and nonfiltered leachates were analyzed for yearly test intervals between 5 and 9 years. Only 2 to 6% of the released uranium passed through a 5-nm filter, with the remaining fraction being released in particulate form or reprecipitated as secondary uranyl phases on the test vessel walls. Examinations of filtered residues revealed the presence of UO_2 granules and elongated uranium silicate grains. The latter phase probably formed on the sample surface as crystals and became dislodged by dripping water during the biweekly leachate injections.

Leachate concentrations of Mg, Ca, K, and Si were found to be depleted relative to the starting EJ-13 leachate. The concentrations were typically reduced to ~10, 30, 30, and 55%, respectively, of the original EJ-13 composition values. Investigations by scanning electron microscopy (SEM) combined with EDS indicated that these cations had been incorporated into a distinct series of uranyl-bearing and clay alteration phases that had formed on the UO_2 pellet surfaces. Alteration minerals developed on the top surface of a sample exposed for 8 years were dominated by the phase boltwoodite $[\text{K}(\text{H}_3\text{O})\text{UO}_2(\text{SiO}_4) \cdot n\text{H}_2\text{O}]$, with lesser amounts of dehydrated schoepite $[\text{UO}_3 \cdot 0.8\text{H}_2\text{O}]$, other complex uranyl silicates, and clays.

Testing will proceed past the ninth year to determine if uranium release rates continue to vary and if the alteration products change. Archived spent fuel samples from these tests will be cross-sectioned to examine grain boundary corrosion, identify alteration minerals within the grain boundaries, and measure alteration depth.

2. Unsaturated Tests with Spent Fuel Samples

The objective of these tests is to measure the reactivity of spent fuel under a range of potential repository conditions. These drip tests employ fragments of two types of irradiated fuel, ATM-103 and ATM-106, which represent the majority of spent fuel types. The average burnup of each fuel is 30 MW-day/kg U for ATM-103 and 43 MW-day/kg U for ATM-106. The spent fuel and leachate have been examined at approximately six-month intervals for the last two years. The spent fuel matrix is reacting to form more stable mineral phases, analogous to the alteration products of unirradiated UO_2 (Sec. IV.C.1). A small fraction of the actinides are being released into the leachate, where they appear as dissolved species, colloids, and sorbed materials on the vessel walls. There appears to be a difference in actinide release behavior for the two fuel types, although both fuels produce colloidal material.

Phases similar to those identified as alteration products in weathered zones of uranium ore deposits and in the dissolution of unirradiated UO_2 formed as the spent fuel particles reacted and released their constituent elements into solution. Attached to one spent fuel particle was schoepite, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, which may have contained La, Ce, Pr, Nd, Sm, Am, and Cm. A second phase, which was deposited on the Zircaloy retainer, incorporated Cs, Ba, and Mo. This

phase was identified by AEM as a billietite-related alkali uranyl hydroxide hydrate of the form, $R(VO_2)_6O_4(OH)_6 \cdot xH_2O$, where R is an alkali metal.

The maximum fractions for the actinides and cesium released during four test intervals are shown in Table IV-1 for each fuel type. The maximum fraction released equals the ratio of the sum of the ionic, colloidal, and sorbed material in the leachate to the original amount in the fuel. The cesium fraction reflects the fraction of the reacted UO_2 matrix. The data indicated that the maximum fractions for Am, Cm, and Np are larger than the fraction for plutonium. In addition, the plutonium fraction for ATM-103, which included a large amount of colloidal material, after 581 days of reaction was an order of magnitude greater than that for ATM-106. Nonetheless, the cesium fractions for the two fuel types were the same order of magnitude.

Table IV-1. Maximum Fraction of Actinides and Cesium Released from Spent Fuels in Drip Tests (90°C and 0.75 mL water every 3.5 days) as a Function of Total Reaction Time

ATM-106	Maximum Fraction Released ^a			
	113 days	271 days	482 days	581 days
Am-241	2E-7	7E-7	6E-7	4E-7
Cm-244	2E-7	2E-46	1E-6	1E-6
Np-237	N.A. ^b	N.A.	2E-5	7E-6
Pu-239	8E-8	2E-7	5E-7	1E-7
U-238	7E-8	4E-7	N.A.	N.A.
Cs-137	1E-6	1E-5	9E-5	2E-4
ATM-103	120 days	275 days	482 days	581 days
Am-241	6E-6	2E-8	7E-8	1E-5
Cm-244	8E-5	2E-7	2E-7	4E-5
Np-237	N.A.	N.A.	7E-6	3E-4
Pu-239	1E-8	2E-9	8E-9	9E-7
U-238	1E-7	1E-8	N.A.	N.A.
Cs-137	5E-6	1E-6	8E-6	2E-4

^aFractions released during intervals between reaction times.

^bN.A. indicates data are not available.

The estimated reaction rates were 0.04-0.5 mg/(m²•day) for ATM-103 and 0.3-1.2 mg/(m²•day) for ATM-106. These values are similar to those obtained for unirradiated UO_2 under unsaturated conditions (Sec. IV.C.1) but greater than those previously reported for

unirradiated UO_2 reacted under saturated conditions⁷ during intervals when the uranium release rates were the lowest.

The actinide contents of the colloids released during the 482-to-581 day interval were determined as a function of size by sequential filtration through 1000, 100, and 50 nm filters, followed by a separate filtration through a 5 nm filter. There were some similarities and some differences for the two fuels. The similarities included (1) a bimodal distribution for curium, with 50% of the released curium in particles $\geq 1000 \mu\text{m}$ and 50% in particles $< 50 \text{ nm}$, and (2) the neptunium particles were $< 100 \text{ nm}$. One difference was that the Am and Pu particles from ATM-103 were $< 100 \text{ nm}$ but were $> 100 \text{ nm}$ from ATM-106. With the exception of neptunium, the majority of the transuranic elements in the leachate was associated with colloids.

The results indicate that the alteration products on the spent fuel are similar to the products found during oxidative dissolution of uranium ore deposits and during the unsaturated dissolution of unirradiated UO_2 . The spent fuel reaction rate in the unsaturated tests appears to be greater than that observed under saturated conditions. Our tests have also shown that colloids can be significant means of release for the transuranics. The current tests will be continued for an undetermined period, and additional spent fuel will be obtained for testing.

D. *Vitrification of Low-Level Waste*

1. Development of Low-Level Glass Waste Forms

The goal of this activity is to demonstrate the feasibility of vitrifying several types of low-level mixed wastes (LLMW) generated as a result of research activities at the ANL-East site. (Mixed wastes contain both hazardous and radioactive components.) Past laboratory studies using simulated wastes have shown that this LLMW can be successfully vitrified and the toxic components treated. Furthermore, these studies concluded that treatment of LLMW would result in significant overall volume reductions of the waste streams. This advantage adds an economic incentive to using vitrification as a treatment technology.

The objectives of the present study were to identify and produce glass formulations made with actual LLMW from the ANL-East site. These glass formulations were designed such that together they comprise a compositional envelope that could eventually be used in the full-scale vitrification of LLMW. Several criteria were used to select glass formulations for inclusion in the compositional envelope: (1) the formulation melts at temperatures available with commercially available vitrification systems, (2) the melted mixture has a viscosity amenable to pouring at the melt temperature, and (3) the resultant waste form passes the Toxicity Characteristic Leaching Procedure (TCLP), which constitutes the regulatory basis for determining whether a material is hazardous.

⁷ D. W. Shoesmith and S. Sunder, *An Electrochemistry-Based Model for the Dissolution of UO_2* , Swedish Nuclear Fuel and Waste Management Report SKB 91-63 (1991).

During the past year, 15 crucible melts were produced in crucibles at 1100°C. Nine of the melts were prepared with actual LLMW to identify the glass compositional envelope, and six melts were "spiked" with additional hazardous metals to demonstrate that these metals can be stabilized. All the glasses were examined to determine whether they had fully melted and could be poured from the melt crucible. The melts were further tested for their leachability characteristics with the TCLP.

The chemical composition of the 15 glasses are presented graphically in Fig. IV-2 for the phase diagram $\text{SiO}_2 + \text{Al}_2\text{O}_3/\text{B}_2\text{O}_3/\text{R}_2\text{O}$, where R denotes an alkali metal. The light gray region indicates the known glass-forming region for this system. The stars denote the three ANL waste streams: storage tank sludge (STS), evaporator concentrator bottoms (ECB), and high efficiency air particulate filter media (HEPA). The circles with dots labeled SWA and SWB are two blends of STS, ECB, and HEPA that were mixed for this study. The formulations of SWA and SWB represent the estimated annual generation of the individual waste streams that will require vitrification. The expanded portion of the diagram (right side) indicates the compositions of the individual crucible melts that were produced (Nos. 1 to 15). The black circles with white numbers indicate crucible melts, and the white circles with black numbers indicate spiked melts. The dark gray region indicates the compositional envelope containing between 72 and 90 wt% of SWA or SWB, with the balance being glass-forming additives. All melts could be poured, but melts 4, 8, and 9 poured with some difficulty. All as-cast glasses easily passed the TCLP. In the future, tests will be performed on these glasses to show that the radioactive components have been stabilized.

Fig. IV-2. Compositional Envelope for Glasses Suitable in Treatment of Argonne Mixed Wastes. (See text for explanation.)

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

Waste forms made of glass-crystal composite are being investigated for the eventual disposal of LLMW materials. These waste forms are being developed as an alternative to traditional vitreous and cementitious waste forms, because a wider range of wastes can be treated. The composite combines both the excellent durability exhibited by predominantly crystalline waste forms, such as Synroc, with the advantages of using vitrification for waste processing. In the composite (Fig. IV-3), crystalline phases such as iron-rich spinels $[(\text{Fe}, \text{Zn}, \text{Cd}, \text{Ni})(\text{Al}, \text{Fe}, \text{Ti}, \text{Cr})_2\text{O}_4]$, zirconolite $(\text{CaZrTi}_2\text{O}_7)$, titanite (CaTiSiO_5) , perovskite (CaTiO_3) , feldspar [anorthite variety $(\text{CaAl}_2\text{Si}_2\text{O}_8)$], augite $[(\text{Ca}, \text{Mg}, \text{Fe}, \text{Ti}, \text{Al})_2(\text{Si}, \text{Al})_2\text{O}_6]$, and pseudobrookite $(\text{Fe}_2\text{TiO}_5)$ can host the majority of the radioactive elements and hazardous metals present in the LLMW streams. The glass fraction of the composite serves as a binder for the crystals and also incorporates elements excluded from the crystal structures.

Fig. IV-3. Scanning Electron Microscope-Backscattered Electron Image of Unreacted Sample: (a) Unidentified Ca-Na-U Phase, (b) Uranium-Rich Zirconolite, (c) Iron-Rich Magnetite, and (d) Titanite

Synthesis experiments to date have shown that Cr, Ni, Pb, Cd, U, and Ce (as a surrogate for Pu) from simulated waste streams can be incorporated into crystals, with all elements except lead being strongly fractionated into the crystalline phases. Crystalline phases also have the potential to incorporate other hazardous elements into their structures, including Tc, As, Ba, and Th, and glass network-breaking elements, such as Na, F, S, and P.

The composites have been subjected to static leach tests at 90°C and vapor hydration tests at 200°C, and the durability results compared with those from other waste materials. The composites were also tested with the TCLP to determine their applicability for Environmental Protection Agency (EPA) licensing. Results from the durability tests indicated that the composites have corrosion-resistant properties for Si, Al, U, and Na that are similar to, or better than, those of simulated high-level waste glasses (e.g., SRL 202U). Figure IV-4 shows the much lower uranium release achieved in two composites (one with zirconolite, the other without) compared with a borosilicate glass initially doped with a similar concentration of uranium (SRL 202U). Samples that have incorporated uranium into crystalline phases, such as zirconolite, have the lowest overall uranium release rates, as also shown in Fig. IV-4. This finding reflects the high durability of the crystalline phases relative to predominantly glassy materials. In the vapor hydration tests, the formation of secondary reaction products on the composite sample surfaces is minimal, with most of the alteration phases being composed of clays, iron oxides, and calcium-bearing phases. Radionuclide and hazardous elements in these phases are also minimal, and are thus being retained in the composite waste form. Results from TCLP tests indicate release rates for the hazardous metals that are generally below EPA-established limits for mixed waste declassification. Exceptions occur when waste loadings of specific elements are unusually high, for example, 16% NiO and 20 to 25% CdO. Samples with these higher concentrations are being tested to find the maximum waste loadings that will still allow the composites to pass the TCLP test.

Fig. IV-4.

Normalized Uranium Release for Two Samples of Glass-Crystalline Composites during Static Leach Tests at 90°C. Both samples have near identical compositions, except Zr and Ti have been added to the G2 sample to induce the formation of zirconolite. Also shown is release for SRL 202U glass.

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

The objective of this effort is to assess the long-term durability of borosilicate waste glasses being developed by Pacific Northwest Laboratory (PNL) for stabilization of low-level radioactive waste. An extensive suite of tests is being performed with a wide range of compositions for the candidate waste glass. Short-term corrosion testing has been used to assess the effects of the B, Al, and Ca concentrations in the glasses on their durabilities. Static leach tests are being performed at temperatures of 20, 40, 70, and 90°C for reaction times up to, or beyond, one year. The extent of glass corrosion in these tests will be determined by using

leachate analyses, and the corrosion mechanism will be determined from the results of glass analyses. In addition, vapor hydration tests are being performed at temperatures of 70, 120, 150, 175, and 200°C for reaction times up to, or beyond, one year. These tests will help identify alteration phases formed and their effect on the glass corrosion rate. The static and vapor hydration tests will provide information regarding the temperature and time dependence of the corrosion rate, and these results will be used to describe the long-term durability of the low-level waste forms.

E. *Characterization of Contaminated Soils and Residues*

Electron microscopy techniques are being used to examine uranium contamination at two weapons production sites (Fernald, OH, and Portsmouth, OH); plutonium-contaminated coral sand from a weapons testing site (Johnston Atoll); and incinerator residues from Los Alamos National Laboratory and Rocky Flats Plant. Optical microscopy, SEM, and AEM are used in characterizing these radionuclide-contaminated materials.

During 1994, the focus was on analyzing soils surrounding an incinerator at the Fernald site. The uranium-bearing phases were identified as uranyl(VI) phosphate (meta-autunite), uranium(IV) oxide (uraninite), uranyl(VI) silicate (soddyite), and uranium(IV) metaphosphate [$\text{U}(\text{PO}_3)_4$]. A tetragonal calcium uranyl phosphate was determined to be the major uranium-bearing phase. Carbonate leaching in an oxygen environment removed some of the U(IV) phases; however, $\text{U}(\text{PO}_3)_4$ was not affected by any chemical remediation technology.

Analytical electron microscopy has also been used to determine the effect of chemical treatment on the uranium phases in the soil. High-resolution TEM imaging revealed no evidence of surface alteration in the uranium metaphosphate particles from treated soil; however, in uranium oxide particles, the surface was oxidized and was etched in many regions. In some cases, uranium was only partially leached from the mineral phases. These observations suggest that an additional physical extraction procedure must be applied to remove all the uranium.

We have also studied the Pu and U contamination that resulted from the abort of a nuclear device over Johnston Atoll in the Pacific Ocean in the early 1960s. Plutonium and uranium contamination occurs in "hot spots," which are fragments of bomb components. The Pu and U have both been oxidized by exposure to the environment. Using characterization techniques that included radiochemical and wet chemical analysis, we found that plutonium is migrating from the metal into the sand, possibly through complexation with carbonate.

Incinerator residues from Rocky Flats have also been characterized. Plutonium was mainly in the form of a reduced oxide PuO_{2-x} . Other plutonium-bearing phases were also found, including evidence of plutonium incorporation into a silicate glass in the ash.

In summary, our characterization techniques can help design an optimal remediation approach for a particular contaminated site, because they provide information on the form of the contaminant and the likely success of any remediation method. We are proposing that the techniques used in characterizing radionuclides in the Fernald and Johnston Island soils be applied at other DOE remediation sites.

V. SEPARATION SCIENCE AND TECHNOLOGY

A high-priority need exists to develop processes that can be applied to restore DOE sites to conditions that meet state and federal environmental regulations. The Division's work in separation science and technology is concerned with developing such processes for radioactive, mixed, and hazardous wastes. The TRUEX (TRansUranic EXtraction) solvent extraction process continues to be developed and demonstrated for recovering TRU elements from solutions containing a wide range of nitric acid and nitrate salt concentrations. An important part of this effort is developing and validating the Generic TRUEX Model (GTM). The GTM allows users to design flowsheets for specific waste streams and estimate the cost and space requirements for implementing a site- and feed-specific TRUEX process. The GTM is also a useful tool for plant operators to vary, monitor, and control the process once it is in place. Flowsheets for other solvent extraction processes are also being designed and tested.

Our other work in separation science and technology includes the development of (1) a process based on sorbing modified TRUEX solvent on magnetic beads to be used for separation of contaminants from radioactive and hazardous waste streams, (2) evaporation/concentration technology for processing radioactive solutions, and (3) a process that uses low-enriched uranium targets in place of high-enriched uranium for production of ^{99}Mo for nuclear medicine uses. Several other projects are also underway to develop advanced processes for treating radioactive, mixed, and hazardous wastes.

A. *Development of Solvent Extraction Processes*

Although our separation science and technology activities have broadened into several new areas, solvent extraction R&D is still a significant fraction of our development work, in particular, the TRUEX process. The TRUEX extractant is octyl(phenyl)-N,N-diisobutylcarbamoyl-methylphosphine oxide (abbreviated as CMPO), which is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX solvent. The TRUEX flowsheet includes multistage extraction/scrub sections that recover and purify the TRU elements from the waste streams and multistage strip sections that separate TRU elements from each other and the solvent. The GTM continues to be improved to make it more accurate and easier to use for TRUEX flowsheet calculations of user-specified waste streams. In addition, our ability to design and run flowsheet demonstrations in multistage centrifugal contactors has moved beyond the TRUEX process to other solvent extraction processes such as the strontium extraction process (SREX), newly invented by Chemistry Division personnel.

1. Improvements to Generic TRUEX Model

The main function of the GTM is flowsheet calculations for user-specified waste streams to be treated by TRUEX or other solvent extraction processes. The GTM was assembled with user-friendly spreadsheet software (based on Microsoft Excel) and operates on a Macintosh or IBM-compatible personal computer. During 1994, we released two new versions of the GTM, designated 3.0.1 and 3.1. In GTM version 3.0.1, we improved the models used for determining the distribution ratios of (1) Zr and F for the TRUEX process and (2) Rb, Cs, Na, and Ca for the

TRUEX-SREX process (see Sec. V.A.4). The new distribution ratio models for these components were based on new experimental data obtained for these processes by the ANL Chemistry Division. Other improvements included the elimination of convergence problems when the extraction efficiency was less than 85% and the ability to change the number of iterations needed to converge a flowsheet calculation. Also added were the capabilities to specify, in the user-friendly front end, multiple organic feeds, reroute of aqueous or organic effluents, and solvent composition; these capabilities, although available in the previous version, could not be easily accessed through the front end.

The major upgrade to GTM version 3.1 was the addition of many new species to our speciation model. In prior versions of the GTM, the calculation method for speciation was limited by the maximum size of an equation in a single cell within an Excel spreadsheet. The new method, included in this version, removes this limitation. This gives us the ability to easily calculate the extraction behavior of more species. All the new species added to the speciation model are listed in Table V-1. Also improved in this version is the model used to calculate the loading of the solvent for the TRUEX-SREX process.

Future work will include adding components that are found in the high-level waste that was generated by the Idaho Chemical Processing Plant (e.g., Hg and Cl) and improving the extraction models for species already in the GTM (e.g., Bi and Zr).

2. Validation of the Generic TRUEX Model

The purpose of this validation study was to compare the results predicted by the GTM for three countercurrent flowsheet experiments run at the Power Reactor and Nuclear Fuel Development Corp. (PNC) of Japan. The PNC experiments were performed without our TRUEX processing knowledge or the use of the GTM. As a result, the PNC flowsheets ran into problems, such as precipitation in the scrub section, and did not meet processing goals in the stripping of plutonium.

Flowsheet conditions for the PNC experiments were simulated by using the GTM. Since no information was available regarding stage efficiency for the mixer-settlers used by PNC, we ran the GTM with four stage efficiencies (70%, 80%, 90%, and 100%). The results allowed us to identify which value best simulated the PNC experiments. Fig. V-1 shows the concentration profiles calculated for cerium in the organic phase of the extraction/scrub; also shown are the PNC experimental results. Figure V-2 shows a similar comparison for the strip section. From these two figures and calculated and measured data for the aqueous phase, we concluded that stage efficiency of 90% best describes the cerium profile for the extraction section and 100% for the strip section.

Results similar to Fig. V-1 were obtained for Eu and Cm in the extraction section. For the strip section, results similar to Fig. V-2 were obtained for Am, Cm, and Eu.

All the flowsheets were simulated by using GTM version 3.0.1. This version of the GTM does not account for nitrate complexation. This caused the GTM to overestimate the amount of rare earth being stripped. In earlier work on developing a TRUEX flowsheet for

Table V-1. New Species Included in GTM Version 3.1
(Ox = oxalate, RE = rare earth)

AlF_3	NpF_3^+
AlF_4^-	NpF_4
Bi^{3+}	NpNO_3^{3+}
$\text{Bi}(\text{F})_3^{3+}$	NpOx_3^{2-}
$\text{Bi}(\text{F})_2^{2+}$	NpOx_4^{4-}
$\text{Bi}(\text{NO}_3)_2^{2+}$	PuNO_3^{3+}
$\text{Bi}(\text{NO}_3)_2^+$	$\text{RE}(\text{NO}_3)_2^+$
$\text{Bi}(\text{OH})_2^{2+}$	$\text{RE}(\text{NO}_3)_3$
$\text{Bi}(\text{OH})_2^+$	$\text{RE}(\text{NO}_3)_4^-$
$\text{Bi}(\text{OH})_3$	$\text{RE}(\text{F}_3)$
$\text{Bi}(\text{OH})_4^-$	$\text{RE}(\text{F}_4^-)$
$\text{Bi}(\text{SO}_4)_2$	$\text{RE}(\text{NO}_3)_2^{2+}$
$\text{Bi}(\text{SO}_4)_2^{2+}$	$\text{Th}(\text{NO}_3)_2^{2+}$
$\text{Cd}(\text{NO}_3)_2$	ThF_3^+
CdNO_3^+	ThNO_3^{3+}
FeF_3	ThOx_3^{2-}
FeNO_3^{2+}	UO_2NO_3^+
$\text{Np}(\text{NO}_3)_2^{2+}$	$\text{Zr}(\text{NO}_3)_2^{2+}$
$\text{Np}(\text{NO}_3)_3^+$	$\text{Zr}(\text{NO}_3)_4^+$

recovering TRU elements from aluminum-clad PuO_2 targets,¹ the americium stripping in the presence of high concentrations of rare earth was also underestimated. We assumed that this problem is due to overestimating the nitrate activity in the aqueous strip solution because rare earth-nitrate complexes were ignored. The formation of rare earth-nitrate complexes lowers the amount of uncomplexed or free nitrate. Thus, GTM version 3.1 (which includes the nitrate complexation) was used to recalculate our PNC-related predictions for the strip section. As expected, by including nitrate complexes, we significantly improved the GTM's fit to the PNC stripping data. Details of this GTM validation study will be published in 1995.

¹ L. K. Felker and D. E. Benker, *Application of the TRUX Process to Highly Irradiated Targets*, Oak Ridge National Laboratory Report ORNL/TM-12784 (March 1995).

Fig. V-1.

Concentration Profile for Cerium in Organic Phase as Function of Stage Efficiency for Extraction/Scrub Section. Shown in this figure are the GTM simulations for 70%, 80%, 90%, and 100% stage efficiency and the experimental results obtained by PNC for one countercurrent run (circles).

Fig. V-2.

Concentration Profile for Cerium as a Function of Stage Efficiency for Organic Phase in Strip Section. Shown in this figure are the GTM simulations for 70%, 80%, 90%, and 100% stage efficiency and the experimental results obtained by PNC for one countercurrent run.

3. Technical Support

The TRUEX process has been selected as the reference treatment for the high-level liquid and calcined wastes being stored at Idaho National Engineering Laboratory (INEL). A research effort is underway there to design TRUEX flowsheets for removing actinides from the sodium-bearing waste and the dissolved calcine at INEL's Idaho Chemical Processing Plant. The GTM is being used as a guide to this experimental program.

The extraction behavior of mercury in the TRUEX process is of interest because of its high concentration in the INEL high-level wastes. Significant quantities of mercury (two metric tons of mercury at concentrations of 100 to 900 mg/L) have accumulated in the sodium-bearing high-level waste as a result of reprocessing DOE and naval fuels. Mercury was used as a catalyst in the dissolution of aluminum-clad fuels and, following uranium recovery, was contained in radioactive raffinate streams. Calcination of the raffinates and subsequent nitric acid scrubs of the off-gas treatment concentrated the mercury in the tanks containing the sodium waste. Also present in the waste at significant concentrations is chloride. Neither chloride nor mercury has been included in the GTM.

In experimental studies at INEL on mercury extraction from nitric acid and simulated sodium-bearing waste, Herbst et al.² have shown that mercury is effectively extracted as a chlorocomplex in solutions with excess chloride compared with the mercury concentrations. The GTM is being expanded to include mercury and chloride by adding models for the extraction behavior of these two species and all their aqueous-phase speciation. The extraction model for mercury will be developed from our own data and those of Herbst et al.² Data on the extraction of hydrochloric acid are available from the literature, as are metal-chloride and mercury-anion complexation constants.

4. Flowsheet Demonstrations

We are demonstrating the new flowsheets being developed for the cleanup of nuclear waste by Horwitz and coworkers in the ANL Chemistry Division. These flowsheets are the TRUEX-SREX process, which combines the TRUEX and the SREX (strontium extraction) extractants; the SREX-NEPEX process, which combines the SREX and NEPEX (neptunium-plутonium extraction) extractants; and the SREX process by itself. The TRUEX extractant, CMPO, selectively extracts and partitions Am, Pu, and U along with bismuth and the lanthanides. The SREX extractant, a crown ether called 4,4'(5')-di-*t*-butylcyclohexano-18-crown-6 (also referred to as CE), selectively extracts and partitions Sr, Pb, and, to some extent, Tc. The NEPEX extractant, tributyl phosphate (TBP), selectively extracts and partitions Np(IV), Pu, and U. Combining extractants appropriately would reduce the number of steps in the pretreatment of the dissolved sludge waste in Hanford single-shell tanks while achieving the same waste segregation. Pretreatment would greatly reduce the amount of nuclear waste that has to be vitrified, with an attendant major reduction in waste disposal costs.

In multistage minicontactor (2-cm dia) tests, both the TRUEX-SREX and the SREX-NEPEX processes exhibited major problems that had not been evident in batch tests. For each process, areas were identified where further work is required. In the TRUEX-SREX test, the extraction of strontium by the crown ether was less than expected, a second organic phase formed in the extraction section, and some bismuth oxalate precipitated in the scrub section. In the SREX-NEPEX process, the strontium formed a sticky precipitate with the crown ether that completely shut down one contactor stage.

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).

To solve the precipitation problem encountered in testing the SREX-NEPEX process, a SREX process was developed for a solvent (PS 19) of 0.10M CE in 1-octanol. Because it has neither TBP nor CMPO, this solvent does not extract Np or Pu. The key goals were to remove strontium from the aqueous raffinate by a factor of 10^5 and to remove barium from the strontium by a factor of 10. We also sought to separate strontium from the transuranic and lanthanide elements. This last goal was attained easily as there was neither CMPO nor TBP in the PS 19 solvent. The final flowsheet for this SREX process, shown in Fig. V-3, was demonstrated in a 24-stage minicontactor. The separation of strontium from barium was achieved with

Fig. V-3. SREX Flowsheet for 24-Stage Minicontactor Test using 0.1 M Crown Ether in 1-Octanol as Solvent. Flow rates in milliliters per minute are shown as numbers in parentheses.

good hydraulic performance throughout the test. The strontium concentration in the strip effluent was 40 times higher than that for barium, which exceeded our design goal. Conversely, the barium concentration in the aqueous raffinate from the extraction section was 40 times higher than that for strontium. While this extraction separation was good and represents a decontamination factor of 10^3 for strontium, our goal was a factor of 10^5 . Thus, the extraction section was not as effective in removing strontium as expected. Modeling of this test with the GTM indicated that the results could be explained by assuming a stage efficiency for strontium extraction of about 60%. At this stage efficiency, one would need 12 to 14 more extraction stages to reach a strontium decontamination factor of 10^5 . Since the TRUEX-SREX results also indicate a stage efficiency of 60% for strontium extraction by crown ether, more contact time may be needed to

achieve the desired high stage efficiency for strontium in the extraction section. If this is the case, the centrifugal contactor can be redesigned to give a longer residence time in the mixing zone. With a suitably redesigned contactor, more extraction stages might not be required.

Except for Sr and Pb, the other metal ions in the feed to the SREX process (Bi, Np, Sm, Tc, and U) ended up in the aqueous raffinate along with the barium. The Sr and Pb, which are both extracted by the crown ether, were expected to be stripped out by the low acid scrub and end up in the strip effluent. This was true for strontium and for some of the lead. However, most of the lead, which is extracted more strongly than strontium by the crown ether, ended up in the acid rinse effluent and the organic effluent. Further SREX work is needed to find an appropriate stripping agent for lead so that it all appears in the strip effluent. Overall, these results show that the SREX process works. It also points to several areas where further work is needed to optimize the process and achieve the design goals in an efficient manner. We will soon be starting work on the CSEX-SREX process, where the CSEX extractant is a new crown ether that selectively extracts cesium and, to some extent, sodium.

5. Centrifugal Contactor Development

We have been modifying the basic design of the ANL centrifugal contactor as necessary to adapt it for specific solvent extraction processes as well as for related uses. (See previous report³ for schematic of basic contactor design.) This past year we built multistage 2-cm contactors for Pacific Northwest Laboratory (PNL) and Lockheed Idaho Technology Co. (LITCO). These contactors were designed so that PNL and LITCO could carry out pilot-scale tests of solvent extraction flowsheets, especially the TRUEX process, for cleaning up the nuclear wastes at their sites. The basic design for the 2-cm centrifugal contactor was modified based on PNL requests and on our own testing experience with the original design. A 12-stage bank of the improved contactors is shown in Fig. V-4.

Because of programmatic changes, PNL has not had a chance to use their 2-cm contactor; LITCO is now setting up their 2-cm contactor. We will be working with LITCO as they use the 2-cm contactors to evaluate TRUEX and SREX processes for waste cleanup.

B. *Development of Separation Technologies for Radioactive and Hazardous Wastes*

1. Magnetically Assisted Chemical Separation

The magnetically assisted chemical separation (MACS) process is being developed for treating radioactive and hazardous waste streams, including waste tank sludges and supernatants in underground storage tanks at the DOE Hanford site. Transuranic-containing waste is of primary concern because of its potential hazard resulting from the long-lived radioactive components. This project will develop compact, economic, in-tank or near-tank processes for

³ M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1991*, Argonne National Laboratory Report ANL-92/15, p. 103 (1992).

Fig. V-4. Twelve-Stage Bank of Improved 2-cm Contactors

removing contaminants (TRU, Cs, Sr) from waste solution for remediation efforts at Hanford and other DOE sites.

The MACS process combines the selective and efficient separation afforded by chemical sorption with the physical separation provided by magnetic recovery of ferromagnetic particles. The recovery of Cs, Sr, and TRU uses magnetic particles coated with either a (1) selective ion exchange material (e.g., silicotitanates, resorcinol) or (2) an organic-complexant-containing solvent such as CMPO and TBP. These coatings selectively extract the contaminants from solution based on their chemical nature. Once the particles are removed from solution with a magnet, the contaminant can either be (1) left on the loaded particles and added to a glass feed slurry or (2) stripped into a small volume of solution to regenerate the extracting particles. Our efforts during 1994 focused on developing a new contactor/separator design for the MACS process and evaluating TRU and cesium separation with magnetic particles.

a. Contactor/Separator Design

We have designed a fluidized-bed system for laboratory-scale testing of the MACS process (Fig. V-5). In the fluidized bed, paramagnetic charcoal/magnetite particles coated with CMPO will be mixed with TRU elements in solution. The fluidized bed is designed for a 10-L capacity operated in a batch countercurrent fashion. The TRU elements are extracted by the CMPO, and once loaded, the charcoal/magnetite particles are easily separated from solution by the application of an external magnetic field. The process operates like a conventional multistage pulsed column used in solvent extraction, except that one phase is a solid, and pulsing is done magnetically rather than mechanically. The magnetically stabilized fluidized bed permits a

Fig. V-5. Diagram for MACS Fluidized-Bed Process

compact design and a limited number of mechanical parts compared to those needed for solvent extraction and ion exchange separation.

b. Evaluations of Element Separation with Magnetic Particles

During the past year, we evaluated the performance of polymeric-coated magnetic particles containing an absorbed layer of CMPO diluted by TBP. In a series of experiments, these particles were tested for their ability to extract Am and Pu from nuclear waste solutions similar to those at the Hanford site (i.e., waste from the Plutonium Finishing Plant, supernatant from the single-shell tank, and dissolved sludge from the single-shell tank). In general, the partition coefficients obtained (i.e., concentration of TRU element on magnetic particles divided by concentration of TRU element remaining in solution) were quite high, up to 16,000 for americium and 40,000 for plutonium. These values are greater than those expected based on results of conventional liquid/liquid extraction studies. Also, the extraction proceeded with rapid kinetics. The absorbed Pu and Am were stripped from the magnetic particles by using alcohols. In a one-batch stripping operation, we recovered 95% of the americium and 99% of the plutonium. The overall extraction/stripping operation reduced the TRU-containing waste volume by a factor of 400. Overall, the results indicate that a suitable MACS particle for TRU separation from Hanford waste had been found.

In a collaborative study with Bradtec, Inc., we sought to develop magnetic particles coated with absorbents selective for cesium removal from the supernatant in the Hanford tank wastes. Measurements of partition coefficients at Bradtec indicated that MACS particles

coated with either crystalline silicotitanate or resorcinol formaldehyde show limited promise for removing cesium from the Hanford supernatant. In gamma-irradiation tests at CMT, Bradtec-manufactured MACS particles were exposed to a gamma dose equivalent to 100 cycles of use. This irradiation decreased the loading capacity and partition coefficients for the particles by more than 75%. The particles demonstrated high sensitivity to radiolytic damage owing to the degradation of the polymeric regions. These results were supported by optical microscopy measurements of the gamma-irradiated particles. Overall, use of MACS particles for cesium separation under nuclear waste conditions appears to be only marginally effective. No further work on the MACS process is planned.

2. Advanced Evaporator Technology

A program was started during 1994 to determine whether a Compact Processing Unit (CPU) containing an evaporator and concentrator would remove the significant amount of water that will likely be added to nuclear waste solution in underground storage tanks during retrieval operations at Hanford. The initial focus was on processing supernatants from Hanford's underground storage tanks to remove cesium by ion exchange and prepare it for disposal. However, early estimates indicated that the volume of waste would increase by at least a factor of three through water addition. Further, approximately 30 wt% of the current waste inventory at Hanford is already water. To minimize the volume of waste requiring treatment and disposal, this water must be removed. In fact, before waste processing in the low-level vitrification facility at Hanford, the water must be removed to improve operation of the melters and reduce the size of the facility's off-gas system. Decontaminated water recovered from the evaporators could be recycled to support further retrieval operations and/or discharged to an effluent treatment plant on the site.

A conceptual design for the evaporator/concentrator CPU is shown in Fig. V-6. The bulk of the water is removed by the evaporator; additional concentration (water removal) is completed in a concentrator specially designed to handle high solids concentrations (slurries). The slurry discharged from the evaporator/concentrator system would be capable of being fed directly

Fig. V-6. Processing Scenario for Evaporator/Concentrator Unit

into a vitrification plant. If a high solids slurry is not desired, the concentrate from the evaporator can be routed around the concentrator unit, as shown by the dotted line in Fig. V-6. Distillate from the concentrator would be returned to the evaporator for reprocessing. In addition to processing cesium-free salt solutions, the evaporator/concentrator system is designed to test the feasibility of processing nitric acid regeneration (product) solutions from the cesium removal process.

Based upon evaluations this year, we determined that an evaporator/concentrator CPU for processing DOE tank waste might take several forms, depending on availability of auxiliary services, desired bottoms-product consistency, desired distillate-product purity, etc. For example, where a thick bottoms slurry is desired (e.g., where bottoms are fed to a melter), the evaporator should be followed by a concentrator. Whether that concentrator should be closely linked to the evaporator or located in a melter facility needs to be considered because of storage and handling problems associated with the thick concentrator-bottoms slurry. In some cases, other processing (e.g., neutralization of evaporator bottoms) is necessary between the evaporator and the concentrator. In other cases (e.g., where bottoms containing very few precipitated solids are desired), no concentrator is needed. No further work on an evaporator/concentrator CPU is planned; however, we will assist Oak Ridge National Laboratory in the design and testing of a new mobile evaporator.

3. 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 the decontamination and decommissioning (D&D) of plants and equipment. One such development effort in CMT focuses on the *in situ* decontamination of equipment (e.g., piping systems, storage tanks) in production plants. Our work will address the problem on two fronts: (1) the pursuit of suitable methods for reducing the interior contamination, and (2) the design of a treatment system for processing waste solutions that result from the decontamination efforts. Initial D&D activities will center around the decontamination of TRU-contaminated equipment, with the focus on plutonium contamination and the subsequent processing of the liquid wastes. Based upon what we learn from literature surveys and laboratory tests, these processes may be applicable to many other types of equipment contaminated by radioactive and possibly hazardous components.

Two types of radioactivity are expected in the equipment to be decontaminated: activity that is easily removed from the surface by rinsing or washing, and activity that is incorporated into the granular structure of the material. This second type is generally contained within the first 3-5 μm of material. One possible method for removing this activity is "chemically milling" the interior surface of the equipment. Once the material is removed, any residual activity can be flushed from the system.

Treatment of the solutions coming from chemical milling or other D&D operations will focus on volume reduction and production of a waste form suitable for disposal at DOE's Waste Isolation Pilot Plant. The treatment system must be designed for portability, ease of operation and maintenance, operator protection, and criticality safety. Our past experience with

agitated-film concentrators has shown that the Artisan Rototherm⁴ mounted in a glovebox may be capable of fulfilling these criteria.

4. Closed-Loop Off-Gas System

A conceptual design has been developed for a closed-loop process that will prevent the direct release of toxic off-gases during incineration or vitrification of hazardous and mixed radioactive wastes. This process would virtually eliminate the potential for release of hazardous or radioactive materials to the environment during high-temperature thermal treatments. A closed-loop off-gas system (Fig. V-7) has been added to an existing 250,000 Btu/h (75 kW thermal) fluidized-bed combustor to demonstrate this CMT-designed process. In initial tests, the combustor

Fig. V-7. Schematic for Closed-Loop Off-Gas System

⁴ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, p. 84 (1994).

was operated in an open loop (top half of Fig. V-7) to demonstrate the removal of combustion-product CO_2 in a fluidized bed of CaO (lime), and particulates were removed with hot gas candle filters. An absorbent solution treatment system (bottom half of Fig. V-7) is now being developed for removing CO_2 from a side loop. High CO_2 concentrations can be maintained in the recirculating gases, and this improves the performance of the commercial processes that are used to purify gases and produce CO_2 . With the absorbent solution process, CO_2 and water vapor go through two changes of state before release, effectively separating these combustion products from contaminants released during incineration or vitrification. Oxygen is added to support combustion and minimize off-gas volume; contaminants are separated by precipitation and filtration and recycled for further treatment. Incineration systems with the closed-loop off-gas process would have a high throughput and accommodate more hazardous and more radioactive waste streams than possible with a conventional incinerator. Testing of the complete process is planned for the near future.

C. *Technical Support to Argonne's Waste Management*

We are involved in several different projects in support of ANL's Waste Management Program. The emphasis is on establishing a treatment scenario for all radioactive and hazardous liquids that have been, are, or will be generated at ANL. Our work during 1994 included testing a mixed-waste treatment facility; assisting ANL Waste Management in installing, testing, and training personnel to operate two evaporators and two concentrators for treating on-site waste waters; and designing a facility for treating liquid TRU waste.

1. Mixed-Waste Treatment

A mixed-waste treatment system was designed in CMT and installed at Argonne's Waste Management Operations Building. This system is designed to treat aqueous mixed wastes that contain hazardous metals (Pb, Cd, Cr, Ag, and Hg) and/or have a corrosive composition ($\text{pH} > 12.5$ or < 2). It consists of a chemical treatment which adjusts the pH and precipitates the metals by alkaline sulfide precipitation.⁵ The chemical treatment is followed by filtration, in which the solids are separated from the liquid by a variety of filters. A modular design allows the filtration scheme to be varied for research purposes and for treatment of different influents.

Two separate wastes from ANL's Center for Mechanistic Biology and Biotechnology were successfully treated. The initial concentrations of lead (100 and 1000 ppm) and cadmium (20 and 1000 ppm) in the supernatant were reduced to < 0.02 ppm, which is well below their Resource Conservation and Recovery Act (RCRA) limits of 5 and 1 ppm, respectively. In addition, Davies-Grey wastes were successfully treated. [Davies-Grey is a titration procedure that titrates U(IV) to U(VI) using dichromate.] The chromium in the supernatant was reduced from 21 to 0.12 ppm, also well below the RCRA limit of 5 ppm. The pH for all these waste solutions was increased from < 2 to 10-11. In addition, the precipitates generated during the treatment passed the Toxic Characteristic Leaching Procedure (TCLP). Thus, these mixed wastes were

⁵ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 82-84 (1994).

converted into two low-level waste streams, one solid and the other liquid. This system will continue to be operated by ANL's Waste Management Program to process additional mixed wastes.

2. Upgrade for Evaporator/Concentrator

Argonne's Waste Management Program has two low-level-waste (LLW) evaporators and one LLW concentrator, which are more than 30 years old and in need of replacement. We are providing technical support in the specification, purchase, testing, and documentation of two new LLW evaporators and two new concentrators, one for LLW and one for mixed waste. The evaporators are being purchased from LICON, Inc., and the concentrators from Artisan Industries, Inc.

Figure V-8 presents a schematic of the LLW evaporator/concentrator system. A typical batch of LLW will contain about 5700 L of liquid with about 0.2 wt% solids. This waste will come from a number of sources, including contaminated retention tanks and waste from laboratory experiments. The evaporators will process waste at about 6.0 L/min. Distillate from

Fig. V-8. Schematic for Evaporator/Concentrator Processing of Low-Level Waste (LLW). The symbol LPM indicates liters per minute.

the evaporators will be sufficiently free of activity to allow disposal in Argonne's waste treatment plant. The evaporator bottoms from the batch, about 285 L with about 4 wt% solids, will be fed to the LLW concentrator, which will produce a thick slurry of toothpaste consistency. Concentrator distillate will be reprocessed in the evaporators. Overall, 5700 L of waste will be concentrated to about 19 L of high solids waste, which will be disposed of at the Hanford site. The feed to the mixed-waste concentrator will come from laboratory wastes in small batches (10-200 L) and will be processed to a thick slurry at about 0.26 L/min.

The new evaporators and concentrators have been designed, fabricated, and tested at the manufacturers' facilities. The purpose of this testing was to verify that the equipment operated as expected and met the specifications. Part of the testing involved processing a simulated waste feed (which included Ca, Cu, K, Li, Mg, Mn, Na, Ni, Sm, F, Cl, SO₄, NO₂, NO₃, HCO₃, SiO₃, B₄O₇, and H₂PO₄) in each of the units. Samarium was added to the feed because it can be measured at very low concentration by using neutron activation analysis. This testing established that decontamination factors in the range of 10⁵-10⁷ for samarium could be attained in the evaporators. The design goal for the system was to achieve a decontamination factor of 10⁵ for samarium. Achieving this decontamination factor for samarium means that the decontamination factor for all nonvolatile metals will be similar. The testing also established that the concentrators can evaporate a simulated waste feed to a dry powder if desired. Delivery and installation of the systems at ANL have been completed, and startup testing is underway. All units should be ready for treating actual waste early in 1995.

3. Transuranic-Waste Treatment

Currently, no disposal site will accept wastes with a TRU concentration >100 nCi/g. However, Argonne as part of its ongoing research activities generates wastes with a TRU concentration >100 nCi/g. This waste is stored on site, much of it in highly acidic solutions, and requires stabilization for long-term storage until a permanent disposal site is available. In addition, Argonne's LLW treatment and disposal system is limited to wastes with a TRU concentration of <0.1 nCi/g. Therefore, wastes with a TRU concentration >0.1 nCi/g are also stored on site. A process was developed to treat all these wastes. The process coprecipitates the TRU elements by using magnetite. First, the waste solution is made alkaline by adding sodium hydroxide. Then, a mixture of ferric and ferrous salts is added to the alkaline waste solution. Magnetite precipitates, carrying the TRU isotopes with it. This process has yielded very high decontamination factors (>10⁶) for plutonium. Multiple treatments can be used to reduce the supernatant TRU concentration to <0.1 nCi/g. This process concentrates the TRU isotopes in a non-corrosive solid phase suitable for long-term storage until a permanent disposal facility is available. The <0.1 nCi/g supernatant can be treated and disposed of in Argonne's LLW system. Facilities for treating these wastes by magnetite coprecipitation will be installed and tested in 1995.

D. *Production of ⁹⁹Mo 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 pertechnetate ion (TcO₄⁻) and then suitably changed to other chemical forms, depending

upon the application. The TcO_4^- is washed from an alumina-column generator that contains the parent ^{99}Mo by elution with a saline solution. At present, 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 17 years at ANL and many countries throughout the world. The major objective is 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 and many more are in the process. As conversions of reactor fuel have proceeded, the amount of HEU being exported from the United States for ^{99}Mo production has become an ever more visible proliferation concern.

As a part of the RERTR program, we are studying two LEU target materials for ^{99}Mo production: uranium-metal foil and uranium silicide (U_3Si_2). Either UO_2 or various UAl_x alloys are used in current HEU targets. The silicide fuel is being developed as a LEU substitute for UAl_x alloys, and the uranium metal foil is being developed as a LEU substitute for UO_2 . Processing of the target materials entails dissolution and molybdenum separation and purification steps.

1. Processing of Uranium Foil Target

Our R&D effort on processing of uranium foil targets is focused on developing post-irradiation chemical procedures for the production of ^{99}Mo . The new chemical procedures are expected to resemble closely the Cintichem process previously used for HEU targets. Work in CMT has focused on establishing acid dissolution procedures for the irradiated LEU target. In particular, we measured the dissolution rate, the heat evolved, and the gaseous products from the dissolution of uranium foil by nitric/sulfuric acid mixtures. Figure V-9 shows the effect of sulfuric acid concentration and temperature on the dissolution rate of uranium foil. As shown, this dissolution rate is increased significantly by increasing the temperature and adding sulfuric acid. Collaborative work at the University of Illinois has focused on purification of molybdenum by its precipitation from the dissolver solution by using alpha benzoinoxime. Thus far all results

Fig. V-9. Effects of Temperature and Sulfuric Acid Concentration on the Dissolution Rate of Uranium Foil

indicate that substitution of an LEU-foil target for the current HEU target is possible; future experiments are being performed to optimize the process. Demonstrations of this technology are scheduled to begin at facilities in Indonesia in the summer of 1995.

2. Processing of U_3Si_2 Target

The LEU silicide target is aimed at replacing the HEU- UAl_x alloy, which is in the HEU dissolution process practiced by the Institut National des Radioelements (Fluerus, Belgium); Comision Nacional de Energia Atomica (Buenos Aires, Argentina); and the Atomic Energy Corp. (South Africa). The difficulty with uranium silicide targets is that the conditions used to dissolve UAl_x targets are not applicable for the silicide targets. The targets do not readily dissolve in base. In acid, silica is precipitated in the dissolution process, and the ^{99}Mo cannot be recovered from the solution.⁶

We have been developing a two-step basic dissolution method for the silicide target. The first step in recovering ^{99}Mo from a silicide target is to remove the aluminum cladding and aluminum powder in the fuel meat by basic dissolution. This procedure for basic dissolution of aluminum was developed in the 1950s,⁷ and slight variations of it are practiced all over the world. The second step entails dissolving the uranium silicide powder by a combination of sodium hydroxide and hydrogen peroxide. During the dissolution process, two chemical reactions occur, the autodestruction of hydrogen peroxide and the dissolution of uranium silicide. A literature search revealed very little data about the autodestruction of hydrogen peroxide in sodium hydroxide solutions. One source simply reported that the autodestruction reaction is catalyzed in base, but no quantitative data were given.⁸ A limited kinetic study of dilute hydrogen peroxide (0.01 M) in 0.5-6.0 M NaOH at room temperature indicated that hydrogen peroxide was stable in highly basic solutions.⁹

We have completed experiments to quantify the autodestruction rate in various NaOH solutions (0.128-2.57 M) over the temperature range 70-100°C. The autodestruction reaction is exothermic, and its kinetics must be understood to optimize the U_3Si_2 dissolution and design a dissolver with the proper heat transfer characteristics so that the dissolution process can be safely controlled. Results showed that, as the concentration of NaOH is increased from 0.128 to 2.57 M, the autodestruction rate decreases by a factor of about 20—showing an approximate inverse relationship between the rate and NaOH concentration. The effect of temperature on the autodestruction rate is greater as the NaOH concentration is increased from 0.128 to 2.57 M. The

⁶ 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, IAEA-TECDOC-515, pp. 115-128 (1987).

⁷ S. Stroller and R. Richards, Eds., *Reactor Handbook: Fuel Reprocessing*, Interscience Publishers, New York (1961).

⁸ W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, *Hydrogen Peroxide*, Interscience Publishers, New York (1955).

⁹ D. G. Karraker, *Radiation Effects on the Solubility of Plutonium in Alkaline High Level Waste*, Westinghouse Savannah River Center Report WSRC-MS-94-0278X (1994).

dissolution of U_3Si_2 was also measured. The dissolution was slowed by higher concentrations of sodium hydroxide, the rate depending on the hydrogen peroxide concentration.

Optimized conditions were selected for unirradiated U_3Si_2 powder based on the experimental results, and these conditions were tested on an irradiated miniplate sample that had been stored at ANL for about 9 years. The miniplate sample had undergone 42.2% burnup in the 30 MW Oak Ridge Reactor (ORR) and contained uranium enriched to 19.84% ^{235}U before irradiation. The short-lived fission products, including ^{99}Mo , have completely decayed. Unlike the unirradiated U_3Si_2 target, the irradiated miniplate did not dissolve readily by use of our optimized procedure. The decladding procedure did work as expected. However, after the cladding was removed, the silicide fuel looked like a monolith, not the particles obtained during the unirradiated testing. This monolith was resistant to dissolution. Even after the monolith was broken into pieces, the dissolution was very slow. It appears that either the long irradiation or the long storage has produced a new phase, which is difficult to dissolve. High temperatures encountered either during irradiation or in storage (decay heat) could have accelerated the formation of the new phase. The possible candidate for the new phase is a solid solution of $U_3(Si,Al)_2$. Additional experiments are necessary to determine whether the alkaline peroxide method will dissolve irradiated LEU- U_3Si_2 targets.

Because of the difficulty in dissolving irradiated U_3Si_2 , we are investigating the use of uranium foil targets for ^{99}Mo producers whose target processing begins with basic dissolution. The use of sodium hydroxide with hydrogen peroxide appears very promising as a means of dissolving a target in less than an hour. The foil will also eliminate the problems in later processing caused by the presence of silicate. Research on basic dissolution of both uranium foil and U_3Si_2 target will be carried out in 1995.

VI. ELECTROMETALLURGICAL TECHNOLOGY

As part of the effort to develop the Integral Fast Reactor (IFR), the CMT Division developed an electrometallurgical treatment for recovering Pu and U from spent core and blanket fuel, removing fission products from the recycled fuel, and incorporating them into suitable waste forms for disposal. The electrometallurgical flowsheet for treating IFR fuel is being extended to other metallic spent nuclear fuels such as Experimental Breeder Reactor-II (EBR-II) and N-Reactor; no major changes in the basic flowsheet are foreseen. Previous reports in this series have given details of the process flowsheet and chemistry, for which refinement is continuing.

The current reference treatment may be summarized as follows. Spent fuel in its cladding is mechanically reduced to pieces of approximately quarter-inch size, which are placed in an anode basket. The basket is introduced into an electrorefiner containing molten LiCl-KCl electrolyte salt (at 500°C) along with sufficient oxidant, such as UCl_3 , to convert the active fission products (alkali, alkaline earth, and rare earth) metals to their chlorides. During electrorefining, these remain in the salt, which also contains 2 mol% of actinide chlorides. The basket is connected to the positive pole of a dc power supply, then current is passed to a solid cathode, where nearly pure uranium metal is deposited by reduction of uranium chloride. An equivalent amount of actinide metal from the basket is simultaneously oxidized to its chloride. In the same way, a liquid cadmium cathode is used to remove a mixture of uranium and transuranic (TRU) metals; this mixture is contaminated with small amounts of rare earth metals. Cladding hulls and noble metal fission products remain in unoxidized form throughout the process. After the electrotransport process, they are removed from the anode basket and melted under a chloride flux that contains an oxidant, such as CuCl_2 . Because actinides and any active metals accumulate in the salt phase, the electrorefiner salt is periodically reduced to recover them for return to the electrorefiner feed. The recovered metal phase, which is nearly actinide-free, is cast into a metal waste ingot. Also, the electrorefiner salt is periodically purified by reducing the actinide chlorides into a circulating cadmium stream, extracting residual transuranic actinides by means of uranium in cadmium, and removing the active metal fission products by ion exchange with zeolite A in a column. The column contents are converted to a mineral waste form. Waste volumes are low because this process 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.

A. *Process Development Studies*

The process development studies include laboratory tests to develop a high-efficiency cathode for collecting TRU elements and a technique for monitoring electrolyte composition.

1. Development of Liquid Cadmium Cathode

During the past year, a series of 40 runs was completed in a laboratory-scale (15-cm dia) electrorefiner in which a liquid cadmium "pounder" cathode was used to collect transuranic elements. This cathode is a 5-cm ID crucible that contains a cadmium pool (200-250 g of cadmium). The "pounder" design incorporates an axial and rotating motion agitator

located above the electrolyte-cadmium interface in the electrode. The pounder agitator is basically an insulated ceramic cylinder that moves up and down and rotates about the cathode current lead. The agitator prevents the uncontrolled growth of heavy metal dendrites into the electrolyte phase above the cadmium interface and causes the cathode deposit to accumulate at high concentration in the cadmium phase.

In a plant-scale electrorefiner, a noncritical 3-kg batch of transuranics, uranium, and rare earth fission products will be collected in the liquid cadmium cathode. If the cathode is operated only up to the solubility limit of plutonium in cadmium at 500°C, then 80.3 kg of cadmium (10.4 L) would be the required size of the cathode. This is a large cathode and requires a long retorting time to separate the cadmium (by vaporization) from the nonvolatile actinides. When the solubility of transuranics such as plutonium in cadmium is exceeded, an intermetallic compound (e.g., PuCd₆) forms as a precipitate solid phase. One important goal of this development work was to show that a liquid cathode with the pounder design could handle the formation of solid in the liquid. The goal was to load at least 10 wt% transuranics into the cadmium, which would produce about 25 vol% solids in the cathode. The plant-scale cathode would be 3.5 L, and only 27 kg of cadmium would be needed to collect the actinides.

Table VI-1 gives the highlights of the 40 runs made in development of the pounder cathode. The first 22 runs were discussed in the previous report of this series.¹ The purpose of

Table VI-1. Summary of 40 Runs with Pounder Cathode

Runs	Purpose ^a	Result	Problems
1-10	Test operation feasibility (Pu/U >1)	High loading, >10 wt% Pu	Product ingots difficult to remove from low taper BeO
11-22	Investigate scaleup (Pu/U ≈ 2)	Determined limits	Product ingots difficult to remove from low taper BeO
23-26	Repeat with 4° taper and AlN crucible (Pu/U ≈ 2)	Good release of ingot	
26-31	Increase open area 10% - 18% (Pu/U ≈ 2)	Highest loading >16 wt% Pu, >3 wt% U	
32-40	Run at lower Pu/U with rare earths in electrolyte (Pu/U <1)	Test termination due to short circuiting	Al ₂ O ₃ - conductive AlN reaction

^aThe Pu/U ratios apply to cell inventory at start of runs.

these runs was to establish operational feasibility of the pounder design and to investigate geometric and operational variables that are important to cathode scaleup. During these 22 runs,

¹ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 89-90 (1994).

>10 wt% plutonium was routinely collected by the cathode. However, because the cathode crucible was made from dense BeO and had little taper on the inside cylindrical surface, the cadmium ingots containing the heavy metals (U and Pu) were difficult to remove. After Run 22, an AlN crucible with a 4° taper was substituted. Thereafter, the ingots released easily from the crucible. The taper was more important than the crucible material since the cadmium ingot does not bond to either BeO or AlN.

For Runs 23-31 the heavy metal loading in the cadmium was increased, and testing included a "pounder" cathode with a greater open area (18% vs. 10% in earlier runs). Increasing the open area did not decrease the performance of the pounder in handling the solids, but it did decrease the cell resistance slightly, as expected. Run 31 achieved the highest loading in the cadmium ingot: 16 wt% Pu and 3 wt% U. This gave 51 vol% solids in the cadmium ingot. This finding indicates that, for a plant-scale facility, the cathode size would be a manageable volume, 2.2 L, and only 15.7 kg of cadmium would be needed to collect the transuranics.

The collection efficiency for most of these runs was determined from the following equation:

$$\frac{\text{Wt. Heavy Metal Measured}}{\text{Wt. Heavy Metal Calculated}} \times 100\%$$

where the denominator is calculated from the total ampere-hours passed in a given run.

The average collection efficiency for 26 of the runs from Runs 1-31 was 97.5%. (For four of the runs, no data are available, and an unexplained low value obtained in one run is not included.) The attainment of a predictable collection efficiency is important in transuranic collection in the plant-scale electrorefiner for criticality reasons. The number of ampere-hours passed can be used to limit the deposition in the cathode to a noncritical batch. The attainment of near 100% collection efficiency in this experimental work shows that use of the pounder design is practical.

After Run 31, the uranium inventory in the electrorefiner was increased from 56 to 166 g, and rare earth chlorides were added to the electrolyte. It was necessary to terminate Runs 32-40 early because of short circuiting; these shorts were due to metal deposition along a narrow path either in the interior surface of the AlN crucible in the electrolyte phase or on the Al₂O₃ surface of the pounder cathode. The conductive path results from the reduction of the aluminum compounds by the uranium chloride in the salt. In earlier runs using only BeO for the fabrication of all the cathode parts, this problem did not occur. This materials modification should eliminate the short-circuiting problem.

2. Process-Monitoring Instrumentation

In the electrometallurgical treatment, monitoring of electrolyte composition is critical because it is used to control the composition of the liquid cadmium cathode product.

Voltammetric techniques are thus being developed to allow monitoring of electrolyte composition, essentially on-line, with little or no delay in obtaining analytical results.

Voltammetric techniques can measure multiple species with only three electrodes (for our purposes, a tungsten working electrode, a reference electrode, and a cadmium pool electrode). Also, these techniques measure concentration of species, not chemical activity as in potentiometric techniques (where concentrations can be determined only if activity coefficients of each species are known). In all voltammetric techniques a potential waveform is applied to the working electrode, and the resulting current is measured. The resulting current is usually proportional to concentration, not chemical activity.

Because square-wave voltammetry was found to be the preferable technique, this technique will be described briefly. In square-wave voltammetry, a potential waveform is applied at the working electrode in an electrochemical cell. This waveform results from the superposition of square and staircase waveforms. The duration of each step must be the same as one-half the period of the square wave. The current is sampled near the end of each half cycle, i.e., near the end of the "forward" and "reverse" pulses. The key waveform parameters are the square-wave amplitude and period and the amplitude of the step in the staircase waveform. The "forward" and "reverse" current can be plotted as a function of the applied potential, or the "forward" minus "reverse" current can be plotted as a function of the applied potential. The latter method gives a curve that somewhat resembles a chromatogram, where peak heights are proportional to concentration and the peak position indicates the chemical species.

Semi-quantitative simulations of square-wave voltammetry analysis of electro-refiner salt after ten pins of spent IFR fuel had been processed have been performed by R. Mariani (ANL-West). The simulated response is shown in Fig. VI-1. Note that there are well-resolved individual peaks for U^{3+}/U , Np^{3+}/Np , and Pu^{3+}/Pu . The rare earths, Sm^{3+}/Sm^{2+} , and Am^{3+}/Am peaks are discernible but not always well resolved. Figure VI-2 shows an experimental square-wave voltammogram taken for a $CsCl-LiCl-NaCl$ melt after addition of small amounts of $PuCl_3$, UCl_3 , and $DyCl_3$. The concentrations for U, Pu, and Dy as determined by sample analysis were 0.1, 0.06, and 0.05 wt%, respectively. (The $DyCl_3$ was added to help identify the mixed rare earth peak.) The order of peaks in Fig. VI-2 as well as the peak shape agrees with the simulation in Fig. VI-1. For example, examine the U^{4+}/U^{3+} and the U^{3+}/U peaks in Figs. VI-1 and -2. In both cases, the U^{4+}/U^{3+} is three times broader and one-third the height of the U^{3+}/U peak. Also, the sample analysis indicates that the U^{3+}/U peak should be 1.6 times as tall as the Pu^{3+}/Pu peak. The measured peak height ratio is 1.65. Thus, the agreement is quite good, even at low concentrations.

Square-wave voltammetry can also be used to track changes in concentration during a drawdown of heavy metals and rare earths from electrolyte salt. Figure VI-3 shows how the U^{3+}/U and Pu^{3+}/Pu peaks decreased at three points during a drawdown. The uranium concentration is clearly decreasing as current is passed in the drawdown operation. Future work will focus on obtaining more quantitative results and on generating a calibration curve by use of standard additions of $PuCl_3$ and UCl_3 to electrolyte.

Fig. VI-1. Simulated Square-Wave Voltammetry Response for Rare Earths, Transuranics, Uranium, and Plutonium after Processing of Ten Pins of U-Pu-Zr Fuel. (Adapted from figure of Mariani, ANL-West.)

Fig. VI-2. Experimental Square-Wave Voltammogram of Molten Salt Containing U, Pu, Dy, and Zr. Identification of zirconium peak is speculated but has not been confirmed.

B. Tests with Engineering-Scale Electrorefiner

Process development studies were conducted with an engineering-scale electrorefiner (capable of transporting 10 kg of uranium to a solid cathode) to investigate a heavy metal draw-down step for the electrolyte, to develop conditions for obtaining a uranium product with low salt content, and to test advanced electrorefiner concepts.

Fig. VI-3. Experimental Square-Wave Voltammograms Taken during Drawdown in Test Cell. Note the decrease in uranium waves with increasing amount of charge passed.

1. Drawdown Operations

The electrometallurgical treatment involves electrorefining spent fuel in a molten-salt electrolyte (LiCl-KCl-U/PuCl_3) at 500°C . At some point, the concentrations of alkali, alkaline earth, and rare earth fission products in the salt must be reduced to lower the amount of heat generated in the electrorefiner. The heavy metal concentration in the salt must be reduced before fission products are removed from the salt.

In the drawdown operation (Fig. VI-4), a Li-Cd alloy (5.8 wt% lithium) that is solid at 500°C is loaded into anodic dissolution baskets and rotated in the molten electrolyte;

Fig. VI-4. Schematic of Electrorefiner for Drawdown Operation

current is driven from the anodic dissolution baskets to a solid-mandrel cathode that has a ceramic catch crucible below to collect products that fall from the solid cathode. The design criteria that must be met for the drawdown operation include (1) control of the reduction rate by lithium, (2) good separation between uranium and rare earths, and (3) the collection of uranium and rare earths over a wide range of salt concentrations.

As shown in Table VI-2, the concentrations of uranium in the cathode deposits from the drawdown runs fell into three ranges: low (<0.1 wt%), medium (31.8-39.2 wt%), and high (70-89.3 wt%). For the high range, the uranium concentrations in the salt were from 1.75 to 6.68 wt%, and the concentrations of rare earth metals (Ce, Nd, and Y) in the cathode deposits were low (1.2 wt% or less). For the medium range, the uranium concentrations in the salt were 0.14 to 1.30 wt%, and the concentrations of rare earth metals in the cathode deposits were 1.8-2.8 wt%. For the low range, the concentration of uranium in the salt was 0.015 wt%, and the concentration of rare earths in the deposit was high (31.8 wt%). In sum, the test results indicate that *in situ* drawdown can reduce the uranium concentrations to 0.1 wt% without removing significant quantities of rare earths in the salt. Further reduction to ~0.01 wt% uranium in the salt (99.9% removal) is possible by removing 13% of the rare earths along with the uranium.

Table VI-2. Results from Drawdown Operations in the Engineering-Scale Electrorefiner

Run No.	U in Cathode Deposit, wt%	U in Salt, wt%	Rare Earths in Cathode Deposit, wt%
65	High 89.3	4.33	<0.01
71		1.75	1.2
58		6.68	<0.01
70		2.98	1.1
75	Medium 39.2	0.72	1.8
76		0.14	2.7
72		1.3	2.8
77	Low <0.1	0.015	31.8

2. Production of Low Salt Deposits

The engineering-scale electrorefiner was also used to determine conditions for depositing, on a solid iron cathode, a uranium product having low salt content (1-5 wt% vs. 10-15 wt% for typical deposits). When unclad U-Zr or stainless-steel clad U-Zr is the anode feed material, cathodes with high, low, or no zirconium can be obtained. To determine the optimum conditions for the low salt deposit, the following parameters were varied: mixing rates for salt (0-150 rpm) and cadmium (0-50 rpm), electrodeposition current (20-300 A), voltage (0.2-0.8 V), and quantity of electricity (698-2517 Ah/kg uranium) passed through the electrorefiner.

The salt mixing rate (0-20 rpm), electrodeposition current (50 A), and voltage (0.2-0.3 V) required for the low salt deposit were lower than those needed to produce the typical IFR solid-cathode deposit. On the other hand, the quantity of electricity passed through the electrorefiner for the low salt deposit was greater than that used to produce the typical IFR solid-cathode deposit (1108-1263 Ah vs. 698-865 Ah per kilogram of uranium).

A comparison of the low salt process with that used for simultaneous transport of U and Zr to the solid mandrel cathode² also shows some major differences. The low salt process uses a much lower electrodeposition voltage than that used in the U-Zr codeposition process (0.2-0.3 V vs. 0.7 V). The quantity of electricity passed through the electrorefiner is also less for the low salt process than that for the U-Zr codeposition process (1108-1263 Ah vs. 1466-2517 Ah per kilogram uranium).

The processing steps used to produce uranium deposits with low salt concentration will be incorporated into an advanced electrorefiner design. The requirements of high throughput (>40 kg uranium per hour) and large batch size (100 kg uranium) for these electrorefiners can be met best with the low salt deposits, which are expected to have a higher packing density (5 to 7 g uranium per cubic centimeter) than that achieved with the typical IFR uranium deposit (1 g uranium per cubic centimeter). The lower salt content of these cathode deposits will also reduce the processing time in the cathode processor, which is used to consolidate the heavy metal and to separate the salt from the heavy metal. The high-throughput electrorefiner will be particularly useful for treating large amounts of spent nuclear fuels, such as the blanket in EBR-II and, especially, the N-Reactor fuel (see Sec. VI.B.3).

3. Testing of Advanced Electrorefiner Concepts

The electrometallurgical treatment was originally developed by ANL for recovery and recycle of actinide elements contained in spent IFR fuel. Recently, it has been proposed that the same process could be effectively applied to treating a large quantity of spent fuel from a defense materials production reactor, the N-Reactor at the Hanford site, that has been shut down. There are important differences between the two fuels that influence operational parameters for the electrorefining process. The IFR fuel is clad with stainless steel, and the fuel material is an alloy of zirconium with the heavy metal (HM) at a HM/Zr weight ratio of about 9/1. The Zircaloy-clad unalloyed uranium fuel of the N-Reactor has a HM/Zr ratio of about 32/1, if cladding and fuel are combined. Thus, in processing N-Reactor fuel, about one-third as much zirconium must be handled compared with processing IFR fuel.

In the anodic dissolution process, the zirconium metal in the N-Reactor fuel cladding will oxidize into the salt at the appropriate voltage and then deposit on the cell cathode. The uranium in the N-Reactor fuel is anodically dissolved out of the cladding after it is breached by some mechanical means so as to provide electrolyte access. The breached clad slugs are loaded into porous stainless-steel baskets, which become the anode, and are then dissolved in the

² J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 93-94 (1994).

electrorefiner cell. This method works well for metallic fuels, where >99.99% of the heavy metal is easily dissolved out of the insoluble cladding.

Anodic dissolution of the Zircaloy depends on the cell operating voltage. It is desirable to find operating conditions that electrotransport uranium, while leaving the Zircaloy behind in the anodic dissolution baskets. In this way, no further separations processing is needed for the Zircaloy. Ways to maximize this effect have been found experimentally through controlling the electrode configuration and operating conditions imposed on the electrorefining cell.

Six anodic-dissolution tests were completed with a slug of unirradiated N-Reactor fuel that had been sawed into pieces of different length and diameter. These tests were run in the engineering-scale electrorefiner to determine the operating characteristics needed to provide spent fuel segments that are suitable for a high-throughput electrorefiner.

The average dissolution current for these six tests ranged from 3 to 35 A. When the uranium concentration in the fuel segment was reduced to a low level (<7 wt%), the resistance of the cell increased. At <7 wt% uranium, the maximum dissolution voltage varied between 0.3 and 0.8 V, and about 28% of the Zircaloy cladding was dissolved at less than 0.4 V. At >7 wt% uranium, no dissolution of the Zircaloy was detected below 0.5 V, but between 0.53 and 0.8 V, about 81% of it dissolved. The quantity of electricity needed to dissolve the uranium in these tests varied between 405 and 500 Ah per kilogram of uranium dissolved. Further tests are needed to determine the effect of fuel-segment diameter and length on the uranium dissolution rate.

The test results were employed in developing a conceptual design of a plant-scale facility to process N-Reactor spent fuel. In this design, the vessel size of the electrorefiner is about 1.5-m diameter by 1.5-m height. A 3-metric-ton batch of N-Reactor spent fuel could be loaded into 42 anodic dissolution baskets and electrorefined at a rate of about 40 kg uranium per hour. Testing of the electrode configuration used in this conceptual design has begun in the engineering-scale electrorefiner. Design of a prototype electrorefiner with these electrodes was initiated and will be used to demonstrate the treatment of spent N-Reactor fuel and EBR-II blankets (19.5 metric tons of heavy metal) in the Fuel Cycle Facility at ANL-West.

C. *Electrorefiner Waste Treatment Processes*

As spent fuel batches are processed in the electrorefiner, fission products accumulate in the vessel. As a consequence, fission products of alkaline earths, alkali metals, and rare earths build up in the electrolyte salt. The transition metal fission products tend to remain in the anode baskets together with the cladding hulls. Periodically, the electrolyte salt must be removed from the electrorefiner for treatment to recover any TRU elements and remove a sufficient quantity of heat-generating fission products so that the salt can be recycled. During this reporting period, process development studies have been carried out on (1) the use of a "pyrocontactor" (high-temperature centrifugal contactor) to perform salt/metal extractions and (2) the pumping and filtration of molten salt and cadmium. Also, a new facility, the Waste Form Development

Laboratory, is being built to house engineering-scale equipment associated with the preparation and testing of mineral (zeolite) and metal waste forms.

1. Salt Extraction

Several steps in treating the salt from the electrorefiner employ pyrocontactors to perform salt/metal extractions and recover TRU elements from the salt. During the past year, three series of extraction tests were run with molten salt and cadmium at 500°C in a single-stage pyrocontactor (4-cm dia rotor). In the first test series, cerium was dissolved in cadmium, and CdCl_2 was mixed with LiCl-KCl eutectic salt. In the second test series, lithium was dissolved in cadmium, and CeCl_3 was mixed with the eutectic salt. The objective of these two test series was to demonstrate that the pyrocontactor could effectively mix liquid metal and salt, effect extractions of select species, and separate the metal and salt at 500°C. The third test series used cerium in cadmium to separate lanthanum from yttrium in eutectic LiCl-KCl containing LaCl_3 and YCl_3 . The objective was to simulate the use of uranium in cadmium to separate the TRU elements from the rare earths in the electrorefiner spent salt. This simulation is possible because the separation factors for TRU and rare earths relative to uranium are similar to those for lanthanum and yttrium relative to cerium.³

During each test series, extraction efficiencies were determined from the ratio of the measured transfer of a species compared to the predicted transfer. The predicted transfer at equilibrium conditions was derived from the XTRACT code.⁴ For the measured transfer, samples of feed and effluent streams were collected and analyzed by inductively coupled plasma/atomic emission spectroscopy. In the first test series, the extraction efficiencies were determined from the measured and calculated transfer of cerium from the metal to the salt phase. The average extraction efficiencies were 20, 70, and 90% at contactor speeds of 2100, 2400, and 2700 rpm, respectively. In the second test series, the extraction efficiencies were determined for the transfer of lithium from the metal to the salt and cerium from the salt to the metal. The average extraction efficiencies were 50, 70, and 90% at contactor speeds of 2100, 2400, and 2700 rpm, respectively. In the third test series, the extraction efficiencies were determined for the Ce, La, and Y transfer in the metal and salt phases. The average extraction efficiencies were 41, 47, and 70% at contactor speeds of 2100, 2400, and 2700 rpm, respectively. In this $\text{Ce-LaCl}_3\text{-YCl}_3$ test series, lanthanum was successfully extracted from the test salt, with yttrium remaining in the salt. Because this system is an effective surrogate for the $\text{U-(TRU)Cl}_3\text{-(rare earth)Cl}_3$ system, the results indicate that it should be possible to use the pyrocontactor to extract the TRU elements from the rare earths in the electrorefiner spent salt.

The test results also showed that the contactor provided good mixing and separation of the metal and salt at high contactor speeds, with efficiencies of 90% achieved at

³ L. S. Chow, J. K. Basco, J. P. Ackerman, and T. R. Johnson, "Continuous Extraction of Molten Chloride Salts with Liquid Cadmium Alloys," *Proc. of Global '93 Int. Conf. and Technology Exhibition on Future Nuclear Systems*, Seattle, WA, September 12-17, 1993, Vol. 2, pp. 1080-1083 (1993).

⁴ J. P. Ackerman, "PYRO--A System for Modeling Fuel Reprocessing," *Proc. of the Winter Meeting of the Am. Nucl. Soc.*, San Francisco, CA, November 26-30, 1989, Vol. 60, pp. 168-169 (1990).

contactor speeds of 2700 rpm. Most of the extraction efficiency data fall within $\pm 20\%$ of the mean values. The material balance data are mostly within $100 \pm 10\%$. The trend of extraction efficiency increasing with increasing contactor speed was consistent throughout these tests. The pyrocontactor ran smoothly without any sign of vibration at speeds up to 2700 rpm.

A multistage (4-stage) pyrocontactor is being developed. This multistage contactor will replace the single-stage unit. The design of the four-stage pyrocontactor is complete, and fabrication of the contactor unit is underway.

2. Salt/Cadmium Filtration

Various steps in the processing of spent fuels involve filtering small amounts of insoluble constituents from the salt or cadmium. These constituents include oxides, nitrides, or carbides, which need to be filtered out of the electrorefiner salt along with any metal particles that may escape from the anode baskets. It may also be necessary to periodically filter insoluble materials, such as noble metals, from the cadmium. Hence, six salt and cadmium filtration tests have been carried out with commercially available filter elements. Four of these tests employed filter elements of sintered stainless steel (manufactured by Pall Corp.), and two used filter elements of woven-wire mesh stainless steel (manufactured by Norman Equipment Co.). Two pore sizes for each type of element were employed, 10 and 35 μm . Five of the six tests involved filtering salt, and in one test, cadmium was filtered. In each filtration test, flow and pressure data were obtained at various pump speeds. Each test involved filtration times of 20-48 h for a cumulative pumping/filtration time of 180 h for the six tests.

The filters were attached to a pump assembly by a freeze seal connection. The pump/filter assembly was installed in a stripper vessel described previously.⁵ The stripper vessel contained approximately 19 L of cadmium and 57 L of LiCl-KCl eutectic salt, which had been used in previous stripping tests. The pump assembly can be positioned so that either salt or cadmium can be pumped from the stripper vessel through the filter and then returned to the stripper vessel. During the first three tests, problems were encountered with leaks in the filter occurring in the region where the sintered metal filters were welded. The problem was solved with a design change.

A flow probe was used to measure the flow through the filter assembly. This probe functions by measuring the force exerted by the moving fluid on a spherical probe placed in the flow path. There were some mechanical problems with the flow probe, but modifications have been made, and the flow probe operated satisfactorily for several tests.

A pressure probe was used to measure the pressure in the filter assembly housing. This pressure measurement is the sum of the pressure drop across the filter element plus a pressure drop along the fluid return path. Measurement of the filter housing pressure can aid in determining the flow rate through the filter. In some tests, the pressure data were as expected,

⁵ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 97-98 (1994).

i.e., increasing pressure with increased pump speed. However, in other tests, the filter housing pressure drifted down and decreased with time and sometimes even became negative. It is believed that this behavior is due to a siphon being established in the discharge line of the filter under conditions where the resistance downstream of the filter is larger than the resistance of the filter. Under these conditions, it will be necessary to rely solely on the flow probe for measuring the fluid flow.

After testing, two of the housings for the sintered stainless steel filters were cut open and examined. Both showed evidence of filtration of particulate material. In one filter (35- μm pore size), a residue had remained in the housing during the filtration of cadmium and was found to contain a uranium-iron-intermetallic particulate, UFe_2 , ranging in particle size from 0.1 μm up to 10 μm . In the other filter (10- μm pore size), a thin layer of black material had remained in the housing during the filtration of salt and contained UO_2 as one of the major components. These results are very encouraging because they indicate that these filters can be used to remove particulate materials from both the salt and cadmium streams. Further testing of filters is planned.

3. Demonstration of Engineering-Scale Process

A new facility, the Waste Form Development Laboratory, is being built to house engineering-scale equipment for demonstrating waste removal and waste-form preparation. Three argon atmosphere gloveboxes will be used. The first glovebox will contain the multistage (countercurrent flow) centrifugal pyrocontactor that will be used to demonstrate salt/metal extractions. The second glovebox will hold a high-temperature (tilt-pour) furnace for induction melting and casting. This furnace is capable of operating at 2200°C, which can melt and alloy 2.5 kg of simulated waste-form materials under a molten salt flux. The third glovebox will house a zeolite ion exchange column that will be used in testing various pelletized zeolites (including binder materials). Additional equipment associated with preparing mineral waste forms will include apparatus to remove excess salt from the loaded zeolite, high-temperature blending equipment, and a hot isostatic press capable of operation at high temperature (1450°C) and pressure (200 MPa). Operation of this laboratory is expected early in 1995.

D. *Development of High-Level Waste Form*

Two waste forms--a mineral form and a metal form--are being developed to contain the fission products from the electrometallurgical treatment of spent nuclear fuel. The mineral form will contain the fission products--rare earths, alkali and alkaline earth metals, halogens, and chalcogens--that accumulate in the electrolyte salt; the metal form will contain the cladding hulls, zirconium, and noble metal fission products, which are chemically unaffected by the electrometallurgical process.

1. Mineral Waste Form

Glass-bonded zeolite and sodalite are candidate materials for the mineral waste form; both are fabricated from zeolite A. The fission products are removed from the spent electrolyte salt by ion exchange with zeolite A that has been pre-equilibrated with LiCl-KCl . The fission product-

loaded zeolite and whatever liquid salt wets its surface are mixed with zeolite A at about 450°C to sorb the liquid salt. The resulting material is either (1) mixed with glass powder and formed into a monolith of glass-bonded zeolite or (2) converted to sodalite by heat treatment. Work conducted during this report period focused on preparation and laboratory-scale testing of glass-bonded zeolite and sodalite.

a. Glass-Bonded Zeolite

Glass-bonded zeolite was prepared from zeolite A powders and a borosilicate glass frit containing 7 wt% strontium and 8 wt% calcium. The samples were then evaluated following a standard leach test (MCC-1 procedure) for 28 and 56 days at 90°C in deionized water and in a concentrated brine (NaCl-KCl-MgCl₂) solution. The test results are summarized in Table VI-3, where performance is reported as a normalized (to concentrations, test duration, and surface area) release rate.

Table VI-3. Normalized Release Rates for Glass-Bonded Zeolite in Water and Brine Leach Tested at 90°C

	In Water, g/(m ² •day)		In Brine, g/(m ² •day)	
	28 days	56 days	28 days	56 days
Al	0.30	0.13	0.28	BDL ^a
Ba	0.21	0.08	0.22	0.43
B	0.31	0.19	0.35	0.49
Ca	0.19	0.14	0.17	0.70
Cs	0.60	0.32	0.61	0.57
K	0.73	0.38	0.63	b
Li	0.60	0.35	0.54	0.42
Na	0.67	0.37	0.71	b
Si	0.25	0.11	0.23	0.15
Sr	0.23	0.11	0.24	0.51

^aBDL = below detection limit.

^bIons in brine.

In the deionized water leach tests, the normalized release rates for all elements were less than 1 g/m²•day; the rates for the 56-day tests were about half of the 28-day tests. This finding indicates that the initial release predominates, as it does in the borosilicate glass being considered for disposal of high-level nuclear waste (Sec. IV).

The brine leach tests were run to determine if the zeolite phase functioned as an ion exchanger. The normalized release rates in brine were about the same as those in

deionized water for the elements in the zeolite phase (Ce and Li) but higher for the elements in the glass phase (B and Ca). This finding suggests that ion exchange with the zeolite is not significant, and that the ion exchange values of the glass are greater than those of the zeolite. The normalized release rates in brine were also determined for glass-bonded zeolite prepared with rare earths (Ce, La, Nd, and Y) and were found to be less than $0.01 \text{ g}/(\text{m}^2 \cdot \text{day})$ for all the rare earths. The rates for the other elements were about the same as in Table VI-3.

The kinetics of fission-product ion exchange into zeolite was studied in batch-exchange experiments, in which clay-bound zeolite pellets were immersed in a simulated spent salt at 500°C for 10 min to 72 h. The results (Fig. VI-5) indicate that the ion exchange process can be approximated by first-order kinetics. The divalent cations (Ba and Sr) go through a concentration maximum after 6 h, then steadily decline; they are displaced by the trivalent cations (rare earths). Cesium exchange was rapid; its concentration remained constant throughout the test. The ion exchange studies showed more than adequate removal of all fission products by the zeolite, albeit with rates that imply residence times of hours rather than seconds.

Fig. VI-5.

Ion Exchange Kinetics for Zeolite A Pellets Immersed in Molten Spent Salt (R.E. represents rare earths)

b. Sodalite

Sodalite powders were synthesized from salt-occluded zeolite A, which was blended with dehydrated zeolite A to reduce the chloride ion content of the zeolite to the capacity of sodalite, nominally two chloride ions per sodalite unit cell. The zeolite mixtures were heated to $> 425^\circ\text{C}$ for at least 24 h. X-ray diffraction analysis of the resulting powders indicated that sodalite was the major crystalline phase, with nepheline usually present as a minor phase. Washing of the powders indicated significant residual free salt after synthesis, particularly in samples with a high nepheline content. The powders were consolidated by hot-pressing, resulting in hard, polishable samples. There were no changes in composition between the initial powders and the resulting pellets after hot pressing at 1050°C .

The sodalite samples were leached in deionized water for 28 days at 90°C . Mass losses were much lower for samples that had been washed to remove residual free salt prior to hot pressing. This indicates that residual free salt remains a problem in the production of a sodalite-based waste form.

Preparations are underway for engineering-scale testing of zeolite columns in the Waste Form Development Laboratory (Sec. VI.C.3).

2. Metal Waste Form

Recent work on the metal waste form has focused on an alloy composed of the stainless steel, zirconium, and noble metal fission products intrinsic to the spent fuel. The waste form alloy is an Fe-Zr-Cr-Ni alloy with additions from the noble metal fission products and minor elements in the fuel cladding. A systematic study of this alloy system is being carried out to understand its physical metallurgy and to develop optimal processing parameters.

Three types of stainless steel (HT9, 304, and 316) have been used to represent EBR-II blanket and driver cladding materials that are being considered for conditioning into a metal waste form. Some fuel alloys contain significant amounts of zirconium, which would be directed to the metal waste form. Simulated waste form alloys with compositions ranging from 5 up to 20 wt% zirconium were generated to represent potential waste-form compositions for spent nuclear fuels with stainless-steel cladding; the Zr-Fe system has a eutectic at ~15 wt% Zr. In addition, 304 stainless steel alloys with 67, 83, and 92 wt% zirconium were generated to represent potential waste forms for spent nuclear fuels with Zircaloy cladding; the Zr-Fe system has another eutectic at ~87 wt% Zr. Several alloys of each type were generated; the elements Ru, Pd, and Ag were added to simulate the noble metal fission products. The microstructure in the alloy samples that have been examined to date have been uniform, and the phase structures are being characterized.

General corrosion tests were performed on the waste form alloys. Samples (15 to 20 g) were immersed in simulated J-13 well water of pH 6-8 at 90°C. The J-13 well water is representative of the groundwater at the Yucca Mountain site in Nevada that is proposed for a high-level nuclear-waste repository (Sec. IV). After 28 days of testing, the waste form corrosion rates were very low, at the limits of analytical resolution for the tests, and further testing is proceeding. A casting furnace and glovebox equipment have been designed and fabricated to scale up the experiments to 2.5 kg alloys. The experiments to be conducted in this facility (see Sec. VI.C.3) will investigate alloying, fluxing, TRU extraction, and casting relevant to the metal waste form.

VII. ACTINIDE RECOVERY

Many different types of spent nuclear fuels are now in storage at several Department of Energy sites. The actinide elements, particularly the transuranic (TRU) elements, because of their long half-lives and high toxicity levels, constitute the primary hazard in disposal of these spent fuels. Recovery of the TRU elements for placement in a stable, low-volume waste form offers substantial benefits to repository disposal of these spent fuels. For example, the spent-fuel fission products decay to a minimal toxicity level after several hundred years. In contrast, for the TRU elements to reach a similar toxicity level requires several million years. The TRU elements, once separated from the fuel or waste, can be combined into a low-volume waste form that is leach resistant and diversion resistant, and this waste form can then be sent for ultimate repository disposal. Work has been conducted in the Chemical Technology Division to develop an electrometallurgical process for separating TRU elements from oxide spent fuel. This process is also applicable to other types of non-oxide fuels with appropriate head-end treatment. Recent work has concentrated on development of the process flowsheet, a laboratory-scale demonstration of the process with 0.5 kg of simulated fuel, and design and fabrication of an engineering-scale system for testing the process at a larger scale (20 kg). Experiments have also been done to help understand the rare earth chemistry in the reduction salt.

A. *Process Chemistry and Flowsheet Development*

A flowsheet (Fig. VII-1) was developed for a lithium-based process for separating actinides from oxide spent fuels. In the flowsheet, lithium metal is used to reduce the oxide fuel to metal, and electrorefining is used to isolate purified uranium and a product rich in TRU elements.

The advantages of the lithium process over calcium-based processes, which were previously considered, include lower temperature required (650°C vs. 800°C); steel containment as opposed to expensive tungsten or ceramic containers; and a waste salt form that is compatible with the mineral waste form being developed for other electrometallurgical processes (Sec. VI). The reduction is conducted at 650°C to permit use of LiCl (melting point of 605°C) as the reduction salt. Although lower temperatures have more favorable thermodynamics, mixing KCl with the salt to lower the melting temperature resulted in excessive evaporation of potassium. Addition of alkaline earth chlorides to reduce the salt temperature was undesirable because they lower the solubility for the Li₂O reduction product. To obtain complete reduction of TRU oxides at 650°C, the final Li₂O concentration is limited to 4.5 mol% (solubility is 12 mol%).

The present concept is to introduce the fuel into the reduction vessel as a chopped or shredded mixture of fuel and cladding contained in a basket. Following reduction, the salt is transferred to another vessel for recovery, and the precipitated metals and cladding are washed with recycled salt to remove most of the remaining Li₂O and excess lithium in preparation for introducing the metal to the electrorefining step. The basket containing the fuel is designed to serve as an anode. In electrorefining, purified uranium is collected on a steel cathode. This uranium is subsequently melted (1200°C), cast, and separated from occluded salt, which is recycled. The transuranic actinides are collected in a cadmium cathode along with some of the

uranium. The TRUs and associated uranium are recovered by distilling off the cadmium at 750°C. The cladding and those fission products that are reduced during the reduction step remain in the basket. These are melted along with the basket to produce a metallic waste form. According to DOE policy decisions, the TRU product may be added to this waste.

Spent reduction salt is electrochemically processed to decompose the Li_2O and recover the lithium metal. Removal of virtually all of the Li_2O has been demonstrated in the laboratory, but the reference flowsheet assumes 95% removal. After Li_2O removal, the salt is filtered to remove insoluble rare earth elements and recycled. A portion of the salt (<1%) is discarded to control the concentration of soluble fission products. After KCl is added to lower the salt melting temperature, this salt and the filter cake containing rare earths are fixed on zeolite and bonded with glass for disposal. The lithium process flowsheet will be continually refined in response to results from laboratory-scale testing.

Fig. VII-1. Lithium Process Flowsheet

B. Laboratory-Scale Testing

1. Process Demonstration

A 0.5 kg-scale experiment was conducted to demonstrate most of the steps of the flowsheet shown in Fig. VII-1. To reduce 0.5 kg of simulated oxide fuel on the laboratory scale, it was necessary to conduct seven reduction runs involving 75 g fuel charges each. The combined charges for these seven experiments included UO_2 , PuO_2 , and selected fission products as detailed in Table VII-1. The reduction experiments were conducted at 650°C and employed pure LiCl with a final Li_2O concentration of 4.6 mol%. The metal particles produced in each reduction were separated from the salt by use of a 200-mesh stainless steel screen. The screened product was mostly metal, but it also contained some salt that had wet the metal particles and did not drain off. The combined metal product from all seven reductions was washed twice with fresh LiCl to minimize any Li_2O , which is undesirable in the electrorefining step.

Table VII-1. Combined Charge for Laboratory-Scale Electrorefining Experiment

Species	Weight, g
UO_2	499.72
PuO_2	2.01
NpO_2	0.351
AmO_2	0.024
Nd_2O_3	2.11
CeO_2	1.63
ZrO_2	2.18
RuO_2	1.27
MoO_3	2.30
BaO	0.94
SrO	0.39

The next step demonstrated in the laboratory-scale experiment was electrotransporting the uranium away from the TRU elements. The electrorefining was conducted in a stainless steel beaker containing a LiCl -40 wt% KCl salt. The uranium was added on the anode, which was a flat stainless-steel plate. The cathode was a steel rod that had a roughened surface to which the collected uranium was intended to stick. Previous attempts at electrorefining uranium had demonstrated that the uranium dendrites which formed on the cathode had a tendency to fall off before they could be collected. Hence, a catch crucible was placed under the cathode, as shown in Fig. VII-2. A 9.0 wt% concentration of UCl_3 was generated in the salt by

adding FeCl_2 . This FeCl_2 reacted with the uranium, TRU elements, and any rare earth elements that were present and generated the chlorides of these elements. During the experiments, electrorefining was conducted at 1.0 V with currents that varied between 1 and 3 A. The dendrites and any adhering salt were collected several times a day and combined. At the conclusion of the experiment, filtered samples of the salt, bulk samples of the salt, and a portion of the dendrites were submitted for analysis by inductively coupled plasma/atomic emission spectrometry. The combined dendrites and salt were then placed in a retort and melted, resulting in a uranium ingot.

Fig. VII-2.

Schematic of Uranium Electrorefining Apparatus (SS = stainless steel)

The analytical results for this demonstration are summarized in Table VII-2. We anticipated that the TRU elements (Pu, Am, and Np) would be present in the salt phase after electrorefining, and this appears to be true, except for an unexpectedly large amount of americium retained in the reduction salt. Since we had not had any previous experience with electrorefining uranium in the presence of neptunium, and because U and Np are chemically similar, it was gratifying to find only a minor amount of neptunium in the uranium deposits (0.001 g). The concentrations of TRU elements in the salt were too low to extract by use of a liquid cadmium cathode, as has been done in previous electrorefiner experiments for the Integral Fast Reactor Program. In an actual plant operation, the uranium electrorefining would continue until a sufficient concentration of the TRU elements was obtained to warrant their removal on a liquid cadmium cathode.

As shown by the bottom two rows of Table VII-2, the material balances for most of the elements are reasonable, considering the analytical uncertainties of $\pm 10\%$, and these results would appear to confirm the feasibility of the lithium process. Laboratory-scale experiments will be continued to understand and improve on the steps of the process. Particular emphasis will be placed on obtaining a TRU-free uranium product.

Table VII-2. Analytical Results for Laboratory-Scale Experiments

	U, g	Pu, g	Am, mg	Np, g	Ce, g	Nd, g	Ru, g	Mo, g	Zr, g	Ba, g	Sr, g
Reduction Salt	<0.3	<0.01	9.64	<0.01	1.20	0.84				0.84	0.33
Filtered Electrolysis Salt	45.6	1.40	7.90	0.21	0.38	0.60	<0.08	<0.08	.038	0.017	<0.08
Anode Salt	30.3	0.32	2.50	0.07			0.90	1.74	1.66	<0.013	<0.013
Dendrites	336.3	0.007	0.024	0.001	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03	<0.03
Total	412.2	1.73	20.06	0.28	1.58	1.44	0.90	1.74	1.70	0.86	0.33
Amount Charged	440.5	1.77	21.21	0.35	1.33	1.81	0.96	1.53	1.61	0.84	0.33

2. Behavior of Rare Earth Fission Products

During studies of the reduction of simulated oxide spent fuel by the lithium process, a water-insoluble solid phase of the general formula LiLnO_2 was found with the metallic uranium product, where Ln is one of the rare-earth fission products. The behavior of these compounds during the reduction process has been investigated by reacting the solid lanthanide sesquioxides, Ln_2O_3 , with a molten mixture of metallic lithium, lithium oxide, and lithium chloride at 650°C . The lanthanide concentration of the molten salt was much greater than would be expected if the solution was in equilibrium with either the sesquioxide or the mixed oxide compound, and the lanthanide concentration increased as the amount of Li_2O added to the salt was increased. In the case of Nd_2O_3 , the sesquioxide was found in the water-insoluble residue when the amount of Li_2O added to the LiCl was less than about 6 mol%, while LiNdO_2 was the residue when the amount of added Li_2O was greater than 6 mol%.

These experimental observations are consistent with the following reactions:

These reactions indicate that two neodymium oxide species are formed in the molten salt solution and that, when the concentration of the LiNdO_2 becomes large enough, solid LiNdO_2 precipitates from the molten salt solution. The Li_3NdO_3 species, which has not been experimentally identified in the salt, was assumed to be soluble in the salt. As shown in Fig. VII-3, the experimental values for the total neodymium content of the molten salt agree well with the predictions based

Fig. VII-3. Experimental and Calculated Concentrations of Neodymium in Molten Li_2O - LiCl Salt Mixtures

on this theory. The break in the calculated curve occurs where the equilibrium solid phase changes from Nd_2O_3 to LiNdO_2 .

When the reaction of europium sesquioxide, Eu_2O_3 , with Li and Li_2O dissolved in molten LiCl was studied, the europium content of the molten salt was much greater than observed for Nd_2O_3 and decreased by about 10% as the amount of added Li_2O was increased from about 2 to 8 mol%. The stability of divalent europium suggests that under the conditions of these experiments, the sesquioxide is converted to the dichloride:

The dichloride then reacts with the excess liquid lithium to establish the following equilibrium:

The small decrease in the europium content as the amount of Li_2O in the molten salt was increased is due to the dilution of the LiCl content of the molten salt, which shifts the

above equilibrium to the right. At the largest addition of Li_2O , the observed europium content of the molten salt was slightly greater than the value computed on the basis of the above equilibrium. This is probably due to the formation of LiEuO_2 in solution; the much greater concentration of europium owing to the EuCl_2 almost completely obscures the formation of the mixed oxide species, which is the main reaction for the other rare earths where the divalent state is not stable. Future work will examine the chemistry of Sm_2O_3 and CeO_2 in this system.

3. 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.

Thirteen experiments were performed to investigate electrowinning of lithium metal from Li_2O in molten LiCl salt at a constant cell voltage of 3.0 V. Anode performance is one of the key factors that has to be improved to successfully regenerate the reduction salt and lithium metal by electrowinning. The objective of this set of thirteen experiments was to evaluate different anode materials (graphite, LiFeO_2/Cu , Fe_3O_4 , and Pt-10 wt% Rh). The results show that good electrochemical performance was always achieved when a graphite anode was employed as a consumable carbon anode for the electrowinning process; however, carbon contamination of the electrolyte salt from this anode was a problem. A cermet of copper and LiFeO_2 was tested as a nonconsumable oxygen anode. The results showed that this anode was chemically unstable; the copper from the cermet participated in the electrochemical process, but the LiFeO_2 was essentially not attacked. Two experiments were conducted to investigate the performance of a Fe_3O_4 rod as an inert oxygen anode. Preliminary results showed that the Fe_3O_4 anode was attacked during electrolysis, and the current efficiency for the recovery of lithium metal was low. The reactions which occurred at the anode during electrolysis have yet to be explained.

Of the three inert oxygen anode materials tested during this period, the Pt-Rh anode was the most stable. Therefore, six electrolysis experiments were performed with a Pt-Rh tube anode. One of these experiments (EW-39) was conducted to demonstrate the electrowinning process using simulated recycle salt, which included tellurium and iodine fission products. The result of Experiment EW-39 indicated that tellurium compounds formed an insulation layer on the anode surface that would stop the process. It may be necessary to remove the tellurium by using a sacrificial anode such as zirconium or molybdenum prior to electrowinning the Li_2O with the Pt-Rh anode. The other five experiments were performed in molten LiCl salt that did not contain any tellurium to obtain information pertinent to the planned engineering-scale tests (Sec. VII.C). The cell setup (as shown in Fig. VII-4) for these experiments was a laboratory-scale simulation of the engineering-scale design. The Pt-Rh anodes in these experiments achieved good electrowinning performance. The test results also demonstrated a close correspondence between the magnitude of the cell current and the actual Li_2O concentration in the electrolyte (see Table VII-3). At the end of electrolysis, when the cell current showed a rapid decrease to 0.3 A, the analytical results indicated that the final Li_2O concentration in the electrolyte was below 0.1 wt%.

Fig. VII-4. Schematic of Experimental Cell for Electrolysis Experiments (SS = stainless steel)

Table VII-3. Correlation between Cell Current and Li_2O Concentration in Molten LiCl Electrolyte at Different Stages of Operation

	Start (t = 0)	After 11 h	After 32 h (accelerated current decrease)	Conclusion (t = 50 h)
Li_2O Conc., ^a wt%	3.85	2.58	0.25	0.097
Cell Current, A	6.0	2.5	0.93	0.3
Current Density, mA/cm^2	237	100	36.8	12
Accumulated Ah	0	31.6	72.6	79.11

^aNot corrected for effect of lithium dissolved in the electrolyte.

Our future work will focus on improving the consumable carbon anode by fast removal of anode gases, better containment and removal of carbon dust from the anode region, and optimization of the anode shroud porosity, pore size, and material. We will also continue selection and evaluation of alternative anodes, such as non-consumable anodes (e.g., ferrites and ceramic/metal composites) and consumable metal anodes that are compatible with the lithium process.

4. Development of Laboratory-Scale Retort

A high-temperature vacuum furnace (retort) has been put into service as a distillation and melting furnace for use in development of the actinide recovery processes. This laboratory-scale retort is capable of distilling up to 1 L and consists of a ceramic primary crucible

inside a graphite susceptor and secondary vessel, all within an induction coil. During distillation runs, a condensing and collecting section is placed on top of the secondary crucible.

After the electrorefining step in the lithium process, the purified uranium dendrites are melted and consolidated into an ingot, so the major use of this retort will be in melting uranium. Tests of the retort conducted to date have involved melting a uranium standard, a uranium precipitate produced during reduction of UO_2 , and uranium dendrites produced during electrorefining.

The melting of uranium standards showed that the retort atmosphere and crucible material (BeO) were adequate to produce a uranium ingot. The melting of the uranium reduction precipitate indicated that residual Li_2O in the precipitate re-oxidizes the uranium metal when at or near melting conditions, and this oxide is sufficient to prevent complete consolidation of the precipitate. Under conditions where the precipitate was thoroughly washed in water and methanol to remove Li_2O , a very high fraction of the precipitate was converted to an ingot (93%), but without washing the conversion was only about 60%.

The melting of the uranium dendrites yielded high-quality ingots. In two experiments, dendrites produced by reduction followed by electrorefining of simulated spent fuel (30 and 320 g) were consolidated. The larger batch size produced a solid uranium ingot, as well as some undefined side product. The smaller batch did not produce a visible side product. Future work will be directed toward obtaining good uranium ingots from the various feed materials.

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. The goals of the overall process are to recover >99.9% of the TRU elements and yet minimize the quantities of waste generated. The demonstration experiments are to be conducted in a large (7.6 x 2.4 x 2.6 m) argon-filled glovebox and a smaller (2.4 x 1.1 x 2.9 m) nitrogen-filled glovebox with an interconnecting transfer lock. The tests in these gloveboxes will demonstrate each process step individually (reduction, retorting, casting, and electrowinning), and the gloveboxes will have the capability of storing the process materials between steps. The argon glovebox was completed at the end of FY 1993, and a demonstration reduction was run with a natural UO_2 -based simulated fuel. This 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. A second experiment is planned for early FY 1995 and will use a plutonium-containing simulated fuel. This experiment will demonstrate, within the large enclosure, the reduction and the salt regeneration steps at 650°C with pure LiCl , and is expected to provide a larger, more-readily processed precipitate.

To meet the experimental goals, the nitrogen-filled glovebox and new equipment had to be designed, fabricated, and installed during FY 1994. This equipment included the electrochemical vessel and anode assembly for the electrowinning of lithium and recovery of the spent salt,

two casting stations capable of accepting 25 L of molten salt per cast (one to accept the melt from the reduction crucible and one to accept melt from the electrochemical crucible), and three transfer lines to transfer the melt between the reduction, electrochemical, and casting station vessels. Devices for upending the casting mold to obtain the ingots, crushing the ingot material into pea-size product, and sampling the crushed product for analytical purposes were also incorporated into the argon glovebox. In addition, provisions were made to add a retort and electrorefiner to the argon glovebox without having to expose the plutonium-containing interior. The nitrogen glovebox connects to the argon glovebox through a vacuum lock and is to be used both as an entryway for equipment and supplies into or out of the gloveboxes and as a place to perform processes that, if done in the argon glovebox, would compromise the high-purity atmosphere. For this second purpose the nitrogen glovebox was designed to have an oxidation furnace, which will be added at a later date.

VIII. APPLIED PHYSICAL CHEMISTRY

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

A. *Thermophysical Property Studies of Metallic Nuclear Fuel*

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. Thermodynamic analysis of phase equilibria in metallic nuclear fuels has progressed to the study of the Fe-U-Zr ternary system.¹ This analysis draws upon our previous analyses of the three binary subsystems: U-Zr,² Fe-U,³ and Fe-Zr.⁴ A related analysis of the Pu-U system has also been published.⁵

The general methods used in our analysis have been discussed previously²⁻⁵ and will be briefly summarized here. The calculations were performed with programs of the F*A*C*T (Facility for the Analysis of Chemical Thermodynamics) computer system based in Montreal⁶ to determine equations for the Gibbs energy of all phases existing in a system as functions of temperature and composition. A least squares optimization of all available thermodynamic and phase equilibrium data provides a self-consistent polynomial for the thermodynamic properties of the liquid and expressions for the Gibbs energies of the solid phases. Binary phase diagrams are derived from the thermodynamic properties of the phases by calculating the lowest common tangents to the Gibbs energy-composition curves. This procedure ensures thermodynamic consistency of the resulting phase diagram and provides a powerful means for assessing conflicting data.

We calculated excess Gibbs energies in the liquid and solid phases of the Fe-U-Zr system by substituting the values for the three binary systems into either the Kohler equation⁷ or the Toop equation.⁸ These equations are based on extensions of regular solution theory and have been used extensively in the literature for ternary alloy systems. We also assumed that the Fe-U-Zr system has no ternary compounds, despite the preliminary report of the existence of such a compound.⁹ We are studying this possibility.

¹ A. D. Pelton, P. K. Talley, L. Leibowitz, and R. A. Blomquist, *J. Nucl. Mater.* **210**, 324 (1994).

² L. Leibowitz, R. A. Blomquist, and A. D. Pelton, *J. Nucl. Mater.* **167**, 76 (1989).

³ L. Leibowitz and R. A. Blomquist, *J. Nucl. Mater.* **184**, 47 (1991).

⁴ A. D. Pelton, L. Leibowitz, and R. A. Blomquist, *J. Nucl. Mater.* **201**, 218 (1993).

⁵ L. Leibowitz, R. A. Blomquist, and A. D. Pelton, *J. Nucl. Mater.* **184**, 59 (1991).

⁶ C. W. Bale, A. D. Pelton, and W. T. Thompson, *F*A*C*T Guide to Operations*, McGill University/École Polytechnique, Montreal (1985).

⁷ F. Kohler, *Monatsh. Chemie* **91**, 738 (1960).

⁸ N. J. Olson and G. W. Toop, *Trans. Metal. Soc.-AIME* **266**, 590 (1966).

⁹ L. R. Kelman, "Further Work on ANL on Fast Reactor Fuels," in *Plutonium 1965*, Eds., A. E. Kay and M. B. Waldron, Chapman and Hall, London, p. 525 (1967).

It was not clear what assumptions should be made about the mutual solubilities of Fe_2U and Fe_2Zr for the ternary system. Both of these compounds have the same structure (the Laves phase Cu_2Mg), and the atomic radii of Zr and U are similar; hence, some mutual solubility is expected. Two limiting cases were examined: (1) the compounds were assumed to have no mutual solubility, and (2) they were assumed to be completely miscible in an ideal solid solution. The liquidus projection of the calculated Fe-U-Zr phase diagram for the first case is shown in Fig. VIII-1a. The diagram for the second case is given in Fig. VIII-1b. The two diagrams show relatively little difference except near the Fe_2U - Fe_2Zr join.

For both diagrams, the liquidus surface is dominated by the Fe_2Zr and the $\text{U}(\gamma)/\text{Zr}(\beta)$ phase fields. Small phase fields of Fe_3Zr , FeZr_2 , Fe_2U , FeU_6 , $\text{Fe}(\gamma)$, and $\text{Fe}(\delta)$ are also seen, and a univariant skirts very close to the U-Fe binary. At the binary eutectic at 721°C ,³ only 0.025 at.% Zr will dissolve in the liquid before Fe_2Zr precipitates. The binary peritectic at 810°C is lowered by only 1°C when 0.12 at.% Zr is added, yielding a ternary peritectic. The binary eutectic at 1071°C is lowered to a ternary eutectic at 1046°C with 1.8 at.% Zr. The Fe_2U - Fe_2Zr system is quasi-binary, with a saddle point at 1176°C . The univariant separating the Fe_2Zr and the $\text{U}(\gamma)/\text{Zr}(\beta)$ phase fields is nearly constant in temperature at just below 1000°C over a wide range of compositions. There is a saddle point (maximum temperature) on this univariant at 996°C .

With reference to the U-Zr binary in Fig. VIII-1, when iron is added, a small amount enters into solution in the $\text{U}(\gamma)/\text{Zr}(\beta)$ phase. The binary invariant temperatures are each lowered by about 1°C with the addition of approximately 0.2 at.% Fe in solution, at which point the solution becomes saturated and FeZr_3 precipitates.

The assumptions made in calculating the ternary phase diagram are all well founded. All of the binary optimizations have good precision; thus, the calculated ternary diagram should also have good precision. In comparing the phase diagram where Fe_2U and Fe_2Zr form an ideal solid solution (Fig. VIII-1b) with that where they are immiscible (Fig. VIII-1a), we find that the calculated liquidus surface in the former case is up to 80°C higher in the vicinity of the Fe_2U - Fe_2Zr join. However, as the distance from this join increases, the differences rapidly become much smaller. In the vicinity of the saddle point at 996°C , for example, the liquidus temperature changes only by the order of 1°C . In uranium-rich solutions (above 70% uranium), the liquidus increases by less than 5°C . In reality, Fe_2U and Fe_2Zr probably exhibit limited mutual solubility (with positive deviations from ideal solution behavior), and the true phase diagram lies between the two extremes. This question could best be resolved by a few liquidus measurements in the vicinity of the Fe_2U - Fe_2Zr join. Experiments are planned to explore this question, as well as the existence of a previously reported ternary compound.⁹

B. *Development of Synchrotron Analytical Capabilities*

Over the past year, CMT has been collaborating with Louisiana State University (LSU) in constructing a synchrotron X-ray beamline at the Center for Advanced Microstructures and Devices (CAMD). This project grew from earlier work at the National Synchrotron Light Source (NSLS) of Brookhaven National Laboratory, where a team of Argonne researchers developed techniques to examine small-scale structures in diffusion zones of a variety of materials. These

Fig. VIII-1. Liquidus Surface of Calculated Fe-U-Zr Phase Diagram Based on Assumption of (a) No Solid Solution between Fe_2U and Fe_2Zr and (b) Ideal Solution between Fe_2U and Fe_2Zr . All temperatures in $^{\circ}\text{C}$. E_n = ternary eutectic, e = binary eutectic, P_n = ternary peritectic, and p = binary peritectic.

materials included metallic-fuel/cladding and fission-product-lanthanide/cladding interfaces, as well as aluminum-coated iron-based alloys. Three separate NSLS beamlines were used, since no single beamline allowed simultaneous X-ray fluorescence and diffraction experiments. Nevertheless, with X-ray spot sizes as small as 5 μm , the NSLS experiments successfully demonstrated that synchrotron radiation can be used to reveal both composition and structure in diffusion zones of materials at a microscopic scale.

The ANL/CAMD synchrotron beamline will be the first dedicated facility to take advantage of the techniques developed at the NSLS. Significant progress has been made over the last year in designing and constructing a white-beam facility for X-ray fluorescence work. Thus far, the beamline and experiment hutch have been installed, a vibration-control kinematic table has been delivered, and an X-ray detector system has been procured. During 1995, a major upgrade of the ANL/CAMD beamline will take place. Specifically, focusing optics will be added to intensify the X-ray flux on the sample, and a monochromator will be added to tune the beam to a single X-ray wavelength. The monochromator will be the heart of the ANL/CAMD beamline. In its most basic use, the monochromator allows X-ray diffractometry for the determination of crystal structures. This technique has already proved useful in identifying intermetallic phases in the diffusion zones between metallic nuclear fuel and cladding materials.¹⁰ In a typical experiment at CAMD, a high-energy X-ray beam would be used for fluorescence to locate a specific microstructural feature of a sample. The monochromator would then be tuned to a lower energy for diffractometry of that feature. With a channel-cut monochromator, this change in X-ray energy would cause a vertical shift of the beam position on the sample. For the well-defined microstructure of a diffusion couple, this shift could be compensated for by a translation of the sample, though translation errors would always cause uncertainties in the final beam position on the sample. An improved technique would be the use of a double-crystal, fixed-exit monochromator, which provides a constant beam position regardless of the X-ray wavelength. As the ANL/CAMD experiments shift away from nuclear reactor-related diffusion couples, this feature will become more critical. Moreover, a fixed-exit monochromator with a fast energy-scanning capability opens a wide range of research areas that would not otherwise be possible. X-ray absorption spectroscopy, for example, requires scanning a fixed sample location through a range of energies. Extended X-ray absorption fine structure, in particular, is a powerful tool for determining the local arrangement of atoms and has been used to study aqueous corrosion of nuclear waste glasses and to examine the structure of industrial catalysts. Other techniques requiring a fixed-exit monochromator include surface extended X-ray absorption fine structure, X-ray absorption near-edge structure, and X-ray standing waves. The dependability, flexibility, and accuracy of the ANL/CAMD beamline monochromator will allow for diverse X-ray techniques that can provide structural information on a wide range of materials, including glasses, batteries, fuel cells, and weldments. Several CMT researchers have expressed interest in pursuing these possibilities at CAMD.

¹⁰ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, pp. 112-113 (1994).

C. *Fusion-Related Research*

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 lithium-containing ceramics (e.g., Li_2O , LiAlO_2 , Li_4SiO_4 , and Li_2TiO_3) as breeder materials.

1. Tritium Release from Ceramic Breeders

Lithium-containing ceramics are among the leading candidates for use as tritium-breeding materials in a fusion reactor. Breeder blanket designs utilizing lithium ceramics also employ a beryllium neutron multiplier to ensure a tritium-breeding ratio greater than one. For these designs to be acceptable from an economic and safety perspective, the tritium inventory in the ceramic and in the beryllium should be low. The SIBELIUS experiment is a U.S./European community collaborative test designed to assess the compatibility of beryllium/lithium ceramics and beryllium/steel compacts in a neutron environment. The test has provided the opportunity to assess the tritium inventory in several candidate ceramic breeder materials and in beryllium and to determine whether any interactions between the ceramics and beryllium affect the tritium inventory in these materials.

Tritium inventory measurements at the blanket end-of-life provide important data for designers and modelers. However, sample characteristics, such as grain size, may be affected by changes in the test conditions, such as temperature or purge gas composition, which may complicate the interpretation of the end-of-life inventories. The SIBELIUS data set is unique in that the samples were subjected to a minimal number of temperature changes and operated under constant purge-gas composition.

The design of the irradiation capsules and the experimental conditions have been reported previously.^{11,12} Results summarized here concern the beryllium/ceramic specimens (the tested ceramics are Li_2ZrO_3 , Li_2O , Li_4SiO_4 , and LiAlO_2). These specimens were irradiated for 1690 h at a neutron flux of 1.1×10^{14} n/cm²·s (thermal) and 1.0×10^{14} n/cm²·s (fast, >1 MeV). The irradiation temperature was maintained at 550°C (823 K) for most of the experiment. One set of temperature transients was performed near the end of the irradiation period: the temperature for the LiAlO_2 was decreased to 500°C (773 K) then returned to 550°C (823 K), that of the Li_4SiO_4 and Li_2ZrO_3 was decreased to 450°C (723 K) then returned to 550°C (823 K), and that for the Li_2O remained constant at 550°C (823 K). After irradiation, the ceramic specimens were removed from the experimental stack and examined, and tritium analysis was carried out on sections of the samples by either high-temperature annealing or dissolution, followed by liquid scintillation counting.

¹¹ N. Roux, M. Briec, M. Bruet, T. Flament, C. Johnson, M. Masson, A. Terlain, and F. Tournebize, *J. Nucl. Mater.* **179**, 329 (1991).

¹² N. Roux, J. J. Abassin, M. Briec, D. Cruz, T. Flament, and I. Schuster, *J. Nucl. Mater.* **191**, 168 (1992).

The tritium inventories determined from the dissolutions and the anneals are tabulated in Table VIII-1. The lithium oxide results in the table have been corrected to give the inventory prior to any hydrolysis of the sample. This correction increases the tritium inventory from 21.7 to 34.8 MBq/g for the dissolution tests and from 22.6 to 36.2 MBq/g for the anneal samples. The ternary ceramics are much less hygroscopic than lithium oxide and are expected to have undergone only slight hydrolysis during handling and storage. In addition, if hydrolysis occurred, the percentage of weight gained due to hydrolysis is much less than that for lithium oxide. As a result, errors in determining the tritium per unit weight of sample are reduced. As shown in Table VIII-1, the tritium inventories for the Li_2O are in excellent agreement, with differences of less than 5%. The results indicate that all of the tritium was released during the high-temperature anneals, and that losses due to tritium in the gas phase (either as HT or HTO) for the dissolution method are insignificant. For Li_4SiO_4 , the agreement between the two methods is also very good. The greatest difference occurred for the inventories of the LiAlO_2 samples, with a difference of about 20%. This difference is most likely due to the small amount of aluminate sample that dissolved (6 mg) and the inherent errors involved in the partial dissolution. No dissolution analysis was done for the Li_2ZrO_3 sample.

Table VIII-1. Tritium Inventories in SIBELIUS Ceramics at End-of-Life

	Inventory, MBq/g		
	Dissolution	Anneals	Average
LiAlO_2	2029 ± 203	1659 ± 116	1844 ± 185
Li_4SiO_4	874 ± 87	947 ± 66	911 ± 37
Li_2O	34.8 ± 3.5	36.2 ± 2.6	35.5 ± 0.7
Li_2ZrO_3	a	7.8 ± 0.6	a

^aNot defined.

As indicated in Table VIII-1, the tritium inventory increased in the order $\text{Li}_2\text{ZrO}_3 < \text{Li}_2\text{O} < \text{Li}_4\text{SiO}_4 < \text{LiAlO}_2$. These inventories are all within the range of values observed for other in-pile tests where beryllium was absent¹³⁻¹⁶ and suggest that the beryllium has little or no effect on the tritium retention in the ceramic. Also, while the inventories for the Li_4SiO_4 and LiAlO_2 are about two orders of magnitude higher than those for the Li_2ZrO_3 and Li_2O , they are still below levels that would cause safety problems.

Post-test examination of the beryllium/ceramic system indicated that it had remained stable at 550°C (823 K) for the irradiation fluence investigated. The lithium ceramics

¹³ 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.

¹⁴ R. A. Verrall, J. M. Miller, I. J. Hastings, D. S. MacDonald and D. H. Rose, in *Advances in Ceramics: Fabrication and Properties of Lithium Ceramics*, Vol. 27, Eds., G. W. Hollenberg and I. J. Hastings, American Ceramic Society, Westerville, OH, p. 299 (1990).

¹⁵ H. Kwast, A. Kout, R. P. Muis, M. P. Stijkel, A. J. Flipot, and J. D. Elen, *Fusion Eng. Design* **8**, 359 (1989).

¹⁶ H. Kwast, R. Conrad, R. May, S. Casadio, N. Roux, and H. Werle, *J. Nucl. Mater.* **212-215**, 1010 (1994).

survived the irradiation intact without fractures. The ceramic disks were easily separated from the adjacent beryllium disks, with no macroscopic evidence for interactions between the ceramic and beryllium. Examinations with scanning electron microscopy indicated no changes in the ceramic microstructures at the beryllium/ceramic interface; however, some roughening of the beryllium surfaces was noted. The stability of the beryllium/ceramic couple is probably due to a protective coating of BeO, which appears to be unaffected by irradiation damage at the fluence investigated.

Because reliable tritium inventory data are so few, we can not draw firm conclusions at this time. Nonetheless, it appears that intimate contact between beryllium and lithium ceramics considered for tritium breeding materials has no detrimental effects on the performance of the ceramics, chemical interactions between the ceramics and the beryllium also are negligible, and the tritium inventories should cause no safety problems.

2. Desorption of Hydrogen from Lithium Oxide

Lithium oxide is one of the leading candidates for use as a tritium breeding material in a fusion reactor. Many experiments have demonstrated the relative ease of tritium recovery from this material. Tritium release is particularly facile when the purge gas (argon or helium) contains hydrogen, typically at levels of about 0.1%. However, addition of hydrogen to the purge gas has a penalty associated with the tritium purification process. In particular, a large amount of hydrogen in the purge gas will necessitate a larger tritium purification unit and, therefore, higher costs. Optimizing tritium release while minimizing the amount of hydrogen necessary in the purge gas requires a better understanding of the tritium desorption step and the interactions of hydrogen with the lithium oxide surface.

In an effort to gain information about the species present on the surface and their relationship to tritium desorption, we have turned to a study of hydrogen (and deuterium) adsorption and desorption from lithium oxide by using a combination of temperature programmed desorption (TPD) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). From the shape and position of the desorption peak in the TPD spectra, one can obtain information about the energetics of the desorption process.¹⁷ However, this technique provides no information on the identity or form of the species that is desorbing from the surface; DRIFTS fills this gap.

For the TPD measurements, hydrogen (deuterium) was adsorbed on a lithium oxide sample at 250°C (523 K) for 3 to 24 h. The purge gas was then changed to pure Ar or Ar plus 0.1% D₂ (or Ar plus 0.1% H₂), and the temperature increased up to 750°C (1023 K) linearly while the outlet gas stream was continuously monitored by mass spectroscopy.

For the TPD experiments into a purge gas of pure argon, one narrow peak was observed for temperature increases up to 750°C (1023 K) at heating rates of 2, 5, and 10°C/min. For a heating rate of 1°C/min, one peak with what might be a second small peak near the

¹⁷ J. L. Falconer and J. A. Schwarz, Catal. Rev., Sci. Eng. 25(2), 141 (1982).

temperature limit of the experiment was observed. The main peak was narrow, and we were unable to calculate a consistent activation energy for this peak by comparing results from line-shape analysis and plots of $\ln(T_m^2/H)$ vs. $1/T_m$, where T_m is the temperature of the peak maximum, and H is the heating rate. This suggests that desorption into pure argon is not a simple first-order desorption process.

The TPD experiments performed in a purge gas of Ar plus 0.1% H_2 exhibit more than one peak in the desorption spectra. The main peak occurs at temperatures close to those seen in pure argon; however, additional peaks occur at higher temperatures and at temperatures near the maximum temperature for the experiment (Fig. VIII-2). For the main peak, plots of $\ln(T_m^2/H)$ vs. $1/T_m$ give a much lower activation energy compared with line-shape analysis. This suggests that the mechanism for desorption of this species is also not a simple first-order desorption. For the second peak, an activation energy of 73 kJ/mol was calculated from both line-shape analysis and plots of $\ln(T_m^2/H)$ vs. $1/T_m$. The other peaks were too close to the temperature limit to be able to calculate activation energies by these methods.

Fig. VIII-2.

Spectra from Temperature Programmed Desorption of OD from Li_2O at Heating Rate of 1 K/min with Purge Gas of Ar plus 0.1% H_2

The DRIFTS experiments were performed by exposing the ceramic to Ar plus 0.1% H_2 or Ar plus 0.1% D_2 at temperatures between 100°C (373 K) and 400°C (673 K) and recording the infrared spectra. Kinetic experiments were also performed by switching the purge gas (e.g., from Ar plus 0.1% H_2 to pure Ar or Ar plus 0.1% D_2), then recording the spectra at selected time intervals.

Figure VIII-3 shows the hydroxyl region of the DRIFTS spectra of a lithium oxide powder after exposure to a purge gas of Ar plus 0.1% D_2 and Ar plus 0.1% H_2 at 365°C (638 K). Several different absorptions are observed for OH and OD. Under different conditions, other peaks appear more prevalent. Deconvolution of the curves in Fig. VIII-3 indicates four different OH absorptions: 3657, 3604, 3480, and 3400 cm^{-1} . Corresponding OD peaks were observed at 2695, 2659, and 2560 cm^{-1} . (The OD peak corresponding to the OH peak at 3400 cm^{-1} has not

Fig. VIII-3.

Infrared Spectra of Li_2O after Exposure to Argon Purge Gas Containing H_2 and D_2

yet been observed, probably because the intensity of this OH peak is very low under the conditions investigated.) These results indicate four different OH species on the surface. We propose that these are OH species with coordination numbers of 2, 4, 6, and 8, respectively. The strength of the OH bond and, therefore, the OH vibration frequency will depend on the electron density on the oxygen. As the electron density on the oxygen is reduced by coordination to lithium atoms in the lattice, the O-H bond strength should decrease, decreasing the frequency of the absorption. This is similar to the effect seen for infrared absorptions of terminal versus bridging carbonyl groups.

Under certain conditions, we have seen infrared absorptions in the region where a Li-H stretch is expected. These infrared absorptions (at 1245 to 1212 cm^{-1}) are shifted to slightly lower frequencies than that observed for lithium hydride (1280 cm^{-1}). The hydride absorption in the infrared region generally occurred when hydrogen was present in the purge gas and temperatures were above 380°C (653 K). The presence of a Li-H species suggests that hydrogen is adsorbed on the surface heterolytically to form H^+ (OH^-) and H^- (Li-H). Preliminary quantum mechanical calculations suggest that this type of heterolytic adsorption could be on some lithium oxide surfaces.

In our preliminary kinetic studies, the decomposition of the hydroxyl species was followed at 400°C (673 K) by recording the spectra at about 10-min intervals (see Fig. VIII-4). The preliminary data for the decomposition of the main peak at 3657 cm^{-1} appear consistent with a first-order desorption, the rate of which is an order of magnitude lower than that for the decomposition of bulk LiOH ; however, more data are needed. The decompositions of the secondary peaks do not appear to follow first-order processes. Before these peaks start to decay, the secondary hydroxyl peaks tend to remain constant until the peak at 3657 cm^{-1} has decayed substantially. This complicated kinetics may be the reason for the difficulty in interpreting the sharp peaks seen in the TPD curves and requires more study.

Fig. VIII-4.

Hydroxyl Region of Infrared Spectra of Li_2O in Ar plus 0.1% H_2 after Temperature Increase to 400°C (673 K) as Function of Time

As part of a preliminary study to determine the applicability of a combined TPD-DRIFTS experiment, a quasi-TPD experiment was performed while the diffuse reflectance infrared spectra were recorded during a temperature increase from 250°C (523 K) to 400°C (673 K). The TPD curve and the DRIFTS results suggested that the TPD peak observed at about 390°C (663 K) is mainly due to removal of the OH species at 3657 cm^{-1} from the surface. The observation of this species at the surface and the observed change in the concentration of this species with time indicate that the rate-controlling mechanism for the disappearance of this peak is not bulk diffusion. The TPD and DRIFTS results also indicated that the hydride species is not observed until the OH species at 3657 cm^{-1} is absent. One possible explanation is that these hydroxide groups occupy the sites at which H^- adsorbs.

Limitations in the TPD-DRIFTS apparatus relegated the experiment to a maximum temperature of 400°C (673 K) and resulted in a temperature increase that was not quite linear. Thus, no quantitative information regarding the activation energies could be obtained. However, the results do provide qualitative findings, indicating that the technique of combined TPD-DRIFTS should be pursued further.

In future work, the TPD-DRIFTS studies will be extended to higher temperatures, which are more relevant to fusion blanket studies, and DRIFTS experiments will be performed to determine the kinetics of exchange reactions on the Li_2O surfaces.

3. Dissociative Hydrogen Adsorption on Lithium Oxide

As discussed earlier, use of hydrogen in the purge gas enhances the release of tritium from lithium ceramics such as Li_2O . Despite this benefit, the hydrogen addition causes problems associated with tritium separation from the purge gas (because of the large hydrogen/tritium ratio) and tritium containment (arising from the presence of the reduced form of tritium and potential permeation loss). To overcome these problems, we need to gain an understanding of the mechanism through which hydrogen enhances tritium release. Therefore, we are investigating the process of hydrogen adsorption onto lithium oxide surfaces. This study is

being carried out with *ab initio* Hartree-Fock calculations and a slab model. In this model, the semi-infinite crystal is simulated by a finite number of atomic layers parallel to the exposed face, reproducing the crystal geometry. During the last year, our efforts were concentrated on the (110) and (111) crystal surfaces.

Figure VIII-5 shows a part of the extended top layer of the (110) terrace, where the unit cell is defined by the basis vector $\mathbf{a}_1 = (3.23, 0.0, 0.0)\text{\AA}$ and $\mathbf{a}_2 = (0.0, 4.57, 0.0)\text{\AA}$. In the figure, the adsorption locations of the dissociative hydrogen sites are represented by 1, 2, 3, and 4. Dissociative hydrogen sites may then be described by the formalism H(1)H(2), H(1)H(3), and H(1)H(4). For example, H(1)H(2) means that, at location 1, one of the hydrogen atoms is on top of the oxygen, and another hydrogen atom is on top of the lithium at location 2. Note that the model was set up such that the dissociative hydrogen atom appears only on the top of surfaces; no hydrogen appears below the surface.

Fig. VIII-5. Model of Hydrogen Chemisorption on Top Layer of (110) Surface of Li_2O Crystal

Calculated results on the heterolytic sites, Li-O site, of n -layer (110) slabs (where $n \geq 2$) suggest that the heat of adsorption of the dissociative hydrogen is endothermic. For a one-layer (110) slab, the heat of adsorption is exothermic, -0.93 eV, forming OH^- and Li^+HLi^+ . Investigation on the heterolytic sites of three-layer (111) slabs indicates that hydrogen chemisorption is endothermic.

Figure VIII-6 illustrates the density of states for a one-layer (110) slab before and after chemisorption. Before chemisorption (fine lines), the uppermost valence bands are the O 2p bands indicated by three peaks of $2p_x$, $2p_y$, and $2p_z$ bands. The O $2p_z$ orbital (not shown in Fig. VIII-6) lies perpendicular to the surface, while the O $2p_x$ and $2p_y$ orbitals are oriented parallel to the surface. The thicker lines in Fig. VIII-6 are the density of states in the presence of dissociative hydrogen adsorption at H(1)H(3) (see Fig. VIII-5). The narrow band between -16.770 and -16.410 eV represents the formation of OH^- as a result of overlapping between the O $2p_z$ and H 1s orbitals. The highest band represents the H^- that bonds with the two cations in

Fig. VIII-6. Calculated Density of States for One-Layer (110) Slab before (thin lines) and after (thicker lines) Hydrogen Chemisorption on Li_2O Surface

the form of $\text{Li}^+\text{H}^-\text{Li}^+$. The OH and LiH bond lengths are 0.96 and 1.54 Å, respectively, which are closely comparable with the bond lengths reported for the gas phase.¹⁸

Calculations for the homolytic sites of the terrace, such as Li-Li and O-O, indicate no dissociative hydrogen chemisorption. For dissociative hydrogen chemisorption to occur on the homolytic sites, it has to be in the form of either two H^+ or two H^- ions, where each of them attaches to two oxygens or to two lithiums. Such phenomena do not occur for this material under equilibrium conditions since it would require transferring electrons into the surrounding crystal environment. Our calculations indicate that, at equilibrium, this electron transfer is too energetically prohibitive.

In summary, dissociative hydrogen chemisorption on the (110) and (111) Li_2O terraces is endothermic. Exothermic chemisorption with 100% coverage takes place for the case of a one-layer (110) slab around the Li-O site. This is caused by the lower coordination of the oxygen and nearest neighbor adsorbate-adsorbate interactions. Although the one-layer (110) slab represents an unphysical surface, this model illustrates that a lower coordination environment, as in surface step structures such as kinks and ledges, may play an important role in the hydrogen chemisorption process. This will be investigated in the next stage of our work.

¹⁸ Warren J. Hehre, *Ab Initio Molecular Orbital Theory*, John Wiley, New York, pp. 138 and 210 (1986).

IX. BASIC CHEMISTRY RESEARCH

Basic chemistry research is being pursued in three areas: (1) catalytic chemistry associated with molecular energy resources and novel pre-ceramic polymers; (2) materials chemistry of high-temperature superconducting oxides, electrified metal/solution interfaces, molecular sieves, and impurity metals that need to be removed from scrap copper and steel; and (3) geochemical processes involved at mineral/fluid interfaces and in water/rock interactions occurring in active hydrothermal systems.

A. *Fluid Catalysis*

This program uses *in situ* kinetic and spectroscopic techniques to explore catalytic reaction chemistry at the high pressures and temperatures that are frequently employed in industrial processes. Recent accomplishments include (1) the first measurements by *in situ*, high-pressure nuclear magnetic resonance (NMR) of the Shell Process for the hydroformylation of olefins, (2) the development of a new technique for investigating ceramic precursor processes at high pressures, and (3) the synthesis of some highly electrophilic and unusually reactive poly-fluorophthalocyanine complexes designed to achieve the controlled functionalization of aliphatic hydrocarbons.

1. Catalytic Chemistry in Supercritical Fluids

The largest scale industrial process for homogeneous catalysis is the oxo process for the hydroformylation of olefin; the total world oxo capacity is about 5 million tons/year. We have recently initiated the first *in situ*, high-pressure NMR studies of the phosphine-modified cobalt hydroformylation process. This process was invented and is used exclusively by Shell Chemical Company.¹ It produces agricultural chemicals, industrial solvents (e.g., 1-butanol), and detergent-range alcohols from C₁₁-C₁₄ olefins in accord with

As shown in this equation, the catalyst adds one mole of CO and two moles of H₂ to the olefin (in this case a terminal one, in which the double bond lies at the end of the chain) to produce the next higher homologous alcohol; that is, *n* in Eq. 1 is increased by 1. The phosphine-modified catalyst differs from the conventional unmodified cobalt (oxo) catalyst in that the presence of a tertiary phosphine improves the selectivity toward linear products.

The phosphine-modified catalysts operate at higher temperatures than other types. The Shell catalysts operate at 150-210°C, compared to 140-180°C for the unmodified cobalt

¹ I. Kirshenbaum and E. J. Inchalik, "Oxo Process," in *Encyclopedia of Chemical Technology*, 3rd ed., Vol. 16, John Wiley & Sons, New York, pp. 637-653 (1981).

catalyst, and about 100°C for the newer catalysts based on rhodium catalysts.² At the higher process temperatures, the phosphine-modified catalysts produce mainly alcohols, whereas the other catalysts produce aldehydes, which often need to be further processed to yield alcohols by use of a separate hydrogenation step involving an additional catalyst, such as copper chromite.

Our own interest in the phosphine-modified cobalt catalysts stems from our recent research on the conventional oxo catalyst, which would benefit from comparable data on the phosphine-modified systems. 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 Shell catalyst would not only result in the first definitive scrutiny of the component steps in this important industrial process, 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 relevant cobalt carbonyl complexes.

One such case where thermodynamic measurements would be helpful is the hydrogenation equilibrium:

The enthalpy change for this reaction can be used to calculate the bond energy of the Co-H bond in the key hydride-containing species, $\text{H}-\text{Co}(\text{PBu}_3)(\text{CO})_3$, by using the known H-H bond energy for H_2 and the enthalpy change for the homolytic bond dissociation reaction:

Other reactions that occur with the use of the phosphine-modified catalysts, while probably not connected directly to steps in the catalytic pathway, warrant investigation because their occurrence would seem to detract from catalyst efficiency. Two such reactions are

² R. Fowler, H. Connor, and R. A. Baehl, *Hydrocarbon Proc.* 55(9), 247 (1976).

Preliminary high-pressure NMR experiments on the tributylphosphine-modified catalyst indicate that many of the organometallic species can be observed and quantified by ^{31}P NMR. Figure IX-1 presents the spectra we obtained from a ^{31}P NMR study of the Shell-type catalyst at initial partial pressures of H_2 and CO of 6.9 MPa and various temperatures. Although it is too early to describe this system quantitatively, some comparisons with the unmodified catalyst can already be made. For example, the NMR effects associated with the radical, $\bullet\text{Co}(\text{PBU}_3)(\text{CO})_3$, are not so readily apparent in the phosphine-modified system as they are with $\text{Co}_2(\text{CO})_8$ in the absence of phosphine.³ Thus, if dissociation to produce radicals (Eq. 3) proceeded as readily as it does with $\text{Co}_2(\text{CO})_8$, the signal for $\text{Co}_2(\text{CO})_6(\text{PBU}_3)_2$ with increasing temperature (Fig. IX-1) would have (1) broadened, (2) contact shifted, and (3) merged with the resonance for $\text{HCo}(\text{CO})_3\text{PBU}_3$. None of these effects seem to be very significant in Fig. IX-1, even at 225°C. These observations indicate that the Co-Co bond in the phosphine-substituted dimer is probably significantly stronger than the 80 kJ/mol measured for $\text{Co}_2(\text{CO})_8$.³ The process leading to the broadening of the ^{31}P resonance of $\text{HCo}(\text{CO})_3\text{PBU}_3$ in Fig. IX-1 has not yet been identified but could result from rapid proton exchange with bases, such as $\text{Co}(\text{CO})_4^-$. This line broadening has made it more difficult to integrate the hydride resonance and derive the enthalpy change for the hydrogenation equilibrium in Eq. 2, but preliminary measurements indicate a value close to the 19.7 kJ/mol measured for $\text{Co}_2(\text{CO})_8$.⁴ This enthalpy change depends upon the relative strengths of the Co-H and Co-Co bonds of the species in Eq. 2. Thus, if the Co-Co bond in the phosphine-substituted dimer is stronger than that in $\text{Co}_2(\text{CO})_8$, then the enthalpy change

Fig. IX-1.

In Situ ^{31}P NMR Spectra of Shell-Type Catalyst at Temperatures of 75 to 225°C (initial partial pressures of H_2 and CO , 6.9 MPa)

³ R. J. Klingler and J. W. Rathke, *J. Am. Chem. Soc.* **116**(11), 4772-4785 (1994).

⁴ J. W. Rathke, R. J. Klingler, and T. R. Krause, *Organometallics* **11**, 585-588 (1992).

implies that the Co-H bond in the phosphine-substituted hydride is also stronger than that in HCo(CO)_4 . Figure IX-1 also indicates that the ionic products of Eqs. 4 and 5 are not favored at higher temperatures. Additional measurements indicate that the reactions in Eqs. 4 and 5 equilibrate under these conditions, and that the enthalpy changes for both reactions are negative.

In future research, we hope to quantify the observations described here. We also intend to begin the first measurements on supercritical versions of a phosphine-modified catalyst.

2. High-Resolution Detector for Studying Ceramic Precursor and Other Chemistry

Previous work in this activity has demonstrated that toroid cavity detectors have unique properties for *in situ* NMR spectroscopic analysis under forcing conditions of high pressure and temperature.⁵⁻⁷ More recent work has illustrated the potential of toroid cavity NMR detectors to achieve higher spacial resolution⁸ for magnetic resonance imaging than was previously attainable for solid polymer samples. The toroid cavity detector has a wide range of applications in the characterization of surface layers and in the production of advanced materials. Potential uses include *in situ* NMR monitoring of growth sites during ceramic formation processes, analysis of the oxygen annealing step for wires coated with high-temperature superconductors, and investigation of the reaction chemistry as a function of distance within the diffusion layer for electrochemical processes. Current work has removed the only remaining technical factor that limited the general applicability of this high-sensitivity NMR detector.

Over the years, many powerful two-dimensional (2-D) NMR procedures have been developed to resolve the intricate bonding structure of complex biomolecules. These indispensable 2-D NMR techniques were not usable with toroid NMR detectors because it was not possible to homogeneously focus the nuclear magnetization of the NMR sample within a toroid cavity by using a simple radio-frequency (r.f.) transmitter pulse. We have now developed composite pulse sequences for toroid cavity detectors that are capable of orienting the sample's nuclear magnetization in a phase-correlated manner with better than 98% efficiency. This latter achievement allows the full manifold of 2-D NMR experiments that have been developed for conventional NMR detectors to be employed at the higher sensitivities attainable with toroid cavity detectors.

Both toroid coils and the closely related device, the toroid cavity detector of Fig. IX-2, exhibit increased sensitivity when compared with conventional solenoid or Helmholtz coil NMR receivers.⁵⁻⁹ Furthermore, because of their special geometry, toroid cavities exhibit a graded r.f. field (B_1) that is strongest near the central conductor of the toroid detector and drops off as the inverse of the radius r ($B_1 = A/r$, where A is a proportionality constant). This well-defined gradient in the B_1 field forms the basis of the distance-imaging capability of this type of

⁵ J. W. Rathke, J. Mag. Reson. **85**, 150-155 (1989).

⁶ R. J. Klingler and J. W. Rathke, Prog. Inorg. Chem. **39**, 131-180 (1991).

⁷ K. Woelk, J. W. Rathke, and R. J. Klingler, J. Magn. Reson. A **109**, 137 (1994).

⁸ K. Woelk, J. W. Rathke, and R. J. Klingler, J. Magn. Reson. A **105**, 113 (1993).

⁹ T. E. Glass and H. C. Dorn, J. Magn. Reson. **51**, 527 (1983).

Fig. IX-2.

Schematic Drawing of Toroid Cavity
Detector and the Enclosed Sensitive Volume

NMR detector.⁸ However, an unfortunate consequence of this B_1 field gradient is that only 60-75% of the theoretically possible signal intensity is obtained from a single-pulse NMR experiment, because any single r.f. pulse affects the sample located at different radii with varying degrees of effectiveness. Similarly, it is only possible to affect 30-40% inversion of the equilibrium magnetization with a single r.f. pulse. Quantitative magnetic spin inversion is a necessary requirement for many 2-D NMR techniques. One approach to this problem is to employ composite r.f. pulses. Composite pulses are trains of transmitter pulses that function much like a single pulse but are specially designed to compensate resonance offsets, inhomogeneities of the detector, or deviations of the pulse width from its nominal value. Furthermore, various composite pulses have been designed¹⁰ to compensate for inhomogeneous B_1 fields in other types of detectors. However, none of the sequences described in the literature sufficiently compensates for the large B_1 differences that occur in toroid detectors. We have now developed two new efficient composite pulse sequences for toroid detectors. The first pulse sequence allows reception of more than 98% of the theoretically possible signal intensity (composite 90° pulse), and the second achieves up to 99% inversion of the equilibrium magnetization (composite 180° pulse).

The composite 90° pulse consists of five individual components with a set relationship between their duration and relative r.f. phase angle. (In the notation of Ernst¹¹ it may be described as $(\beta)_0(2\beta)_{120}(2\beta)_{180}(2\beta)_{210}(2\beta)_{225}$, where subscripts indicate the transmitter phase angles.) Similarly the composite 180° pulse consists of nine individual components with a set

¹⁰ M. H. Levitt and R. Freeman, *J. Magn. Reson.* **33**, 473 (1979).

¹¹ R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One or Two Dimensions*, Clarendon Press, Oxford, p. 135 (1987).

phase relationship, $(\beta)_0(2\beta)_{120}(2\beta)_{180}(2\beta)_{210}(4\beta)_{225}(2\beta)_{210}(2\beta)_{180}(2\beta)_{120}(\beta)_0$. As an example of these pulse sequences, calculations were performed using 100 vectors representing the nuclear spin magnetization of 100 volume elements located at different radii equally spaced between the inner and outer wall of the toroid cavity in Fig. IX-2 (with $r_1 = 0.71$ mm and $r_2 = 6.35$ mm). Initially, all 100 magnetization vectors are coincident with the origin and the positive z-axis of the rotating coordinate frame. The objective of the 180° pulse sequence is to invert the sample's magnetization. This corresponds to gathering up all of the individual magnetization spin vectors and regrouping them to point down the negative z-axis. The plots in Fig. IX-3 depict the location of the tips of the magnetization vectors after the seventh through the ninth component of the composite 180° pulse sequence. It is readily evident from these plots that each pulse within the composite sequence dramatically affects the distribution of the spin vectors. Significantly, the cumulative combination of the nine component pulses results in efficient spin inversion

Fig. IX-3. Tip Portions of 100 Vectors Representing the Magnetization in Toroid-Cavity NMR Detector after (a) Seventh, (b) Eighth, and (c) Ninth Pulses of Composite 180° Sequence

throughout the entire sample, with all of the spin vectors landing quite close to the negative z-axis (Fig. IX-3c). Efficient spin inversion is a necessary requirement for many state-of-the-art 2-D NMR experiments. Furthermore, even though the pulse sequences have been developed for toroid detectors, they are also applicable to other NMR detectors that exhibit large B_1 gradients (e.g., the surface coils that are useful for NMR imaging of biological samples).

Future work in this area will employ these pulse sequences in conjunction with the toroid cavity detectors to examine the near-electrode chemistry that occurs in lithium polymer-electrolyte batteries. The central conductor of the toroid cavity of Fig. IX-2 is nearly ideally suited as the working electrode in an *in situ* NMR electrochemical device. This combination will be used to probe ion transport mechanisms in polymer-electrolyte systems.

3. Hydrocarbon Activation Chemistry

Metallophthalocyanines have been used as catalysts for various oxidation and reduction processes. The principal objective of this project is to study the activation and the functionalization of hydrocarbons by soluble metallophthalocyanines. We have previously shown^{12,13} that hydrogen and hydrocarbons are activated by $[(R_8Pc)Rh]_2$ according to

where R_8Pc^{2-} is the dianion of 1,4,8,11,15,18,22,25-octapentylphthalocyanine. The dimeric rhodium hydride, $(R_8PcH)RhRh(R_8Pc)H$, that is generated in Eqs. 6 and 7 exists in the solid state and in benzene solutions and can be converted to a monomeric rhodium hydride in tetrahydrofuran (THF):

Fig. IX-4 shows the structure of the rhodium hydride dimer as determined by single-crystal X-ray diffraction study. The long Rh-Rh distance (3.35 Å) implies a very weak bonding or non-bonding between the two Rh's and, therefore, the possibility of a bridging hydride between the two Rh nuclei. The X-ray diffraction data do not allow us to locate the N-H or the Rh-H hydrogen. However, our low-temperature NMR experiments have revealed the presence of

¹² M. J. Chen and J. W. Rathke, J. Chem. Soc. Chem. Comm. 4, 308-309 (1992).

¹³ M. J. Chen and J. W. Rathke, Organometallics 12, 4875-4880 (1994).

Fig. IX-4. X-ray Structure of $(R_8PcH)Rh(\mu-H)Rh(R_8Pc)$

two N-H and four Rh-H resonances at temperatures of -35°C and strongly suggest that there are four isomers at -35°C , and that the hydride ligands are bridging hydrides in these complexes.

In an earlier study,¹² we observed the dynamic NMR processes of benzene solutions of $(R_8PcH)RhRh(R_8Pc)H$ in the temperature range of 25 – 110°C , including the exchange between the N-H and the Rh-H protons. We have extended this study of the hydride dimer to -55°C in toluene- d_8 solutions. Interestingly, as the temperature is lowered, the broad hydride resonance at -38.1 ppm for the hydride ligand in $(R_8PcH)RhRh(R_8Pc)H$ gradually shifts to higher values in the NMR spectra, and at 5°C a new broad resonance appears at -40.5 ppm. Each of these resonances further splits into two resonances at -35°C , resulting in four hydride resonances (-38.1 , -39.1 , -40.6 , and -40.9 ppm). Therefore, there are four kinds of hydrides in the solution at -35°C . The resonances at -40.6 and -40.9 ppm even show fine features due to couplings with two asymmetrically bonded rhodium nuclei. We now believe that the hydride ligands in all these dimer complexes should be formulated as bridging hydrides. Furthermore, we believe that the two unresolved broad resonances (at -38.1 and -39.1 ppm) are associated with two rotamers of $(R_8PcH)Rh(\mu-H)Rh(R_8Pc)$, i.e., the eclipsed and the staggered forms, and the two resonances at -40.6 and -40.9 ppm to two rotamers of $(R_8Pc)_2(\mu-H)_2Rh_2$.

Further NMR experiments and simulation of the spectra are planned to confirm these assignments. Neutron diffraction studies are also planned to locate the hydride ligand in solid $(R_8PcH)Rh(\mu-H)Rh(R_8Pc)$. In the hydrocarbon activation study, we will extend our study to electrophilic activation and catalytic hydrocarbon auto-oxidation by $(CF_3)_8PcM$ and $(CF_3)_8PcMX$ ($M = Rh, Fe, \text{ and } Mn$; $X^- = \text{an anion}$) complexes, exploiting the highly electrophilic character of these fluorinated metallophthalocyanines. Enhancement of catalytic activity by

fluorination has been observed for structurally related metalloporphyrins in the auto-oxidation of hydrocarbons.¹⁴

B. *Materials Chemistry*

The materials chemistry program encompasses fundamental research on the phase chemistry of high-critical-temperature (T_c) superconducting oxides, 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. Studies of High- T_c Superconducting Materials

The discovery of high- T_c superconducting oxides has generated numerous efforts throughout the world to improve the synthesis/processing methods for these novel materials. We are conducting electromotive force (emf) measurements of oxygen fugacity as a function of oxygen stoichiometry and temperature in selected bismuth cuprate materials, namely, $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Bi-2223) and $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (Bi-2212). A coulometric titration technique employing yttria-doped zirconia electrolyte is being used to investigate the thermodynamic properties and nonstoichiometric behavior of these promising cuprate compositions as a function of oxygen partial pressure (10^{-6} atm to 1 atm), oxygen stoichiometry, and temperature ($T = 700\text{--}815^\circ\text{C}$). There are very few quantitative data concerning (1) the dependence of oxygen partial pressure and temperature on the nonstoichiometric behavior of bismuth cuprates or (2) the effect of oxygen stoichiometry on phase relationships and stability in these high- T_c systems. Such data could prove useful in determining optimum processing conditions for producing silver-sheathed Bi-2223 or Bi-2212 wires capable of carrying high critical currents.

During the past year, we completed emf measurements on lead-doped and lead-free Bi-2212 compositions. The as-received materials were found to be single phase by powder X-ray diffraction analysis at room temperature. Analysis by inductively coupled plasma/atomic emission spectroscopy combined with iodometric analysis gave the following compositions:

The results of our emf measurements are shown in Fig. IX-5, where oxygen partial pressures at 815°C (a commonly used processing temperature for Ag/Bi-2223 composite conductors) are plotted as a function of x for both lead-doped and lead-free Bi-2212 samples. The results in Fig. IX-5 reveal very large changes in oxygen partial pressure over a composition range

¹⁴ P. E. Ellis, Jr., and J. E. Lyons, *J. Chem. Soc. Chem. Comm.* **17**, 1315-1316 (1989).

Fig. IX-5. Oxygen Partial Pressure as Function of Oxygen Stoichiometry for Lead-Free and Lead-Doped $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ at 815°C

that is relatively small as x approaches (above/below) the plateau regions. The shapes of the isotherms prior to reaching the plateau regions indicate single-phase nonstoichiometric compositions. The sharp change in oxygen partial pressure over a narrow composition range can be attributed to cations that have different and varying valences in these systems. Thermodynamic assessments of the partial molar entropy and enthalpy of solution of oxygen in these compositions derived from our measurements indicate that the plateau regions can be represented by the binary $\text{CuO}/\text{Cu}_2\text{O}$ system, in excellent agreement with our earlier measurements on lead-doped Bi-2223.¹⁵ The results to date show that processing or annealing lead-doped and lead-free Bi-2212 compositions at 815°C and oxygen pressures ranging from approximately 3×10^{-3} to 0.2 atm should preserve these materials as single-phase compositions. The results indicate a narrower range of composition homogeneity for lead-free Bi-2212 compared to lead-doped Bi-2212 and Bi-2223 compositions in the single-phase region.

Thermogravimetric and differential thermal analysis will be undertaken to check whether the shapes of the isotherms above the plateau regions shown in Fig. IX-5 indeed represent single-phase lead-doped and lead-free Bi-2212. In addition, future studies will be concerned with investigating the thermodynamic behavior and stability of other promising high- T_c superconducting materials, such as $\text{TlBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8.5\pm\delta}$, by means of emf and related measurements.

¹⁵ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, p. 129 (1994).

2. 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 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 vibrational 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.

Synchrotron X-ray absorption spectroscopy was carried out on nickel oxides and hydroxides which were meant to represent the various phases that may be formed during the corrosion of nickel or during the cyclic charging and discharging of the nickel electrode in batteries. Among the compounds that we have characterized are NiO, α - and β -Ni(OH)₂, β - and γ -NiOOH, Ni₃O₂(OH)₄, NiO₂, Ni₃O₄, Ni₂O₃, and KNiIO₆. They will be used as standard samples for the *in situ* analysis of surface films formed on nickel during corrosion in aqueous solutions. Our results indicate three distinct Ni-O bond distances that are characteristic of Ni²⁺, Ni³⁺, and Ni⁴⁺. Also, some of the higher valency oxides (e.g., NiOOH, NiO₂, Ni₃O₄) appear to be a mixture of Ni²⁺ and Ni³⁺ with varying proportions of each. The latter finding will be further explored by diffraction anomalous fine structure measurements. This work is being carried out in collaboration with the Naval Warfare Surface Center.

In collaboration with Exxon Research and Engineering Co., we have analyzed synchrotron diffuse X-ray scattering (DXS) data obtained during electrochemically induced localized corrosion (pitting) of copper surfaces in 0.01 M NaHCO₃. The pits were modeled as cylindrical objects with a certain size and depth distribution; the depth of any pit was assumed to be uncorrelated with that of any other one or with the pit's lateral size. We found the pits to be quasi-randomly distributed on the copper surface and to exhibit a short range correlation. The DXS profiles were fitted to obtain the average size and depth of the pits, as well

as the average separation distance between correlated pits. These DXS-derived parameters were confirmed by scanning electron microscopy of the pitted sample. Thus, we have demonstrated for the first time the utility of DXS for investigating localized corrosion. Further studies will be carried out to delineate the nucleation and growth steps, as well as to determine the potential dependence of the pitting processes.

In collaboration with researchers at the University of Poitiers (France) and the University of Auckland (New Zealand), we continue to carry out *in situ* far-IR spectroscopy studies with a synchrotron source on a platinum electrode in 0.5 M HClO₄ solution. We employed CO as a test molecule but were unable to observe the Pt-CO vibrational mode in the far-IR spectra. However, we were able to observe a band at about 370 cm⁻¹ for a platinum-containing species in the so-called "oxide region" (~0.8 to 1.4 V vs. standard hydrogen electrode), which appears to shift slightly to higher frequency as the potential is increased to 1.6 V. This band was assigned to a hydroxide species, presumably Pt(OH)₄, which is consistent with previously published mid-infrared data.¹⁶ The band shift at higher potential (1.6 V) may be due to the formation of an oxide species, e.g., PtO₂. Future work will examine the adsorption of small molecules (such as SCN⁻, OCS, and OCN) at electrode surfaces *in situ* by using synchrotron far-IR spectroscopy.

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 over 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, coulometric, or potentiostatic pulse transients; ac-impedance measurements; and the rotating-disk-electrode technique, combined with computerized data-evaluation methods. The interfacial structural studies use synchrotron X-ray measurements, such as surface scattering and standing-wave techniques. Heterogeneous charge-transfer reactions are the essential chemical reactions in many energy-related technologies, such as batteries for electric vehicles and fuel cells for primary electrical power generation. They are also involved in corrosion of these and other energy technologies. Clearly, a fundamental understanding of the dynamics of these reactions could result in improvements in many energy technologies.

During 1994, we continued our kinetic studies of the Cu²⁺/Cu⁰ electrode reaction, 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. Earlier¹⁷ we determined that the reaction rate is controlled by the Cu²⁺/Cu⁺

¹⁶ J. B. Benzinger, F. A. Pascal, S. L. Bainasek, M. P. Soriaga, and A. T. Hubbard, *J. Electroanal. Chem.* **198**, 65 (1986).

¹⁷ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1992*, Argonne National Laboratory Report ANL-93/17, p. 166 (1993).

charge transfer step and that, under suitable experimental conditions, the other elementary steps can be considered in pseudo-equilibrium. This reaction was found to be strongly catalyzed by traces of chloride ions in the solution.¹⁸ Our results also indicate that the removal of chloride impurities below the part-per-million range is needed to obtain meaningful comparisons with theory. This year, we developed a high-temperature/high-pressure method for kinetic measurements in which the chloride effect is eliminated. We also carried out a mechanistic study of the catalytic effect coordinated with theoretical modeling (see Sec. IX.B.2.c) and determined that the probable cause is increased electronic coupling due to the closer approach of the chloride-bridged ion to the electrode surface. In coordination with the theoretical modeling described in Section IX.B.2.c, we are now starting high-temperature/high-pressure kinetic measurements with and without the chloride effect.

In a collaborative effort with the ANL Materials Science Division, we also continued to use synchrotron X-ray techniques in probing electrified interfaces that are buried under or within condensed phases. In prior years, X-ray reflectivity techniques were used to investigate the metal side of the interface and the structure of the solution side of the electrical double layer.¹⁹ This year we initiated a similar study using a complementary technique involving X-ray standing waves (XSW). The combination of the two X-ray techniques will permit us to investigate the double-layer structure over five orders of magnitude of concentration range and at a distance from the electrode surface ranging from a few angstroms to tens of thousands of angstroms. We have designed and built an X-ray/electrochemical cell suitable for XSW measurements. This is a thin-layer cell, with a solution layer thickness on the order of 10^{-4} cm between the working electrode surface and the covering membrane, a design completely different from the cells used earlier with the reflectivity technique. During 1995, XSW measurements will be initiated with the goal of providing a comparison of competing double-layer theories.

The interaction of X-rays with the system under investigation (e.g., radiolysis of the solution or photoelectrochemical phenomena at the surface) has been generally ignored by researchers conducting electrochemical/synchrotron X-ray measurements. Recently, we carried out qualitative experiments to determine the extent and nature of this interaction. A significant amount of radiolysis was found at high photon fluxes. Figure IX-6 shows the current generated by X-ray irradiation of a platinum electrode held at its rest potential in 0.1 M perchloric acid. These results indicate that bulk solution radiolysis dominates over any photoelectrochemical phenomena. The effect can be safely ignored for most measurements carried out at present-day bending-magnet beam lines ($<10^{10}$ photons/second). However, as higher-flux beam lines are developed, the X-ray interference with the system under investigation will have to be considered on a case-by-case basis. In the meantime, we have identified a way to minimize this radiolytic effect, i.e., continuous, high-speed flushing of the test solution to carry away most of the radiolytic products before they can diffuse to the metal/solution interface. (Our previously developed transmission-geometry X-ray/electrochemical cells¹⁷ are particularly suited for such

¹⁸ J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, p. 132 (1994).

¹⁹ M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1991*, Argonne National Laboratory Report ANL-92/15, p. 178 (1992).

Fig. IX-6. Current at Open-Circuit Potential and its Relaxation during X-ray Irradiation of Platinum Electrode in 0.1 M Perchloric Acid. X-ray flux on for 4 to 8 min, starting at 0.5 min

experiments.) This will be especially important on future beamlines at the Advanced Photon Source under construction at ANL.

c. Theoretical Studies of Electrode Reactions

The $\text{Cu}^{2+}/\text{Cu}^0$ electron transfer reaction is known to influence stress corrosion cracking in light water nuclear reactors. A theoretical investigation was carried out to gain insight into how chloride ions catalyze electron transfer during the copper deposition reaction. Electron transfer rates, k_{ET} , are dependent on the product of the square of an electronic coupling energy, $V(r)$, and a Franck-Condon weighted density of states.²⁰ We have investigated the electronic coupling, $V(r)$, for several homogeneous electron transfer reactions that are approximate models for the copper deposition reaction. The electronic coupling was calculated for three possible reactions: (1) direct interaction, (2) outer-sphere electron transfer (water-water bridge), and (3) inner-sphere electron transfer (chloride bridge). For all three reactions, the copper-copper distance was varied, and the electronic coupling for both the $\text{Cu}^{1+}/\text{Cu}^0$ and the $\text{Cu}^{2+}/\text{Cu}^{1+}$ reactions was calculated by means of *ab initio* molecular orbital theory. The electronic

²⁰ V. O. Levich, *Advances in Electrochemistry and Electrochemical Engineering*, John Wiley, New York, Vol. 4, p. 249 (1966).

coupling was estimated from the difference in orbital energies of the symmetric and anti-symmetric combination of the donor and acceptor orbitals.²¹ The coupling for the direct interaction was calculated based on a copper dimer. The coupling for the outer-sphere electron transfer was calculated from the interaction of two $\text{Cu}(\text{H}_2\text{O})_6$ complexes in an apex-apex configuration, and that for the inner-sphere electron transfer was calculated by replacing the two apex water molecules in the outer-sphere reaction with a chloride ion. Likely closest approach distances for the copper deposition reaction were obtained by examining the potential energy surfaces of complexes that emulate the possible participants in the reactions.

The results show that an increased coupling for the chloride-bridged $\text{Cu}^{2+}/\text{Cu}^{1+}$ reaction is due to the shorter copper-copper distance rather than intrinsic chemical effects. This conclusion is based on the finding of little difference, as a function of intermetallic distance, between the coupling due to the water bridge and that due to the chloride bridge. The increase in coupling results from the closer approach that is possible for the chloride bridge compared to the water bridge. At the "most probable" approach distance for the chloride bridge, coupling is an order of magnitude larger than that for the water complex.

In the case of the $\text{Cu}^{1+}/\text{Cu}^0$ electron transfer, the inner- and outer-sphere reactions have similar electronic coupling at the "most probable" approach distance. This suggests that chloride ions should have no catalytic effect for this electron transfer reaction, a finding that is consistent with experiment.²² The results also suggest that the $\text{Cu}^{1+}/\text{Cu}^0$ direct interaction has a favorable electronic coupling, which is due, in part, to its close approach distance.

The electronic mechanism for electron transfer was studied by using the McConnell superexchange model based on localized natural bond orbitals.^{23,24} The pathways through the localized orbitals were examined. This work indicates that the electron transfer for the inner-sphere reaction occurs through chlorine 3s and 3p bonding orbitals (Fig. IX-7, bottom), while that for the outer-sphere reaction occurs largely through OH σ^* antibonding orbitals of water (Fig. IX-7, top). In future work we intend to investigate the effects of other ions (such as Br^- and I^-) on catalysis of the $\text{Cu}^{2+}/\text{Cu}^0$ electron transfer reaction and to consider the heterogeneous reaction.

3. 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, metal halides, thin-film diamond growth mechanisms, and molecular cluster studies. One of the methods that has been developed, Gaussian-2 (G2) theory,²⁵ is now being widely used in universities and industry for

²¹ L. A. Curtiss, C. A. Naleway, and J. R. Miller, *J. Phys. Chem.* **97**, 4050 (1993).

²² J. E. Battles et al., *Chemical Technology Division Annual Technical Report, 1993*, Argonne National Laboratory Report ANL-94/15, p. 133 (1994).

²³ H. McConnell, *J. Chem. Phys.* **35**, 508 (1961).

²⁴ C. A. Naleway, L. A. Curtiss, and J. R. Miller, *J. Phys. Chem.* **95**, 8434 (1991).

²⁵ L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *J. Chem. Phys.* **94**, 7221 (1991).

Fig. IX-7. Illustration of Most Important Electron Pathways for Inner- and Outer-Sphere $\text{Cu}^{1+}/\text{Cu}^0$ Reactions. Inner-sphere reaction shown in bottom graph, outer-sphere reaction on top.

the accurate calculation of thermochemical data. This method is based on *ab initio* molecular orbital theory and is accurate to ± 2 kcal/mol for calculating reaction energies.

a. Development of Gaussian-2 (G2) Theory

The performance of G2 theory²⁵ was improved by inclusion of higher level theoretical methods for correlation effects, geometries, and zero-point energies. A higher level of correlation treatment was examined by using Brueckner doubles and coupled cluster methods rather than the quadratic configuration interaction [QCISD] method used in G2 theory. We also examined geometries optimized at the QCISD level rather than at the second-order Møller-Plesset level (MP2) and MP2 zero-point energies rather than Hartree-Fock (HF) zero-point energies. The experimental data (energies for 125 molecules) used for validation of the original G2 theory was employed to test these new variations of G2 theory. Inclusion of higher levels of correlation treatment had little effect except in cases involving multiply-bonded species. In these species, better agreement was obtained in some cases and poorer agreement in others, so that there was no improvement in the overall performance of G2 theory. The use of QCISD geometries gave significantly better agreement with experiment for several cases, including the ionization potentials of CS and O₂, electron affinity of CN, and dissociation energies of N₂, O₂, CN, and

SO₂. This leads to a better overall agreement with experiment. The use of MP2 zero-point energies gave no overall improvement in the performance of G2 theory. These new methods will be useful for investigations of specific species.

In collaboration with AT&T Bell Laboratories, we also used G2 theory to calculate accurate energies of small elemental clusters. In particular, we extended previous work on Si_n clusters to include the n=6 and n=7 clusters.²⁶ As shown in Table IX-1, the theoretical binding energies are in good agreement with recently measured values.^{27,28} The structures and binding energies of Al_n clusters (n=2 to 7), along with their ionization energies, are also in good agreement (± 0.1 eV) with experiment.²⁶ Finally, G2 theory was used to calculate binding energies of carbon clusters containing up to seven carbon atoms. Again, good agreement with experiment was found. The study of clusters with methods capable of attaining chemical accuracy, such as G2 theory, is still in its infancy, but it is clear from our results that these methods can provide a satisfactory framework for interpreting a variety of experimental measurements.

Table IX-1. Binding Energies (in eV) of Silicon Clusters
Calculated by Gaussian-2 Theory

Silicon Clusters	Expt. ^a	Theory (G2)
Si ₂	3.32 $\pm$ 0.07, 3.17 $\pm$ 0.13 ^b	3.19
Si ₃	7.34 $\pm$ 0.17, 7.3 $\pm$ 0.4 ^b	7.41
Si ₄	12.02 $\pm$ 0.23	11.95
Si ₅	16.16 $\pm$ 0.25	16.15
Si ₆	20.54 $\pm$ 0.21	20.65
Si ₇	25.19 $\pm$ 0.25	24.95

^aFrom Ref. 27 unless otherwise noted.

^bFrom Ref. 28.

b. Molecular Sieve Materials

Zeolites are solid acid catalysts that are widely used in the petrochemical industry for hydrocarbon cracking. This process, which is not yet well understood, can be divided into the following steps: (1) adsorption of a hydrocarbon molecule at the zeolitic Brønsted acid site, (2) proton transfer from the zeolite to the adsorbed molecule, (3) subsequent reaction of the

²⁶ K. Raghavachari and L. A. Curtiss, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy: Understanding Chemical Reactivity*, Ed., S. R. Langhoff, Kluwer Academic Publishers, Netherlands, pp. 173-208 (1995).

²⁷ R. W. Schmude, Q. Ran, and K. A. Gingerich, to be published in *J. Chem. Phys.*

²⁸ M. W. Chase et al., *JANAF Thermochemical Tables*, Third ed., *J. Phys. Chem. Ref. Data*, Vol. 14, Suppl. 1 (1995).

protonated hydrocarbon with other species inside the zeolite, and (4) return of a proton to the zeolite framework. Since protonated hydrocarbons are intermediates in the acid-catalyzed cracking process, a detailed understanding of their structure and stability should give useful information about the reactions they undergo inside the zeolite. As part of a larger effort to understand the energetics of proton transfer and acid catalysis in zeolites, we are investigating the equilibrium geometries of protonated alkanes (carbonium ions) and have computed their proton affinities by using G2 theory. Figure IX-8 shows the calculated potential energy surface of protonated ethane, $C_2H_7^+$. The curve indicates four local minima in the potential energy surface -- one corresponding to protonation in the C-C bond, and the other three corresponding to protonation at the terminal carbon position. Calculation of the proton affinity of the lowest energy structure gave 141.0 kcal/mol, in good agreement with the experimental value of 139.6 kcal/mol.²⁹ Theoretical investigations are underway on larger hydrocarbons, such as C_3 and C_6 species, that have been studied experimentally in ZSM-5 zeolite. We will also be investigating the interaction of these carbonium ions with Brønsted acid sites in large aluminosilicate clusters representing the zeolite ZSM-5.

Fig. IX-8. Potential Energy Surface of Protonated Ethane (G2-calculated relative energies, in kcal/mol)

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 other molecules such as ammonia, water, and methanol. We have investigated proton transfer to water in aluminosilicate clusters containing up to 28 aluminum atoms. Previous studies³⁰ on smaller clusters from other groups are unclear on whether the neutral species (H_2O) or the protonated form is the most stable in the zeolite, and whether there is an energy barrier to proton

²⁹ K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.* **98**, 6119 (1976).

³⁰ A. Ison and R. J. Gorte, *J. Catal.* **89**, 150 (1984).

transfer. Experimental studies³¹ are also inconclusive. Our G2 calculational studies based on larger clusters suggest that the protonated form, H_3O^+ , exists only as a transition state for proton movement from one acid site to another. This transition state is about 5 kcal/mol higher in energy than the minimum for the adsorbed H_2O molecule. This is in contrast to the situation for ammonia, where we have found no barrier to transfer of the proton to ammonia to form NH_4^+ . The desorption energy of water was calculated (using G2 theory) to be 13 kcal/mol, in good agreement with the experimental value of 12 kcal/mol.³¹ The adsorbed H_2O molecule bonds to the OH group of the acid site and another oxygen of the framework to form a cyclic bonded complex.

In future work, we will consider the interaction of other molecules (such as methanol and carbonium ions) with the acid site. Carbonium ions important in hydrocarbon cracking (such as methyl pentane) will be investigated.

4. Enhanced Metallurgical Processes

a. Removal of Copper from Scrap Steel

America's huge inventory of scrap steel is a major resource for the production of steel at competitive prices. However, impurities in scrap, especially copper, hinder its use for high value products, such as sheet steel. The presence of more than 0.1 wt% copper leads to undesirable properties in the production of sheet steel. A major minimill (Nucor Corp., the fourth largest steelmaker in the United States) has devised a method for producing sheet steel from scrap. However, this method is limited by the availability and cost of low copper scrap. We are developing a process that will remove copper from scrap by using an aluminum sulfide-based matte and are investigating other processes that might economically remove copper from steel.

We have measured copper distribution coefficients between mattes and steel in molten mixtures of Al_2S_3 with FeS and other sulfides. Our initial measurements led to distribution coefficients of 24-31 at 1365°C. However, the original sulfide mattes were contaminated with oxygen, and solution theory calculations suggested that such contamination should lower the distribution coefficients. Our current apparatus is hermetically sealed to avoid contamination and can be pumped out and then filled with pure argon. Measurements were performed at 1365-1400°C on high carbon steel in equilibrium with mattes containing 80-90 wt% Al_2S_3 , 10-20 wt% FeS, and 0-10 wt% MgS or CaS. Three measurements with relatively low oxygen levels in the matte led to distribution coefficients of 24, 32, and 40. We observed that a steel/matte weight ratio of 4 always yielded copper contents in the steel between 0.05 and 0.09 wt%, where the initial value was 0.4 wt%. These compositions are within the range needed for the production of sheet steel. For cases in which the distribution coefficients were 32 and 40, the copper contents in the steel were 0.05 and 0.08 wt%. Further measurements are underway to increase the distribution coefficients by increasing the FeS content. Using fundamental principles of solution chemistry in silicates, we are also devising compositions of silicate-based slags that might extract copper efficiently from steel. Since silicate slags are already widely used in

³¹ A. G. Pelmenshikov and R. A. van Santen, J. Phys. Chem. **97**, 10678 (1993).

steelmaking, they are likely to be readily accepted by industry if we are successful in devising a composition for which the distribution coefficient of copper is high.

b. Removal of Lead from Brass or Copper Scrap

We have also deduced molten salt compositions that remove lead from solid copper and brass surfaces at about 350°C and are exploring the chemistry of this process. With these molten salts, we have been able to remove over 90% of the surficial lead from polished lead-bearing brass. Treated brass samples were tested by an Environmental Protection Agency procedure for estimating the hazard derived from the leaching of lead from metals in contact with drinking water. Test results indicated that our method of lead removal could be used for the pretreatment of brass parts for water systems. Further work is underway to improve the performance of the molten salt so that we might remove 99% of the leachable lead. In addition, we investigated another molten salt composition that, in principle, should convert molten scrap brass to the more valuable commodity, copper, by the removal of all alloying elements at about 1100°C.

C. *Geochemistry*

The geochemistry research in CMT is focused on experimental studies of mineral-fluid interfaces. The approach is to observe reacting mineral surfaces *in situ* by use of synchrotron X-ray radiation. The objective is to gain a better fundamental understanding of chemical processes occurring at mineral-fluid interfaces, which 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.

1. Trace Elements in Calcite

Knowledge of the crystallographic locations of minor and trace elements within minerals and at their surfaces is important for a wide range of applications in the earth and environmental sciences. We used the X-ray standing waves generated by dynamical Bragg diffraction to directly measure lattice locations of trace elements within and at the surface of a mineral single crystal.³² These high-precision measurements were made on natural Iceland spar calcite cleaved along the (10 $\bar{1}$ 4) plane and reacted with a dilute aqueous lead solution. These

³² Y. Quin, N. C. Sturchio, R. P. Chiarello, P. F. Lyman, T.-L. Lee, and M. J. Bedzyk, *Science* **265**, 1555-1557 (1994).

experiments were performed at the National Synchrotron Light Source, Brookhaven National Laboratory. Within the bulk crystal, naturally occurring trace manganese was found within (10 $\bar{1}$ 4) planes, consistent with its substitution for calcium. At the crystal surface, sorbed lead was found to be highly ordered and mostly within (10 $\bar{1}$ 4) planes. This demonstrates a powerful application of synchrotron radiation in the earth and environmental sciences. With the advent of much brighter X-ray sources such as the ANL Advanced Photon Source, we anticipate significant increases in the sensitivity of the X-ray standing wave technique.

2. Heteroepitaxial Nucleation and Growth of Otavite on Calcite

Here we present some results of X-ray scattering measurements made at mineral-water interfaces. This particular study demonstrated a new and accurate approach for measuring *in situ* precipitation rates and growth mechanisms in mineral-water systems. X-ray reflectivity and diffraction were used to characterize an otavite overgrowth during its precipitation from aqueous solution onto the calcite (10 $\bar{1}$ 4) cleavage surface. Otavite growth was initiated when approximately 1 mL of an otavite-saturated solution, which had 100% CO₂ bubbled through it for two days prior to use, was added to a reaction cell. As CO₂ diffused out of the solution through a small vent at the top of the cell, otavite became oversaturated and precipitated on the calcite cleavage surface. X-ray reflectivity and diffraction scans were measured during 4585 min of growth. Specular X-ray reflectivity was measured by monitoring changes in the reflected X-ray intensity as a function of perpendicular momentum transfer ($Q_{\perp}$). Reflectivity was used to determine the properties of thin films, including the film thickness, interfacial roughness, and real-space electron density profile across interface(s). X-ray reflectivity is ideal for determining thin film thickness as a function of time (growth rate). From the reflectivity measurements,³³ we determined the otavite growth rate to be 15 Å/h during the first 540 min of growth. After 540 min, the growth slowed considerably.

The calcite structure is rhombohedral and can be discussed conveniently in terms of the hexagonal unit cell. The calcite lattice constants are $a = 4.99$ Å and $c = 17.059$ Å.³⁴ Otavite has the calcite structure, and the otavite lattice constants are $a = 4.92$ Å and $c = 16.298$ Å. If the otavite overgrowth forms with the bulk otavite lattice constants, then the otavite (10 $\bar{1}$ 4) reflection would have a diffraction maximum at $Q_{\perp} = 2.13$ Å⁻¹. The calcite (10 $\bar{1}$ 4) reflection has a diffraction maximum at $Q_{\perp} = 2.07$ Å⁻¹. These $Q_{\perp}$ values correspond to lattice spacings of 3.04 Å and 2.95 Å for calcite (10 $\bar{1}$ 4) and otavite (10 $\bar{1}$ 4), respectively.

Figure IX-9 shows the specular diffraction scans that we recorded during otavite growth. The intense, narrow peak at $Q_{\perp} = 2.07$ Å⁻¹ is due to the diffraction maximum of the calcite (10 $\bar{1}$ 4) reflection. The full width at half maximum (FWHM) intensity of this peak was limited by instrumental resolution. The second peak in Fig. IX-9, which appears at higher $Q_{\perp}$ (2.13 Å⁻¹), is due to diffraction from the otavite overgrowth. The peak position is nearest to otavite

³³ R. P. Chiarello and N. C. Sturchio, *Geochim. Cosmochim. Acta* **58**, 5633-5638 (1994).

³⁴ R. W. G. Wyckoff, *Crystal Structures*, John Wiley, New York (1964).

Fig. IX-9.

Diffracted X-ray intensity (log scale) vs. Perpendicular Momentum Transfer ($Q_{\perp}$). The data are offset for clarity. Vertical dashed lines at $Q_{\perp} = 2.07$ and $2.13 \text{ \AA}^{-1}$ indicate the $(10\bar{1}4)$ reflections of calcite and otavite, respectively. The inset shows percent compression of the measured otavite overgrowth d-spacing (relative to bulk otavite) vs. the measured longitudinal coherence length (i.e., thickness) of the overgrowth.

$(10\bar{1}4)$, indicating that the otavite formed with its $(10\bar{1}4)$ direction parallel to the calcite $(10\bar{1}4)$ direction. With increasing time, the FWHM of this peak became narrower, and the peak position shifted to lower $Q_{\perp}$.

To quantify these observations, the otavite peaks were fit by using a Voigt function. The relevant fit parameters were the otavite FWHM and peak position. The FWHM was used to estimate the average domain size (L) of the otavite in the direction perpendicular to the $(10\bar{1}4)$ diffraction planes (using the Scherrer equation³⁵), and the peak position was used to determine the d-spacing ($d_{10\bar{1}4}$) of the otavite in the direction perpendicular to the $(10\bar{1}4)$ diffraction planes. We found that L , determined from diffraction, and D , determined from reflectivity were in good agreement up to 540 min. This finding indicates that L provides an acceptable estimate of film thickness. The results also indicated that $d_{10\bar{1}4}$ was equal to $2.885 \text{ \AA}$ ($L = 36.6 \text{ \AA}$) after 173 min of growth and $2.934 \text{ \AA}$ ($L = 63.4 \text{ \AA}$) after 381 min. As shown by the inset in Fig. IX-9, at a thickness of $36.6 \text{ \AA}$, the otavite was compressed by 2.2% in the direction perpendicular to the calcite surface. The otavite $(10\bar{1}4)$ compression served to relieve lateral strain in the overgrowth. The lateral strain occurred because the cadmium atoms in the otavite structure were aligned with calcium atom positions of the underlying calcite, i.e., the interface was coherent. At a thickness $63.4 \text{ \AA}$, the lateral and longitudinal strain in the otavite was relieved. The relief of strain at a critical thickness is commonly observed in semiconductor systems.

Several off-specular diffraction scans were measured for the otavite after 4585 min of growth. The off-specular diffraction maxima indicate that the otavite formed as a single crystal

³⁵ B. E. Warren, *X-ray Diffraction*, Addison-Wesley, Reading, PA (1969).

overgrowth. From rocking curve scans at off-specular diffraction peaks, the in-plane crystal mosaic was 0.45° . The out-of-plane crystal mosaic was determined to be 0.41° from rocking curve scans measured at the otavite $(10\bar{1}4)$ diffraction peak. The lattice constants determined from the off-specular peak positions were nearly identical to those of bulk otavite. These results indicate that the otavite grew as a single crystal heteroepitaxially on the calcite $(10\bar{1}4)$ cleavage surface. Future work in this area will involve studies of $\text{Cd}_x\text{Ca}_{1-x}\text{CO}_3$ solid-solution formation and the nucleation and growth kinetics of clay minerals.

X. ANALYTICAL CHEMISTRY LABORATORY

A. *Introduction*

The Analytical Chemistry Laboratory is a full-cost-recovery service center, with the primary mission of providing a broad range of analytical chemistry support services to the scientific and engineering programs at ANL. The ACL also does research in analytical chemistry, conducts instrumental and methods development, and provides analytical services for governmental, educational, and industrial organizations. The ACL handles a wide range of analytical problems. Although some routine or standard analyses are done, many Argonne programs generate unique problems that can require development of methods or adaptation of techniques to obtain useful analytical data.

The ACL is administratively within CMT, its principal ANL client, but provides technical 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 the group lines, as do many projects with the ACL.

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 applies 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 determinations use X-ray diffraction and fluorescence of solids. The Organic Analysis Group employs a number of complementary techniques to separate organic compounds and measure them at trace levels in samples such as complex organic mixtures, pesticides, potentially hazardous wastes, and drugs. Personnel in the Organic Analysis Group also develop methods for such purposes as continuously monitoring incinerator emissions and determining volatile organic compounds in the headspace gas of DOE waste containers. Chemometric techniques are used for extracting useful information from sensor response data. The Environmental Analysis Group analyzes environmental, hazardous waste, and coal samples for the inorganic constituents. The group also provides quality assurance support to DOE and other clients for various kinds of analytical data.

New ACL capabilities established in 1994 include an automated flashpoint tester to meet an Environmental Protection Agency (EPA) method requirement for determination of the hazard level of volatile waste materials, a platinum-lined oxygen combustion bomb for more accurate determination of trace metals in waste and environmental samples, a liquid scintillation counter for screening the α and β activities in environmental samples, and a germanium detector for γ -emitting nuclides. In addition, the scanning electron microscope user facility was upgraded this year.

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 1994 are summarized here. A more complete account of research topics is given in another report.¹

1. Engineering Studies of Electrometallurgical Treatment of Spent Nuclear Fuels

In the electrorefining of spent metallic fuels for fast reactors (see Sec. VI), fuel pins are chopped into small segments and placed in a basket that is introduced into molten salt (LiCl-KCl) at 500°C. The basket is connected to a dc power supply and made anodic; nearly pure uranium is removed from the spent fuel by electrotransport to solid cathodes, followed by electrotransport of the plutonium and any remaining uranium to liquid cadmium cathodes. Engineering-scale studies are being conducted in CMT (Sec. VI) to develop processes to recover transuranic (TRU) elements from the spent electrolyte salt and metal discharged from the electrorefiner and to separate the fission products so that the treated salt and metal can be recycled. The ACL has contributed to this effort by determining elements of interest in samples from the halide-salt electrolyte, cadmium anode, and the cathode product. Special dissolution procedures are followed for each type of sample matrix, and separation schemes based on solvent extraction and ion exchange are used to isolate the desired elements from matrix components and, subsequently, to separate these elements. Cations, including U and Pu, are determined in samples with an inductively coupled plasma/atomic emission spectrometer (ICP/AES) configured to analyze radioactive solutions. The mass spectrometric isotope dilution technique is used whenever higher precision and accuracy than attainable with ICP/AES are required.

Experiments to which ACL contributed during the past year include studies on the extraction efficiency of a specially designed centrifugal contactor ("pyrocontactor") for carrying out extractions of selected elements from molten salt and cadmium. The analytical results showed good separation between the desired elements. These tests demonstrated the feasibility of extracting transuranics from the rare earths chlorides and uranium. Studies were also undertaken to demonstrate the feasibility of electrochemically reducing UCl_3 and PuCl_3 in the electrorefiner salt by using Li-Cd alloy (5.9 wt% Li) as an anode material. Analytical results showed that the U and Pu content in the salt had been reduced by a factor of 150, and the rare earth elements (Y, Sm, Gd, Nd, Ce, and La) had been reduced by a factor of four. These results demonstrate the possibility of purifying spent electrorefiner salt by using this stripping process.

2. Analytical Certification of Special Reference Materials

The Analytical Laboratory in the Fuels and Engineering Division at ANL-West has developed methods for analyses that will be required for process control and materials

¹ D. W. Green et al., *Analytical Chemistry Laboratory Progress Report for FY 1994*, Argonne National Laboratory Report ANL/ACL-94/3 (December 1994).

accountability during the planned demonstration of processing of spent nuclear fuels at ANL-West. To help in methods development/validation and to provide a source of quality-control samples for use during the demonstration, CMT has prepared two sets of "Special Reference Materials," each consisting of specified analytes in a matrix typical of samples that will be generated during the planned demonstration. It is the task of the ACL to characterize each batch of materials by chemical analysis and provide reference values for the concentrations of individual constituents in each matrix.

In 1993, CMT researchers prepared samples of two special reference materials, designated SRM-A (containing enriched uranium in a LiCl-KCl salt matrix) and SRM-B (containing U, Pu, Am, and a mixture of simulated fission products and process elements in the same salt matrix). To provide accurate and precise U and Pu assays in this work, we applied the mass spectrometric isotope dilution method with a special internal-standard technique for the mass-spectrometric measurements of uranium. Furthermore, americium was determined by γ -spectrometry; metals and rare earths by ICP/AES; and Cs and Rb by flame emission or atomic absorption after separation from U and Pu.

All of the uranium isotopic and compositional analyses on SRM-A have been completed. The results of uranium assays on 10 SRM-A samples (analyzed in duplicate) show a mean concentration of 2.5058 wt% U, with a standard deviation of only 0.0022 wt%. The remaining SRM-A "standards" were sent to ANL-West, and the analytical laboratory there is testing and validating methodology at their laboratory for comparable uranium assays.

3. Thermal Treatment Systems for Organic Effluents

The ACL has developed a continuous emission monitor based upon Fourier transform infrared (FTIR) technology. This on-stream device will monitor stack gases from thermal treatment systems 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 performance. 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 used to characterize the effluent, such as use of a volatile organic sampling train followed by gas chromatograph/mass spectrometer (GC/MS) analysis in the laboratory. This method, which is required under current procedures, only provides a one-time analysis.

During 1994, we contributed to an EPA protocol for continuous emission monitoring with FTIR technology. The EPA also asked us to prepare and submit a procedure to them for validation. An EPA procedure is not required; however, when such a procedure is followed and quality control is within the specified limits, the EPA guarantees acceptance of the data (unlike a protocol). Our procedure for continuous emission monitoring was submitted in September 1994, and validation is now underway. Validation requires analysis of data collected from stack gas measurements to verify that they meet quality control limits. We anticipate that data generated with our FTIR system will be compliant with EPA requirements.

A Cooperative Research and Development Agreement (CRADA) to commercialize the FTIR system was reached in October 1994 with Clean Air Engineering and Martin Marietta Energy Systems, the operators of a DOE incinerator at the K-25 site in Oak Ridge, TN. The research and development done under the CRADA, in combination with the EPA acceptance of the data, will help make the system commercially available, and more widespread application of this technology should facilitate public acceptance of thermal treatment facilities.

4. Characterization of Used HEPA Filters for Disposal

High-efficiency particulate-air (HEPA) filters provide the final stage of containment on many laboratory exhaust systems in ANL facilities by preventing escape of chemical and radioactive materials entrained in the exhausted air. For a number of years, used HEPA filters removed from these systems have accumulated in ANL's Environment and Waste Management Program (EWM), because no facility could be found that would accept them for disposal. A little over a year ago, EWM 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 in EWM 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.

The composite samples generated during repackaging of the HEPA filters by EWM consist of portions of 12 to 14 individual filters, which must be homogenized for analysis. Homogenizing the composite sample is quite difficult because of the fibrous, fabric-like nature of the HEPA filter media. For containment during the cutting process, the manual operations are performed in a closed glovebag in a laboratory fume hood.

From the homogenized composite, representative subsamples are taken for determining specific characteristics or contaminants in the HEPA filter media. In particular, we prepared a slurry according to protocol and determined pH, as well as the concentrations of metals, inorganic anions, sulfide, cyanide, semivolatile organic compounds, polychlorinated biphenyls, and radionuclides. For some samples, sufficiently high concentrations of heavy metals were present to require testing with the EPA Toxicity Characteristic Leaching Procedure so that a proper hazard classification can be assigned to the waste.

During 1994, EWM initiated a campaign to dispose of historical HEPA filter waste, which generated about 100 composite samples for analysis. By the end of FY 1994, the ACL had characterized approximately 60 samples, and EWM had shipped 44 bins of used filters to Hanford. This campaign has resulted in a major reduction of the historical waste inventory at the ANL site.

5. Development of "Smart" Chemical Sensors

Current ACL research efforts in chemometrics (the use of mathematics, statistics, and formal methods of logic for analysis of chemical data) are focused on the development of an optimized software system for designing automated monitoring algorithms for spectroscopic, chromatographic, electrochemical, and radiochemical sensors that are of interest to the DOE

Office of Arms Control and Nonproliferation. The objective of this work is to produce "smart" sensors that provide real-time data analysis and can be linked to systems that collect and analyze data from multiple sensors. Smart sensors have obvious advantages for both invasive and noninvasive monitoring scenarios. The software system, referred to as the Sensor Algorithm Generation Environment (SAGE), provides a unique workbench that will allow users to selectively combine and experiment with various types of signal processing procedures, including digital filtering, pattern recognition, and multivariate quantitative techniques. The results can be used to produce customized algorithms that analyze data from a particular sensor. These algorithms can then be implemented in software via the computer controlling the sensor, or they 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. The SAGE workbench is expected to save time, effort, and expense in producing optimized, smart sensors capable of automated data analysis and decision making. Although the SAGE workbench is still under development, novel algorithms have been successfully designed for qualitative processing of data from a passive FTIR sensor used for remote monitoring of chemical emissions and for quantitative processing of data from an extractive FTIR system used for continuous emission monitoring (Sec. X.B.3).

6. Development of the 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 for DOE's Office of Environmental Management (EM), Analytical Services Division. The program is designed to provide information on the quality of radiological and nonradiological analytical data being produced by all laboratories on which DOE is relying for analysis of environmental restoration and waste management samples. The ACL is assisting the two lead DOE laboratories in the development of the program requirements and strategies for implementation, especially in the nonradiological portions of the program. The ACL is also collaborating on developing strategies for compiling and analyzing the performance evaluation results, and for monitoring to assure that needed corrective actions are taken.

The Interagency Agreement between ANL and Region V of the EPA was renewed for FY 1994. This agreement allows us to nominate laboratories performing analyses for EM into performance evaluation programs and to access the relevant information about these laboratories from the Water Supply and Water Pollution programs of the Environmental Monitoring Systems Laboratory (Cincinnati, OH). Historical and current data from these programs are now routinely transferred electronically from the EPA data base at Research Triangle Park (North Carolina) to the data base at ANL.

7. Analytical Procedures for Waste Minimization and Pollution Prevention

Procedures exist for waste characterization, but waste minimization and pollution prevention have not usually been considered in the development of these procedures. The DOE expects to require several million characterizations over a 30-year period to accomplish the Department's goals for environmental restoration and waste management. The waste generated

by the analytical procedures used for characterizations is a significant source of new DOE waste. Success in reducing the volume of secondary waste and the costs of handling this waste would significantly decrease the overall cost of this DOE program. We have begun investigating several methods to reduce these secondary wastes, one of which is a microanalytical method that incorporates a direct-injection nebulizer in a flow injection method.

The determination of the inorganic constituents of environmental and waste samples usually involves multielement analytical techniques, such as ICP/AES or inductively coupled plasma/mass spectrometry (ICP/MS). These techniques provide simultaneous determination of inorganic constituents, such as heavy metals, in aqueous solution. Both techniques use a nebulizer that converts the sample into an aerosol, which is injected into the high-temperature plasma. In the standard method, the sample is continuously pumped into a nebulizer having 1% utilization efficiency. However, the combination of a flow injection technique and a direct-injection nebulizer allows introduction of sample aliquots of less than a milliliter with a 100% utilization efficiency. That is, all of the sample aliquot will be converted to an aerosol for analysis. Verification results for this new method will be reported next year.

8. Gross α/β Analysis of Environmental and Mixed-Waste Samples

In 1994, the ACL evaluated improved equipment and techniques for microwave digestion of samples for gross α/β analysis. Laboratories are receiving many requests for such analyses as a result of DOE's environmental restoration and waste management activities. The new techniques could allow laboratories to respond to such requests more quickly.

Gross α/β activity measurements are used as a screening procedure before analysts initiate determinations of radionuclides, as well as a hazard characterization prior to determinations of metals or volatile organics. Therefore, gross α/β determinations often become the rate-determining step in these analytical protocols. Traditional methods for the gross α/β analysis of environmental and mixed-waste samples require repetitive leaching, which is time-consuming and generates large volumes of secondary wastes.

An alternative to leaching is microwave digestion, but in the past microwave technology has had limited application in the radiochemical laboratory because of limitations on sample size and pressure. However, new microwave vessel designs allow for larger sample sizes and for very high pressures, on the order of 1500 psi (~10 MPa). Results obtained by the ACL indicate that the microwave digestion procedure meets performance requirements for several matrix types and provides precision and detection limits that are equivalent to traditional hot-plate methods. Moreover, analyst time was decreased by a factor of three, while turnaround time was improved by a factor of two. Secondary waste generation was dramatically reduced by a factor of nine or more. Therefore, this new digestion technique clearly allows the analyst to prepare the sample in a fraction of the time with significantly less acid and with a lower potential of cross-contamination.

9. Microwave-Assisted Extraction of Semivolatile Organic Compounds from Soil

Microwave-assisted extraction has been investigated as an alternative to conventional soxhlet and sonication methods for extracting, from soils, semivolatile organic compounds regulated by the Resource Conservation and Recovery Act (RCRA). This method minimizes the amount of secondary waste generated during the extraction and analysis of environmental and waste samples. Only 30 mL of solvent is needed for microwave-assisted extraction, compared to up to 300 mL for the conventional techniques.

Extensive studies have been carried out to determine extraction efficiencies under a variety of conditions for both semivolatile organic compounds spiked on blank soil and for commercially available reference materials. Three solvent systems have been studied: methylene chloride, methylene chloride/acetone, and hexane/acetone mixtures. The optimum conditions for extraction have been determined from studying the effects on extraction efficiency of variations in temperature, microwave power, extraction time, and moisture content.

Extraction efficiencies comparable to conventional methods were obtained with all three solvent systems. Methylene chloride extractions were improved (up to 30% for some compounds) by adding a small amount of water (10%) to the soil. For a marine sediment standard (NIST 1941a), extraction efficiencies with the new procedure averaged only about 50% of the certified values. For the soils, the results were mixed; for most compounds, efficiencies were equal to or better than those obtained by standard extraction techniques, but some were much lower.

When microwave-assisted extraction is applied to the whole range of semivolatile organic compounds spiked on blank soil, extraction efficiencies are comparable to soxhlet and sonication methods. Extraction yields of many of the more polar acids and bases are poor; however, this is also true for conventional techniques.

10. Characterization of Products and Residues 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 side 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 and are 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. An FTIR microscope is used 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 from polyvinylchloride and acrylonitrilebutadienestyrene standards to spectra from reconstituted plastics from the process. Other analytical methods are applied to

determine specific contaminants in the foams, oils, and fines. Heavy metals and 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, they are determined by ICP/AES or cold vapor atomic absorption 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 polyurethane foams from the shredder fluff and (2) a comprehensive characterization of shredder fines to determine their suitability for disposal by incineration in a cement kiln.

11. Analysis of Highly Acidic Mixed Waste

The ACL assisted Argonne's EWM in developing methods for analyzing mixed-waste (hazardous and radioactive) samples that pose special analytical problems. These samples are contaminated with americium at a level that exceeds the maximum level of radioactivity for analysis in our laboratory. In addition, the sample matrix is highly acidic. Because of the contamination level and acidity, we had to develop new ways of analyzing these samples for volatile and semivolatile organic compounds. For volatile organics, we are developing an off-line purge-and-trap method for use in a hot laboratory. This method involves purging the volatile organic compounds in the corrosive water sample onto a trap in a hot laboratory. Traps are then surveyed and sent to our laboratory for analysis. For semivolatile analysis, we have focused on solid-phase extraction, because this method, compared to traditional separatory funnel methods, is much less complicated and time consuming. This method will reduce the analyst's exposure during sample preparation and will allow for quick and easy setup in a laboratory that is equipped for handling high-level radioactive samples.

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

The ACL is collaborating with ANL's Energy Systems Division and the U.S. Army at the Rocky Mountain Arsenal to develop a method that distinguishes among As(III), As(V), and organo-arsenic compounds in soil samples. The Army wants to distinguish between the arsenic originating from lewisite, a chemical warfare agent, and that originating from other sources. They will use this information to examine the impact of the chemical form of the arsenic on remediation activities. The approach chosen was a combination of high-pressure liquid chromatography (HPLC) and inductively coupled plasma/mass spectrometry (ICP/MS). This approach permits separation of the arsenic species by HPLC, followed by sensitive (as low as 0.2×10^{-12} g) detection of arsenic by ICP/MS.

13. Stand-off Detection

The U.S. Army's Edgewood Research, Development and Engineering Center has an ongoing program in stand-off detection of chemical plumes. The objective of this program is to support their effort by testing instrumentation. This testing includes determining the sensitivity of newly designed passive-remote FTIR spectrometers and enhancing the ability of existing spectrometers to detect chemical plumes in the presence of interferences.

We have constructed an analyte data base consisting of quantitative data at different black-body temperatures for dimethyl methylphosphonate and diisopropyl methylphosphonate, which are two surrogates for more toxic compounds. Data were collected in the laboratory and in the field under different background conditions. We will use this data set to determine the ability of FTIR spectrometers to detect analytes under different background conditions. The black-body emission spectra will be correlated with different field emission data.

14. Analysis of Soil Samples for Special Volatile Organics

During the closure process of an on-site area (referred to as 317), the ACL analyzed soil samples taken by Argonne's EWM for several volatile organic compounds that are not normally determined during a closure process. However, these special analytes could not be analyzed by the traditional purge-and-trap methods because of their poor purge efficiencies from water. Two methods were developed to allow fast analysis yet still meet the quality assurance requirements set forth by RCRA. One method involved a modified purge-and-trap procedure, and the other involved a decane extraction.

Several data packages were prepared from analysis of nearly 50 samples, which were mostly soil or sand. The analysis data helped EWM characterize the 317 Area soil for several special volatile organics: methanol, ethanol, 2-butanone peroxide, 1-butanol, and 2-ethoxyethanol. This information assisted EWM in determining what, if any, cleanup was needed.

15. Transition Metal Speciation in Textile Mill Wastewater

Under the new Stream Quality Standards enforced by the 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 "pre-metallized"; that is, the dye molecules contain either Cu, Cr, or Co as part of the chromophore. With support from the AMTEXTTM partnership (an initiative based on a CRADA between the 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. Of particular interest are toxic metals whose chemical form allows uptake by biological systems ("bioavailable"). Collected data will be used to assess the bioavailability (and environmental impact) of the metals. These data will also provide a basis for formulating an effective process by which bioavailable toxic metals can be removed from the wastewater.

16. Determination of Uranium in Dissolver Solutions for Production of ^{99}Mo from Low-Enrichment Uranium

Molybdenum-99 is a radioisotope (half-life of 2.75 days) used frequently in nuclear medicine. The production of this isotope requires neutron irradiation of targets containing high-enrichment uranium; however, the use of this uranium will soon be curtailed to reduce the risk of further nuclear weapons proliferation. It is possible to produce ^{99}Mo from targets containing low-enrichment uranium, but the process is only economical if the yield of ^{99}Mo is comparable to that obtained from high-enriched uranium targets. High-density uranium silicide (U_3Si_2) targets, developed at ANL in 1985, offer a practical substitute for high-enriched uranium, and CMT is investigating the recovery of ^{99}Mo from these materials (Sec. V.D). The ACL is supporting these investigations by using ICP/MS to determine the uranium present in dissolver solutions of alkaline hydrogen peroxide. These uranium data have been used to determine the chemical conditions (i.e., temperature and solvent composition) that are optimal for target dissolution; future experiments will examine the recovery of molybdenum from the dissolved targets.

17. Determination of Volatile Organic Compounds in Headspace for WIPP Project

An important part of the analytical work that must be done as part of the Waste Isolation Pilot Plant (WIPP) project involves the analysis of material destined for the WIPP site (Carlsbad, NM) to show that it meets the requirements of regulating agencies with respect to toxic components and does not constitute mixed waste that must be handled separately. Of particular interest are volatile organic compounds, which have appreciable vapor pressure at room temperature and, if released, could migrate quickly from a point of confinement. To test the level of volatile organic compounds in waste drums, gas samples are drawn from the drums into special sample canisters and shipped to laboratories for analysis. The ACL is one of several laboratories participating in a performance demonstration program whose purpose is to establish qualification to do analysis of the drum headspace gas. The analysis for volatile organic compounds involves making quantitative additions of diluent and standards to the gas sample, trapping the analytes on a molecular-sieve adsorbent, and heating the adsorbent to release the compounds to a gas chromatograph/mass spectrometer, where they are identified and quantified. The ACL has maintained qualification as a participating laboratory in this program.

18. Development of an Analytical Scheme to Determine Actinides in Soil

The Department of Energy is sponsoring a program to develop methods for the chemical characterization of environmental samples. A primary focus of this project is to develop faster and cheaper radioanalytical methods. As part of this project, the ACL, in collaboration with groups from ANL's Chemistry and Environmental Research Divisions, has developed an improved method to isolate and separate the actinide elements from soil for analysis. This method includes sample preparation that is useful for subsequent measurement by either alpha spectrometry or inductively coupled plasma/mass spectrometry (ICP/MS).

The new analytical scheme uses a series of extraction chromatographic materials, such as Tru-Spec and Teva-Spec, and ion exchange resins, such as Diphonix and BioRad Ag 1-X8. These materials allow sequential isolations of the individual actinides for α -spectrometry and group separations for ICP/MS. Hydride adducts, $^{238}\text{UH}^+$ and $^{232}\text{ThH}^+$, were found to interfere with the determination of ^{239}Pu and ^{233}U by ICP/MS. Because of the relatively short half-life of ^{241}Am , ICP/MS is not a suitable detection method for this isotope at ambient environmental levels. Therefore, the trivalent actinides are isolated for α -spectrometry determinations prior to further group separation for ICP/MS measurements. Additionally, the separation schemes were designed to allow analysis of the actinides in soil, whether the soils had been leached with an acid solution or had been totally dissolved through a sodium hydroxide fusion.

The Diphonix resin offers several advantages. Diphonix is selective for actinides in highly acidic solutions, even in the presence of complexing agents. The ability to use hydrochloric acid makes it easier to maintain large soil samples in solution. Diphonix also remains effective in the presence of hydrofluoric acid, which makes it possible to process sample solutions that contain considerable quantities of silica. In more traditional methods, silica is removed through volatilization of silica tetrafluoride. However, in this analytical scheme, silica is kept in solution, and this reduces fume hood emissions.

19. Methods for Determining Metals in Waste Oil

Many ANL programs depend on vacuum pumps, hydraulic systems, or lubricated 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 methods for decomposing oils to provide a single aqueous solution that could be used in all the hazardous metal analyses. We then applied two methods (Parr-oxygen-bomb combustion and microwave-assisted acid decomposition) in the preparation of metal-containing oil standards to evaluate the recovery of 20 metals. For this project, elemental measurements were done by using graphite furnace atomic absorption, cold vapor atomic absorption, or inductively coupled plasma/atomic emission spectrometry. Low recoveries were observed for several metals when the samples were prepared by the Parr-oxygen-bomb methods. However, with the microwave preparation methods, recoveries between 90 and 100% were obtained for all target metals.

20. Support for High-Temperature Superconductor Development

The ACL continued providing extensive analytical support to high-temperature superconductivity programs in the Energy Technology and Chemical Technology Divisions. Much of this work involves analysis of starting materials, process samples, and products related to fabrication and characterization studies on various ceramic compositions, including $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ("123-compound") and lead-doped bismuth/strontium/calcium/copper oxides ("BSCCO" ceramics). Our measurements include determining elemental composition by ICP/AES or classical methods, anions by ion chromatography, carbon with a LECO 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.

This past year, researchers have concentrated on the study of the BSCCO ceramics, which exhibit several superconducting phase compositions [e.g., $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ and $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$]. Researchers at ANL, often in collaboration with scientists at universities and commercial organizations, are investigating new ways to prepare the BSCCO ceramics and are studying the chemical and physical properties of the specimens they obtain. New analytical challenges have arisen from these studies, especially in determining the oxygen coefficient by iodometric titration. It seems that in the BSCCO ceramics, bismuth may slowly form an iodobismuthite ion, which consumes titrant and causes an indistinct endpoint. We found that adding ethylenediaminetetraacetic acid to complex bismuth before titration greatly improved the endpoint behavior and allowed precise measurement of the oxygen coefficient.

In general, the BSCCO system exhibits potential for forming mixed phases and has a more complicated chemistry than the 123-compound. Compositional changes can arise from variations in metal stoichiometry (e.g., noninteger stoichiometry numbers for one or more metals) as well as from variations in the valence of Pb, Bi, or Cu. This range of compositional variation in the BSCCO materials makes chemical analysis of individual specimens very important to understanding and comparing results. Our experience with these materials suggests that more precise methodology is needed for their compositional analysis, as well as new approaches to characterize the metal valences that occur in them. The ACL plans to pursue development of capabilities to satisfy these needs.

21. Orphan Waste Disposal

Many ANL facilities have waste materials left behind by programs that are no longer funded or materials whose origin is unknown or inadequately documented. In support of these orphan waste projects, the ACL is conducting chemical and radiological analyses to provide the composition and hazards-classification data needed by treatment/storage/disposal (TSD) facilities that will ultimately process the wastes. Working closely with Argonne's EWM to ensure that information and procedural requirements of the appropriate TSD 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 EWM staff in interpreting the analysis results for waste handling.

Wastes characterized by the ACL this year have included approximately 30 five-gal pails of soil samples that were archived over decades of radiological characterization projects in ANL's Environment Safety and Health Division, as well as hundreds of smaller waste items from various laboratories and storage areas. Many of these small items were unlabeled containers of solids, aqueous or organic liquids, and oils or sludges. When the material in these containers appeared to be pure chemical compounds or simple mixtures, we pursued an analytical approach that would directly identify the material and then relied on a material safety data sheet to obtain pertinent hazards information. For solids, X-ray fluorescence and X-ray diffraction analysis often gave the necessary information; for liquids and oils, several techniques (such as GC/MS and FTIR spectroscopy) were often employed. However, many wastes either could not be identified

or contained complex mixtures of components; such wastes were evaluated for the RCRA characteristics of ignitability, corrosivity, toxicity, and reactivity. Wastes from radiological-controlled areas required determination of the identity and quantity of radionuclides that might be present; these wastes were analyzed by α -spectrometry, gas proportional counting, liquid scintillation counting, and/or α pulse height analysis. Through its Orphan Waste work projects, EWM has helped ANL divisions dispose of tens of thousands of pounds of waste materials.

22. Facility Closure

Under the RCRA, facilities or areas that have been involved in the storage, treatment, or disposal of hazardous wastes must undergo a formal closure and a sequence of characterization, remediation, and recharacterization, before they are returned to general use. The ACL provided both laboratory services and technical support to several of these activities.

In the 317 Area of the ANL site, RCRA closure of two areas was completed. One of these, the "Shoot-and-Burn Pile," consisted of a large mound of sand on which shock-reactive waste chemicals had been detonated by rifle shot in past years as a means to render the chemicals safe for disposal. The other area, the "Alkali Metal Passivation Tank," is a concrete structure that had held water for the purpose of neutralizing water-reactive chemicals. Chemical analyses of numerous samples of water, sand, soil, and sludge from these areas were required to complete their RCRA closures. Most of these analyses involved commonly applied EPA methods. However, for the Shoot-and-Burn Pile, special methods had to be devised to provide data on specific materials known to have been detonated on the sand pile.

Involvement by the ACL in these RCRA closures extended beyond performing laboratory measurements on samples. The ACL also participated in the selection and specification of methods for the analysis of samples, interacted with contractors that performed the sampling and remediation activities or provided third-party oversight of the closure process, and assisted in evaluation or interpretation of analysis results. The data that the ACL provided helped to determine how waste generated during the cleanup would be disposed, and whether the remediation achieved decontamination standards established in the closure plan. The successful closure of these facilities is a significant milestone in ANL's efforts to remediate environmental concerns related to past operations.

23. Wastewater Treatability Studies

Wastewater from facilities on the ANL site is segregated into two distinct sewer systems, which collect either sanitary wastewater or laboratory wastewater for separate treatment and discharge. In coming years, ANL plans to upgrade its facilities for treating the effluents from these sewer systems. Among the planned improvements is construction of a wastewater treatment plant that would process the laboratory-system wastewater to remove potential contaminants such as heavy metals, volatile organic compounds, suspended solids, and other substances that are regulated under ANL's National Pollution Discharge Elimination System (NPDES) permit.

To help choose among alternative technologies and operational designs (e.g., batch-mode vs. continuous-mode processing) for the proposed plant, Argonne's EWM commissioned

an on-site engineering study of laboratory wastewater treatability. In this study, the compatibility and effectiveness of various treatment processes were examined with actual wastewater effluents from the ANL site. The ACL provided laboratory support by analyzing samples of treated and untreated water for the contaminants of interest. Because adjustments to treatment conditions required feedback data from previous tests, short turnaround times and close cooperation were important to the study's success. In all, the ACL analyzed more than 500 samples in support of this effort. Process recommendations from this study will help ensure that the plant will operate effectively.

24. Measurement of Calcium Isotope Ratios in Canine Blood Serum

Researchers in Argonne's Center for Mechanistic Biology and Biotechnology are studying the effects of ovary removal and cadmium exposure on the metabolic uptake of calcium into the body. In one study designed to measure intestinal calcium uptake in canine subjects, isotopically enriched, stable calcium tracers were administered orally (^{44}Ca) and intravenously (^{42}Ca) to groups of dogs having different treatment histories. Blood was drawn from each animal at an appropriate time after the tracers were administered. The relative amounts of each tracer present in the withdrawn blood provide the desired measure of calcium absorption through the digestive pathway.

Key to the application of this approach to measuring calcium uptake is the ability to precisely determine the extent of isotopic enrichment or depletion of calcium in the blood-serum samples from each subject. In 1993, the ACL determined $^{44}\text{Ca}/^{42}\text{Ca}$ ratios on a number of samples by ICP/MS. In 1994, we established procedures for measuring calcium isotope ratios in the blood-serum samples by thermal ionization mass spectrometry (TIMS). For these measurements, an oxalate precipitation procedure was used to isolate calcium ($\sim 30\ \mu\text{g}$) from a 0.3 mL portion of serum. For TIMS analysis, 3 μg of this calcium was loaded on a high-purity rhenium side filament and analyzed in triple-filament configuration with a rhenium-ionizing filament. Instrumentally induced mass fractionation was corrected for in each analysis run by normalizing all measured ratios to a reference value for $^{40}\text{Ca}/^{48}\text{Ca}$ in natural calcium. This normalization could be applied to the tracer-doped samples as well as to control samples because ^{40}Ca and ^{48}Ca were not present at significant levels in the tracers. With the normalization of ratios, run-to-run precision for ratios involving the tracer isotopes was quite good, showing a relative standard deviation of about 0.2% for duplicate measurements on 14 serum samples. Also, TIMS data obtained for natural calcium samples were in excellent agreement with literature values.² The TIMS analysis uses about a factor of 30 less sample than the ICP-MS measurements and provides precise data ($\pm 0.2\%$) on all calcium isotopes in each sample. Agreement between the ICP/MS and TIMS values for the $^{44}\text{Ca}/^{42}\text{Ca}$ ratios was remarkably good. The analytical results demonstrate that ICP/MS isotopic analysis for calcium is viable in appropriate cases.

² L. J. Machlan and L. B. Moore, *Anal. Chem.* **44**, 2291-2296 (1972).

XI. ADDENDUM.**CHEMICAL TECHNOLOGY DIVISION
PUBLICATIONS --- 1994**

The Division's publications and oral presentations for 1994 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—1994

A. Journal Articles, Books, and Book Chapters

Waste Removal in Pyrochemical Fuel Processing for the Integral Fast Reactor

J. P. Ackerman, T. R. Johnson, and J. J. Laidler

Actinide Processing: Methods and Materials, Eds., B. Mishra and W. A. Averill, The Minerals, Metals, and Materials Soc., Warrendale, PA, pp. 261–266 (1994)

Structure and Dynamics of Molten Aluminum and Gallium Trihalides II. Raman Spectroscopy and *Ab Initio* Calculations

A. D. Alvarenga, M.-L. Sabounji, L. A. Curtiss, M. Grimsditch, and L. E. McNeil
Mol. Phys. **81**(2), 409–420 (1994)

Climatic, Eustatic, and Tectonic Controls on Quaternary Deposits and Landforms, Red Sea Coast, Egypt

R. Arvidson, R. Becker, A. Shanabrook, W. Luo, N. C. Sturchio, M. Sultan, Z. Lotfy,
A. M. Mahmood, and Z. El Alfy
J. Geophys. Res. **99**, 12,175–12,190 (1994)

Pyrometallurgical Processes for Recovery of Actinide Elements

J. E. Battles, J. J. Laidler, C. C. McPheeters, and W. E. Miller

Actinide Processing: Methods and Materials, Eds., B. Mishra and W. A. Averill, The Minerals, Metals, and Materials Soc., Warrendale, PA, pp. 135–151 (1994)

The Adsorption of CO and H₂O on Polycrystalline Gold as Studied by Synchrotron Infrared Spectroscopy

B. Beden, C. A. Melendres, G. A. Bowmaker, C. Liu, and V. A. Maroni

Synchrotron Techniques in Interfacial Electrochemistry, Eds., C. A. Melendres and A. Tadjeddine, NATO ASI Series, Vol. 432, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 433–450 (1994)

Theoretical and Inelastic Neutron-Scattering Studies of Tetraethylammonium Cation as a Molecular Sieve Template

H. V. Brand, L. A. Curtiss, L. E. Iton, F. R. Trouw, and T. O. Brun
J. Phys. Chem. **98**(4), 1293–1301 (1994)

Identification of Uranium-Bearing Colloids from the Dissolution of Spent Fuel and UO₂

E. C. Buck and J. K. Bates
Micro. Res. Technol. **27**, 352 (1994)

Characterization of Ni on Si Wafers: Comparison of Surface Analysis Techniques

W. F. Calaway, S. R. Coon, M. J. Pellin, D. M. Gruen, M. Gordon, A. C. Diebold, P. Maillot,
J. C. Banks, and J. A. Knapp
Surf. Interface Anal. **21**, 131–137 (1994)

Reversible Hydrocarbon Activation by Rhodium Phthalocyanine Dimer [(R₈Pc)Rh]₂ (R₈Pc²⁻ = Dianion of 1,4,8,11,15,18,22,25-Octa-*n*-Pentylphthalocyanine)

M. J. Chen and J. W. Rathke
Organomet. **13**(12), 4875–4880 (1994)

Quartz Crystal Microbalance and Synchrotron X-ray Reflectivity Study of Water and Liquid Xenon Adsorbed on Gold and Quartz

R. P. Chiarello, J. Krim, and C. Thompson
Surf. Sci. **306**, 359-366 (1994)

Epitaxial Growth of Otavite on Calcite Observed *In Situ* by Synchrotron X-ray Scattering

R. P. Chiarello and N. C. Sturchio
Geochim. Cosmochim. Acta **58**(24), 5633-5638 (1994)

Neutral Copper Cluster Sputtering Yields: Ne^+ , Ar^+ , and Xe^+ Bombardment

S. R. Coon, W. F. Calaway, and M. J. Pellin
Nucl. Instr. Methods B **90**, 518-522 (1994)

Hydride Interference on the Determination of Minor Actinide Isotopes by Inductively Coupled Plasma Mass Spectrometry

J. S. Crain and J. Alvarado
J. Anal. At. Spectrom. **9**, 1223-1227 (1994)

Fabricating Multifilamentary High- T_c Superconducting Bismuth Cuprate Tapes by Metalorganic Chemical Spray Pyrolysis

L. P. de Rochemont, V. A. Maroni, M. Klugerman, R. J. Andrews, and W. C. Kelliher
Appl. Supercond. **2**(3/4), 281-294 (1994)

A Theoretical Study of Triatomic Carbon-Silicon Mixed Clusters. Relative Energies and Binding Energies

P. W. Deutsch and L. A. Curtiss
Chem. Phys. Lett. **226**, 387-391 (1994)

Asymptotic Power Spectrum Analysis of Chaotic Behavior in Fluidized Beds

J. Ding and S.-W. Tam
Int. J. Bifurcation and Chaos **4**(2), 327-341 (1994)

Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the MnO-SiO_2 and CaO-SiO_2 Systems

G. Eriksson, P. Wu, M. Blander, and A. D. Pelton
Can. Metall. Q. **33**(1), 13-22 (1994)

Characteristics of Colloids Generated during the Corrosion of Nuclear Waste Glasses in Groundwater

X. Feng, E. C. Buck, C. J. Mertz, J. K. Bates, J. C. Cunnane, and D. J. Chaiko
Radiochim. Acta **66/67**, 197-205 (1994)

Effects of Salt Solutions on Glass Dissolution

X. Feng and I. L. Pegg
Phys. Chem. Glasses **35**(2), 98-103 (1994)

Colloidal Products and Actinides Species in Leachate from Spent Nuclear Fuel

P. A. Finn, E. C. Buck, M. Gong, J. C. Hoh, J. W. Emery, L. D. Hafenrichter, and J. K. Bates
Radiochim. Acta **66/67**, 189-195 (1994)

Quality Assurance

A. A. Frigo
Chapter 13 in *Guidelines for Gloveboxes*, AGS-G001-1994, American Glovebox Soc., Denver, CO, pp. 131-137 (1994)

Fullerenes as Precursors for Diamond Film Growth without Hydrogen or Oxygen Additions

D. M. Gruen, S. Z. Liu, A. R. Krauss, J. S. Luo, and X. Z. Pan
Appl. Phys. Lett. **64**, 1502 (1994)

Deposition and Characterization of Nano-Crystalline Diamond Films

D. M. Gruen, X. Z. Pan, A. R. Krauss, S. Z. Liu, J. S. Luo, and C. M. Foster
J. Vac. Sci. Technol. A **12**, 1491 (1994)

Advanced Batteries for Electric Vehicles

G. L. Henriksen, W. H. DeLuca, and D. R. Vissers
CHEMTECH **24**, 32-38 (1994)

Lithium-Aluminum/Iron Sulfide Batteries

G. L. Henriksen and D. R. Vissers
J. Power Sources **51**, 115-128 (1994)

Removal of VOCs from Groundwater Using Membrane-Assisted Solvent Extraction

J. C. Hutter, G. F. Vandegrift, L. Nunez, and D. H. Redfield
AIChE J. **40**(1), 166-177 (1994)

Tritium Release from Beryllium Discs and Lithium Ceramics Irradiated in the SIBELIUS Experiment

C. E. Johnson, D. L. Baldwin, and J. P. Kopasz
J. Nucl. Mater. **212-215**, 966-970 (1994)

Tritium Transport and Release from Lithium Ceramic Breeder Materials

C. E. Johnson, J. P. Kopasz, and S.-W. Tam
Nucleotecnica **14**(26), 7 (1994)

Pyrochemical Recovery of Actinide Elements from Spent Light Water Reactor Fuel

G. K. Johnson, R. D. Pierce, D. S. Poa, and C. C. McPheeters
Actinide Processing: Methods and Materials, Eds., B. Mishra and W. A. Averill, The Minerals, Metals, and Materials Soc., Warrendale, PA, pp. 199-214 (1994)

Thermodynamic Modeling of Chemical Interactions between CaO-TiO₂ Ceramics and Molten Salts

I. Johnson and P. S. Maiya
J. Mater. Res. **9**(3), 739-745 (1994)

High-Pressure NMR Investigation of Hydrogen Atom Transfer and Related Dynamic Processes in Oxo Catalysis

R. J. Klingler and J. W. Rathke
J. Am. Chem. Soc. **116**, 4772-4785 (1994)

Tritium Release from Lithium Titanate, A Low Activation Tritium Breeding Material

J. P. Kopasz, J. M. Miller, and C. E. Johnson
J. Nucl. Mater. **212-215**, 927-931 (1994)

Spatial Tritium Transport in Single Crystal LiAlO₂

J. P. Kopasz, C. A. Seils, and C. E. Johnson
J. Nucl. Mater. **212-215**, 912-916 (1994)

Fundamentals of Fuel Cell System Integration

M. Krumpelt, R. Kumar, and K. M. Myles
J. Power Sources 49, 37-51 (1994)

Conditioning of Spent Nuclear Fuel for Permanent Disposal

J. J. Laidler
J. Franklin Inst. 331A, 173-181 (1994)

A Spreadsheet Algorithm for Stagewise Solvent Extraction

R. A. Leonard and M. C. Regalbuto
Solvent Extr. Ion Exch. 12(5), 909-930 (1994)

Abundance and Depth of Origin of Neutral and Ionic Clusters Sputtered from a Liquid Gallium-Indium Eutectic Alloy

T. B. Lill, W. F. Calaway, M. J. Pellin, and D. M. Gruen
Phys. Rev. Lett. 73, 1719 (1994)

Microstructure and Superconducting Properties of Attrition-Milled $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$

J. S. Luo, H. G. Lee, and S. N. Sinha
J. Mater. Res. 9(2), 297-304 (1994)

Composition and Microstructural Evolution of Nonsuperconducting Phases in Silver-Clad $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ Composite Conductors

J. S. Luo, N. Merchant, E. Escorcia-Aparicio, V. A. Maroni, B. S. Tani, W. L. Carter, and G. N. Riley
J. Mater. Res. 9(12), 3059-3067 (1994)

Kinetic Energy Distribution of Sputtered Indium Atoms and Clusters

Z. Ma, W. F. Calaway, M. J. Pellin, and E. I. von Nagy-Felsobuki
Nucl. Instrum. Methods B 94, 197-202 (1994)

Sputtering of Neutral and Ionic Indium Clusters

Z. Ma, S. R. Coon, W. F. Calaway, M. J. Pellin, and D. M. Gruen
J. Vac. Sci. Technol. A 12, 2425-2430 (1994)

XAFS Spectra and the Oxidation State of Nickel in Some of Its Oxy Compounds

A. N. Mansour, C. A. Melendres, M. Pankuch, and R. Brizzolara
J. Electrochem. Soc. 141, L69 (1994)

Chemistry of Passive Films on Amorphous $\text{Al}_{90}\text{Fe}_7\text{Ce}_3$ Alloy Induced Using Potentiodynamic Polarization Techniques by XPS

A. N. Mansour, C. A. Melendres, M. Pankuch, S. J. Poon, Y. He, and G. J. Shiflet
Surf. Sci. Spectra 2, 184 (1994)

Defining a Metal-Based Waste Form for IFR Pyroprocessing Wastes

S. M. McDevitt, J. Y. Park, and J. P. Ackerman
Actinide Processing: Methods and Materials, Eds., B. Mishra and W. A. Averill, The Minerals, Metals, and Materials Soc., Warrendale, PA, pp. 305-319 (1994)

Electrode Materials for the Reduction of CaO and Li₂O for Actinide Pyroprocessing

S. M. McDeavitt, J. L. Smith, C. C. McPheeters, R. D. Pierce, and D. S. Poa

Actinide Processing: Methods and Materials, Eds., B. Mishra and W. A. Averill, The Minerals, Metals, and Materials Soc., Warrendale, PA, p. 215 (1994)

Future Prospects for the Application of Synchrotron Techniques to Interfacial Electrochemistry

C. A. Melendres

Synchrotron Techniques in Interfacial Electrochemistry, Eds., C. A. Melendres and A. Tadjeddine, NATO ASI Series, Vol. 432, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 469-474 (1994)

Synchrotron Techniques in Interfacial Electrochemistry

C. A. Melendres and A. Tadjeddine, editors

Synchrotron Techniques in Interfacial Electrochemistry, Eds., C. A. Melendres and A. Tadjeddine, NATO ASI Series, Vol. 432, Kluwer Academic Publishers, Dordrecht, The Netherlands (1994)

Reaction Induced Texture of (Bi,Pb)₂Sr₂Ca₂Cu₃O_{10+δ}/Ag Composite Conductors

N. Merchant, J. S. Luo, V. A. Maroni, G. N. Riley, and W. L. Carter

Appl. Phys. Lett. **65**(8), 1039-1041 (1994)

Effects of Oxygen Pressure on Phase Evolution and Microstructural Development in Silver-Clad (Bi,Pb)₂Sr₂Ca₂Cu₃O_{10+δ} Composite Conductors

N. Merchant, J. S. Luo, V. A. Maroni, S. N. Sinha, G. N. Riley, and W. L. Carter

Appl. Supercond. **2**(3/4), 217-225 (1994)

Cell Design for *In Situ* X-ray Scattering Studies of Metal/Solution Interfaces under Electrochemical Control

Z. Nagy, H. You, and R. M. Yonco

Rev. Sci. Instrum. **65**(7), 2199-2205 (1994)

Thermodynamic Analysis of Phase Equilibria in the Iron-Uranium-Zirconium System

A. D. Pelton, P. K. Talley, L. Leibowitz, and R. A. Blomquist

J. Nucl. Mater. **210**, 324-332 (1994)

Chapter 8: Air Emissions from Pressurized Fluidized Bed Combustors

W. F. Podolski, W. M. Swift, and S. A. Miller

Fundamentals of Pressurized Fluidized Bed Combustion, Ed., E. J. Anthony, Blackie Academic and Professional, Glasgow, Scotland (1994)

Lattice Location of Trace Elements within Minerals and their Surfaces with X-ray Standing Waves

Y. Qian, N. C. Sturchio, R. P. Chiarello, P. F. Lyman, T.-L. Lee, and M. J. Bedzyk

Science **265**, 1555-1557 (1994)

High Pressure NMR Studies of Homogeneous Catalytic Processes

J. W. Rathke, R. J. Klingler, M. J. Chen, and K. Woelk

Trends in Organometallic Chemistry **1**, 117-130 (1994)

Stability of Pu(VI) in Selected WIPP Brines

D. T. Reed, S. Okajima, and M. K. Richmann

Radiochim. Acta **66/67**, 95-101 (1994)

Orientational Phase Transitions in Alloys

M.-L. Saboungi, G. K. Johnson, and D. L. Price

Statics and Dynamics of Alloy Phase Transformations, Eds., P. E. A. Turchi and A. Gonis, Plenum Press, New York, pp. 195-201 (1994)

Portable X-ray Fluorescence for Determination of Lead and Other Metals on Small-Arms Firing Ranges

J. F. Schneider, J. D. Taylor, S. D. Zellmer, and D. A. Bass

Am. Environ. Lab., pp. 35-36 (1994)

Three-Color and 1 + 1 Resonance Ionization Mass Spectrometry of Zirconium Sputtered from Refractory Carbides

D. R. Spiegel, W. F. Calaway, G. A. Curlee, A. M. Davis, R. S. Lewis, M. J. Pellin, D. M. Gruen, and R. N. Clayton

Anal. Chem. **66**, 2647-2655 (1994)

Survival of Polyanions in Expanded Liquid Alloys

M. Stolz, O. Leichtweib, R. Winter, M.-L. Saboungi, J. A. Fortner, and W. S. Howells

Europhy. Lett. **27**(3), 221 (1994)

Development of Self-Absorption Coefficients for the Determination of Gamma-Emitting Radionuclides in Environmental and Mixed Waste Samples

W. E. Streets

Nucl. Instrum. Methods Phys. Res. A **353**, 702-705 (1994)

Uranium-Series Ages of Travertines and Timing of the Last Glaciation in the Northern Yellowstone Area, Wyoming-Montana

N. C. Sturchio, K. L. Pierce, M. T. Murrell, and M. L. Sorey

Quat. Res. **41**, 265-277 (1994)

Thermodynamic and Nonstoichiometric Behavior of the Lead-Doped Bi-2223 System

M. Tetenbaum, M. C. Hash, B. S. Tani, J. S. Luo, and V. A. Maroni

Physica C **235-240**, 321-322 (1994)

Solubility of AgCl in Molten NaCl-AlCl₃ and KCl-AlCl₃

P. J. Tumidajski, M. Blander, and D. S. Newman

J. Electrochem. Soc. **141**(4), 895-900 (1994)

The Toroid Cavity NMR Detector

K. Woelk, J. W. Rathke, and R. J. Klingler

J. Magn. Reson. A **109**, 137-146 (1994)

Processing Technology Interview: Argonne National Laboratory Offers Solution for the Conversion of Spent Catalysts to Marketable Products

D. J. Wronkiewicz

The Catalyst Review Newsletter, pp. 9-11 (October 1994)

Yields of Sputtered Metal Clusters: The Influence of Surface Structure

A. Wucher, Z. Ma, W. F. Calaway, and M. J. Pellin

Surf. Sci. Lett. **304**, L439-L444 (1994)

Oxidation-Reduction-Induced Roughening of Platinum(111) Surface

H. You and Z. Nagy

Phys. B **198**, 187-194 (1994)

In-Situ X-ray Reflectivity Study of Incipient Oxidation of Pt(111) Surface in Electrolyte Solutions

H. You, D. J. Zurawski, Z. Nagy, and R. M. Yonco

J. Chem. Phys. **100**(6), 4699-4702 (1994)

Theoretical Studies of Hydrogen-Bonded Complexes of $\text{H}_3\text{SiO}(\text{H})\text{AlH}_3$ with OH_2 , NH_3 , and CH_4

S. A. Zygmunt, H. V. Brand, D. J. Lucas, L. E. Iton, and L. A. Curtiss

J. Mol. Struc. (Theochem.) **314**, 113-123 (1994)

B. Patents

Process to Remove Rare Earth from IFR Electrolyte

J. P. Ackerman and T. R. Johnson

Patent No. 5,336,450, issued August 9, 1994

Oxygen Partial Pressure Sensor

D. W. Dees

Patent No. 5,344,549, issued September 6, 1994

Synthesis of Highly Phase Pure (Bi,Pb)-Sr-Ca-Cu-O Superconductor

S. E. Dorris, R. B. Poeppel, B. C. Prorok, M. T. Lanagan, and V. A. Maroni

Patent No. 5,354,535, issued October 11, 1994

Method to Synthesize Dense Crystallized Sodalite Pellet for Immobilizing Halide Salt Radioactive Waste

T. Koyama

Patent No. 5,340,506, issued August 23, 1994

Transition Metal Sulfide Loaded Catalyst

V. A. Maroni, L. E. Iton, J. W. Pasterczyk, M. Winterer, and T. R. Krause

Patent No. 5,306,683, issued April 26, 1994

Solid Oxide Fuel Cell with Single Material for Electrodes and Interconnect

C. C. McPheeters, P. A. Nelson, and D. W. Dees

Patent No. 5,330,859, issued July 19, 1994

Electrolytic Recovery of Reactor Metal Fuel

W. E. Miller and Z. Tomczuk

Patent No. 5,348,626, issued September 20, 1994

The Use of Ion Conductors in the Pyrochemical Reduction of Oxides

W. E. Miller and Z. Tomczuk

Patent No. 5,282,937, issued February 1, 1994

Variable Pressure Thermal Insulating Jacket

P. A. Nelson, R. F. Malecha, and A. A. Chilenskas

Patent No. 5,347,816, issued September 20, 1994

Thermal and Chemical Remediation of Mixed Waste

P. A. Nelson and W. M. Swift

Patent No. 5,335,609, issued August 9, 1994

Process for Measuring Low Cadmium Levels in Blood and Other Biological Specimens

D. P. Peterson, E. A. Huff, and M. H. Bhattacharyya

Statutory Invention Registration No. H1310, issued May 3, 1994

Electrochemical Cell

L. Redey, D. R. Vissers, and J. Prakash

Patent No. 5,283,135, issued February 1, 1994

Electrochemical Cell, Bromine or Iodine Containing Additives Incorporated during Charging to Improve Cell Capacity or Power

L. Redey, D. R. Vissers, and J. Praksah

Patent No. 5,340,668, issued August 23, 1994

Recovery of UO_2/PuO_2 in IFR Electrorefining Process

Z. Tomczuk and W. E. Miller

Patent No. 5,356,605, issued October 18, 1994

C. Reports

Practical Superconductor Development for Electrical Power Applications, Annual Report for FY 1994

T. R. Askew, Y. S. Cha, S. E. Dorris, J. T. Dusek, J. E. Emerson, K. C. Goretta, K. E. Gray, J. D. Hettinger, J. G. Hu, J. R. Hull, R. T. Kampwirth, D. S. Kupperman, M. T. Lanagan, J. S. Luo, M. Martinelli, V. A. Maroni, R. L. McDaniel, N. Merchant, D. J. Miller, R. C. Niemann, J. J. Picciolo, J. L. Routbort, D. Singh, J. P. Singh, M. Tetanbaum, V. R. Todt, K. L. Uherka, and C. A. Youngdahl

ANL-94/39 (October 1994)

Determination of the Toxicity Characteristic for Metals in Soil—A Comparison of the Toxicity Characteristic Leaching Procedure and Total Metal Determination

D. A. Bass and J. D. Taylor

ANL/ACL-94/3 (December 1994)

ANL Technical Support Program for DOE Environmental Restoration and Waste Management Annual Report, October 1992–September 1993

J. K. Bates, W. L. Bourcier, C. R. Bradley, N. R. Brown, E. C. Buck, S. A. Carroll, J. C. Cunnane, N. L. Dietz, T. DiSanto, W. L. Ebert, J. W. Emery, X. Feng, T. J. Gerding, M. Gong, L. D. Hafenrichter, J. C. Hoh, J. J. Mazer, L. Newton, B. L. Phillips, R. Pletcher, and D. J. Wronkiewicz

ANL-94/19 (June 1994)

High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics. Volume III

J. K. Bates, C. R. Bradley, E. C. Buck, J. C. Cunnane (compiler and editor), W. L. Ebert, X. Feng, J. J. Mazer, D. J. Wronkiewicz, J. Sprull, W. L. Bourcier, B. P. McGrail, and M. K. Altenhofen

U.S. Department of Energy, Office of Waste Management, Report No. DOE-EM-0177
(March 1994)

High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics. Volume II

J. K. Bates, C. R. Bradley, E. C. Buck, J. C. Cunnane (compiler and editor), W. L. Ebert, X. Feng, J. J. Mazer, D. J. Wronkiewicz, J. Sprull, W. L. Bourcier, B. P. McGrail, and M. K. Altenhofen

U.S. Department of Energy, Office of Waste Management, Report No. DOE-EM-0177
(March 1994)

High-Level Waste Borosilicate Glass: A Compendium of Corrosion Characteristics. Volume I

J. K. Bates, C. R. Bradley, E. C. Buck, J. C. Cunnane (compiler and editor), W. L. Ebert, X. Feng, J. J. Mazer, D. J. Wronkiewicz, J. Sprull, W. L. Bourcier, B. P. McGrail, and M. K. Altenhofen

U.S. Department of Energy, Office of Waste Management, Report No. DOE-EM-0177
(March 1994)

Nuclear Waste Programs Semiannual Progress Report, April–September 1992

J. K. Bates, C. R. Bradley, E. C. Buck, N. L. Dietz, W. L. Ebert, J. W. Emery, X. Feng, P. A. Finn, T. J. Gerding, M. Gong, L. D. Hafenrichter, J. C. Hoh, J. J. Mazer, C. J. Mertz, and D. J. Wronkiewicz

ANL-94/14 (May 1994)

Nuclear Waste Programs Semiannual Progress Report, October 1991–March 1992

J. K. Bates, C. R. Bradley, E. C. Buck, N. L. Dietz, W. L. Ebert, J. W. Emery, X. Feng, P. A. Finn, T. J. Gerding, J. C. Hoh, J. J. Mazer, and D. J. Wronkiewicz

ANL-93/37 (November 1993)

Chemical Technology Division Annual Technical Report, 1993

J. E. Battles et al.

ANL-94/15 (April 1994)

Applied Research and Development Private Sector Accomplishments, Final Summary Report

N. J. Beskid, J. S. Devgun, M. M. Zielke, and M. D. Erickson

DOE/CH-9303 (December 1993)

Critical Review of Glass Performance Modeling

W. L. Bourcier

ANL-94/17 (July 1994)

Analytical Electron Microscopy Characterization of Uranium-Contaminated Soils from the Fernald Site, FY 1993 Report

E. C. Buck, J. C. Cunnane, N. R. Brown, and N. L. Dietz

ANL-94/38 (October 1994)

Performance Specifications for Technology Development: Application for Characterization of Volatile Organic Compounds in the Environment

S. E. Carpenter, P. V. Doskey, M. D. Erickson, and P. C. Lindahl

ANL/ER/TM-3 (July 1994)

Electric Vehicle Battery Testing and Development Project at Argonne National Laboratory, 1993 Annual Report

C. C. Christianson, W. H. DeLuca, K. R. Gillie, J. E. Kulaga, A. F. Tumillo, and C. E. Webster

Electric Power Research Institute Report EPRI RP-3150-01 (1994)

Effect of Glass Composition on Waste Form Durability: A Critical Review

A. J. G. Ellison, J. J. Mazer, and W. L. Ebert

ANL-94/28 (November 1994)

Glassy Slags for Minimum Additive Waste Stabilization Interim Progress Report, May 1993–February 1994

X. Feng, D. J. Wronkiewicz, J. K. Bates, N. R. Brown, E. C. Buck, N. L. Dietz, M. Gong, and J. W. Emery

ANL-94/24 (May 1994)

Analytical Chemistry Laboratory Progress Report for FY 1994

D. W. Green, A. S. Boparai, D. L. Bowers, D. G. Graczyk, and P. C. Lindahl (with contributions from ACL Staff)

ANL/ACL-94/4 (December 1994)

Applied Physical Chemistry Progress Report, October 1991–September 1992

C. E. Johnson, H. M. Attaya, M. C. Billone, R. A. Blomquist, J. P. Kopasz, L. Leibowitz, M. F. Roche, and C. A. Seils

ANL-94/4 (December 1993)

Tritium Release from Beryllium Discs and Lithium Ceramics Irradiated in the SIBELIUS Experiment

C. E. Johnson, J. P. Kopasz, and D. L. Baldwin

Fusion Reactor Materials Semiannual Progress Report for the Period Ending September 30, 1993, DOE/ER-0313/15, p. 373 (1994)

Performance of Ceramic Breeder Materials in the SIBELIUS Experiment

J. P. Kopasz, C. E. Johnson, and D. L. Baldwin

Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1994, DOE/ER-0313/16, p. 385 (1994)

Tritium Release from Lithium Titanate, A Low Activation Tritium Breeding Material

J. P. Kopasz, C. E. Johnson, and J. M. Miller

Fusion Reactor Materials Semiannual Progress Report for the Period Ending September 30, 1993, DOE/ER-0313/15, p. 366 (1994)

Measurement of Alkali Vapors in PFBC Exhaust Final Report

S. H. D. Lee and W. M. Swift

ANL/FE-94-01 (January 1994)

Basic TRUEX Process for Rocky Flats Plant

R. A. Leonard, D. B. Chamberlain, J. A. Dow, S. E. Farley, L. Nunez, M. C. Regalbuto, and G. F. Vandegrift

ANL-94/33 (August 1994)

Development Program for Magnetically Assisted Chemical Separation: Evaluation of Cesium Removal from Hanford Tank Supernatant

L. Nunez, B. A. Buchholz, M. Ziemer, G. R. Dyrkacz, M. D. Kaminski, G. F. Vandegrift, K. J. Atkins, F. M. Bos, G. R. Elder, and C. A. Swift

ANL-94/47 (December 1994)

The Determination of PCBs in Rocky Flats Type IV Waste Sludge by Gas Chromatography/Electron Capture Detection, Part II

K. J. Parish, D. V. Applegate, P. D. Postlethwait, A. S. Boparai, and G. T. Reedy

ANL/ACL-94/2 (December 1994)

Methods for Removing Transuranic Elements from Waste Solutions

S. A. Slater, D. B. Chamberlain, C. J. Conner, J. Sedlet, B. Srinivasan, and G. F. Vandegrift

ANL-94/43 (November 1994)

Proceedings of the *Ad Hoc* Workshop on Ceramics for Li/FeS₂ Batteries

J. A. Smaga, editor

Argonne National Laboratory Report (1994)

Separation Science and Technology Semiannual Progress Report, April–September 1992

G. F. Vandegrift, S. E. Betts, D. L. Bowers, D. B. Chamberlain, C. J. Conner, J. M. Copple, J. A. Dow, S. E. Farley, S. Howard, J. C. Hutter, D. A. Johnson, R. A. Leonard, L. Nunez, D. Redfield, M. C. Regalbuto, J. Sedlet, B. Srinivasan, S. Weber, and D. G. Wygmans

ANL-94/29 (September 1994)

Separation Science and Technology Semiannual Progress Report, October 1991–March 1992

G. F. Vandegrift, S. E. Betts, D. B. Chamberlain, J. M. Copple, J. A. Dow, L. Everson, S. E. Farley, J. C. Hutter, R. J. Jaskot, R. A. Leonard, L. Nunez, D. Redfield, M. C. Regalbuto, J. Sedlet, B. Srinivasan, M. A. Tranovich, E. H. Van Deventer, S. Weber, and D. G. Wygmans

ANL-93/38 (January 1994)

D. Abstracts and Proceedings Papers

Development of a Catalytic Partial Oxidation Reformer for Methanol Used in Fuel Cell Propulsion Systems

S. Ahmed, R. Kumar, and M. Krumpelt

Program and Abstracts of the Fuel Cell Seminar, San Diego, CA, November 28–December 1, 1994, pp. 593–596 (1994)

Carbon Isotopic Composition of n-Alkanes and Isoprenoids in Slightly Biodegraded Crude Oils from the Phillipstown Fields (Illinois Basin)

A. J. Bakel, R. M. Dyer, T. E. Ruble, and R. P. Philip

Organic Geochemistry—Poster Sessions from the 16th Int. Meeting on Organic Geochemistry, Ed., K. Oygard, pp. 91–94 (1994)

Determination of the Forward Reaction Rates of Glasses by Single-Pass Flow-Through Tests

A. J. Bakel, J. J. Mazer, and D. J. Wronkiewicz

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19–21, 1994, Vol. 2, pp. 881–884 (1994)

Evaluation of Accuracy of Carbon Isotopic Measurements for Individual n-Alkanes by Gas Chromatography/Isotope Ratio Mass Spectrometry

A. J. Bakel, P. H. Ostrom, and N. E. Ostrom

Proc. of the Am. Chem. Soc. Meeting, Compound Specific Isotope Analysis in Biogeochemistry and Petroleum Research, Organic Geochemistry, Vol. 21, pp. 595–602 (1994)

Modification of a Graphite Furnace Atomic Absorption Spectrophotometer for the Analysis of Low-Level Mixed Waste Samples

D. A. Bass, L. B. TenKate, and A. M. Wroblewski

Abstracts of the 35th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 11–13, 1994, p. 53 (1994)

Results of Drip Tests on Sludge-Based and Actinide-Doped Glasses

J. K. Bates and E. C. Buck

Proc. of the Fifth Annual Int. Conf. on High-Level Radioactive Waste Management, Las Vegas, NV, May 22–26, 1994, pp. 1088–1101 (1994)

Waste Glass Weathering

J. K. Bates and E. C. Buck

Mater. Res. Soc. Symp. Proc. **333**, 41–53 (1994)

Applicability of Slags as Waste Forms for Hazardous and Mixed Wastes

J. K. Bates, E. C. Buck, N. L. Dietz, X. Feng, D. J. Wronkiewicz, C. Whitworth, K. Filius, and D. Battleson

Proc. of the Spectrum '94 Conf., Nuclear and Hazardous Waste Management Int. Topical Meeting, Atlanta, GA, August 14–18, 1994, Vol. 3, pp. 2222–2231 (1994)

A Statistical Mechanical Theory for Molten Silicate Solutions

M. Blander and I. Bloom

Proc. of the Ninth Int. Symp. on Molten Salts, 185th Electrochem. Soc. Meeting, San Francisco, CA, May 22–27, 1994, Vol. 94-13, pp. 1–7 (1994)

Molten Sulfate-Carbonate Liquids in the Effluents of Wood Combustion for Power Production

M. Blander, A. D. Pelton, R. Cole, J. A. Libera, and K. W. Ragland

Extended Abstracts, Ninth Int. Symp. on Molten Salts, 185th Electrochem. Soc. Meeting, San Francisco, CA, May 22-27, 1994, Vol. 94-1, pp. 8-15 (1994)

Sealant Development for Solid Oxide Fuel Cells

I. Bloom, K. L. Ley, and R. Kumar

Program and Abstracts of the Fuel Cell Seminar, San Diego, CA, November 28-December 1, 1994, pp. 597-601 (1994)

AEM Characterization of a Thorium Contaminated Soil

N. R. Brown, B. J. Carlson, E. C. Buck, N. L. Dietz, and J. K. Bates

Proc. of the Waste Management '94 Conf., 20th Annual Nuclear Waste Symp., Tucson, AZ, February 27-March 3, 1994, pp. 901-904 (1994)

SEM and EDS Characterization of a Low-Level Radioactive Fluorosilicate Glass Altered in a Saturated Environment

N. R. Brown, J. J. Mazer, D. J. Wronkiewicz, and J. K. Bates

Proc. of the Scanning Microscopy Meeting, Scanning Microscopy Int., Toronto, Canada, May 7-12, 1994 (1994)

Secondary Phase Formation Due to the Reaction between Low-level Radioactive Fluorosilicate Waste Glasses and Water Vapor

N. R. Brown, D. J. Wronkiewicz, J. J. Mazer, and A. J. Bakel

Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19-21, 1994, Vol. 1, p. 657 (1994)

Colloid Formation during the Corrosion of SRL 200 Glass

E. C. Buck, J. K. Bates, and X. Feng

Trans. of the 96th Annual Meeting and Exposition of the Am. Ceram. Soc., Environmental and Waste Management, Issues in the Ceramic Industry, Indianapolis, IN, April 24-28, 1994 (1994)

The Distribution of Uranium-Bearing Phases in Fernald Soils

E. C. Buck, N. R. Brown, and N. L. Dietz

Mater. Res. Soc. Symp. Proc. **333**, 437-444 (1994)

Supporting Soil Remediation by Electron Beam Methods

E. C. Buck, N. R. Brown, N. L. Dietz, and J. C. Cunnane

Proc. of the Waste Management '94 Conf., 20th Annual Nuclear Waste Symp., Tucson, AZ, February 27-March 3, 1994, pp. 2131-2135 (1994)

Microscopic Characterization of Radionuclide-Contaminated Soils to Assist Remediation Efforts

E. C. Buck, N. R. Brown, N. L. Dietz, J. A. Fortner, and J. K. Bates

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19-21, 1994, Vol. 1, pp. 581-583 (1994)

Analysis of Reacted Nuclear-Waste Glass Using Electron Beams

E. C. Buck, N. L. Dietz, and J. K. Bates

Proc. of the 52nd Annual Meeting of the Microscopy Soc. of America, New Orleans, LA, July 31-August 5, 1994, pp. 656-657 (1994)

Analytical Electron Microscopy of Solid Reaction Products from SRL200 Waste Glasses

E. C. Buck, J. A. Fortner, J. K. Bates, X. Feng, N. L. Dietz, C. R. Bradley, and B. S. Tani
Mater. Res. Soc. Symp. Proc. **333**, 585-593 (1994)

Uranium Removal from Soils: An Overview from the Uranium in Soils Integrated Demonstration Program

D. J. Chaiko and C. Francis

Proc. of the Waste Management '94 Conf., Tucson, AZ, February 27-March 3, 1994 (1994)

Soil Decontamination Using Aqueous Biphasic Separation

D. J. Chaiko, R. Mensah-Biney, and D. Gupta

Proc. of the Waste Management '94 Conf., 20th Annual Nuclear Waste Symp., Tucson, AZ, February 27-March 3, 1994, Vol. 3, pp. 2257-2260 (1994)

The Mineral-Fluid Interface: New Applications of Synchrotron X-ray Scattering

R. P. Chiarello and N. C. Sturchio

Abstracts, Fall Meeting of the Materials Research Soc., Boston, MA, November 28-December 2, 1994, p. 754 (1994)

In Situ Crystal Truncation Rod Measurements at the Calcite-Fluid Interface

R. P. Chiarello and N. C. Sturchio

Proc. of the Am. Phys. Soc. Meeting, Pittsburgh, PA, March 21-25, 1994 (1994)

In Situ Crystal Truncation Rod Measurements during Calcite Dissolution in Aqueous Fluids

R. P. Chiarello and N. C. Sturchio

Trans. of the Am. Geophys. Union, EOS, Baltimore, MD, May 23-27, 1994 (1994)

Removal of CO₂ in Closed Loop Off-Gas Treatment Systems

M. K. Clemens, P. A. Nelson, and W. M. Swift

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19-21, 1994, Vol. 1, pp. 167-170 (1994)

Treatment of Mixed and Transuranic Wastes at Argonne National Laboratory

C. J. Conner, D. B. Chamberlain, J. C. Hutter, J. Sedlet, S. A. Slater, B. Srinivasan, G. F. Vandegrift, and D. G. Wygmans

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19-21, 1994, Vol. 1, pp. 161-162 (1994)

Hydrogeochemical Characterization of the Alvord Basin Geothermal Area, Harney County, Oregon, USA

M. L. Cummings, A. St. John, and N. C. Sturchio

Proc. of the 15th New Zealand Geothermal Workshop, Eds., K. C. Lee, M. G. Dunstall, and M. P. Hochstein, pp. 119-124 (1994)

Theoretical Studies of Long-Distance Electron Coupling

L. A. Curtiss, C. Naleway, and J. R. Miller

Proc. of the 17th DOE Solar Photochemistry Research Conf., Brainerd, MN, June 6-10, 1993 (1994)

The Challenge: Collection of Quantitative Chemical Release Field Data

J. C. Demirgian, S. Macha, and S. Darby

Proc. of the Third Workshop on Stand-Off Detection for Chemical and Biological Defense, Williamsburg, VA, October 17-21, 1994, pp. 299-306 (1994)

Management of Radioactive Waste from Nuclear Power Plants: An Overview

J. S. Devgun

Proc. of the 29th Intersoc. Energy Conversion Eng. Conf., Monterey, CA, August 7-12, 1994, Part 3, pp. 1193-1198 (1994)

Technology Applications for Radioactive Waste Minimization

J. S. Devgun

Proc. of the Spectrum '94 Conf., Nuclear and Hazardous Waste Management Int. Topical Meeting, Atlanta, GA, August 14-18, 1994, Vol. 2, pp. 1391-1396 (1994)

How Clean is Clean? Cleanup Standards, Guidelines, and Pathway Analysis Models, Summary of the Workshop

J. S. Devgun and G. Subbaraman

Proc. of the Waste Management '94 Conf., 20th Annual Nuclear Waste Symp., Tucson, AZ, February 27-March 3, 1994, Vol. 3, pp. 2329-2331 (1994)

Disposition of Actinides Released from High-Level Waste Glass

W. L. Ebert, J. K. Bates, E. C. Buck, M. Gong, and S. F. Wolf

Trans. of the 96th Annual Meeting and Exposition of the Am. Ceram. Soc., Environmental and Waste Management, Issues in the Ceramic Industry, Indianapolis, IN, April 24-28, 1994, Vol. 45, pp. 231-241 (1994)

Laboratory Testing of Glass Corrosion; Effects of Experimental Parameters

W. L. Ebert and J. J. Mazer

Mater. Res. Soc. Symp. Proc. **333**, 27-40 (1994)

Faster Radiochemical Methods

M. D. Erickson, J. H. Aldstadt, J. S. Alvarado, J. S. Crain, K. A. Orlandini, and L. L. Smith

Proc. of the Cost-Efficient Acquisition and Utilization of Data in the Management of Hazardous Waste Sites Conf., Herndon, VA, March 22-25, 1994 (1994)

Performance Specifications for Technology Development

M. D. Erickson, S. E. Carpenter, P. V. Doskey, and P. C. Lindahl

Abstracts, 35th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 11-13, 1994, p. 76 (1994)

Development of Vitro-Ceramics as Final Waste Forms for Mixed Wastes

X. Feng

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19-21, 1994, Vol. 1, pp. 235-239 (1994)

Structural Bond Strength Model for the Development of Final Waste Forms

X. Feng

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19-21, 1994, Vol. 1, pp. 29-31 (1994)

Surface Layer Effects on Waste Glass Corrosion

X. Feng

Mater. Res. Soc. Symp. Proc. **333**, 55-68 (1994)

Chemical Durabilities of Tailored Slags Versus High-Level Waste Glasses

X. Feng, J. K. Bates, D. J. Wronkiewicz, N. R. Brown, E. C. Buck, M. Gong, and W. L. Ebert
Extended Abstracts, 185th Electrochem. Soc. Meeting, San Francisco, CA, May 22-27, 1994, Vol. 94-1, pp. 912-913 (1994)

Effects of S/V on the Corrosion Mechanism and Secondary Phase Formation of Waste Glasses

X. Feng, E. C. Buck, J. K. Bates, M. Gong, and I. L. Pegg
Trans. of the 96th Annual Meeting and Exposition of the Am. Ceram. Soc., Environmental and Waste Management, Issues in the Ceramic Industry, Indianapolis, IN, April 24-28, 1994 (1994)

Glassy Slag: A Complementary Waste Form to Homogeneous Glass for the Implementation of MAWS in Treating DOE Low-Level/Mixed Wastes

X. Feng, G. Ordaz, and P. Krumrine
Proc. of the Spectrum '94 Conf., Nuclear and Hazardous Waste Management Int. Topical Meeting, Atlanta, GA, August 14-18, 1994 (1994)

Glassy Slags as Novel Waste Forms for Remediating Mixed Wastes with High Metal Contents

X. Feng, D. J. Wronkiewicz, J. K. Bates, N. R. Brown, E. C. Buck, M. Gong, and W. L. Ebert
Proc. of the Waste Management '94 Conf., 20th Annual Nuclear Waste Symp., Tucson, AZ, February 27-March 3, 1994, pp. 1541-1550 (1994)

Comparison of Glassy Slag Waste Forms Produced in Laboratory Crucibles and in a Bench-Scale Plasma Furnace

X. Feng, D. J. Wronkiewicz, N. R. Brown, M. Gong, C. Whitworth, K. Filius, and D. Battleson
Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19-21, 1994, Vol. 2, pp. 872-875 (1994)

Elements Present in Leach Solutions from Unsaturated Spent Fuel Tests

P. A. Finn, J. K. Bates, J. C. Hoh, J. W. Emery, L. D. Hafenrichter, E. C. Buck, and M. Gong
Mater. Res. Soc. Symp. Proc. **333**, 399-407 (1994)

Colloidal Products and Actinide Species in Leachate from Spent Nuclear Fuel

P. A. Finn, E. C. Buck, M. Gong, J. C. Hoh, J. W. Emery, L. D. Hafenrichter, and J. K. Bates
Proc. of the Fourth Int. Conf. on Chemistry and Migration Behavior of Actinides and Fission Products in the Geosphere, December 12-17, 1993, pp. 197-203 (1994)

The Effect of Fuel Type in Unsaturated Spent Fuel Tests

P. A. Finn, M. Gong, J. K. Bates, J. W. Emery, and J. C. Hoh
Proc. of the Fifth Annual Int. Conf. on High-Level Radioactive Waste Management, Las Vegas, NV, May 22-26, 1994, pp. 1080-1087 (1994)

Behavior of Spent Fuel Under Unsaturated Conditions

P. A. Finn, J. C. Hoh, J. K. Bates, and S. F. Wolf
Proc. of the Topical Meeting on DOE Spent Nuclear Fuel—Challenges and Initiatives, Am. Nucl. Soc., Salt Lake City, UT, December 13-16, 1994, pp. 421-425 (1994)

EELS Analysis of Local Structure in Nuclear Waste Glasses

J. A. Fortner, E. C. Buck, and J. K. Bates
Proc. of the Am. Phys. Soc. Meeting, Pittsburgh, PA, March 21-25, 1994 (1994)

EELS Analysis of Local Structure in Nuclear Waste Glasses

J. A. Fortner, E. C. Buck, and J. K. Bates

Bull. Am. Phys. Soc. 39(1), 97 (1994)

ISO 9000 Quality Standards Applied to Glovebox Design and Manufacturing

A. A. Frigo

Proc. of the Eighth Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc.,
Raleigh, NC, August 8-11, 1994, p. 77 (1994)**The Use of Design-for-Manufacturability Techniques to Ensure the Quality of Large Gloveboxes**

A. A. Frigo, R. F. Malecha, and E. F. Lewandowski

Proc. of the Seventh Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc.,
Seattle, WA, August 16-19, 1993, p. 40 (1994)**Electrorefining "N" Reactor Fuel**

E. C. Gay and W. E. Miller

Proc. of the Topical Meeting on DOE Spent Nuclear Fuel—Challenges and Initiatives, Am.
Nucl. Soc., Salt Lake City, UT, December 13-16, 1994, pp. 267-274 (1994)**Method for Removal of Heavy Metal from Molten Salt**

E. C. Gay, W. E. Miller, and J. J. Laidler

Proc. of the Ninth Int. Symp. on Molten Salts, 185th Electrochem. Soc. Meeting,
San Francisco, CA, May 22-27, 1994, Vol. 94-13, pp. 721-725 (1994)**Transportation Polymer Electrolyte Fuel Cell Systems for Different On-Board Fuels**

H. K. Geyer, R. Ahluwalia, M. Krumpelt, and R. Kumar

Program and Abstracts of the Fuel Cell Seminar, San Diego, CA, November 28-December 1,
1994, pp. 483-486 (1994)**Analytical Procedures for Waste Minimization and Pollution Prevention**

D. W. Green, L. L. Smith, J. S. Crain, A. S. Boparai, and J. B. Schilling

Proc. of Pollution Prevention Conf. X, Denver, CO, May 3-5, 1994, pp. 1-7 (1994)

Safety Characteristics of Lithium-Alloy/Metal Sulfide Batteries

G. L. Henriksen, D. R. Vissers, and A. A. Chilenskas

Proc. of the Symp. on Lithium Battery Safety/Reliability/Cell Engineering/Environmental
Issues, Seventh Int. Meeting on Lithium Batteries, Boston, MA, May 15-20, 1994 (1994)**The Stability of Calibration Standards for ICP/AES Analysis: A Two-Year Study**

D. R. Huff and E. A. Huff

Proc. of the Tenth Annual Waste Testing and Quality Assurance Symp., Arlington, VA,
July 11-15, 1994, pp. 369-383 (1994)**Tritium Release from Beryllium Discs and Lithium Ceramics Irradiated in the SIBELIUS Experiment**

C. E. Johnson, D. L. Baldwin, and J. P. Kopasz

Proc. of the Third Int. Workshop on Ceramic Breeder Blanket Interactions, Paris, France,
September 22-24, 1993, pp. 145-156 (1994)**Meyer-Neldel Rule for Liquid Semiconductors**

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

Proc. of the Am. Phys. Soc. Meeting, Pittsburgh, PA, March 21-25, 1994 (1994)

Bipolar Li/FeS₂ Component Development

T. D. Kaun, M. C. Hash, W. P. Johll, M. A. Perrine, and D. R. Simon

Proc. of the *Ad Hoc* Workshop on Ceramics for Li/FeS₂ Batteries, Oak Brook, IL, September 29-30, 1993, pp. 55-75 (1994)

Performance of Ceramic Breeder Materials in the SIBELIUS Experiment

J. P. Kopasz, C. E. Johnson, and D. L. Baldwin

Trans. of the 96th Annual Meeting and Exposition of the Am. Ceram. Soc., Fourth Symp. on the Fabrication and Properties of Ceramics for Fusion Energy, Indianapolis, IN, April 24-28, 1994 (1994)

Tritium Release from Lithium Titanate, A Low Activation Tritium Breeding Material

J. P. Kopasz, J. M. Miller, and C. E. Johnson

Proc. of the Third Int. Workshop on Ceramic Breeder Blanket Interactions, Paris, France, September 22-24, 1993, pp. 81-95 (1994)

Aluminum Chloride-1-Butylpyridium Chloride Melts as an Electrolyte for Aluminum/Polyaniline Cells

N. Koura, K. Takeishi, S. Takahashi, L. A. Curtiss, K. Suzuya, M.-L. Saboungi, and D. L. Price

Proc. of the Ninth Int. Symp. on Molten Salts, 185th Electrochem. Soc. Meeting, San Francisco, CA, May 22-27, 1994, Vol. 94-3, pp. 728-735 (1994)

Materials Challenges for Fuel Cell Commercialization

M. Krumpelt

Abstracts, Fall Meeting of the Materials Research Soc., Boston, MA, November 28-December 2, 1994 (1994)

Support Research for Solid Oxide Fuel Cells

M. Krumpelt and T. W. Kueper

Proc. of the Fuel Cells '94 Contractors' Review Meeting, Morgantown, WV, August 17-18, 1994, DOE/METC-94/1010 (1994)

Advances in Research in Solid Oxide Fuel Cells

M. Krumpelt, T. W. Kueper, and R. Doshi

Proc. of the Fuel Cells '94 Contractors' Review Meeting, Morgantown, WV, August 17-18, 1994, DOE/METC-94/1010 (1994)

Sealant Materials for the Solid Oxide Fuel Cell

M. Krumpelt, R. Kumar, I. Bloom, and K. L. Ley

Proc. of the Fuel Cells '94 Contractors' Review Meeting, Morgantown, WV, August 17-18, 1994, DOE/METC-94/1010 (1994)

Pitting Corrosion of Aluminized Seals in Molten Carbonate Fuel Cells

M. Krumpelt, M. F. Roche, and I. Bloom

Proc. of the Fuel Cells '94 Contractors' Review Meeting, Morgantown, WV, August 17-18, 1994, DOE/METC-94/1010, pp. 51-52 (1994)

Molten Carbonate Fuel Cell with High Power Density

M. Krumpelt, M. F. Roche, I. Bloom, H. K. Geyer, and S. A. Johnson

Proc. of the Fuel Cells '94 Contractors' Review Meeting, Morgantown, WV, August 17-18, 1994, DOE/METC-94/1010, pp. 49-50 (1994)

Lithium Ferrate and Lithium Cobaltate Cathodes for Molten Carbonate Fuel Cells

M. Krumpelt, M. F. Roche, I. Bloom, J. E. Indacochea, and G. H. Kucera

Proc. of the Fuel Cells '94 Contractors' Review Meeting, Morgantown, WV, August 17-18, 1994, DOE/METC-94/1010, pp. 41-42 (1994)

Multiply Manifoldd Molten Carbonate Fuel Cells

M. Krumpelt, M. F. Roche, H. K. Geyer, and S. A. Johnson

Proc. of the Fuel Cells '94 Contractors' Review Meeting, Morgantown, WV, August 17-18, 1994, DOE/METC-94/1010, pp. 38-40 (1994)

Modeling of Polymer Electrolyte Fuel Cell Systems

R. Kumar, R. Ahluwalia, H. K. Geyer, and M. Krumpelt

Proc. of the Annual Automotive Technology Development Contractors' Coordination Meeting, Detroit, MI, October 18-21, 1993, Society of Automotive Engineers, SAE Publication P-278, pp. 409-417 (1994)

Sealants for the SOFC

R. Kumar, I. Bloom, K. L. Ley, and M. Krumpelt

Proc. of the Fuel Cells '94 Contractors' Review Meeting, Morgantown, WV, August 17-18, 1994, DOE/METC-94/1010 (1994)

Polymer Electrolyte Fuel Cell Systems for Different Fuels and Fuel Processing Options

R. Kumar, H. K. Geyer, R. Ahluwalia, and M. Krumpelt

Proc. of the Annual Automotive Technology Development Contractors' Coordination Meeting, Dearborn, MI, October 24-27, 1994, pp. 301-308 (1994)

Preliminary Evaluation of FIBROSICTM Candle Filter for Particle Control in PFBC

S. H. D. Lee, P. Eggerstedt, J. F. Zievers, and F. I. Honea

Proc. of the 29th Intersoc. Energy Conversion Eng. Conf., Monterey, CA, August 7-12, 1994, Part 3, pp. 1302-1307 (1994)

Properties of Glass-Bonded Zeolite Monoliths

M. A. Lewis, D. F. Fischer, and C. D. Murphy

Trans. of the 96th Annual Meeting and Exposition of the Am. Ceram. Soc., Indianapolis, IN, April 24-28, 1994 (1994)

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. J. Marr, P. L. Johnson, K. J. Parish, and W. R. Newberry

Abstracts, 35th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 11-13, 1994, p. 48 (1994)

Transmission Electron Microscopy of Pb-doped Bi₂Sr₂Ca₂Cu₃O_x/Ag Composite Conductors Prepared by the Two-Powder Process: The Effect of Lead Addition on Critical Current and Microstructure

J. S. Luo, S. E. Dorris, M. T. Lanagan, and V. A. Maroni

Proc. of the 52nd Annual Meeting of the Microscopy Soc. of America, New Orleans, LA, July 31-August 5, 1994, pp. 798-799 (1994)

Compositional and Microstructural Analysis of Two-Powder Bi(Pb)-2223/Ag Composite Conductors: Effect of Lead Addition Method

J. S. Luo, Y. Feng, S. E. Dorris, A. K. Fischer, D. C. Larbalestier, and V. A. Maroni

Abstracts, Fall Meeting of the Materials Research Soc., Boston, MA, November 28–December 2, 1994 (1994)

Diamond Growth from Fullerene Precursors: A High Resolution Electron Microscopy (HREM) Study

J. S. Luo, D. M. Gruen, A. R. Krauss, X. Z. Pan, and S. Z. Liu

Abstracts, Fall Meeting of the Materials Research Soc., Boston, MA, November 28–December 2, 1994 (1994)

Effect of Lead Loss and Sheath Structure on Phase Formation and Texture Development in $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x(\text{Bi-2223})/\text{Ag}$ Composite Conductors

J. S. Luo, N. Merchant, V. A. Maroni, S. E. Dorris, and M. T. Lanagan

Abstracts, Fall Meeting of the Materials Research Soc., Boston, MA, November 28–December 2, 1994 (1994)

A New Imaging Resonance Ionization Mass Spectrometer for Isotope and Trace Analysis

Z. Ma, R. N. Thompson, W. F. Calaway, K. R. Lykke, M. J. Pellin, A. M. Davis, R. S. Lewis, and R. N. Clayton

Proc. of the 42nd ASMS Conf. on Mass Spectrometry and Allied Topics, Chicago, IL, May 29–June 3, 1994, p. 843 (1994)

Window Design for Custom Modular Gloveboxes

R. F. Malecha and A. A. Frigo

Proc. of the Eighth Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc., Raleigh, NC, August 8–11, 1994, p. 87 (1994)

Installing a Very Large Glovebox in a Very Small Laboratory

R. F. Malecha, A. A. Frigo, E. F. Lewandowski, and S. G. Wiedmeyer

Proc. of the Seventh Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc., Seattle, WA, August 16–19, 1993, p. 39 (1994)

A Study of the Structure and the Morphology of Oxide Films on Amorphous Al-Fe-Ce Alloys by XPS and SEM

A. N. Mansour and C. A. Melendres

Extended Abstracts, 186th Electrochem. Soc. Meeting, Miami Beach, FL, October 9–14, 1994, Vol. 94-2, Abstract No. 147 (1994)

XAFS Investigation of the Structure and Valency of Nickel in Some Oxy Compounds

A. N. Mansour and C. A. Melendres

Abstracts, Eighth Int. XAFS Conf., Berlin, Germany, August 28–September 2, 1994 (1994)

Atomic Structure and Valency of Nickel in Some of Its Oxy Compounds

A. N. Mansour, C. A. Melendres, M. Pankuch, and R. Brizzolara

Extended Abstracts, 185th Electrochem. Soc. Meeting, San Francisco, CA, May 22–27, 1994, Vol. 94-1, Abstract No. 36 (1994)

Evaluation of a Fourier Transform Infrared Continuous Emission Monitor Field Test at a TSCA Incinerator

Z. Mao, J. C. Demirgian, and G. T. Reedy

Proc. of the Incineration Conf. on Evaluation of a Fourier Transform Infrared Continuous Emission Monitor Field Test at a TSCA Incinerator, Houston, TX, May 9–13, 1994 (1994)

Investigations of Structure at Material/Water Interfaces Using Synchrotron Radiation

V. A. Maroni

Abstracts, Fall Meeting of the Materials Research Soc., Boston, MA, November 28–December 2, 1994 (1994)

An Evaluation of Vitrification Technology: Application to Mixed Waste at Argonne National Laboratory

J. J. Mazer, J. S. Devgun, N. J. Beskid, and H. J. No

Proc. of the Waste Management '94 Conf., 20th Annual Nuclear Waste Symp., Tucson, AZ, February 27–March 3, 1994, Vol. 3, pp. 1551–1555 (1994)

Pyrochemical Processing of Reactor Spent Fuels as a Waste Management Tool

C. C. McPheeters, R. D. Pierce, and T. P. Mulcahey

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19–21, 1994, Vol. 1, pp. 387–389 (1994)

Standards for High Level Radioactive Waste Repositories

D. W. Moeller, M. J. Steindler, P. W. Pomeroy, and W. J. Hinze

Proc. of the Fifth Annual Int. Conf. on High-Level Radioactive Waste Management, Las Vegas, NV, May 22–26, 1994 (1994)

Liquid-Fueled SOFC Power Sources for Transportation

K. M. Myles, R. Doshi, R. Kumar, and M. Krumpelt

Proc. of the First European Solid Oxide Fuel Cell Forum, Lucerne, Switzerland, October 3–7, 1994, pp. 983–992 (1994)

Investigation of Incipient Oxidation of Platinum with X-ray Reflectivity Technique

Z. Nagy, H. You, D. J. Zurawski, and R. M. Yonko

Extended Abstracts, 185th Electrochem. Soc. Meeting, San Francisco, CA, May 22–27, 1994, Vol. 94–1, pp. 1285–1286 (1994)

Sodalite as a Waste Form for IFR Fission Products

C. Pereira and J. P. Ackerman

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19–21, 1994, Vol. 2, pp. 867–870 (1994)

Effect of Halide Ions and Sulfur on the Performance of Ni/NiCl₂ Electrode

J. Prakash, L. Redey, and D. R. Vissers

Extended Abstracts, 185th Electrochem. Soc. Meeting, San Francisco, CA, May 22–27, 1994, pp. 1534–1535 (1994)

Precise Lattice Location of Trace Elements within Minerals and at their Surfaces with X-ray Standing Waves

Y. L. Qian, N. C. Sturchio, R. P. Chiarello, P. F. Lyman, T. L. Lee, and M. J. Bedzyk

Abstracts, Fall Meeting of the Materials Research Soc., Boston, MA, November 28–December 2, 1994, p. 749 (1994)

Recent High-Pressure NMR Spectral and Imaging Studies

J. W. Rathke, R. J. Klingler, M. J. Chen, and K. Woelk

Proc. of the Ninth DOE/BES Heterogeneous Catalysis and Surface Chemistry Research Conf., Oconomowoc, WI, May 24–27, 1994, pp. 124–127 (1994)

Resistivity Measurements of Separators

L. Redey

Proc. of the *Ad Hoc* Workshop on Ceramics for Li/FeS₂ Batteries, Oak Brook, IL, September 29–30, 1993, pp. 189–198 (1994)

Performance Enhancement of Na/NiCl₂ Cells by Iodine

L. Redey, J. Prakash, A. Scheglov, D. R. Vissers, and J. DeGruson

Extended Abstracts, 186th Electrochem. Soc. Meeting, Miami Beach, FL, October 9–14, 1994, pp. 218–219 (1994)

Sodium/Nickel-Chloride Battery Development

L. Redey, J. Prakash, D. R. Vissers, and E. J. Dowgiallo

Proc. of the Annual Automotive Technology Development Contractors' Coordination Meeting, Detroit, MI, October 18–21, 1993, Society of Automotive Engineers (1994)

Interactions of Plutonium-Organic-Microbial Mixtures in Simulated Groundwater

D. T. Reed and M. K. Richmann

Trans. of the Am. Geophys. Union, EOS, Baltimore, MD, May 23–27, 1994 (1994)

Orientational Glass Phases in Zintl Compounds

J. W. Richardson, J. A. Fortner, D. L. Price, and M.-L. Saboungi

Proc. of the Am. Phys. Soc. Meeting, Pittsburgh, PA, March 21–25, 1994 (1994)

Molten Carbonate Fuel Cells: Modeling and Research Activities at ANL

M. F. Roche, G. H. Kucera, H. K. Geyer, J. E. Indacochea, M. Krumpelt, and K. M. Myles

An EPRI/GRI Fuel Cell Workshop on Fuel Cell Technology Research and Development, Atlanta, GA, March 22–23, 1994, Paper No. 14, EPRI Report No. TR-103852, Palo Alto, CA (1994)

Compound Specific Isotopic Analysis of Uinta Basin Native Bitumens

T. E. Ruble, A. J. Bakel, and R. P. Philp

Proc. of the Am. Chem. Soc. Meeting, Compound Specific Isotope Analysis in Biogeochemistry and Petroleum Research, Organic Geochemistry, Vol. 21, pp. 661–671 (1994)

Neutron Diffraction from Alkali Metal-Chalcogen Liquid Alloys

M.-L. Saboungi, J. A. Fortner, and W. S. Howells

Proc. of the Am. Phys. Soc. Meeting, Pittsburgh, PA, March 21–25, 1994 (1994)

Phosphate-Bonded Ceramics as Candidate Final Waste Form Materials

A. P. Singh, A. S. Wagh, J. C. Cunnane, M. Sutaria, and S. Kurokawa

Proc. of the 96th Annual Meeting of the Am. Chem. Soc., Indianapolis, IN, April 24–28, 1994 (1994)

Chemically Bonded Phosphate Ceramics for Stabilization of Low-Level Mixed Wastes

D. Singh, A. S. Wagh, and J. C. Cunnane

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19–21, 1994, Vol. 1, pp. 562–564 (1994)

Design Requirements for Bipolar Plates

J. A. Smaga, J. Prakash, and J. Hryn

Proc. of the *Ad Hoc* Workshop on Ceramics for Li/FeS₂ Batteries, Oak Brook, IL, September 29–30, 1993, pp. 76–100 (1994)

Geothermal Systems in the Mammoth Corridor of Yellowstone National Park, USA

M. L. Sorey, Y. Kharaka, W. Stanley, and N. C. Sturchio

Trans. of Geotherm. Research Council **18**, 241-245 (1994)

A Revised Interpretation of the Seasonal Trends of the Carbon and Oxygen Isotopic Composition of Atmospheric CO in 1971

C. M. Stevens

Trans. of the Am. Geophys. Union, EOS, San Francisco, CA, December 5-9, 1994 (1994)

Comparison of Gamma Spectrometry Self-Absorption Models for Environmental Samples

W. E. Streets and A. T. Sherren

Abstracts, 35th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 11-13, 1994 (1994)

Revelations at Mineral-Water Interfaces by X-ray Scattering

N. C. Sturchio and R. P. Chiarello

Abstracts with Programs, Geological Soc. of America Annual Meeting, Seattle, WA, October 24-27, 1994 (1994)

In Situ Observation of Epitaxial Growth of Otavite on Calcite Using Synchrotron X-ray Scattering

N. C. Sturchio and R. P. Chiarello

Trans. of the Am. Geophys. Union, EOS, Baltimore, MD, May 23-27, 1994 (1994)

Ab Initio Calculations for Hydrogen Adsorption on Lithium Oxide Surfaces

A. Sutjianto, S.-W. Tam, P. Ravindra, and L. A. Curtiss

Trans. of the 96th Annual Meeting and Exposition of the Am. Ceram. Soc., Fabrication and Properties of Ceramics for Fusion Energy, Indianapolis, IN, April 24-28, 1994 (1994)

Tritium Transport and Retention in SiC

S.-W. Tam, J. P. Kopasz, and C. E. Johnson

Trans. of the 96th Annual Meeting and Exposition of the Am. Ceram. Soc., Fourth Symp. on the Fabrication and Properties of Ceramics for Fusion Energy, Indianapolis, IN, April 24-28, 1994 (1994)

Treatment of Mixed Radioactive Liquid Wastes at Argonne National Laboratory

G. F. Vandegrift, D. B. Chamberlain, C. J. Conner, J. C. Hutter, R. A. Leonard, H. No, L. Nunez, J. Sedlet, B. Srinivasan, and D. G. Wygmans

Proc. of the Waste Management '94 Conf., Tucson, AZ, February 27-March 3, 1994, Vol. 3, pp. 1579-1585 (1994)

TRUEX Process Development

G. F. Vandegrift and M. C. Regalbuto

Proc. of the Spectrum '94 Conf., Nuclear and Hazardous Waste Management Int. Topical Meeting, Atlanta, GA, August 14-18, 1994 (1994)

Separator Design Requirements

D. R. Vissers, V. S. Battaglia, A. N. Jansen, and T. D. Kaun

Proc. of the *Ad Hoc* Workshop on Ceramics for Li/FeS₂ Batteries, Oak Brook, IL, September 29-30, 1993, pp. 101-114 (1994)

Development of Prototype Management Reports on Analytical Laboratory Performance in Performance Evaluation Programs for the DOE Office of Environmental Restoration and Waste Management

S. Warren, J. Hensley, D. A. Bass, and A. Bunn

Proc. of the Waste Management '94 Conf., Tucson, AZ, February 27-March 3, 1994 (1994)

Ion Replacement Electrorefining

J. L. Willit, Z. Tomczuk, W. E. Miller, and J. J. Laidler

Proc. of the Ninth Int. Symp. on Molten Salts, 185th Electrochem. Soc. Meeting, San Francisco, CA, May 22-27, 1994, Vol. 94-13, p. 713 (1994)

Characterization Studies of Actinide Contamination on Johnston Atoll

S. F. Wolf, J. K. Bates, N. R. Brown, E. C. Buck, N. L. Dietz, and J. A. Fortner

Proc. of the Spectrum '94 Conf., Nuclear and Hazardous Waste Management Int. Topical Meeting, Atlanta, GA, August 14-18, 1994, pp. 453-458 (1994)

Radionuclide Decay Effects on Waste Glass Corrosion

D. J. Wronkiewicz

Mater. Res. Soc. Symp. Proc. **333**, 83-97 (1994)

Effects of Radiation Exposure on SRL 131 Composition Glass in a Steam Environment

D. J. Wronkiewicz, C. R. Bradley, J. K. Bates, and L. M. Wang

Mater. Res. Soc. Symp. Proc. **333**, 259-267 (1994)

Radionuclide and Hazardous Element Retention in Glass-Crystal Composite Waste Forms

D. J. Wronkiewicz, X. Feng, N. R. Brown, and T. DiSanto

Extended Abstracts, Emerging Technologies in Hazardous Waste Management VI Symp., Am. Chem. Soc., Atlanta, GA, September 19-21, 1994, Vol. 1, pp. 645-648 (1994)

The Development of Glass-Crystal Composite Waste Forms for the Disposal of Nuclear and Hazardous Waste Materials

D. J. Wronkiewicz, X. Feng, N. R. Brown, and A. J. G. Ellison

Abstracts with Programs, Geological Soc. of America Annual Meeting, Seattle, WA, October 24-27, 1994, p. A470 (1994)

Effect of Surface Layers on the Dissolution of Nuclear Waste Glasses

S.-B. Xing, A. C. Buechele, and I. L. Pegg

Mater. Res. Soc. Symp. Proc. **333**, 541-548 (1994)

Gross Alpha/Beta Analysis of Environmental and Mixed-Waste Samples by High-Pressure Microwave Dissolution

J. S. Yaeger and L. L. Smith

Abstracts, 35th ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 11-13, 1994 (1994)

E. Papers Presented at Scientific Meetings

Chemistry of Pyroprocessing for Nuclear Waste Transmutation

J. P. Ackerman

Presented at the Int. Conf. on Accelerator-Driven Transmutation Technologies and Applications, Las Vegas, NV, July 25-29, 1994

Waste Removal in Pyrochemical Fuel Processing for the Integral Fast Reactor

J. P. Ackerman, T. R. Johnson, and J. J. Laidler

Presented at the Int. Symp., 123rd Annual Meeting of the Minerals, Metals, and Materials Soc., San Francisco, CA, February 28-March 3, 1994

Radioanalytical Methods Evaluation

J. S. Alvarado, J. S. Crain, J. H. Aldstadt, L. L. Smith, K. A. Orlandini, and M. D. Erickson

Presented at the Outreach to Industry: Partnership for the Future Conf., Seattle, WA, January 25-27, 1994

Variations in Nitrogen Isotope Ratios of Some Southern California Crude Oils: Possible Implications for Reconstruction of Depositional Environments

G. B. Archart and A. J. Bakel

Presented at the Geological Soc. of Am. Annual Meeting, Seattle, WA, October 24-27, 1994

Inorganic Instrumental Techniques in Environmental Analysis

D. A. Bass

Presented at the Department of Educational Programs Workshop, Argonne National Laboratory, April 1994

Pyrometallurgical Processes for Recovery of Actinide Elements

J. E. Battles, J. J. Laidler, C. C. McPheeters, and W. E. Miller

Presented at the Int. Symp., 123rd Annual Meeting of the Minerals, Metals, and Materials Soc., San Francisco, CA, February 28-March 3, 1994

Minimum Additive Waste Stabilization (MAWS) for Mixed and Low-Level Radioactive Wastes

N. J. Beskid, J. J. Mazer, R. Gimpel, and R. Warner

Presented at the American Institute of Chemical Engineers National Meeting, Denver, CO, August 14-17, 1994

Removal of Radioactivity from Radioactive Mixed Waste Samples

A. S. Boparai, M. A. Gritters, Y. Tsai, and S. D. Kent

Presented at the 45th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, February 27-March 3, 1994

Automated Sample Preparation of Radioactive Mixed Waste Samples for Organic Analysis

A. S. Boparai, K. J. Parish, D. V. Applegate, G. T. Reedy, and S. E. Carpenter

Presented at the 45th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, February 27-March 3, 1994

Effect of Alpha-Radiolysis on TRUEX-NPH Solvent

B. A. Buchholz, L. Nunez, and G. F. Vandegrift

Presented at the 208th Am. Chem. Soc. Fall National Meeting, Characterization and Treatment of High-Level Nuclear Waste, Washington, DC, August 21-26, 1994

Effect of Gamma-ray Radiation on the Separation Efficiencies of Coated Magnetic Microparticles

B. A. Buchholz, L. Nunez, and G. F. Vandegrift

Presented at the University of Illinois, Urbana, IL, April 6, 1994

Radiation Effect on the Removal of Transuranics in Solution by Coated Magnetic Micro-Particles

B. A. Buchholz, L. Nunez, and G. F. Vandegrift

Presented at the 208th Am. Chem. Soc. Fall National Meeting, Characterization and Treatment of High-Level Nuclear Waste, Washington, DC, August 21-26, 1994

Electron Beam Microanalysis of Nuclear Waste Glass

E. C. Buck and J. K. Bates

Presented at the 208th Am. Chem. Soc. Fall National Meeting, Washington, DC, August 21-26, 1994

Electron Beam Analysis of Contaminated Soils

E. C. Buck, N. L. Dietz, N. R. Brown, J. A. Fortner, and J. K. Bates

Presented at the INTER/MICRO '94 Conf., Chicago, IL, July 18-21, 1994

Cluster Ejection during Ion Bombardment

W. F. Calaway, Z. Ma, T. B. Lill, and M. J. Pellin

Presented at the Particle Solid Interactions Gordon Conf., Plymouth, NH, July 31-August 5, 1994

Development of Chemometrics-Based Algorithms for Real-Time Analysis of Chemical Sensor Data: An Overview of the SAGE Program

S. E. Carpenter

Presented at the 21st Annual Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory, November 10, 1994

Time-Domain vs. Frequency Domain Analysis of FTIR Data

S. E. Carpenter

Presented at the 45th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, February 27-March 3, 1994

New Separation Process for Decontaminating Soil

D. J. Chaiko

Presented at the Florida Environmental Chem. Conf., Palm Coast, FL, October 25-29, 1994

Characterization of Plutonium-Containing Solid Residues by Analytical Electron Microscopy

D. J. Chaiko, E. C. Buck, N. L. Dietz, and J. K. Bates

Presented at the 14th Annual Pyrochemical Workshop, Boulder, CO, October 31-November 3, 1994

Uranium Recovery from Contaminated Soil

D. J. Chaiko and R. Mensah-Biney

Presented at the Am. Chem. Soc. National Meeting, San Diego, CA, March 13-18, 1994

Mass Transfer in Aqueous Biphasic Systems

D. J. Chaiko, A. Rollins, E. H. Van Deventer, and P. Ward

Presented at the Am. Chem. Soc. National Meeting, San Diego, CA, March 13-18, 1994

Aggregation of Polyethylene Glycol in Aqueous Solutions

D. J. Chaiko and P. Thiyagarajan

Presented at the Am. Chem. Soc. National Meeting, San Diego, CA, March 13-18, 1994

Development of a Portable Evaporation System for Processing Underground Storage

D. B. Chamberlain

Presented at the University of Illinois Nuclear Engineering Department Graduate School Seminar, Champaign, IL, October 11, 1994

Development of a Portable Evaporation System for Processing Underground Storage Tank Waste

D. B. Chamberlain, M. K. Clemens, C. J. Conner, E. Johnson, D. Korch, A. E. V. Rozeveld, D. G. Wygmans, and G. F. Vandegrift

Presented at the 1994 Plutonium/Uranium Recovery Operations Conf., Knoxville, TN, October 17-20, 1994

Treatment of Transuranic and Mixed Wastes at Argonne National Laboratory

C. J. Conner, D. B. Chamberlain, J. C. Hutter, J. Sedlet, S. A. Slater, B. Srinivasan, G. F. Vandegrift, H. No, and D. G. Wygmans

Presented at the 18th Actinide Separations Conf., Durango, CO, May 23-26, 1994

Development of the Generic TRUEX Model: A Method for Designing Solvent Extraction Flowsheets for Treatment of High-Level Waste

J. M. Copple, M. C. Regalbuto, R. A. Leonard, and G. F. Vandegrift

Presented at the Argonne National Laboratory Technical Women's Symp., Countryside, IL, September 13-14, 1994

Determination of Actinides in Environmental Samples with ICP-MS and Automated Batch Preconcentration

J. S. Crain and L. L. Smith

Presented at the ASTM-DOE Symp. on the Application of ICP-MS to Radionuclide Determinations, Gatlinburg, TN, October 13-14, 1994

Enhanced Measurement of Long-Lived Actinides by Inductively Coupled Plasma-Mass Spectrometry

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

Presented at the Third Int. Conf. on Methods and Applications in Radioanalytical Chemistry, Kailua-Kona, HI, April 10-16, 1994

Determination of Actinide Elements in Environmental Samples using Inductively Coupled Plasma-Mass Spectrometry

J. S. Crain, J. S. Yaeger, J. A. Alvarado, L. L. Smith, J. T. Kiely, and F. G. Smith

Presented at the 40th Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Cincinnati, OH, November 13-17, 1994

Continuous Emission Monitoring of Incinerators Using Extractive and Passive-Remote Fourier Transform Infrared Spectroscopy

J. C. Demirgian, C. L. Hammer, E. Y. Hwang, and Z. Mao

Presented at the 45th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, February 27-March 3, 1994

Radiation Principles

J. S. Devgun

Presented at the Illinois Institute of Technology, May 6, 1994

Determination of Radioisotopes in Environmental Samples: Dollars and Sense

M. D. Erickson, J. H. Aldstadt, J. A. Alvarado, J. S. Crain, L. L. Smith, and K. A. Orlandini
Presented at the 21st Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, St. Louis, MO, October 2-7, 1994

Radiochemical Method Evaluation—Industrial Partner Opportunities

M. D. Erickson, M. A. Edgell, P. C. Lindahl, L. L. Smith, and M. H. Carter
Presented at the International Association of Environmental Testing Laboratories Stakeholders Workshop II, Arlington, VA, April 20-22, 1994

DOE-Private Sector Partnerships for Improvement of Radioanalytical Chemistry

M. D. Erickson, M. A. Edgell, and L. L. Smith
Presented at the 40th Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Cincinnati, OH, November 13-17, 1994

Characterization of HEPA Filters for Disposal

A. M. Essling, I. M. Fox, F. P. Smith, D. G. Graczyk, and C. W. Grandy
Presented at the Argonne National Laboratory Technical Women's Symp., Countryside, IL, September 13-14, 1994

Behavior of Spent Fuel Under Unsaturated Conditions

P. A. Finn
Presented at the Argonne National Laboratory Technical Women's Symp., Countryside, IL, September 13-14, 1994

Distribution of Actinides in Spent Fuel Leachate

P. A. Finn, J. C. Hoh, S. F. Wolf, J. K. Bates, and E. C. Buck
Presented at the Spent Fuel Workshop '94 Conf., Montebello, Quebec, August 22-24, 1994

Removal of Actinide Elements from Liquid Scintillation Cocktail Wastes Using Liquid-Liquid Extraction and Demulsification Techniques

K. Foltz, S. Landsberger, B. Srinivasan, and G. F. Vandegrift
Presented at the Winter Conf. of the Am. Nucl. Soc., Washington, DC, November 13-18, 1994

Analytical Microscopy Support of Nuclear Waste Management Programs

J. A. Fortner, E. C. Buck, J. S. Luo, and J. K. Bates
Presented at the ANL/CAMD Synchrotron Application Workshop, Argonne National Laboratory, November 16, 1994

Guideline for Gloveboxes, Section 13: Quality Assurance

A. A. Frigo
Presented at the Eighth Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc., Raleigh, NC, August 8-11, 1994

Glovebox Photographs for the American Glovebox Society (AGS) Standards Development Committee Information Booth

A. A. Frigo and R. F. Malecha
Presented at the Eighth Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc. as part of a Glovebox Display at the Standards Development Committee's Booth, Raleigh, NC, August 8-11, 1994

Design-for-Manufacturability: A Process to Ensure the Smooth Transition from Design to Manufacturing

A. A. Frigo, R. F. Malecha, and E. F. Lewandowski

Presented at the ANL Quality Coordination and Training Meeting, Argonne National Laboratory, January 10, 1994

A Model for Chemical Speciations in the Plasma of an ICP-MS

M. Gong and R. E. Sassoon

Presented at the 21st Annual Conf. of the Federation of Analytical Chemistry and Spectroscopy Societies, St. Louis, MO, October 2-7, 1994

The Leadership Challenge within the Analytical Laboratory

D. W. Green

Presented at the Analytical Laboratory Managers Association Conf., Leesburg, VA, October 19-21, 1994

Turning Soot into Diamonds with Microwaves

D. M. Gruen, A. R. Krauss, J. S. Luo, X. Z. Pan, and S. Z. Liu

Presented at the 29th Microwave Power Symp., Chicago, IL, July 25-27, 1994

Diamond-Film Growth Using Buckyball Precursors

D. M. Gruen, S. Z. Liu, A. R. Krauss, X. Z. Pan, and J. S. Luo

Presented at the Spring Meeting of the Materials Research Soc., San Francisco, CA, April 4-8, 1994

Lessons Learned in Acquiring New Regulations for Shipping Advanced Electric Vehicle Batteries

G. L. Henriksen, C. Hammel, and E. A. Altemos

Presented at the Twelfth Int. Electric Vehicle Symp., Palo Alto, CA, December 5-7, 1994

Ultrasonic Vacuum Extraction of Gases from Water

B. D. Holt and N. C. Sturchio

Presented at the Am. Chem. Soc. National Meeting, San Diego, CA, March 13-18, 1994

Recent Advances in the Separation of Actinides by Liquid-Liquid Extraction, Extraction Chromatography, and Ion Exchange

E. P. Horwitz, R. Chiarizia, H. Diamond, M. L. Dietz, and R. A. Leonard

Presented at the 208th Am. Chem. Soc. Fall National Meeting, Washington, DC, August 21-26, 1994

Chloride Ion Catalysis of the $\text{Cu}^{2+}/\text{Cu}^+$ Redox Reaction

N. C. Hung, Z. Nagy, and D. J. Zurawski

Presented at the 208th Am. Chem. Soc. Fall National Meeting, Washington, DC, August 21-26, 1994

Production of Mo-99 Using Low Enriched Uranium Silicide

J. C. Hutter, B. Srinivasan, M. Vicek, and G. F. Vandegrift

Presented to Dr. Roberto O. Marques, Comision Nacional de Energia Atomica, Gerencia di Area Radioisotoposy Radiaciones, Buenos Aires, Argentina, July 11-15, 1994

Production of Mo-99 Using Low Enriched Uranium Silicide

J. C. Hutter, B. Srinivasan, M. Vicek, and G. F. Vandegrift

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors, Williamsburg, VA, September 18-23, 1994

Development of a Standard Operating Procedure for the Continuous Emission Monitoring of Incinerator Effluents Using FTIR Technology

E. Y. Hwang, J. C. Demirgian, Z. Mao, and G. Plummer

Presented at the 45th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, February 27–March 3, 1994

Tritium Transport and Release from Lithium Ceramic Breeder Materials

C. E. Johnson, J. P. Kopasz, and S.-W. Tam

Presented at the Second Chilean Lithium Symp., Santiago, Chile, May 23–27, 1994

Lithium Actinide Recycle Process Demonstration

G. K. Johnson, R. D. Pierce, and C. C. McPheeters

Presented at the 14th Annual Pyrochemical Workshop, Boulder, CO, October 31–November 3, 1994

Pyrochemical Recovery of Actinide Elements from Spent Light Water Reactor Fuel

G. K. Johnson, R. D. Pierce, D. S. Poa, and C. C. McPheeters

Presented at the Int. Symp., 123rd Annual Meeting of the Minerals, Metals, and Materials Soc., San Francisco, CA, February 28–March 3, 1994

Materials and Mechanisms of High Temperature Lithium Sulfide Batteries

T. D. Kaun, M. C. Hash, G. L. Henriksen, A. N. Jansen, and D. R. Vissers

Presented at the Second Chilean Lithium Symp., Santiago, Chile, May 24–27, 1994

NMR Spectral and Imaging Studies at High Pressure

R. J. Klingler and J. W. Rathke

Presented at the University of Wisconsin, Madison, WI, November 21–22, 1994

High Pressure NMR Spectral and Imaging Studies

R. J. Klingler, K. Woelk, and J. W. Rathke

Presented at the University of Illinois at Chicago, IL, July 14, 1994

An Investigation of the Desorption of Hydrogen from Lithium Oxide Using Temperature Programmed Desorption and Diffuse Reflectance Infrared Spectroscopy

J. P. Kopasz, J. Ortiz-Villafuerte, and C. E. Johnson

Presented at the Fourth Int. Workshop on Ceramic Breeder Blanket Interactions, Los Angeles, CA, June 22–24, 1994

Microwave-induced Plasma Destruction of Organic Compounds

T. R. Krause

Presented at the 47th Annual Gaseous Electronics Conf., Gaithersburg, MD, October 18–21, 1994

Recent ESPIP Survey of Existing Tank Waste Sludge

T. R. Krause

Presented at the DOE Efficient Separations and Processing Integrated Program Workshop on High-Level Waste Tank Sludges, Richland, WA, April 11–12, 1994

A Fuel Cell Overview

M. Krumpelt

Presented at the Northeast Sustainable Energy Association, Providence, RI, October 3–5, 1994

Fuel Cell Materials Development

M. Krumpelt and K. M. Myles

Presented at the DOE/AIST Technical Meeting, Tokyo, Japan, February 1-8, 1994

Modeling of PEM Fuel Cell Systems

R. Kumar

Presented at the Int. Energy Agency Workshop on PEM Fuel Cells, Grenoble, France, May 26-27, 1994; also Diamond Bar, CA, December 5-6, 1994

Reformers for Fuel Cell-Based Propulsion Power Systems

R. Kumar, S. Ahmed, and M. Krumpelt

Presented at the EPRI/GRI Fuel Cell Workshop on Fuel Cell R&D, Atlanta, GA, March 22-23, 1994

Conditioning of Spent Nuclear Fuel for Permanent Disposal

J. J. Laidler

Presented at the Dixy Lee Ray Memorial Symp., Seattle, WA, August 30-September 2, 1994

The Integral Fast Reactor—A Practical Approach to Waste Management

J. J. Laidler

Presented at the Nuclear as a Large-Scale Global Energy Option Workshop, Oak Ridge, TN, September 28-30, 1994

Pyrochemical Processing of DOE Spent Nuclear Fuels

J. J. Laidler

Presented at the DOE Spent Nuclear Fuel Challenges and Initiatives Conf., Salt Lake City, UT, December 13-16, 1994

Use of Pyroprocessing in the Preparation of Spent Fuel for Transmutation

J. J. Laidler

Presented at the Int. Conf. on Accelerator-Driven Transmutation Technologies and Applications, Las Vegas, NV, July 25-29, 1994

Testing Solvent Extraction Flowsheets

R. A. Leonard, C. J. Conner, A. Philippides, and G. F. Vandegrift

Presented at the 18th Actinide Separations Conf., Durango, CO, May 23-26, 1994

Sputtering of Neutral and Ionic Clusters from Liquid Metal Alloys: Abundance and Depth of Origin

T. B. Lill, W. F. Calaway, and M. J. Pellin

Presented at the Spring Meeting of the Illinois Chapter of the Am. Vacuum Soc., Evanston, IL, April 29, 1994

DOE's Performance Evaluation Program Initiatives

P. C. Lindahl

Presented at the Eighth Annual Workshop, Interagency Steering Committee for Quality Assurance for Environmental Measurements, Gaithersburg, MD, August 23-24, 1994

IPEP Implementation

P. C. Lindahl

Presented at the 12th Annual DOE Analytical Managers Meeting, Montvale, NJ, October 4-6, 1994

Development of the Integrated Performance Evaluation Program (IPEP)

P. C. Lindahl and W. R. Newberry

Presented at the Int. Association of Environmental Testing Laboratories Stakeholders Workshop, Arlington, VA, April 20-22, 1994

Analytical Electron Microscopy of Phase Formation and Texture Development of $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ in a Silver Sheath

J. S. Luo, N. Merchant, V. A. Maroni, S. E. Dorris, and M. T. Lanagan

Presented at the TMS Materials Week '94 Meeting, Rosemont, IL, October 3-6, 1994

Materials Development for Pyroprocesses: Metal Waste Forms and Molten Metal Containment

S. M. McDeavitt, D. P. Abraham, J. Y. Park, and J. P. Ackerman

Presented at the 14th Annual Pyrochemical Workshop, Boulder, CO, October 31-November 3, 1994

Defining a Metal-Based Waste Form for IFR Pyroprocessing Wastes

S. M. McDeavitt, J. Y. Park, and J. P. Ackerman

Presented at the Int. Symp., 123rd Annual Meeting of the Minerals, Metals, and Materials Soc., San Francisco, CA, February 28-March 3, 1994

Electrode Materials for the Reduction of CaO and Li_2O for Actinide Pyroprocessing

S. M. McDeavitt, J. L. Smith, C. C. McPheeters, R. D. Pierce, and D. S. Poa

Presented at the Int. Symp., 123rd Annual Meeting of the Minerals, Metals, and Materials Soc., San Francisco, CA, February 28-March 3, 1994

Separation of Actinides from Reactor Spent Fuels by Pyrochemical Methods

C. C. McPheeters, R. D. Pierce, and T. P. Mulcahey

Presented at the 18th Actinide Separations Conf., Durango, CO, May 23-26, 1994

Synchrotron X-ray Scattering Techniques in Corrosion Research

C. A. Melendres

Presented at the DOE-BES Corrosion Contractors' Meeting, Richland, WA, September 7-8, 1994

Reaction Induced Texture in Ag-Sheathed $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}/\text{Ag}$ Composites

N. Merchant, J. S. Luo, V. A. Maroni, G. N. Riley, and W. L. Carter

Presented at the Applied Superconductivity Conf., Boston, MA, October 16-21, 1994

Russian Fuel Fabrication and Reprocessing Capabilities with Mixed Oxide Fuel

C. J. Mertz, R. D. Pierce, and G. F. Vandegrift

Presented at the Review Meeting for Report on Russian Capability to Utilize Mixed Oxide (MOX) Fuel, U.S. DOE, Germantown, MD, September 23, 1994

Russian Reprocessing Capabilities with Mixed Oxide Fuel

C. J. Mertz and G. F. Vandegrift

Presented at the Argonne National Laboratory Technical Women's Symp., Countryside, IL, September 13-14, 1994

Advances in Metal Removal and Separation Science

L. Nunez

Presented at the Technical Association of the Pulp and Paper Institute (TAPPI) Meeting, Argonne National Laboratory, July 11, 1994

Separation Science Activities at Argonne National Laboratory

L. Nunez

Presented at the University of Illinois Nuclear Engineering Department, Radioactive Waste Management, Urbana, IL, March 28, 1994

Characterization and Separation Capabilities of Coated Ferromagnetic Particles for Transuranic and Heavy Metals Applications

L. Nunez, B. A. Buchholz, and G. F. Vandegrift

Presented at the Spring Meeting of the Materials Research Soc., San Francisco, CA, April 4-8, 1994

Actinide Separation of High-Level Waste Using Solvent Extractants on Magnetic Microparticles

L. Nunez, M. D. Kaminski, B. A. Buchholz, S. B. Aase, N. R. Brown, and G. F. Vandegrift

Presented at the 208th Am. Chem. Soc. Fall National Meeting, Characterization and Treatment of High-Level Nuclear Waste, Washington, DC, August 21-26, 1994

Magnetically Assisted Chemical Separation (MACS) Processes for Waste Remediation

L. Nunez and G. F. Vandegrift

Presented at the Technical Information Exchange Meeting of the Efficient Separations and Processing Integrated Program, Dallas, TX, January 10-11, 1994

Magnetically Assisted Chemical Separation (MACS) Processes

L. Nunez and G. F. Vandegrift

Presented at the Technical Information Exchange Meeting with Industry on Environmental Restoration Needs in Northwest United States, Seattle, WA, January 25-27, 1994

Plutonium and Americium Separation Using Organophosphorus Extractant Absorbed onto Ferromagnetic Particles

L. Nunez and G. F. Vandegrift

Presented at the Am. Chem. Soc. National Meeting, San Diego, CA, March 13-18, 1994

PCB Determination in Rocky Flats Plant Mixed Waste Sludges

K. J. Parish

Presented at the 20th Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory-West, Idaho Falls, ID, February 22, 1994

Electrochemical Recovery of Spent Reduction Salt

D. S. Poa, J. L. Smith, S. M. McDeavitt, and R. D. Pierce

Presented at the 14th Annual Pyrochemical Workshop, Boulder, CO, October 31-November 3, 1994

NMR and Supercritical Hydroformylations

J. W. Rathke, R. J. Klingler, and K. H. Woelk

Presented at the Shell Development Company, Houston, TX, October 10, 1994

Fine Tuning the Gas Chromatography/Matrix Isolation-Infrared Spectrometry Technique

G. T. Reedy, S. E. Carpenter, and A. S. Boparai

Presented at the 45th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, February 27-March 3, 1994

Separation and Recovery of Radioactive Materials by the TRUEX Process

M. C. Regalbuto

Presented at the Women in Science Seminar, Spring Arbor, MI, April 22, 1994

TRUEX Process Development

M. C. Regalbuto and J. M. Copple

Presented at the Argonne National Laboratory Technical Women's Symp., Countryside, IL, September 13-14, 1994

The Use of the TRUEX Solvent Extraction Process for Treatment of High-Level Waste

M. C. Regalbuto, R. A. Leonard, J. M. Copple, and G. F. Vandegrift

Presented at the Argonne National Laboratory Technical Women's Symp., Countryside, IL, September 13-14, 1994

TRUEX Process Development

M. C. Regalbuto and G. F. Vandegrift

Presented at the Hanford Summit II Conf., Pasco, WA, June 16, 1994

Cation Segregation in Simulated Radioactive-Waste Zeolite-A Mixtures

J. W. Richardson and M. A. Lewis

Presented at the Int. Zeolite Conf., Garmisch-Partenkirchen, Germany, July 17-22, 1994

The Development of Analytical Applications for Diphonix Resin

A. Rollins, A. Thakker, M. Gula, M. Fern, E. P. Horowitz, R. Chiarizia, H. Diamond, L. L. Smith, and S. Maxwell

Presented at the 40th Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Cincinnati, OH, November 13-17, 1994

Waste Minimization Using Evaporators and Concentrators

A. E. V. Rozeveld, D. B. Chamberlain, D. G. Wygmans, C. J. Conner, M. K. Clemens, and D. Korch

Presented at the Argonne National Laboratory Technical Women's Symp., Countryside, IL, September 13-14, 1994

Alkali-Chalcogenide Semiconductors: From Bulk to Confined Geometries to Liquids

M.-L. Sabounji, D. L. Price, J. A. Fortner, J. W. Richardson, P. Armand, and L. E. Iton

Presented at the Am. Chem. Soc. Meeting, Ann Arbor, MI, June 1-3, 1994

Field-Analytical-Laboratory Screening of Soils and Underground Storage Tanks

J. F. Schneider, N. A. Tomczyk, J. D. Taylor, D. V. Applegate, and L. F. Sytsma

Presented at the 45th Pittsburgh Conf. and Exposition on Analytical Chemistry and Applied Spectroscopy, Chicago, IL, February 27-March 3, 1994

Remembrance of Things Past—The Early Bioassay Conferences

J. Sedlet

Presented at the 40th Annual Conf. on Bioassay, Analytical, and Environmental Radiochemistry, Cincinnati, OH, November 13-17, 1994

Treatment of Transuranic Waste Using Carrier Precipitation at Argonne National Laboratory

S. A. Slater, S. B. Aase, B. Babcock, D. B. Chamberlain, C. J. Conner, J. Sedlet, and G. F. Vandegrift

Presented at the Argonne National Laboratory Technical Women's Symp., Countryside, IL, September 13-14, 1994

Environmental Radioanalytical Method Development: What's New

L. L. Smith

Presented at the 20th Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory-West, Idaho Falls, ID, February 22, 1994

Improved Method for the Determination of Actinide Elements in Soil

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

Presented at the Third Int. Conf. on Methods and Applications in Radioanalytical Chemistry, Kailua-Kona, HI, April 10-16, 1994

Development of a Dissolution Process for Metal Foil Target Containing Low Enriched Uranium

B. Srinivasan, J. C. Hutter, G. K. Johnson, and G. F. Vandegrift

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors, Williamsburg, VA, September 18-23, 1994

New Isotopic Perspectives on Atmospheric Carbon Monoxide

C. M. Stevens

Presented at the 20th Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory-West, Idaho Falls, ID, February 22, 1994

Development of Self-Absorption Coefficients for the Determination of Gamma-Emitting Radionuclides in Environmental and Mixed Waste Samples

W. E. Streets

Presented at the Symp. on Radiation Measurements and Applications, Ann Arbor, MI, May 16-19, 1994

Proposed Scoring Protocols for the Integrated Performance Evaluation Program (IPEP)

W. E. Streets

Presented at the 20th Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory-West, Idaho Falls, ID, February 22, 1994

Stability of Graphite Furnace Calibration Standards

L. B. TenKate and D. A. Bass

Presented at the Society for Applied Spectroscopy Meeting, Villa Park, IL, February 8, 1994

Thermodynamic and Nonstoichiometric Behavior of the Bi-2212 and Bi-2223 Systems

M. Tetenbaum

Presented at the Second Workshop on High Temperature Superconductor Phase Diagrams, Gaithersburg, MD, October 31-November 2, 1994

Thermodynamic and Nonstoichiometric Behavior of the Lead-Doped Bi-2223 System

M. Tetenbaum, M. C. Hash, B. S. Tani, J. S. Luo, and V. A. Maroni

Presented at the Fourth Int. Conf. of Materials and Mechanisms of Superconductivity in High Temperature Superconductors, Grenoble, France, July 5-9, 1994

Thermodynamic and Nonstoichiometric Behavior of the Lead-Doped Bi-2223 System

M. Tetenbaum, M. C. Hash, B. S. Tani, J. S. Luo, and V. A. Maroni

Presented at the Spring Meeting of the Materials Research Soc., San Francisco, CA, April 4-8, 1994

Lithiated Oxides for Lithium-Ion Batteries

M. M. Thackeray

Presented at the 186th Electrochem. Soc. Meeting, Miami Beach, FL, October 9-14, 1994

Lithium Insertion into Transition Metal Oxides

M. M. Thackeray

Presented at Argonne National Laboratory, June 2, 1994

Manganese Oxides for Lithium Battery Applications

M. M. Thackeray

Presented at Argonne National Laboratory, May 5, 1994

Spinel Materials for Lithium Batteries

M. M. Thackeray

Presented at the 11th Int. Seminar on Primary and Secondary Battery Technology and Applications, Deerfield Beach, FL, February 28-March 3, 1994

Transition Metal Oxides for Rocking-Chair Li Cells

M. M. Thackeray, E. Ferg, R. J. Gummow, and A. de Kock

Presented at the Fall Meeting of the Materials Research Soc., Solid State Ionics Symp., Boston, MA, November 28-December 2, 1994

TRUEX Applications

G. F. Vandegrift

Presented at the UST-ID Kickoff Meeting, Knoxville, TN, October 18, 1994

Use of the Generic TRUEX Model to Design Flowsheets for Treating High-Level Wastes

G. F. Vandegrift, R. A. Leonard, M. C. Regalbuto, J. M. Copple, and R. J. Jaskot

Presented at the 208th Am. Chem. Soc. Fall National Meeting, Characterization and Treatment of High-Level Nuclear Waste, Washington, DC, August 21-26, 1994

Metal Distillation and Melting Using an Inductively Heated Vacuum Furnace

M. A. Vest

Presented at the 14th Annual Pyrochemical Workshop, Boulder, CO, October 31-November 3, 1994

Development of Prototype Management Reports on Analytical Laboratory Performance in Performance Evaluation Programs for the DOE Office of Environmental Restoration and Waste Management

S. Warren, J. Hensley, D. A. Bass, and A. Bunn

Presented at the Technology Information Workshop, Kennewick, WA, May 10-12, 1994

***In Situ* Analysis of a Pyroprocess Molten Salt Using Square Wave Voltammetry**

J. L. Willit

Presented at the 14th Annual Pyrochemical Workshop, Boulder, CO, October 31-November 3, 1994

Rotating Frame NMR Microscopy

K. Woelk, J. W. Rathke, and R. J. Klingler

Presented at the Rocky Mountain Conf. on Analytical Chemistry, Denver, CO, July 31-August 5, 1994

Application of Glass-Crystal Composite Waste Forms for the Disposal of Nuclear and Hazardous Waste Materials

D. J. Wronkiewicz

Presented at the Idaho National Engineering Laboratory Seminar, Idaho Falls, ID, November 10, 1994, and Argonne National Laboratory-West, Idaho Falls, ID, November 11, 1994

The Reaction of Simulated Nuclear Waste Glass under Unsaturated Testing Conditions

D. J. Wronkiewicz

Presented at the Northeastern Illinois University Geology Department Seminar Series,
Chicago, IL, April 7, 1994

A Comparison of the Alteration Products Formed during the Dissolution of UO_2 and Spent Nuclear Fuel under Unsaturated Test Conditions

D. J. Wronkiewicz, P. A. Finn, J. K. Bates, and E. C. Buck

Presented at the Spent Fuel Workshop '94 Conf., Montebello, Quebec, August 22-24, 1994

Gross Alpha/Beta Analysis of Environmental and Mixed-Waste Samples by High-Pressure Microwave Dissolution

J. S. Yaeger

Presented at the 21st Annual Analytical Chemistry Laboratory Technical Meeting, Argonne
National Laboratory, November 10, 1994

Oxide Growth and Oxidation-Reduction Induced Roughening at Metal/Solution Interfaces

H. You and Z. Nagy

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA,
November 28-December 2, 1994

F. Papers Accepted for Publication

The Inorganic Chemistry of Wood Combustion for Power Production

M. Blander, K. W. Ragland, R. L. Cole, J. A. Libera, and A. D. Pelton

To be published in Biomass and Bioenergy

Simultaneous Dual-Element Analysis of Refractory Metals in Naturally Occurring Matrices Using Resonance Ionization of Sputtered Atoms

W. F. Calaway, R. C. Wiens, D. S. Burnett, M. J. Pellin, and D. M. Gruen

To be published in J. Vac. Sci. Technol.

Extraction of Technetium from Simulated Hanford Tank Wastes

D. J. Chaiko, Y. Vojta, and M. Takeuchi

To be published in Sep. Sci. Technol.

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

To be published in J. Radioanal. Nucl. Chem.

Energies of C_2H_5O and $C_2H_5O^+$ Isomers

L. A. Curtiss, D. J. Lucas, and J. A. Pople

To be published in J. Chem. Phys.

Superexchange Pathway Calculation of Electronic Coupling through Cyclohexane Spacers

L. A. Curtiss, C. A. Naleway, and J. R. Miller

To be published in J. Phys. Chem.

Effects of Multiple Pulping Variables on the Molecular Weight and Molecular Weight Distribution of Kraft Lignin

D. Dong and A. L. Fricke

To be published in J. Wood Chem. Technol.

Intrinsic Viscosity and the Molecular Weight of Kraft Lignin

D. Dong and A. L. Fricke

To be published in Polymer

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

Meyer-Neldel Rule for Liquid Semiconductors

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

To be published in Appl. Phys. Lett.

Carrier Density Enhancement in Semiconducting NaSn and CsPb

J. A. Fortner, M.-L. Saboungi, and J. E. Enderby

To be published in Phys. Rev. Lett.

Getting Results from Individual Goal Setting

D. W. Green

To be published in Vol. 1 of *Managing the Modern Laboratory*

Safety Characteristics of Lithium Alloy/Metal Sulfide Batteries

G. L. Henriksen, D. R. Vissers, and A. A. Chilenskas

To be published in J. Power Sources

Ultrasonic Vacuum Extraction of Gases from Water for Chemical and Isotopic Analysis

B. D. Holt, N. C. Sturchio, G. B. Arehart, and A. J. Bakel

To be published in Isotope Geosci.

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

To be published in Chem. Phys. Lett.

Electrodeposition and Characterization of Amorphous Fe-Ni-Cr Based Alloys

J. C. Kang, S. B. Lalvani, and C. A. Melendres

To be published in J. Appl. Electrochem.

Performance of Ceramic Breeder Materials in the SIBELIUS Experiment

J. P. Kopasz, C. E. Johnson, and D. L. Baldwin

To be published in J. Nucl. Mater.

Solvent Characterization Using the Dispersion Number

R. A. Leonard

To be published in Sep. Sci. Technol.

Sputtering of Group IIIA-Elements: Properties of the Metal Cluster Formation Mechanism

T. B. Lill, W. F. Calaway, Z. Ma, and M. J. Pellin

To be published in Surf. Sci.

Cluster Emission during Sputtering of the Liquid Gallium-Aluminum Eutectic Alloy

T. B. Lill, W. F. Calaway, and M. J. Pellin

To be published in J. Appl. Phys.

Sputtering of Tin and Gallium-Tin Clusters

T. B. Lill, W. F. Calaway, and M. J. Pellin

To be published in Nucl. Instrum. Methods B

A Study of the Structure and the Morphology of Oxide Films on Amorphous Al-Fe-Ce Alloys by XPS and SEM

A. N. Mansour and C. A. Melendres

To be published in J. Electrochem. Soc.

XAFS Investigation of the Structure and Valency of Nickel in Some Oxy Compounds

A. N. Mansour and C. A. Melendres

To be published in Phys. B

Oxide Reduction and Extraction (Treatment of Oxide Spent Fuels)

C. C. McPheeters

To be published in *Separation Techniques in Nuclear Waste Processing*, Eds., C. Wai, N. Chapman, and T. Carleson, University of Idaho, Moscow, ID

Far Infrared Spectroscopy of a Platinum Electrode *In Situ* using a Synchrotron Source

C. A. Melendres, B. Beden, and G. A. Bowmaker

To be published in *J. Electroanal. Chem.*

X-ray Diffuse Scattering for the *In Situ* Study of Electrochemically Induced Pitting on Metal Surfaces

C. A. Melendres, Y. P. Feng, D. D. Lee, and S. K. Sinha

To be published in *J. Electrochem. Soc.*

Chloride Ion Catalysis of the Copper Deposition Reaction

Z. Nagy, J. P. Blaudeau, N. C. Hung, L. A. Curtiss, and D. J. Zurawski

To be published in *J. Electrochem. Soc.*

Radiolytic Effects on the *In Situ* Investigation of Buried Interfaces with Synchrotron X-ray Techniques

Z. Nagy and H. You

To be published in *J. Electroanal. Chem.*

Waste Remediation Using *In Situ* Magnetically Assisted Chemical Separation

L. Nunez, B. A. Buchholz, and G. F. Vandegrift

To be published in *Sep. Sci. Technol.*

Thermochemistry of (germanium + sulfur) IV. Critical Evaluation of the Thermodynamic Properties of Solid and Gaseous Germanium(II) Sulfide GeS and Germanium(IV) Disulfide GeS_2 , and Digermanium Disulfide $\text{Ge}_2\text{S}_2(\text{g})$. Enthalpies of Dissociation of Bonds in $\text{GeS}(\text{g})$, $\text{GeS}_2(\text{g})$, and $\text{Ge}_2\text{S}_2(\text{g})$

P. A. G. O'Hare and L. A. Curtiss

To be published in *J. Chem. Thermodyn.*

Accurate Theoretical Studies of Small Elemental Clusters

K. Raghavachari and L. A. Curtiss

Book Chapter to be published in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy: Understanding Chemical Reactivity*

Flux Pinning Associated with Y_2BaCuO_5 Precipitates in Melt-Processed $\text{YBa}_2\text{Cu}_3\text{O}_x$

S. Sengupta, D. Shi, J. S. Luo, V. R. Todi, Z. Wang, C. Varanasi, P. J. McGinn, U. Balachandran, and K. C. Goretta

To be published in *Cryogenics*

Improved Separation Method for Determining Actinides in Soil Samples

L. L. Smith, J. S. Crain, J. S. Yaeger, E. P. Horwitz, H. Diamond, and R. Chiarizia

To be published in *J. Radioanal. Nucl. Chem.*

Ab Initio Calculations for Dissociative Hydrogen Adsorption on Lithium Oxide Surfaces

A. Sutjianto, S.-W. Tam, R. Pandey, L. A. Curtiss, and C. E. Johnson

To be published in *J. Nucl. Mater.*

Molecular Orbital Calculations and Raman Measurements for 1-Ethyl-3-Methylimidazolium Chloroaluminates

S. Takahashi, L. A. Curtiss, D. Gosztola, N. Koura, and M.-L. Sabounji

To be published in *Inorg. Chem.*

Tritium Transport and Retention in SiC

S.-W. Tam, J. P. Kopasz, and C. E. Johnson

To be published in J. Nucl. Mater.

Magneto-optical Imaging of Flux Patterns in Multifilamentary $(\text{BiPb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ Composite Conductors

U. Welp, D. O. Gunter, G. W. Crabtree, J. S. Luo, V. A. Maroni, W. L. Carter,

V. K. Vlasko-Vlasov, and V. I. Nikitenko

To be published in Appl. Phys. Lett.

Nitrogen Geochemistry and Isotopic Variations in Organic Matter and Diagenetic Minerals Influenced by Fluid Migration

L. B. Williams, R. E. Ferrell, I. Hutcheon, A. J. Bakel, M. M. Walsh, and H. R. Krouse

To be published in Geochim. Cosmochim. Acta

Distribution for ANL-95/24Internal:

J. P. Ackerman
 J. G. Asbury
 J. K. Bates
 J. E. Battles
 N. J. Beskid
 P. R. Betten (5)
 I. D. Bloom
 A. S. Boparai
 D. L. Bowers
 E. C. Buck
 F. A. Cafasso
 E. L. Carls
 D. J. Chaiko
 D. B. Chamberlain
 Y. I. Chang
 L. D. Chipman
 C. C. Christianson
 J. C. Cunnane
 D. W. Dees
 L. W. Deitrich
 W. H. DeLuca
 H. Drucker
 B. D. Dunlap
 W. L. Ebert
 A. Ellison
 P. A. Finn
 J. Fortner
 F. Y. Fradin
 E. C. Gay
 D. G. Graczyk
 D. W. Green
 D. M. Gruen

J. E. Harmon (2)
 J. E. Helt
 G. L. Henriksen
 G. K. Johnson
 L. R. Johnson
 C. E. Johnson
 T. D. Kaun
 T. R. Krause
 M. Krumpelt
 R. Kumar
 J. J. Laidler (75)
 K. K. Larsen
 S. H. D. Lee
 L. Leibowitz
 R. A. Leonard
 L. G. LeSage
 M. A. Lewis
 P. C. Lindahl
 M. J. Lineberry
 R. F. Malecha
 V. A. Maroni
 W. D. McFall
 C. C. McPheeters
 W. E. Miller
 J. F. Miller
 T. P. Mulcahey
 K. M. Myles
 P. A. Nelson
 W. H. Perry
 W. F. Podolski
 R. B. Poeppel
 J. W. Rathke

L. Redey
 D. T. Reed
 M. F. Roche
 N. F. Sather
 W. W. Schertz
 D. K. Schmalzer
 A. Schriesheim
 W. B. Seefeldt
 M. A. Slawecki
 J. A. Smaga
 D. L. Smith
 M. A. Sodaro
 M. J. Steindler
 D. M. Strachan
 N. C. Sturchio
 T. G. Surles
 W. M. Swift
 S.-W. Tam
 M. Thackeray
 C. E. Till
 Z. Tomczuk
 G. F. Vandegrift
 D. R. Vissers
 D. C. Wade
 L. C. Walters
 R. W. Weeks
 C. L. Wilkinson
 J. L. Willit
 A. M. Wolsky
 R. D. Wolson
 D. J. Wronkiewicz
 TIS Files

External:

DOE-OSTI, per distribution per UC-400 and -500 (92)
 ANL-E Library (2)
 ANL-W Library
 Manager, Chicago Operations Office, DOE
 A. Bindokas, DOE-CH

J. Haugen, DOE-CH
 J. Neff, DOE-CH
 S. L. Webster, DOE-CH
 J. R. LaFevers, DOE-UC
 R. C. Baker, DOE-AAO
 A. L. Taboas, DOE-AAO

Chemical Technology Division Review Committee Members:

E. R. Beaver, Monsanto Company, St. Louis, MO
 D. L. Douglas, Consultant, Bloomington, MN
 R. K. Genung, Oak Ridge National Laboratory, Oak Ridge, TN
 J. G. Kay, Drexel University, Philadelphia, PA
 G. R. St. Pierre, Ohio State University, Columbus, OH
 J. Stringer, Electric Power Research Institute, Palo Alto, CA
 J. B. Wagner, Arizona State University, Tempe, AZ
 R. D. Alkire, University of Illinois, Urbana, IL
 J. Allison, USDOE, Office of Waste Management, Germantown, MD
 T. D. Anderson, USDOE, Office of Technology Development, Germantown, MD
 R. A. Bajura, USDOE, Morgantown Energy Technology Center, Morgantown, WV
 S. Barker, Westinghouse Hanford Company, Richland, WA
 T. F. Bechtel, USDOE, Morgantown Energy Technology Center, Morgantown, WV
 S. E. Berk, USDOE, Office of Fusion Energy, Germantown, MD
 E. Beyma, USDOE, Office of Fossil Energy, Germantown, MD
 A. L. Boldt, Westinghouse Hanford Company, Richland, WA
 D. F. Bowersox, Los Alamos National Laboratory, Los Alamos, NM
 S. A. Butter, USDOE, Office of Basic Energy Sciences, Washington, DC
 M. H. Campbell, Westinghouse Hanford Company, Richland, WA
 K. A. Chacey, USDOE, Office of Environmental Management, Germantown, MD
 S. G. Chalk, USDOE, Office of Transportation Technologies, Washington, DC
 S. W. Chun, USDOE, Pittsburgh Energy Technology Center, Pittsburgh, PA
 S. P. Cowan, USDOE, Office of Waste Management, Germantown, MD
 P. Davis, USDOE, Office of Transportation Technologies, Washington, DC
 L. Dubois, ARPA/DSO, Defense Sciences Office, Arlington, VA
 J. J. Eberhardt, USDOE, Office of Advanced Transportation Materials, Washington, DC
 R. E. Erickson, USDOE, Office of Environmental Management, Germantown, MD
 G. Escobar, LATO Office, Rocky Flats Plant, Golden, CO
 R. C. Ewing, University of New Mexico, Albuquerque, NM
 R. J. Fiskum, USDOE, Building Equipment Division, Washington, DC
 C. W. Frank, USDOE, Office of Technology Development, Washington, DC
 T. Fryberger, USDOE, Office of Technology Development, Germantown, MD
 D. Geiser, USDOE, Office of Technology Development, Germantown, MD
 M. R. Ghate, USDOE, Morgantown Energy Technology Center, Morgantown, WV
 R. Gilchrist, Westinghouse Hanford Company, Richland, WA
 R. Goldstein, Electric Power Research Institute, Palo Alto, CA
 Government Documents Department, University of California, Berkeley, CA
 T. Grobstein Marechaux, USDOE, Office of Advanced Transportation Materials, Washington, DC
 T. J. Gross, USDOE, Office of Transportation Technologies, Washington, DC

T. Grumbly, USDOE, Office of Environmental Management, Washington, DC
 D. Haught, USDOE, Office of Advanced Transportation Materials, Washington, DC
 K. L. Heitner, USDOE, Office of Transportation Technologies, Washington, DC
 T. M. Hohl, Westinghouse Hanford Company, Richland, WA
 G. Jansen, Westinghouse Hanford Company, Richland, WA
 L. J. Jardine, Lawrence Livermore National Laboratory, Livermore, CA
 E. F. Johnson, Princeton University, Princeton, NJ
 E. Jones, Pacific Northwest Laboratory, Richland, WA
 F. Kane, University of Idaho, Moscow, ID
 R. D. Kelley, USDOE, Office of Basic Energy Sciences, Germantown, MD
 R. S. Kirk, USDOE, Office of Transportation Technologies, Washington, DC
 B. Knutson, Westinghouse Hanford Company, Richland, WA
 R. A. Kost, USDOE, Office of Transportation Technologies, Washington, DC
 K. Krist, Gas Research Institute, Chicago, IL
 A. R. Landgrebe, USDOE, Office of Transportation Technologies, Washington, DC
 B. Lee, Institute of Gas Technology, Chicago, IL
 S. C. T. Lien, USDOE, Office of Technology Development, Germantown, MD
 L. Little, USDOE, Nevada Operations Office, Las Vegas, NV
 G. J. Lumetta, Pacific Northwest Laboratory, Richland, WA
 J. E. Lytle, USDOE, Office of Waste Operations, Washington, DC
 J. Milliken, USDOE, Office of Transportation Technologies, Washington, DC
 R. F. Mull, Ford Motor Company, Dearborn, MI
 A. C. Muscatello, LATO Office, Rocky Flats Plant, Golden, CO
 J. B. O'Sullivan, Electric Power Research Institute, Palo Alto, CA
 A. L. Olson, Lockheed Idaho Technology Company, Idaho Falls, ID
 J. Owendoff, USDOE, Office of Environmental Restoration, Washington, DC
 P. G. Patil, USDOE, Office of Transportation Technologies, Washington, DC
 L. Petrakis, Brookhaven National Laboratory, Upton, NY
 S. T. Picraux, Sandia National Laboratories, Albuquerque, NM
 W. M. Polansky, USDOE, Division of Advanced Energy Projects, Germantown, MD
 R. Price, USDOE, Office of Fusion Energy, Germantown, MD
 C. Purdy, USDOE, Office of Technology Development, Germantown, MD
 G. Reddick, Westinghouse Hanford Company, Richland, WA
 P. Rosenfield, Chrysler Corporation, Auburn Hills, MI
 G. Rudins, USDOE, Office of Fossil Energy, Germantown, MD
 R. L. San Martin, USDOE, Dep. Asst. Secy. for Renewable Energy, Washington, DC
 P. S. Schaus, Westinghouse Hanford Company, Richland, WA
 W. C. Schutte, USDOE, Office of Technology Development, Germantown, MD
 L. H. Schwartz, National Institute of Standards and Technology, Gaithersburg, MD
 A. W. Searcy, Lawrence Berkeley Laboratory, Berkeley, CA
 R. Sehgal, Electric Power Research Institute, Palo Alto, CA
 R. W. Shivers, USDOE, Div. of Energy Utilization Research, Washington, DC
 R. R. Shockley, Illinois Clean Coal Institute, Carterville, IL
 J. S. Siegel, USDOE, Office of Fossil Energy, Germantown, MD
 W. A. Siegel, USDOE, Office of Transportation Technologies, Washington, DC
 A. Simmons, USDOE, Las Vegas, NV

M. I. Singer, USDOE, Advanced Research/Special Technologies, Washington, DC
S. N. Sinha, University of Illinois--Chicago, Chicago, IL
E. Slaathug, Westinghouse Hanford Company, Richland, WA
F. D. Stevenson, USDOE, Office of Basic Energy Sciences, Germantown, MD
R. B. Stout, Lawrence Livermore National Laboratory, Livermore, CA
J. P. Strakey, USDOE, Pittsburgh Energy Technology Center, Pittsburgh, PA
R. A. Sutula, USDOE, Office of Transportation Technologies, Washington, DC
R. Swaroop, Electric Power Research Institute, Palo Alto, CA
M. Thomas, US CAR, Dearborn, MI
J. C. Tseng, USDOE, Office of Environmental Management, Germantown, MD
G. P. Turi, USDOE, Office of Environmental Management, Germantown, MD
J. A. Turi, USDOE, Office of Environmental Management, Germantown, MD
M. P. Whelan, Gas Research Institute, Chicago, IL
K. Yeager, Electric Power Research Institute, Palo Alto, CA
R. E. York, General Motors Corporation, Warren, MI
R. J. Harrison, Atomic Energy of Canada, Ltd., Chalk River, Ontario, CANADA
M. Ozawa, Tokai-Works, Ibaraki-ken, JAPAN
M. Tokiwai, CRIEPI FBR Division, Komae-shi, Tokyo, JAPAN