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**Chemical Technology Division
Annual Technical Report**

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2000

Chemical Technology Division

Annual Report

Introduction

The Chemical Technology Division (CMT) is one of eight engineering research divisions within Argonne National Laboratory (ANL), one of the U.S. government's oldest and largest research laboratories. The University of Chicago oversees the laboratory on behalf of the U.S. Department of Energy (DOE). Argonne's mission is to conduct basic scientific research, to operate national scientific facilities, to enhance the nation's energy resources, and to develop better ways to manage environmental problems. Argonne has the further responsibility of strengthening the nation's technology base through developing industrial technology and transferring that technology to industry.

The Chemical Technology Division is a diverse early-stage engineering organization, specializing in the treatment of spent nuclear fuel, development of advanced power

sources, and management of both high- and low-level nuclear wastes. Although this work is often indistinguishable from basic research, our efforts are directed toward the practical devices and processes that are covered by ANL's mission. Additionally, the Division operates the Analytical Chemistry Laboratory, which provides a broad range of analytical services to ANL and other organizations.

The Division is multi-disciplinary. Its people have formal training as ceramists; physicists; material scientists; electrical, mechanical, chemical, and nuclear engineers; and chemists. They have experience working in academia, urban planning, and the petroleum, aluminum, and automotive industries. Their skills include catalysis, ceramics, electrochemistry, metallurgy, nuclear magnetic resonance spectroscopy, and petroleum refining, as

well as the development of nuclear waste forms, batteries, and high-temperature superconductors.

The Division's wide-ranging expertise finds ready application in solving energy and environmental problems. Division personnel are frequently called on by governmental and industrial organizations for advice and contributions to problem solving in areas that intersect present and past CMT programs and activities.

Currently, CMT is engaged in the development of several technologies of national importance. Included among them are

- advanced lithium-ion and lithium-polymer batteries for transportation and other applications,
- fuel cells, with an emphasis on the use of an oxidative reformer and regular gasoline as the fuel supply,
- stable nuclear waste forms suitable for storage in a geological repository, and
- electrochemical and pyrochemical processes for the disposition of spent nuclear fuel.

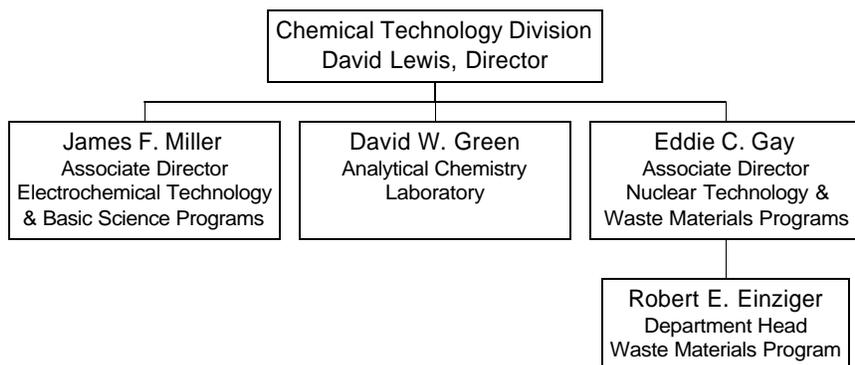
A separate program, in basic science, is engaged with smaller research projects, such

as catalysis and superconductivity, that have the potential to impact future energy systems. Our state-of-the-art Analytical Chemistry Laboratory supports these and other ANL programs.

The Division also serves as technical support in process design and development to the DOE programs in nuclear weapons' materials, isotope separation, and other specialties.

During 2000, CMT had an annual operating budget of approximately \$35 million. Three-quarters of this funding came from DOE, the remainder from other government agencies and private industry. The level of full-time staffing during the past year was 175 full time, and 42 part time. Displayed below is an organization chart for the senior managers of the CMT technical programs. A complete Divisional organization chart appears at the end of this report.

In this annual report we present an overview of the technical programs together with representative highlights. The report is not intended to be comprehensive or encyclopedic, but to serve as an indication of the condition and status of the Division.



Batteries

Rechargeable lithium batteries are becoming increasingly popular as power sources for consumer electronics, such as cellular phones, camcorders, and laptop computers. Because of the commercial success of these batteries in this market, they are being seriously considered for other applications that require high energy and power density, combined with long life, such as vehicles powered by batteries alone or a hybrid of batteries and another technology.

The advanced battery program in the CMT Division has been involved in the research and development of both lithium-ion and lithium-polymer batteries. Lithium-ion batteries use liquid electrolytes and insertion compounds at both positive and negative electrodes. During charge and discharge, lithium ions are shuttled between the host structures of the two electrodes. Lithium polymer batteries make use of a metallic lithium negative electrode, a polyethylene oxide-based solid electrolyte, and metal oxide positive electrode.

Because of its long-standing expertise with lithium batteries, the CMT Division has been given a key role in the multilaboratory DOE program called the Advanced Technology Development Program. This

program is designed to help develop high-power batteries under DOE's Partnership for a New Generation of Vehicles (PNGV). In the PNGV, the federal government and the U.S. auto industry are working together to develop a low-emission passenger car with a fuel economy of 80 miles per gallon. In the area of energy storage, the PNGV is focusing its R&D efforts on high-power lithium-ion batteries to be used in a hybrid electric vehicle. These batteries would meet the energy storage requirements for leveling the load on a prime power source and for capturing regenerative braking energy.

The CMT battery program has a seven-year history of working on lithium-polymer batteries for the electric-vehicle application under a cooperative research and development agreement with 3M Corp. and Hydro-Québec. We have provided technical support in three main areas: electrochemical characterization and modeling of advanced cell designs, testing and evaluation of prototypes, and development of advanced electrode materials.

Another important thrust within the battery program involves fundamental, but directed, research on electrode materials for rechargeable lithium batteries. Recent

efforts have focused on developing an alternative material that is safer than the conventional graphite anode in the lithium-ion battery, particularly when subject to abuse or overcharge conditions. We have discovered a new family of intermetallic electrode materials that appears to eliminate the safety hazards without the problems regarding performance decline upon cycling encountered with other intermetallic materials.

The Division operates the Electrochemical Analysis and Diagnostics Laboratory, which was established to study advanced battery systems for applications such as electric and hybrid vehicles, and power load management for electric utilities. This facility has been cited as a valuable resource by battery users, developers, and program managers who must evaluate and choose battery technologies and research directions. Since it was established more than two decades ago, the laboratory has tested more than 4000 cells, ranging from individual 4-Wh cells to 50-kWh batteries, representing 12 technologies and 18 battery developers. Recently, we have added the capability to test fuel cells up to 50 kW (equivalent to 65 hp).

Development of High-Power Lithium-Ion Batteries

In 1995, the DOE and the U.S. auto industry initiated industrial R&D projects to develop high-power lithium-ion batteries for use as the energy storage device in hybrid electric vehicles, as part of the Partnership for a New Generation of Vehicles (PNGV) program. The PNGV goal is to develop a new class of vehicle with up to three times the fuel efficiency of today's comparable vehicle without compromising performance and cost of ownership. In 1998, members of CMT helped DOE to organize a new program, involving multiple laboratories, to aid in identifying the key factors that limit the inherent safety and calendar life of this promising high-power battery technology. Argonne is the lead laboratory for this Advanced Technology Development (ATD) program. Other participating laboratories include Brookhaven National Laboratory, Idaho National Engineering and Environmental Laboratory, Lawrence Berkeley National Laboratory, and Sandia National Laboratories.

For this program, we developed first- and second-generation chemistries for high-

power cells and transferred this information to industrial producers of cylindrical 0.9-Ah high-power cells. Subsequently, these firms fabricated several hundred cells incorporating the CMT-developed chemistries. We have also participated in the accelerated aging (through calendar and cycle-life testing) of these cells and applied a suite of diagnostic techniques to new and aged cells to help establish the mechanisms that control their safety and life. Table I-1 summarizes the first- and second-generation cell chemistries.

During the last year, we completed the accelerated aging of the first-generation cells along with a variety of diagnostic studies. In addition, the second-generation cell chemistry was defined, and 0.9-Ah cells with this chemistry are being built.

Performance tests of new and aged first-generation cells revealed that this cell chemistry can meet the PNGV performance requirements prior to aging, but that the power performance fades rapidly on aging.

Table I-1. Chemistries for First- and Second-Generation Lithium-Ion Cells Developed for ATD Program

	First-Generation Chemistry	Second-Generation Chemistry
Anode	75 wt% MCMB-6 graphite 16 wt% SFG-6 graphite 9 wt% PVDF binder	92 wt% MAG-10 graphite 8 wt% PVDF binder
Cathode	84 wt% $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ 8 wt% PVDF binder 4 wt% SFG-6 graphite 4 wt% carbon black	84 wt% $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ 8 wt% PVDF binder 4 wt% SFG-6 graphite 4 wt% carbon black
Electrolyte/ Separator	1 M LiPF_6 in EC:DEC (1:1)/ 37 μm polyethylene	1.2 M LiPF_6 in EC:EMC (3:7)/ 25 μm polyethylene

PVDF = polyvinylidene fluoride

EC:DEC = ethylene carbonate: diethyl carbonate

EMC = ethyl methyl carbonate

To identify the factors responsible for the rapid power fade with this cell chemistry, we analyzed the gases formed, the chemical changes in the electrolyte, and the chemical and physical changes in and on the electrode surfaces. The gas and electrolyte analyses showed only minor chemical changes. In tests with three-electrode laboratory cells, micro-reference electrodes developed in CMT revealed the positive electrode to be the main source of an impedance rise (causing the power to decline) in the cell, while AC-impedance measurements with symmetrical cells uncovered the sources of impedance rise as interfacial phenomena at both electrodes (see Fig. I-1).

We employed various techniques to examine the physical and chemical characteristics of the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ positive-electrode surface. High-resolution transmission electron microscopy established that the secondary positive-electrode particles are agglomerates of primary particles and indicated an amorphous film growing in the grain boundaries—between the primary particles—of aged positive electrodes. X-ray photoelectron spectroscopy was used to examine the surface of the secondary particles. After sputtering, the possible

presence of NiO was detected near the surface of particles harvested from aged cells, indicating possible lithium concentration gradients within the particles during high-current charge pulses. These diagnostic studies on first-generation cells continue in an effort to more thoroughly understand the phenomena that control aging with this cell chemistry. Similar accelerated aging and diagnostic studies are planned for the cells that incorporate our second-generation chemistry.

We are also involved in the development of advanced electrodes and electrolytes for these high-power cells. These materials are being tailored to help solve the problems identified with the first- and second-generation cell chemistries.

ANL Participants

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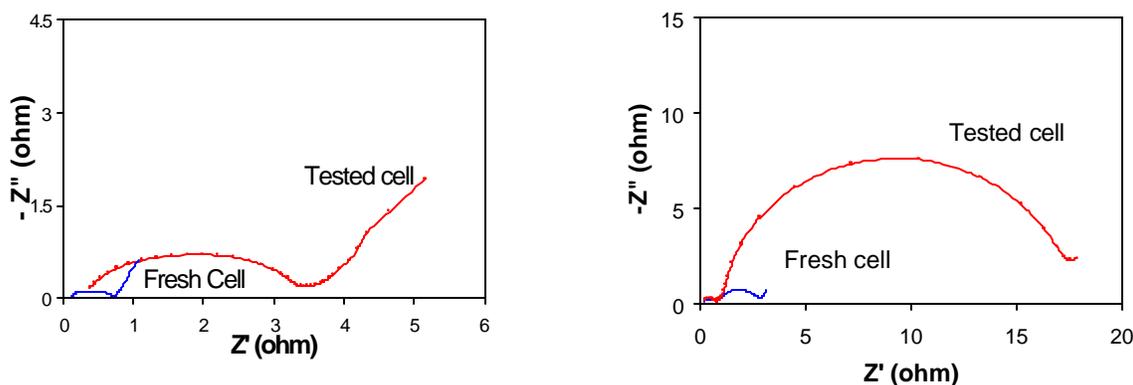


Fig. I-1. Alternating Current-Impedance Spectra Obtained on Negative-Electrode Symmetrical Cell (left) and Positive-Electrode Symmetrical Cell (right). The positive and negative electrodes were harvested from new and aged first-generation cells. For calendar life testing, the aged cell was stored at 60% state of charge and 50°C for four weeks.

Development of Lithium-Polymer Batteries

The lithium-polymer battery (LPB) is a lightweight, high-energy system that can operate at moderate temperatures (typically 60-80°C). With a polymer electrolyte, this all-solid-state battery can be manufactured by using high-speed film-laminate technology. The battery's low weight translates into high specific energy. The Li/Li⁺ redox reaction (negative electrode, -3.0 V) gives the battery its high power. The positive electrode is based on a transition metal oxide, typically a vanadium oxide, that acts as a reversible chemical host for intercalating lithium cations. Thus, during discharge, the lithium cations insert into the host material with simultaneous electrochemical reduction of the host's closest-neighbor redox sites. The host structure is highly reversible to both redox and insertion reactions; this allows the lithium cations to exit upon recharge.

For more than seven years ANL has participated in the development of lithium-polymer batteries for electric and hybrid-electric vehicle applications. Working with Hydro-Québec, 3M Corp., and the U.S. Advanced Battery Corp., ANL has provided technical support over a wide range of advanced battery research and development activities. These include component, cell, and battery testing and characterization; post-test diagnostic analysis; electrochemical cell modeling and battery design; and electrode materials development, evaluation, and optimization.

Component and cell testing and characterization have been carried out by means of electrochemical techniques such as direct-current methods (e.g., constant current or power discharge, peak power measurements, and current interruptions),

variable power studies such as the dynamic stress test, and alternating-current impedance methods. The purpose is to develop a better understanding of the cell characteristics during operation and to provide the critical information needed to focus future research efforts on improving and optimizing the lithium-polymer battery performance. We also conduct high-quality, reliable, and independent testing of prototype full-size cells, modules (Fig. I-2), and battery packs. In addition to the electrochemical studies, thermal effects during the operation of lithium-polymer cells are examined through electrochemical microcalorimetry studies. This work has provided highly accurate simultaneous thermal and electrochemical information on the cells.

Materials development within the LPB project has focused on the synthesis and characterization of metal oxide positive electrodes that offer superior electrochemical behavior to state-of-the-art materials. 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 the stability of the oxygen-ion array and minimum displacements of the transition metal cations in the host are required to ensure good reversibility.

Past major accomplishments include our identification of a superior positive-electrode material with a 30% capacity improvement and a lower irreversible capacity loss upon cycling. We also developed a scaleable process for the

synthesis of the improved material and transferred this technology to 3M.

Electrochemical modeling of lithium-polymer cells has been conducted to elucidate the phenomena occurring in the cells during operation. This work involves simultaneously solving differential mass, charge, energy, and momentum balances on every species in each phase and component of the fundamental electrochemical cell. The time constant for the lithium transport in the lithium-polymer cells is relatively large when compared with liquid-electrolyte battery systems. This is a result of the slow ionic transport in the polymer electrolyte and the positive-electrode active material. These phenomena are difficult to separate and examine experimentally because of the composite positive-electrode structure of carbon, electrolyte, and active material, as well as the thin cell geometry.

Early in the LPB project our modeling effort was very effective in identifying the limitations of the cell and, in particular, the positive-electrode oxide material. We have continued to improve the flexibility, quality, and reliability of the electrochemical model. At this time, it is still the only tool for effectively examining concentration,

potential, and current distributions in the lithium-polymer cell.

This past year, our work on model improvement has concentrated on modeling the mechanical stresses that may develop in the cell during operation. Under this effort significant modifications are being made to the electrochemical model, which require converting it from a single- to a multi-dimensional model. Initial work has concentrated on developing a two-dimensional model because of the limitations imposed by computational speed and our present level of understanding. The newly developed two-dimensional electrochemical model was used to examine the loss in cell performance resulting from various cell edge effects and fabrication imperfections. Future activities will focus on integrating the mechanical and electrochemical models of the lithium-polymer cell.

ANL Participants

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Fig. I-2. Lithium-Polymer Battery Module Fabricated by 3M and Hydro-Québec and Tested at Argonne

Development of Advanced Electrode Materials for Lithium-Ion Batteries

Lithium-ion batteries are being developed and manufactured worldwide for powering electronic devices such as cellular phones and laptop computers and for electric and hybrid vehicles. State-of-the-art lithium-ion batteries use lithiated graphite (LiC_6) negative electrodes coupled to LiCoO_2 positive electrodes via an organic electrolyte. These 4-V batteries are inherently unsafe and require sophisticated electronic circuitry to protect individual cells from being overcharged when the potential of the lithiated graphite electrode reaches that of metallic lithium, and when the LiCoO_2 electrode is extensively delithiated. A need, therefore, exists for alternative electrode materials that reduce the safety hazards as well as improve the performance.

Research at CMT on alternative negative electrode materials to graphite has focused on a new class of intermetallic materials with NiAs- and zinc-blende-type structures. These materials react electrochemically with lithium at a few hundred millivolts above the potential of metallic lithium.

In particular, we discovered that a Cu_6Sn_5 electrode (NiAs-type structure) undergoes a topotactic phase transition at ~ 400 mV (vs.

lithium) to yield Li_2CuSn , in which the CuSn component has a zinc-blende arrangement of atoms (Fig. I-3). Further lithiation of Li_2CuSn results in an expulsion of metallic Cu from the structure and the formation of $\text{Li}_{4.4}\text{Sn}$. Unfortunately, although this reaction is reversible, capacity is lost steadily from the copper-tin electrode during charge and discharge. The capacity loss is attributed to grain growth of the extruded copper, electrode expansion, and loss of contact of the copper with the lithiated Sn particles. We have found that this problem can be minimized when the cycling is limited to the topotactic reaction. In this case, the copper-tin electrode will attain a rechargeable gravimetric capacity of ~ 200 mAh/g, which translates to a volumetric capacity of 1040 mAh/mL based on the density of Li_2CuSn (5.2 g/mL). Although the gravimetric capacity of the copper-tin electrode is inferior to that of lithiated graphite (theoretical value of 372 mAh/g), the practical volumetric capacity exceeds the theoretical value of lithiated graphite (818 mAh/mL). As a result, copper-tin electrodes are attractive for lithium-ion battery applications when volume is a more important consideration than mass.

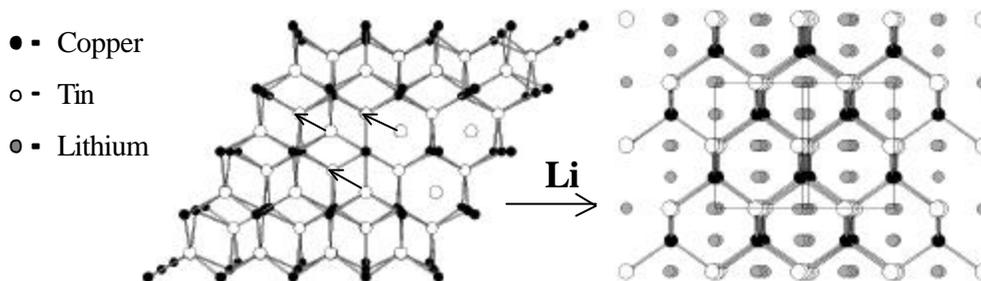


Fig. I-3. Structural Schematic Representing the Cu_6Sn_5 to Li_2CuSn Transformation

Our research on intermetallic electrode materials with a zinc-blende-type structure has focused on the family of antimony-based semiconductors, of which InSb has yielded the most promising results. We determined that the electrochemical reaction with lithium takes place by lithium insertion and indium extrusion from a stable face-centered-cubic Sb array between 900 and 600 mV (vs. lithium), yielding Li_3Sb on complete extrusion of indium (Fig. I-4). What is remarkable about the reaction is that the Sb array expands by only 4.4% during lithiation, and that after one conditioning cycle, the reaction is reversible. Further capacity can be obtained from the electrode if lithiation of the extruded In is allowed to take place (<600 mV vs. lithium). We found that InSb electrodes offer a practical rechargeable gravimetric capacity of ~300 mAh/g, which is equivalent to a volumetric capacity of 1290 mAh/mL, based

on the average density of the InSb electrode after reaction with lithium to form Li_3Sb and In (4.3 g/mL). These results hold great promise for developing an alternative electrode that is safe and able to endure many cycles without capacity decline.

The research on intermetallic electrodes has been sponsored primarily by DOE's Office of Basic Energy Sciences and Office of Advanced Automotive Technologies. This research has led to a Work-for-Others contract with an industrial firm.

ANL Participants

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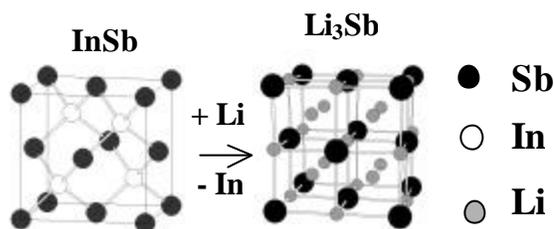


Fig. I-4. Schematic of Structural Relationship between InSb and Li_3Sb

Battery and Fuel Cell Testing and Evaluation

Since 1976, the Electrochemical Analysis and Diagnostics Laboratory (EADL) in CMT has been providing battery developers with reliable, independent, and unbiased performance evaluations of their cells, modules, and battery packs. These evaluations have been performed for DOE, the Partnership for the New Generation of Vehicles (PNGV), the U.S. Advanced Battery Consortium (USABC), and others to provide insight into those factors that limit the performance and life of advanced battery systems. Recently, our capabilities have expanded to fuel cell testing.

The EADL has been used to test large numbers of both small and large batteries and fuel cells fabricated within and outside of ANL. It is a flexible facility with capabilities to conduct 120 concurrent advanced-battery studies under operating conditions that simulate electric-vehicle, hybrid-electric vehicle, utility load-leveling, and standby/uninterruptible power source applications. Each battery is independently defined, controlled, and monitored to impose charging regimes and discharge load profiles that simulate the types of dynamic operating conditions found during actual usage. The testing of groups of cells/batteries is controlled by computers that communicate over high-speed networks with central servers and are controlled by other computer workstations.

The EADL has evaluated many battery technologies, such as Na/S, LiAl/FeS, LiAl/FeS₂, lithium-polymer, lithium-ion, Zn/Cb, Zn/Br₂, Ni/Fe, Ni/Zn, Ni/MH, Ni/Cd, and lead-acid. These represent technologies from over 18 developers throughout the world.

In some of our work on lithium-ion batteries, we characterized and tested prototype lithium-ion batteries made under DOE's Advanced Technology Development (ATD) Program. These batteries were designed for use in hybrid electric vehicles. At present, lithium-ion technology exhibits exceptional power capability and long cycle life, but has very poor calendar life. One of the goals for this project is to gain an understanding of the effect of accelerated calendar-life testing at four temperatures (40, 50, 60, and 70°C) and two states of charge (40% and 60%) on the performance of these batteries.

Performance data under these test conditions were obtained with respect to area specific impedance and power density. Figure I-5 presents a typical profile for power density as a function of open circuit voltage and time. It tracks the decreasing power density with time in a calendar-life test at 60% state of charge and 40°C.

Examining all the test data revealed two basic trends. First, the performance degradation data follow simple parabolic kinetics, which is consistent with thin film growth such as layer formation or the formation of a solid-electrolyte interface. Second, performance degradation depends directly on temperature and is controlled by diffusion. A layer formed at the solid-electrolyte interface could be the source of these observations. These results will be used to project the performance and life of the lithium-ion batteries at ambient temperature and will help industrial battery developers extend the life of these batteries.

ANL Participants

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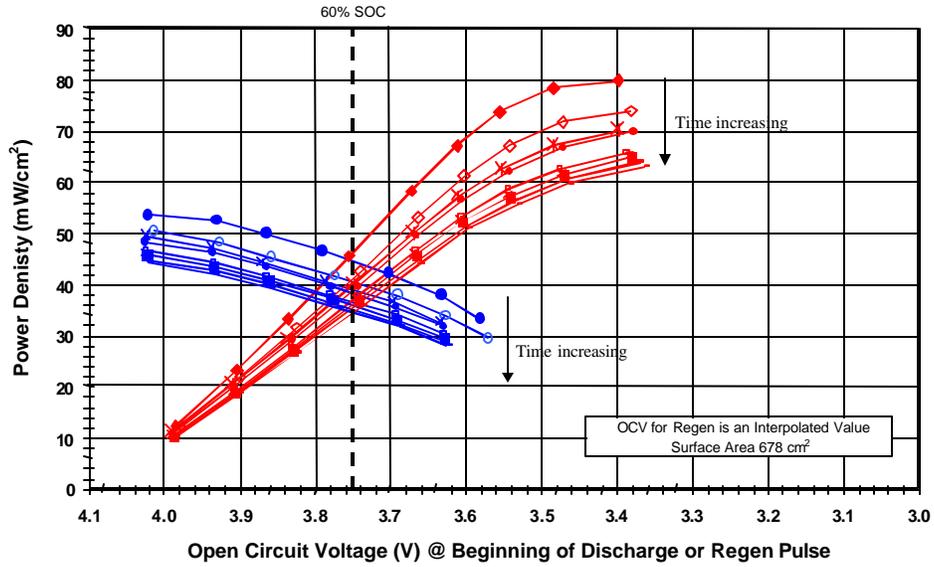


Fig. I-5. Typical power density vs. cell voltage curves in calendar-life test at 60% state of charge (SOC) and 40°C. The lower set of curves is from the “regen” power and the upper, from discharge. Regen stands for charge pulse from regenerative braking.



Fuel Cells

Fuel cells convert hydrogen and oxygen into electricity by electrochemical reactions, eliminating the need for heat engines. They hold the promise of clean electric power not only for cars and other vehicles but also for houses, commercial buildings, and industrial processes. The CMT Division has been a leader in fuel cell research for more than twenty years, drawing on a range of disciplines to create and improve materials and designs for fuel cells.

Because fuel cells are very energy efficient and produce almost no emissions, interest in this technology is growing. The polymer electrolyte fuel cell, in particular, is attracting significant private investment for transportation and residential use. However, the polymer electrolyte fuel cell presents some challenges to widespread adoption. Foremost among them today is providing a suitable fuel. Because no national infrastructure exists to supply hydrogen, the ideal fuel for fuel cells, it has been necessary to develop fuel processors that can convert conventional fuels such as gasoline, alcohols, or natural gas into a hydrogen-rich (reformat) gas.

For the automotive application, the design of the fuel processor must be small, light weight, able to start up rapidly, and responsive to rapidly changing power demands. At the low operating temperature of the polymer electrolyte fuel cells (nominally, $\sim 80^{\circ}\text{C}$), the reformat also has to be free of chemical species that can poison the electrocatalyst. These include carbon monoxide and sulfur-bearing species.

Meeting all these requirements for the automotive fuel cell system is a major challenge, and more than half of our effort is devoted to the development of fuel processing technology. This work encompasses development and demonstration of the individual processes involved, including fuel reforming, chemical shift reaction, sulfur removal, and carbon monoxide removal.

One of our major accomplishments has been the development of an engineering-scale processor with a novel catalytic material that efficiently produces hydrogen from a wide variety of hydrocarbon fuels, including methanol, natural gas, and gasoline. In addition to fuel flexibility, the novel catalyst has demonstrated excellent resistance to

sulfur in the fuel, a property essential for reliable, long-term operation of the processor. We have issued several patents as a result of this work, and industrial firms have already, or are about to, license our fuel processing technology.

In a related effort, we continue to lead the field in analysis and modeling of fuel cell systems integrated into vehicles. These analysis and modeling efforts have looked at the effects of different fuel cell types, fuel compositions, fuel storage methods, fuel processing techniques, and vehicle specifications.

In the development of the more traditional molten carbonate and solid oxide fuel cells for stationary power applications, we are working closely with industrial developers on specific issues related to technology improvement.

Development of Fuel Processor for Fuel Cell Systems

Polymer electrolyte fuel cells (PEFCs) are being developed for many different applications, including portable power such as laptop computers and cellular phones, stationary power for remote locations as well as urban residences, and automotive propulsion. In the absence of a hydrogen refueling infrastructure, these fuel cells will require hydrogen produced from available fuels such as natural gas, liquefied petroleum gas, gasoline, or diesel. The conversion of these fuels into hydrogen needs to be carried out in compact yet efficient fuel processors that start up rapidly and maintain the hydrogen purity through variable power loads.

During the past decade, we have been developing fuel processors for PEFC systems and have pioneered this technology from process definitions, through catalyst development, to hardware design and demonstration. Our fuel processor is based on a series of unit operations and processes (Fig. II-1) where fuel, air, and water feeds

are converted into a hydrogen-rich gas suitable for use with PEFCs. The feeds are first preheated, then autothermally reformed by means of proprietary catalysts (licensed by Sud Chemie Inc.) at 700°C. The hydrogen-rich effluent from the reformer contains hydrogen sulfide (from sulfur present in the fuel) and oxides of carbon. After the H₂S is removed with a suitable reagent, most of the carbon monoxide is converted in a water-gas shifter reactor. A unit then reduces the CO level down to the 10-50 ppm that can be tolerated by the fuel cell. The fuel cell consumes 70-85% of the hydrogen produced to electrochemically generate electricity. The remaining hydrogen is catalytically oxidized to generate heat, which can then be recovered for use within the fuel processor. Challenges overcome in designing the fuel processor included strategically positioning various components operating over a wide temperature spectrum (shown in Fig. II-1) while maintaining a compact and efficient unit.

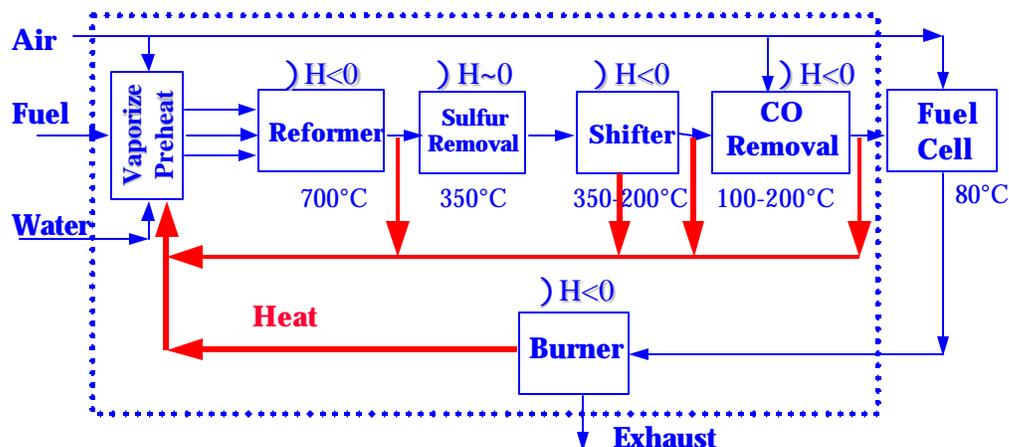


Fig. II-1. Simplified Schematic Showing Fuel Processor with Fuel Cell Stack (where ΔH = heat of reaction)

Figure II-2 shows the fuel processor developed to accept feed streams at ambient conditions and integrate all the unit operations and processes to deliver a product gas ready for the final CO removal. This engineering-scale unit, which has a total volume of 7 L, has been demonstrated to convert gasoline and methanol into sufficient hydrogen for a fuel cell stack operating at 7 and 4 kW(e), respectively. The fuel processor was packed with a novel catalyst developed in CMT for the reforming and water-gas shift reactions.

Figure II-3 shows the composition of the product gas obtained from the fuel processor with gasoline as the fuel. The product

contained 40-45% (dry basis) hydrogen and operated at efficiencies approaching 80%. (Efficiency is defined as the lower heating value of the hydrogen as a percentage of the lower heating value of the fuel.) Several industrial firms have expressed interest in marketing the ANL-developed fuel processor.

ANL Participants

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Fig. II-2. Novel Reforming Catalyst Developed in CMT Being Held next to Integrated Fuel Processor

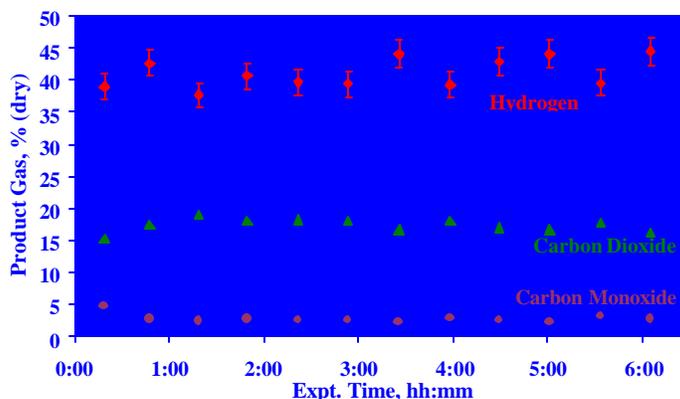


Fig. II-3. Product Gas Composition Obtained from Conversion of Gasoline in the Integrated Fuel Processor

Effects of Fuel Constituents on Fuel Processor Catalysts

Fuel cell vehicles offer the prospect of electric vehicles with very low emissions and high efficiency but require a hydrogen-rich gas as the fuel. On-board reforming of petroleum-based fuels, such as gasoline, remains one of the major challenges to the near-term commercialization of fuel cell vehicles. We have developed and patented an autothermal-reforming catalyst that will convert a wide variety of hydrocarbon fuels into hydrogen.

A typical gasoline formulation consists of paraffins, aromatics, naphthenes, oxygenates, and olefins. Although gasoline can be reformed, some of these constituents, as well as sulfur impurities, may have detrimental effects on the fuel processing catalysts. They may lead to compromised performance and decreased fuel conversion efficiency. In an effort to identify which constituents are beneficial and which are detrimental to the reformer, we are testing various components of gasoline under autothermal-reforming conditions. The results will be used to help define the requirements for a fuel-cell fuel and determine if a special formulation of fuel-cell-grade gasoline would improve overall system performance. We have also entered into cooperative research and development agreements with several oil companies to investigate the reforming of refinery streams and fuel blends.

Short-term (< 20 h) and long-term (>1000 h) reforming tests in a microreactor system have been performed with about 2 g of the ANL catalyst at temperatures from 600 to 800°C. In the short-term tests, all of the gasoline components investigated to date have been converted to a hydrogen-rich gas at 800°C and a gas hourly space velocity of

15,000/h. Conversions were all above 95% under these conditions. However, there are substantial differences in reforming under less severe operating conditions. The effect of temperature on hydrogen production from several gasoline constituents is illustrated in Fig. II-4. The general trend is that aromatic compounds (represented by trimethylbenzene and toluene) require higher temperatures than olefins (1-octene), which require higher temperatures than naphthenes (methylcyclopentane and methylcyclohexane), which require higher temperatures than straight chain and branched paraffins (n-octane and isooctane). As shown in Fig. II-4, hydrogen production from trimethylbenzene decreased the most dramatically with a decrease in temperature.

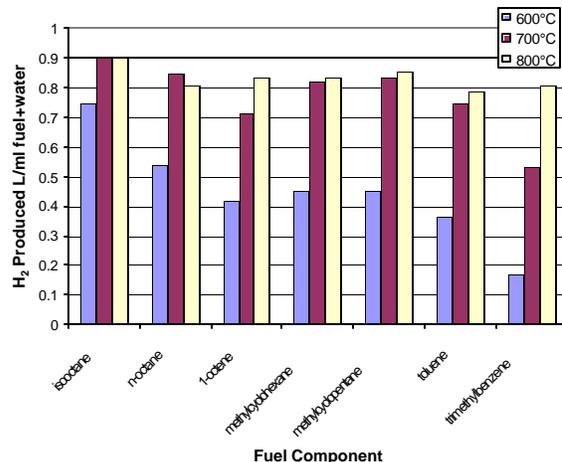


Fig. II-4. Effect of Temperature on Hydrogen Yield from Autothermal Reforming of Gas Constituents

We have also investigated the effect of gas hourly space velocity on autothermal reforming. As was true for temperature, trimethylbenzene was the most sensitive to changes in space velocity. Hydrogen yield

dropped dramatically when the space velocity was increased from 15,000 to 75,000 h⁻¹.

The long-term tests indicated that the catalysts developed at CMT are resistant to coking, even when reforming a fuel containing high concentrations of aromatics. Simulated gasoline blends containing up to 20% aromatics were reformed for over 1000 h, with start-up and shut-down cycles, without any problems regarding coke formation. There was less than a 5% decrease in hydrogen production after 1000 h of operation (Fig. II-5).

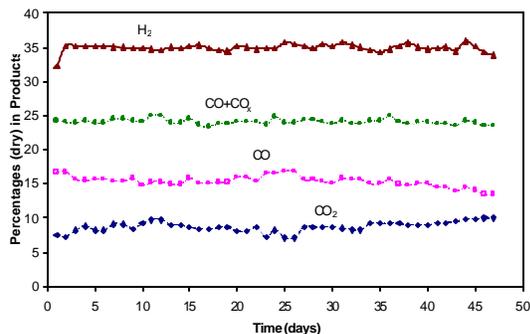


Fig. II-5. Long-Term Performance of ANL Reforming Catalyst with Simulated Gasoline

The effects of sulfur impurities on the ANL autothermal-reforming catalyst were determined by reforming fuels doped with benzothiophene to obtain sulfur levels of 50, 300, and 1000 ppm (by weight). The results indicate that sulfur is not detrimental to the catalyst. Short- and long-term tests indicated that hydrogen production was actually higher for the fuels with sulfur added than for sulfur-free fuels (Fig. II-6). The effects of sulfur on reforming over a nickel catalyst were also investigated. After the fuel was switched to a sulfated fuel, hydrogen production decreased by about 15%. When the fuel was switched back to sulfur-free fuel, the hydrogen production returned to the initial level.

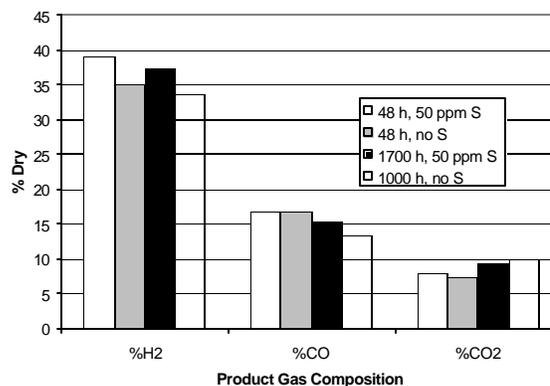


Fig. II-6. Effect of Sulfur on Product Gas Composition in Short- and Long-Term Tests with ANL-Developed Catalyst

In sum, our reforming tests led to the following conclusions. First, all of the major types of chemicals found in gasoline can be autothermally reformed to provide a hydrogen-rich gas. Second, trimethylbenzene requires the most severe reforming conditions, including both high temperature (800°C) and low space velocities. Third, the effect of sulfur impurities in the fuel on catalyst performance depends on the catalyst. Finally, there was no major long-term degradation of the ANL autothermal-reforming catalyst caused by adding unsaturated components or sulfur to the fuel.

ANL Participants

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Design, Analysis, and Modeling of Automotive Fuel Cell Systems

Polymer electrolyte fuel cells are being developed to provide clean, efficient propulsion power in transportation applications. To meet performance targets and other vehicle-related constraints, we must take into account not only the fuel cell stack but also its integration into a vehicle along with a fuel processor, heat exchangers, etc. We are thus carrying out model calculations to address issues of system integration, thermal and water management, and system and vehicle-level efficiencies and fuel economies. For these analyses, we use the GCtool software package developed at Argonne.

One of the major studies conducted this year involved analyses of design and operating parameters needed for a fuel cell/battery hybrid automobile to achieve 80 miles per gallon (34 km/L) of gasoline, one of the goals set by DOE's Partnership for the Next Generation of Vehicles (PNGV).

Our earlier modeling results had shown that, to achieve the PNGV target efficiencies of 38.4% at rated power and 48% at one-fourth of rated power, average operating cell voltages of 0.772 V and 0.896 V would be needed at the respective power levels. At these rather high cell voltages, the

corresponding current and power densities in today's fuel cells are low, requiring a large cell active area and resulting in high cost for the fuel cell stack.

We have reanalyzed the fuel cell in a hybrid system, using a more conservative cell polarization curve. Analyses were conducted for three automobile types: a lightweight vehicle, a heavier but more aerodynamic vehicle, and a lightweight and aerodynamic vehicle. For these vehicles, we determined the fuel economies on the Federal Urban Driving Schedule (FUDS) and the Highway Cycle, as well as the combined fuel economies. The key vehicle characteristics used in the analyses are shown in Table II-1. This table also includes the maximum and average power requirements for the three vehicles on the two driving schedules.

We first analyzed an 80-kW (net) fuel cell system, with 0.7 V/cell at the rated power. Figure II-7 presents the combined fuel economy calculated for the three vehicles powered by this 80-kW system. Figure II-8 shows the effect of using a smaller fuel cell system (40 kW versus 80 kW), as well as one with a lower design-point cell voltage (0.65 V versus 0.7 V).

Table II-1. Physical Characteristics of Conceptual Vehicles and Their Power Requirements

	Lightweight	Aerodynamic	Lightweight and Aerodynamic
Vehicle Weight, kg	1043	1379	1043
Frontal Area, m ²	2.18	2.18	2.18
Drag Coefficient	0.25	0.163	0.163
Rolling Resistance Coefficient	0.0064	0.0064	0.0064
Wheel Radius, mm	326	326	326
Auxiliary Power, kW	0.5	0.5	0.5
Max. (Avg.) Power, kW			
FUDS	27.7 (3.97)	35.2 (4.54)	27.3 (3.77)
Highway	22.9 (8.17)	28.7 (7.68)	22.4 (6.75)

Fuel Cells

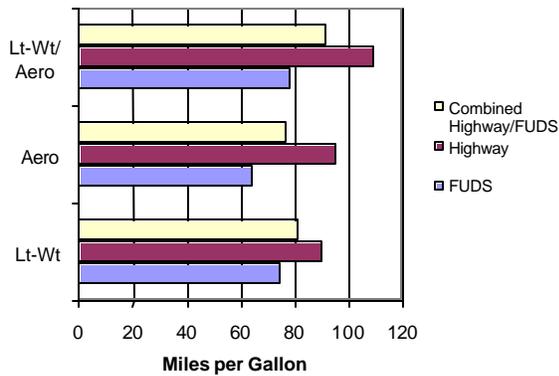


Fig. II-7. Fuel Economy for Three Vehicles (Table II-1) Powered by 80-kW Fuel Cell System

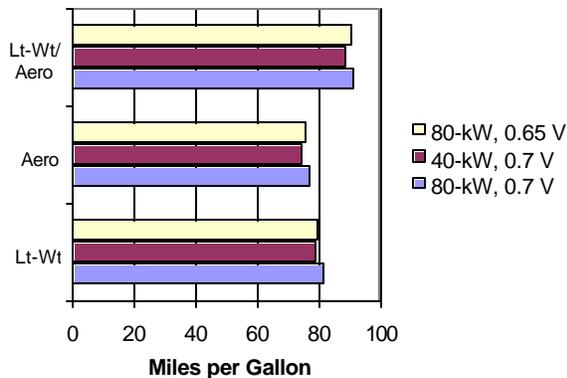


Fig. II-8. Effect of Fuel Cell Power and Design-Point Cell Voltage on the Combined FUDS/Highway Fuel Economy for the Three Vehicles

From these and other system analyses, we arrived at the following conclusions:

- To achieve the target fuel economy set by PNGV (80 mpg on gasoline), an 80-kW fuel cell vehicle will need to be extremely lightweight and highly aerodynamic.
- A 40-kW (or smaller) fuel cell system can meet the power requirements for

urban and highway driving with all three conceptual vehicles, but it will not provide acceptable acceleration.

- The fuel cell system is never operated at the rated power on these simulated driving cycles; average power draw is ~10% of rated power, with short bursts to ~35% of rated power.
- A lower design-point cell voltage has a minor effect on fuel economy, but it would reduce the fuel-cell stack size significantly. The sizes of the fuel processor and the heat exchangers would increase, however, because of the lower efficiency at the design point.
- Using a smaller fuel cell system would decrease system weight, volume, and cost, with a relatively small decrease in fuel economy; however, a larger battery would be required to provide the requisite acceleration and passing performance.

Our modeling activity has received a Transportation Fuel Cell Program Special Recognition Award from the DOE/Office of Advanced Automotive Technologies.

ANL Participants

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Development of Low-Temperature Solid Oxide Fuel Cells

Among the fuel cell systems currently being developed, the solid oxide fuel cell (SOFC) offers significant advantages for residential and auxiliary power units, as well as for larger industrial power applications.

The goal for all fuel cells presently is to reduce both stack and system costs to make them competitive with existing technologies. While the current SOFC operates at 1000°C, this high temperature has limited the materials that can be used for the various cell components (electrolyte, anode, cathode, and interconnect or bipolar plate) to relatively expensive ceramic compositions. In addition, there are concerns with the materials and manufacturing costs of other components within the hot zone of the fuel cell, which are normally ceramic-based (e.g., manifolds, piping, and insulation).

Much of the present R&D activity is focused on developing SOFC materials for use at 800°C, which is low enough that alternative materials become available to reduce cost significantly. Further reduction in operating temperature, to 500-700°C, could yield even greater cost savings.

In addition to materials flexibility and cost, the lower SOFC operating temperatures result in higher Nernst and cell voltages, leading to increased energy conversion efficiencies. Further, the lower operating temperatures would permit close and efficient thermal integration with a fuel reformer for converting hydrocarbon fuels to a hydrogen-rich gas. For example, a typical catalytic-autothermal reformer operates between 750 and 850°C. Thus, a fuel cell operating at about 800°C would be ideally

suited for optimal thermal integration between these two key components. The reduced operating temperature would also improve mechanical robustness and reduce thermal stresses and chemical interactions among the various cell components. However, operating the SOFC at lower temperatures significantly increases the performance requirements for the cell components.

The decrease in the performance of the cathode as the temperature is reduced is the most significant issue facing development of lower temperature SOFCs. The lack of ionic conductivity in the conventional manganite-based perovskites limits their use as the cathode at the lower temperatures. Mixed electronic-ionic conductivity is essential in the cathode material to permit the oxygen reduction to occur over the entire electrode surface rather than being restricted to the three-phase region of electrode, electrolyte, and gas phase.

Current research at CMT is focused on developing alternative cathode materials for use with thin-film electrolytes of gadolinia-doped ceria or yttria-stabilized zirconia, which operate over a temperature range of 500-850°C. Half-cell tests at these temperatures showed promising results for a number of perovskite-based cathodes, as well as some layered structures. Figure II-9 shows the area specific resistances measured for candidate cathode materials with the two electrolytes at various temperatures. The best-performing cathode on yttria-stabilized zirconia was a strontium-doped lanthanum ferrite, which has low resistance, stable performance, and low overpotentials under

galvanostatic conditions. The best-performing cathode on gadolinia-doped ceria was a strontium-doped gadolinium cobaltite, again displaying low resistances with a fairly stable long-term performance. With these alternative cathode materials, the target area specific resistance of $<1 \Omega \cdot \text{cm}^2$ was achieved for yttria-stabilized zirconia at 800°C and gadolinia-doped ceria at 650°C . Further reductions in temperature and area specific resistance for cathodes with both electrolytes are desirable.

Although we have placed a strong emphasis on cathode research, other relevant materials issues for the SOFC are also being investigated in CMT. Anodes that are

tolerant to sulfur in the fuel have gained interest recently because they could potentially remove the fuel reformer from within the system, resulting in reduced costs. Various materials strategies are being explored to attack this problem. The search for an improved metallic interconnect also continues, a necessary component within the stack at lower temperatures.

ANL Participants

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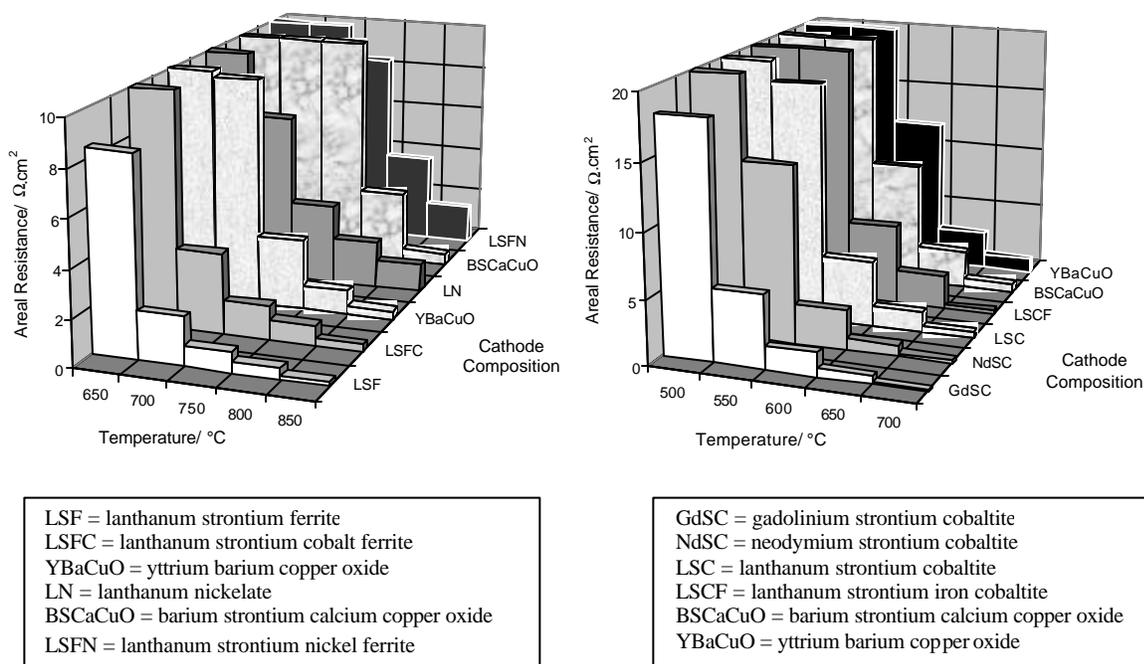


Fig. II-9. Area Specific Resistance for Various Cathode Compositions on Yttria-Stabilized Zirconia Electrolytes (left) and Gadolinia-Doped Ceria Electrolytes (right)



Waste Materials Research

Our primary research on waste materials involves the determination of the corrosion behavior of various nuclear waste forms in adverse atmospheres in support of disposal in approved repositories. This research includes chemical and physical characterization, testing, and analyses of the results in terms of mechanisms of elemental release from the waste forms. Qualification testing is being conducted on all the major waste forms intended for interment: spent nuclear fuel from DOE sites, spent fuel from commercial light water reactors, the ceramic waste form being developed for plutonium disposition, glasses developed for the Defense Waste Processing Facility and the West Valley Demonstration Project, and the ceramic waste form resulting from the electrometallurgical treatment of spent sodium-bonded fuel from Experimental Breeder Reactor-II (EBR-II). Besides this work on spent fuel and high-level waste forms, projects are also underway on characterization and testing of low-level waste forms.

The DOE has stewardship over 200 types of spent fuel from a variety of testing programs and research reactors. Before this waste can

be buried in a geologic repository, its corrosion behavior for long time periods under repository-relevant conditions must be understood. The DOE spent fuels have been divided into groups to facilitate degradation testing. We are performing characterization and groundwater corrosion tests on three groups: metallic uranium, mixed oxide, and uranium aluminide fuels. A major finding was the observation of colloids in the leachate from the tests with the metallic uranium and mixed oxide fuels. These particles are a significant concern because they have the potential to absorb radionuclides from the corroding fuels and transport them through the subsurface environment.

The DOE will file a license application for the candidate repository at Yucca Mountain in Nevada, which will be used primarily for disposing spent fuel from commercial reactors. We are providing key input to the development of the performance assessment models that are to be used to support the site recommendation regarding the Yucca Mountain site. Specifically, we have been responsible for preparing analysis and modeling reports covering a variety of topics: the

corrosion rate of defense high-level waste glass, concentration limits for colloid-associated and mixed-phase dissolved radionuclides released in degradation tests, and hydride-related degradation of the cladding from commercial spent fuel.

The CMT Division also supports the Yucca Mountain Project by characterizing and testing commercial spent nuclear fuel. The objective is to determine how this spent fuel will corrode and release radionuclides under the conditions to which it may be exposed in an unsaturated repository. The tests examine the corrosion of the fuel under conditions that simulate the dripping and humid air environments expected in the repository. We perform an extensive suite of chemical, radiochemical, and electron microscopy analyses to determine the important chemical reactions that are involved in altering the fuel and releasing radionuclides as dissolved or colloidal species. This work has led to the clarification of the net reactions that occur, estimates for the rates of these reactions, and identification of the important role of uranyl alteration products in sequestering radionuclides.

The CMT Division is leading an effort to establish colloid-based radionuclide concentration limits for the waste forms intended for disposal at Yucca Mountain. This effort addresses important concerns related to the fate and transport of actinides via colloids under the anticipated conditions at the proposed Yucca Mountain site. Research is being performed to examine colloids generated from corrosion tests with commercial spent nuclear fuel, to determine colloid formation behavior, to establish key conditions affecting colloid generation and behavior in subsurface conditions similar to those expected at Yucca Mountain, and to characterize the properties of the colloids.

The DOE is considering several alternatives for the disposal of excess plutonium resulting from the dismantlement of nuclear weapons. One alternative is immobilization, where the plutonium is fixed in a titanate-based ceramic. We are conducting tests and analyses to support qualification of this waste form for disposal in a federal high-level waste repository. Corrosion testing continues to support previous observations that the titanate ceramic is extremely durable.

In a spin-off project from the nuclear waste research, the CMT Division is investigating the chemical durability of a dental glass-ceramic in collaboration with scientists at the University of Florida School of Dentistry. Results from aqueous corrosion tests have shown that the chemical durability and, therefore, the clinical performance of this dental ceramic are not acceptable. On the basis of these tests, we recommended use of compositional changes or changes in the fabrication procedure that minimize the amount of glass in the composite.

A glass-bonded sodalite waste form has been developed in CMT to immobilize salt wastes generated during the electrometallurgical treatment of EBR-II fuel (see Sec. IV). We are conducting tests and analyses to support qualification of EBR-II waste forms for disposal in a federal high-level waste repository. The database being generated will be used to show that the ceramic waste form meets the requirements specified in the DOE "Waste Acceptance System Requirements Document." Testing and modeling efforts are also in progress to demonstrate how the impact of these waste forms can be integrated into the DOE "Total System Performance Assessment" that will be performed to support the license application for the repository.

The CMT Division is performing detailed analyses of the contents of more than 30 fissile and neutron-absorbing nuclides that are present in spent nuclear fuel to generate a compositional database of high-burnup fuels. We have analyzed samples excised from 23 fuel segments originating from Three Mile Island-1 and Quad Cities-1 reactors. Results of these analyses are being used, in part, to validate isotopic models that are the basis for criticality scenarios at the proposed Yucca Mountain repository.

The DOE will privatize the separations and immobilization activities for disposing the tank wastes at the Hanford, Washington, site. We are evaluating the durability of glasses that represent likely low-activity waste glasses in support of the performance assessment of the proposed low-level disposal system at Hanford. Also, we have formulated test methods for low-activity product acceptance that will be used by DOE in acceptance testing of the waste products.

Several CMT scientists are also working with the American Society for Testing and Materials to develop standards for waste-form testing and extension of the dry storage of spent fuel.

The Division's waste materials research includes efforts devoted to (1) substitution of low- for high-enriched uranium in the production of molybdenum-99, (2) treatment of radioactive, mixed, and hazardous waste, and (3) novel applications of separation science to industrial processes.

Technetium-99m, the daughter of molybdenum-99, is the most commonly used medical radioisotope in the world. We are working to convert all current processes for molybdenum-99 production, worldwide, from high- to low-enriched uranium. The

program is international, with ongoing and new initiatives with partners in Indonesia, South Africa, the Netherlands, Belgium, Russia, Canada, Korea, Australia, and Argentina. Our particular research deals with fabrication and dissolution of the new targets and conversion of current processes to allow the use of low-enriched uranium. A new target was designed and tested that is significantly cheaper to fabricate than older designs and has improved cooling capabilities. In our cooperation with Argentina, we are modifying their current process to accept the new target.

An alkaline-side solvent-extraction process for ^{137}Cs removal from alkaline tank waste is being tested at CMT in cooperation with Oak Ridge National Laboratory, the Savannah River Technical Center, and the Savannah River Site. This process shows great promise for extracting the cesium from the 34 million gallons of high-level waste now stored in tanks at the Savannah River Site.

The CMT Division also serves as the chemical engineer for Waste Management Operations at ANL. We are currently assisting them in designing and operating a treatment facility for aqueous mixed waste. Ties are also being developed and strengthened with industrial partners for improving processes, waste treatment, and decontamination of equipment.

Corrosion Testing of DOE-Owned Spent Nuclear Fuels for Permanent Disposal at Yucca Mountain

The Department of Energy has approximately 2500 metric tons of spent nuclear fuel that it plans to permanently dispose in the Yucca Mountain repository. The fuel inventory includes over 200 types of fuels, but time and financial resources permit corrosion testing of only three or four types. Currently at Argonne, we are testing metallic uranium, mixed oxide, and aluminum dispersion fuels. We plan to include graphite fuels in our testing program at some future date.

The focus of the work reported here is oxic, hydrologically unsaturated corrosion testing of metallic uranium fuel. In these tests, unirradiated metallic uranium was suspended inside an air-tight steel test vessel, exposed to an air atmosphere at 90°C, and wetted periodically by injected groundwater. One test was continued until the fuel coupon was completely oxidized (77 days). Samples of the solid corrosion products, liquid leachates, and the gas atmosphere were analyzed during the course of the test and at test termination. Results indicated that the metallic uranium oxidized rapidly to a particulate “sludge” composed of uranium oxides and oxyhydroxides, the liquid leachate contained dissolved and colloidal uranium phases, and the corrosion process generated hydrogen gas. These results are significant to the repository license application because current regulations restrict the quantity of particulates in a waste canister and prohibit the presence of potentially explosive gases. Perhaps the most significant result, however,

is the documentation of fuel-derived colloids in the leachate. Using dynamic light scattering and transmission electron microscopy, we identified the major components of the colloidal suspension as uranium oxides and oxyhydroxides with mean particle sizes of approximately 5 and 100 nm (see Figs. III-1 and -2). We also identified a minor component as uranium silicate with a mean particle size of approximately 700 nm. These colloids have the potential to adsorb radionuclides from corroding fuels and transport them as stable, charged, radionuclide-associated colloids through the subsurface environment; hence, they are a significant concern for the repository disposal of spent fuel at Yucca Mountain.

Ongoing and future corrosion tests include applying the methods developed for unirradiated uranium fuel to spent uranium fuel, determining the stability regime of the colloids, and determining the speciation of radionuclides among dissolved, colloidal, and solid phases.

ANL Participants

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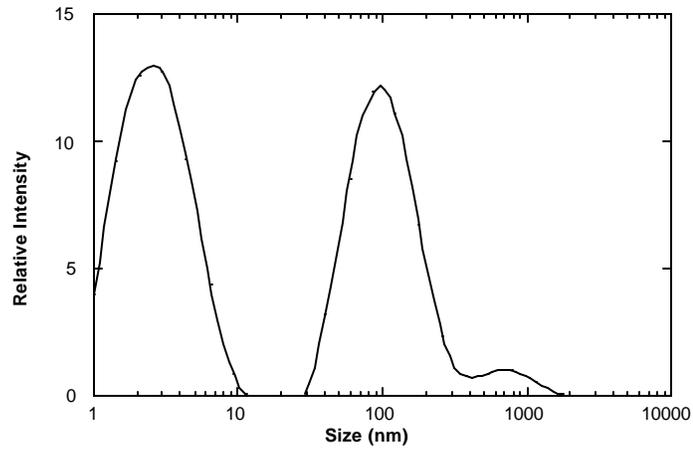


Fig. III-1. Tri-modal Size Distribution of Colloids Generated during Corrosion of Unirradiated Metallic Uranium Fuel as Determined by Dynamic Light Scattering. Colloids were predominantly small particles with mean sizes of approximately 5 and 100 nm, with a minor quantity of larger (approximately 700 nm) particles.

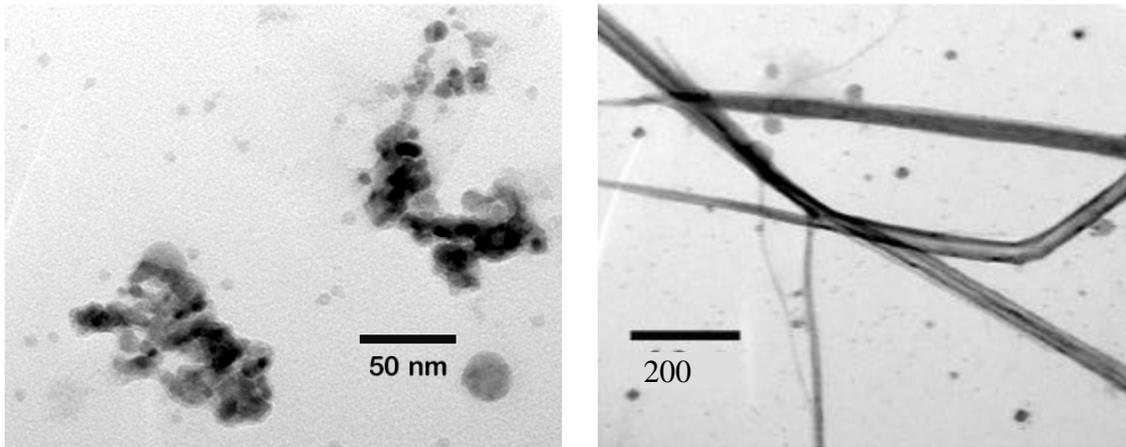


Fig. III-2. Transmission Electron Micrographs of Colloids. Micrograph on left shows individual uranium oxide/oxyhydroxide colloids that are approximately 5-nm dia, with agglomerates of approximately 100 nm. Micrograph on the right shows long needles of uranyl silicates approximately 700-1000 nm in length.

Support for the Yucca Mountain Site Recommendation Decision — Waste Form Analysis and Modeling Reports

The DOE Secretary plans to make a formal recommendation to the President in July 2001 concerning the suitability of the Yucca Mountain Site for development of a repository for disposal of spent nuclear fuel (SNF) and vitrified high-level waste (HLW). The Secretary's recommendation will be based on the results of an assessment (referred to as a "total system performance assessment") of the performance of the site, together with the engineered components of the disposal system, in safely isolating radionuclides in the waste from human contact for many millennia. This assessment requires models that can be used to simulate the processes that may degrade the waste forms and result in radionuclide release from the disposal system. We have prepared analysis and modeling reports that describe the corrosion models and their scientific basis. These models are to be used in determining (1) the degradation rate of vitrified HLW, (2) the role that alteration phases, which are formed when disposed spent fuel degrades, play in sequestering radionuclides and thereby limiting their dissolved concentrations, and (3) the contribution of waste form colloids to the radionuclide release.

The analysis and modeling report for HLW glass describes the scientific basis for a model that has been developed to conservatively bound the dissolution rate of this glass. The scientific basis for the model is experimental evidence, developed at CMT and elsewhere over the past two decades, which shows that glass corrosion can be treated as a classic mineral dissolution process. To model the rate of dissolution of

the vitrified wastes in the repository, we have adapted the well-established mathematical expressions that have been developed for the rate of dissolution of silicate minerals. A key challenge in applying this approach was to estimate the long-term dissolution affinity term in the model for glass waste forms. Short-term experimental tests have shown that this term usually decreases monotonically as the glass corrodes in closed systems. However, because experimental results from accelerated corrosion tests conducted at CMT have shown that the dissolution affinity is influenced by the formation of secondary alteration phases in a way that is not yet fully understood, the modeling approach adopted was to include an empirically determined bounding estimate for the dissolution affinity. In following this approach, we have developed an analytical expression for the dissolution rate containing only three parameters and two variables (temperature and pH). We obtained conservative estimates of the values for each model parameter by analysis of CMT experimental data and the open literature.

Although many of the key radionuclides (e.g., ^{237}Np) are only minor constituents (typically less than 1 wt%) in the waste forms, the rate at which they can be transported away from the corroding waste is constrained by processes that limit their dissolved concentration in the groundwater that may contact the waste. In considering the constraints on the concentrations of radionuclides that may result from the corrosion of commercial light water reactor

(LWR) fuels in the repository, we have assessed the effects of the alteration phases that are formed as the fuel corrodes. Upon exposure to water and an oxidizing atmosphere, LWR fuels corrode by oxidative dissolution and alteration phase precipitation to form U(VI) oxyhydroxides. These compounds are also common in nature, where natural UO_2 (uraninite) has undergone oxidative corrosion and has persisted for hundreds of thousands to millions of years. Experimental studies at CMT discovered trace levels of Np in the U(VI) oxyhydroxide dehydrated schoepite, $(\text{UO}_2)\text{O}_{0.25-x}(\text{OH})_{1.5+2x}$ ($x \leq 0.15$), formed in corrosion tests with spent fuel. Based on crystal-chemical arguments, there is good reason to expect that Np can enter into the structure of uranyl oxyhydroxides. We developed a model for the Np concentration in solution by using a method described by Bruno et al. (Chem. Geol. 151, 277-291, 1998), in which a Henry's law constant of one is assumed for trace elements in a solid that precipitates and dissolves congruently with respect to the major (U) and trace (Np) elements. We have used this model to calculate the total concentration of Np in solution by multiplying the calculated U concentration by the Np/U ratio in the dehydrated schoepite.

Figure III-1 shows the calculated concentration of dissolved Np as a function of solution pH. The solid and dotted lines show the calculated Np concentration when the experimentally determined and theoretical upper limit values are used for the Np/U ratio in the dehydrated schoepite (0.006 and 0.33, respectively). For comparison, the dashed line shows the Np concentration calculated by using a prior approach which assumed that solid Np_2O_5 limits the dissolved Np concentrations. Also given in Fig. III-1 are the experimental Np concentrations reported from batch experi-

ments (solid triangles) and hydrologically unsaturated drip tests (solid circles) with spent UO_2 fuel conducted at CMT.

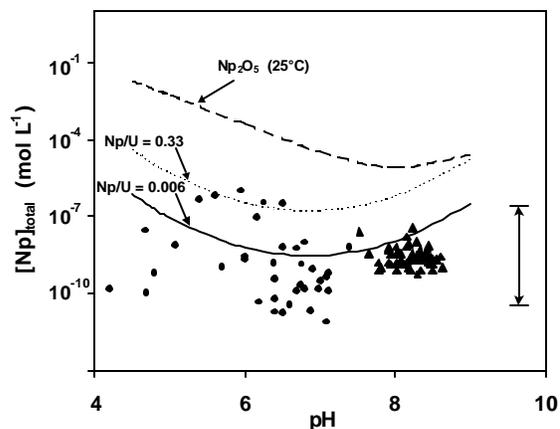


Fig. III-3. Comparison of Calculated (curves) and Experimental (symbols) Data for Np Concentrations in Dehydrated Schoepite. The arrow shows the uncertainty range calculated for the Np data.

Comparison of the calculated and experimental results shows that our model predicts Np concentrations similar to or above the average experimentally determined Np concentration at all pH values. Thus, our model is a relatively conservative estimator of Np concentrations and a significant improvement over the prior model based on the solubility of Np_2O_5 .

The CMT Waste Materials Research Department will continue to participate in the Yucca Mountain Project through experimental and modeling efforts designed to support DOE's application for a license to construct and operate this waste repository.

ANL Participants

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Assessing the Impact of Colloids on the Disposal of Radioactive Waste Glass at Yucca Mountain

Colloidal systems encompass a wide variety of surface-active agents and dispersed particles. Because of their sub-micron size and surface charge properties, colloidal systems have the potential to transport radioactive contaminants from a waste storage or disposal site to the subsurface groundwater. Indeed, recent studies at the Nevada Test Site have confirmed the mobility of colloidal plutonium in the subsurface and accentuate the importance of colloids in the modeling of waste form performance. To evaluate the impact of colloids on radioactive waste disposal at Yucca Mountain, the Waste Materials Research Department in CMT is characterizing the physical and chemical nature of the solution-borne colloids that form during waste-form degradation. The focus of our work is on understanding the formation and properties of radionuclide-bearing colloids that affect their transport and mobility in a subsurface environment.

Over the past several years, static corrosion tests have been underway on several representative compositions of Defense Waste Processing Facility glass in groundwater from Yucca Mountain. These laboratory studies of colloidal properties are important to determine the mechanism of colloid formation and colloid stability during waste form corrosion. A variety of techniques, including transmission electron microscopy (TEM), dynamic light scattering (DLS), and nuclear spectroscopy, have been employed to characterize the colloids generated in the corrosion tests.

Results from the TEM colloid analyses indicated that smectite clay colloids form

during glass corrosion and contain discrete radionuclide-bearing phases incorporated in the clay (Fig. III-4). Americium and plutonium were identified in the brockite inclusion rather than in the clay colloid matrix. The mineralogical composition of the colloids, as determined by TEM analyses, was found to be important for understanding and predicting the stability of the colloids. The DLS results have been instrumental in correlating the bulk-solution colloidal properties (colloid size and concentration) with the compositional results from TEM and the radionuclide distribution from filtration and alpha spectroscopy. In addition, DLS was employed to monitor the rate of colloid growth and changes in the size and diffusion of the colloids as a function of nuclear waste glass corrosion. Under the reaction kinetics of these corrosion tests, stable colloids were observed in low ionic strength solutions (below about 0.05 mol/kg). However, as the ionic strength increased during the glass corrosion, aggregation of the colloidal species occurred. For waste glass corrosion, the colloid stability is thus governed by the properties of the clay and the geochemical environment.

The results from these studies demonstrate the importance of colloids for modeling waste form behavior. Ongoing and future studies include predicting colloid formation and stability in other waste forms under repository-relevant conditions.

ANL Participants

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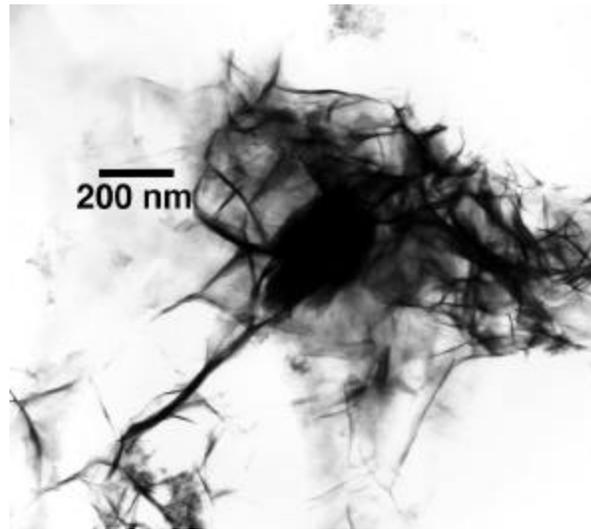


Fig. III-4. Smectite Clay Colloid from a Corrosion Test with Nuclear Waste Glass Showing Entrained Particles of Brockite (thorium calcium orthophosphate mineral, dark regions within clay matrix)

Advanced Applications of ICPMS for Characterization of Nuclear Waste Forms and Their Corrosion Products

The license application for the proposed repository at Yucca Mountain requires data on the corrosion behavior and the isotopic composition of nuclear waste forms. Providing this information requires accurately determining the concentrations of multiple elements and radionuclides in samples possessing complex matrices. One of the challenges in analyzing these samples is the need to determine concentrations of both naturally occurring elements and non-naturally occurring radionuclides, often at very low concentrations (10^{-6} to 10^{-15} g/mL). Other challenges include handling small sample volumes (several milliliters to <0.1 mL) and isobaric interferences. The determination of elemental speciation is also desired to help elucidate the chemical processes involved in nuclear waste form corrosion. We have applied and developed three related techniques to overcome these challenges: inductively coupled plasma mass spectrometry (ICPMS), high resolution-inductively coupled plasma mass spectrometry (HR-ICPMS), and high-performance liquid chromatography with

inductively coupled plasma mass spectrometry (HPLC-ICPMS).

Models being developed for potential repository criticality scenarios require accurate information on the concentrations of fissile and neutron-absorbing nuclides in the waste forms. We have determined the content of 31 nuclides in over 30 spent fuel samples possessing burnups ranging from 30 to 80 GWd/MTU (gigawatt-days/metric ton uranium). We have also applied HPLC-ICPMS to the determination of lanthanide fission products in spent nuclear fuel. Figure III-5 shows a mass chromatogram of lanthanides in a dissolved sample of spent nuclear fuel from Three Mile Island Reactor-1 (TMI-1). This measurement provides information on the lanthanide isotopic distribution so that percent fission burnup can be determined. These analyses will provide validation for isotopic models used to predict the concentrations of important nuclides in the repository.

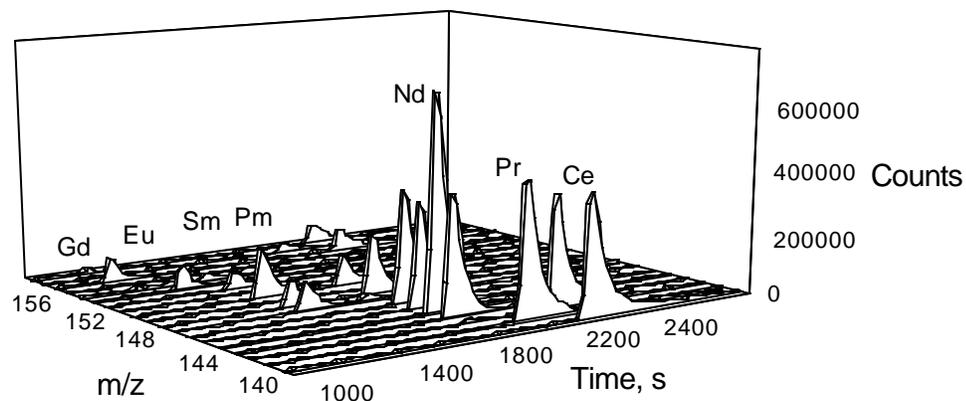


Fig. III-5. Mass Chromatogram of Lanthanide Fission Product Nuclides in Dissolved Sample of Spent Nuclear Fuel from TMI-1

Understanding the long-term behavior of nuclear waste materials in a geological repository has required the development of sophisticated testing methodologies for waste forms. In turn, these tests have required the adaptation and development of sophisticated analytical methods to provide the means for accurately quantifying the release of radionuclides from the waste forms. The mass specificity and high sensitivity of conventional ICPMS allow quantitation of multiple nuclides, elements, and radionuclides with concentrations as low as 10 pg/mL in the corrosion products of nuclear waste materials. However, the low solubility of actinides in groundwater frequently leads to extremely low concentrations of these important radionuclides. To overcome this difficulty, we have developed methods that give us the capability to determine ultra-low concentrations of nuclides in small volume samples. By utilizing low-flow microconcentric nebulization as a method of sample introduction to our new-generation HR-ICPMS (VG Elemental Axiom) we are capable of determining as little as 2.5×10^5 atoms of ^{238}U in 0.1 μL of solution (1 fg/mL). We have utilized ICPMS and HR-ICPMS to quantitatively measure the corrosion rate of a variety of high-level

nuclear waste glasses, plutonium-containing ceramics, and spent nuclear fuels.

The capability to determine the speciation of trace nuclides in waste-form corrosion products facilitates elucidation of chemical processes involved in corrosion. The specificity of ICPMS analysis can be greatly increased with the application of HPLC to separate elements possessing different oxidation states. Because of the ultra-high sensitivity of HR-ICPMS, the hybrid technique HPLC-HR-ICPMS has allowed us to determine trace iodide species in a simulated groundwater with oxidation state specificity. Figure III-6 shows the presence of multiple anionic iodide species in simulated Yucca Mountain groundwater at concentrations ranging from 5 to 0.1 ng/mL. We are currently developing the HPLC-HR-ICPMS technique to allow the determination of the oxidation state of trace-level actinides and size-specific analysis of colloids generated from the corrosion of nuclear waste materials.

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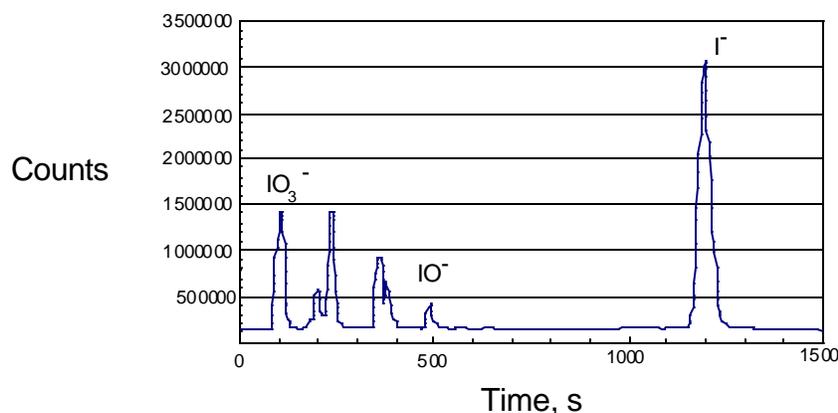


Fig. III-6. Mass Chromatogram of Trace Anionic Iodide Species in Simulated Groundwater Representative of Yucca Mountain Repository

Performance of Titanate Ceramics for Plutonium Disposition

The Department of Energy has selected a two-pronged approach for the disposition of up to 50 metric tons of surplus plutonium. Approximately 13 metric tons will be immobilized in a titanate ceramic; the balance will be fabricated into a mixed oxide fuel and irradiated in commercial light water reactors. Members of the Chemical Technology Division are conducting research to support qualification of the ceramic waste form for disposal in the proposed high-level waste repository at Yucca Mountain.

Part of this qualification effort is to understand the microstructure of the ceramic, and then relate the corrosion behavior of the ceramic to the microstructure. Phases that are typically present in the ceramic include pyrochlore [(Ca,Gd,Pu)(Hf,Pu,U,Gd)Ti₂O₇], the related phase zirconolite, Hf-bearing rutile [(Ti,Hf)O₂], brannerite [(U,Pu,Gd)Ti₂O₆], and minor amounts of PuO₂. A state-of-the-art scanning electron microscope is used to characterize the ceramic.

As part of the testing program, a series of corrosion tests with crushed ceramic (100-125 μm) was completed over a two-year period. The release rates of Pu and Gd from a titanate ceramic during corrosion tests increased rapidly after one year of reaction (Fig. III-7). In contrast, the release of Ca increased linearly. Four possible processes could explain the increasing release rates of Pu and Gd:

- Release of colloids from the waste form might lead to an increase in the measured concentrations of Pu and Gd. The colloids observed in leachates

appeared to be small pieces of ceramic. If the colloids were responsible for the increased Gd and Pu releases, then Al, Ca, Ba, Zr, and Ti release would also increase. Since this was not observed, colloids were probably not responsible for the Gd and Pu behavior.

- Precipitation of solids during testing would decrease the concentration of important elements in solution, possibly leading to an increase in the corrosion rate. However, few precipitates were observed on the reacted ceramic, and they seldom contained major ceramic elements.
- An increase in surface area during tests could have served to increase corrosion. If the surface area increased, then the release rates of all elements would increase. Because this is not observed, an increase in reactive surface area does not adequately explain the observed Gd and Pu release.

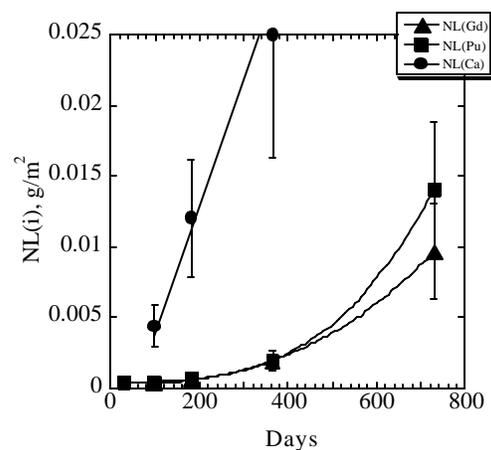


Fig. III-7. Normalized Mass Losses, NL(i), for the Zirconolite-1 Ceramic as a Function of Time

- Dissolution of a less-durable phase is the most likely explanation for the increasing Pu and Gd release. Previous results showed that brannerite dissolves faster than other titanate phases, and brannerite contains both Pu and Gd.

Particles of the ceramic recovered from the two-year corrosion test were examined with scanning electron microscopy. In particular, we were interested in any changes in the brannerite during the test. In the unreacted ceramic, brannerite is surrounded by PuO_2 (Fig. III-8, left). In the reacted ceramic, voids surrounded PuO_2 (Fig. III-8, right); little brannerite was found in the reacted sample.

This absence of brannerite in reacted ceramics is consistent with the Pu and Gd release behavior in these same tests. If the Pu- and Gd-bearing brannerite dissolves faster than any of the other phases in this ceramic, then Pu and Gd would be released at a higher rate than Ca.

The apparent increase in the dissolution rate of brannerite with increasing test duration is somewhat difficult to explain. One possible explanation is that the reacting surface area of the ceramic increased as test duration in-

creased. As a brannerite grain dissolved, voids would have been generated. These voids could have enlarged and connected existing pores. Development of interconnected porosity would have allowed water to move more freely through the ceramic and provided access to a larger surface area of brannerite.

In sum, the dissolution of one phase, brannerite, was shown to control the release of Pu and Gd from this titanate ceramic. On the basis of this conclusion, the absence of brannerite in the final immobilization ceramic would lead to significantly lower Pu and Gd releases. Therefore, we have recommended that steps be taken in the fabrication procedure to minimize the amount of brannerite in the final immobilization ceramic.

ANL Participants

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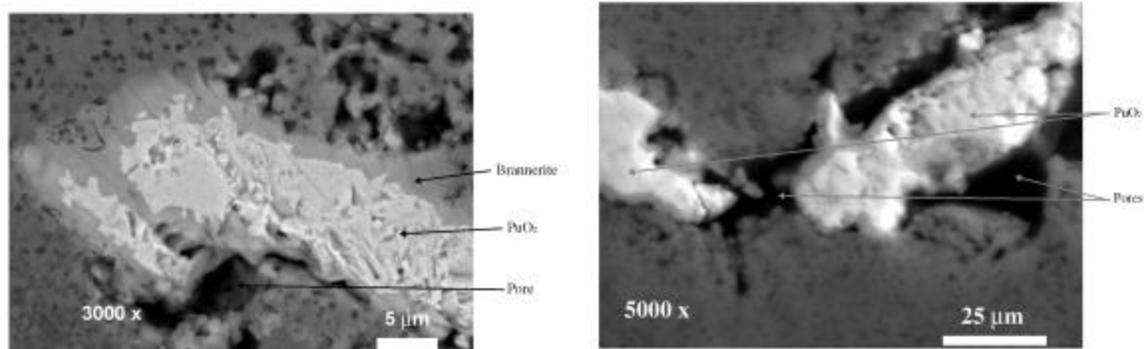


Fig. III-8. Scanning Electron Micrographs of Unreacted Titanate Ceramic Showing Brannerite Surrounding PuO_2 (left) and Particle of the Same Ceramic after Two Years of Corrosion under Product Consistency Test-B Conditions. Note voids surrounding the PuO_2 (right).

Colloidal Release of Plutonium Dioxide from a Ceramic Waste Form

Argonne has developed an electrometallurgical process to convert spent sodium-bonded nuclear reactor fuel into waste forms that can be disposed in a high-level waste repository. One of the waste forms is a ceramic material that consists of about 75 mass% sodalite (incorporating most of the salt), 25 mass% glass binder, and small amounts of halite, clay, and oxides. The qualification of the ceramic waste form (CWF) for disposal requires that ANL identify the physical form and the amounts in which plutonium is released during corrosion of the CWF.

Samples of CWF were prepared with nonradioactive fission product elements as well as the actinides uranium and plutonium. Structural characterization and corrosion tests were performed to determine the effects of uranium and plutonium on the CWF microstructure and corrosion behavior and to determine the release behavior of U and Pu.

The microstructure of the U/Pu-doped CWF was the same as that of nonradioactive CWF with one additional phase. Clusters of polycrystalline 0.020-0.050 μm particles of $(\text{U,Pu})\text{O}_2$ were observed within the glass, usually very near glass-sodalite boundaries. Since these $(\text{U,Pu})\text{O}_2$ particles could be released into aqueous solution as colloids, corrosion testing of the U/Pu-doped CWF was carried out using the Product Consistency Test (PCT), a test method that exposes a large surface area and that can be used to identify colloids in solution. Crushed, sieved, and washed CWF samples were immersed in demineralized water for 7 days to a year at 90 or 120°C. Following each test, solutions were removed and

passed sequentially through 0.45- μm , 0.10- μm , and 0.005- μm filters. The 0.45- μm filtrates were examined by dynamic light scattering and transmission electron microscopy (TEM).

The main conclusions from these tests were as follows:

- Almost all plutonium is released from U/Pu-loaded CWF as colloidal-sized $(\text{U,Pu})\text{O}_2$ particles or as material fixed on test vessel walls. The $(\text{U,Pu})\text{O}_2$ particles are usually attached to amorphous aluminosilicate colloids, as shown in the TEM image of material on a holey carbon grid (Fig. III-9).
- The releases of matrix elements and trace elements as functions of test duration and temperature were similar to corresponding releases from the nonradioactive CWF.
- The largest fractions of the released plutonium were deposited on vessel walls and in the colloidal size range of 0.005-0.10 μm . The mean normalized releases are shown as a function of particle size range in Fig. III-10.

The corrosion tests of U/Pu-loaded CWF have demonstrated the following:

- Microstructural characterization of heterogeneous waste forms must be carried out prior to corrosion testing in order to guide the choice of corrosion tests and to interpret the results of those tests.

- The techniques of sequential filtration, dynamic light scattering, and TEM are appropriate to characterize colloidal releases from heterogeneous waste forms.

ANL Participants

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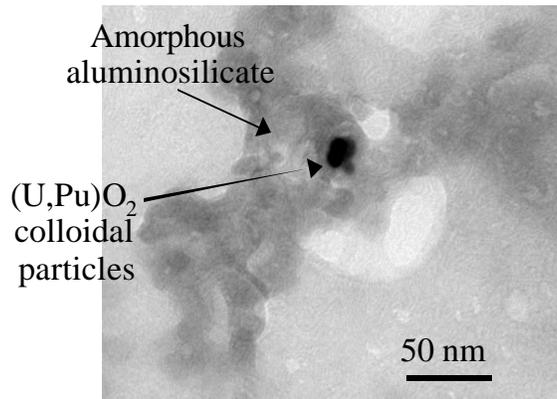


Fig. III-9. Transmission Electron Micrograph of (U,Pu)O₂ and Amorphous Aluminosilicate Colloidal Particles Released after 28 Days in 120°C PCT of Ceramic Waste Form

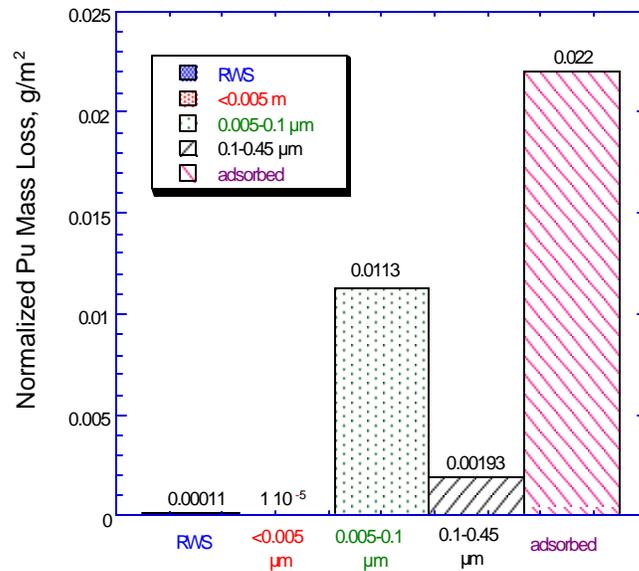


Fig. III-10. Normalized Plutonium Mass Losses after 7 Days in 120°C PCT with Ceramic Waste Form. Bars show rapid water soluble (RWS), sequential filtrate, and adsorbed fractions. Averaged from triplicate tests.

Corrosion Mechanisms of a Bioceramic

The chemical durability of dental ceramics is an important factor in their clinical performance. Under service conditions, dental ceramics are exposed to a wide variety of aqueous environments. The chemical durability of silicate dental ceramics depends on their composition and their microstructure (i.e., the arrangement of crystals). While dental materials must have good long-term corrosion behavior *in vivo*, a great deal of useful information can be gathered through *in vitro* laboratory corrosion studies.

The CMT Waste Materials Research Department is a leader in the study of aqueous corrosion of ceramics and glasses. Recently, we have applied this expertise to a dental ceramic with the goal of describing the processes involved in its corrosion. If these processes are understood, then the dental ceramic can be altered to minimize their impact. For example, the chemical durability of the ceramic might be improved by the replacement of Na and K with Ca to minimize ion exchange, or the addition of Al to minimize matrix dissolution. In addition, changes in the fabrication procedure might improve the microstructure of the dental ceramic.

The corrosion tests in this study were conducted according to the MCC-1 procedure at 90°C for 1, 3, 5, 7, and 14 days. At the end of the test, the pH and cation concentrations of the leachate were measured.

Microscopic examination of a polished cross section of a fluorocanite dental ceramic showed that the microstructure was heterogeneous with two phases present. The interior of the monolith contained tightly packed, fine-grained canasite with glass

between the crystals (area A in Fig. III-11). The microstructure near the edges was quite different and contained large regions of glass and crystals of varying orientations and sizes (area B in Fig. III-11). The cooling history of the dental ceramic, which differs slightly for the edges of the monolith compared with the interior, is the most likely cause of the microstructure.

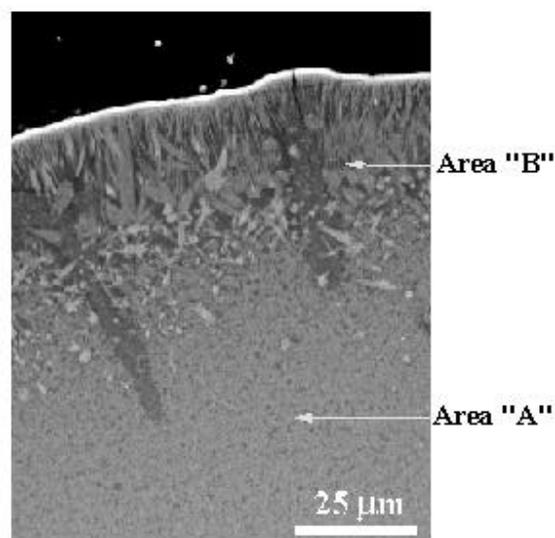


Fig. III-11. Scanning Electron Micrograph of an Unreacted Fluorocanite Dental Ceramic

The losses of five elements from the dental ceramic were quantified as the normalized mass loss $[NL(i), \text{ in } \text{g}/\text{m}^2]$ (amount of ceramic dissolved, based on elemental release, divided by the sample surface area). As shown in Fig. III-12, the $NL(i)$ values for each of the elements increased rapidly from 1 to 7 days. The corrosion rates based on these data were constant between 1 and 7 days and ranged from 0.15 to 0.36 $\text{g}/(\text{m}^2\cdot\text{day})$. These results suggest that the dental ceramic corroded at the maximum attainable rate at the given test conditions.

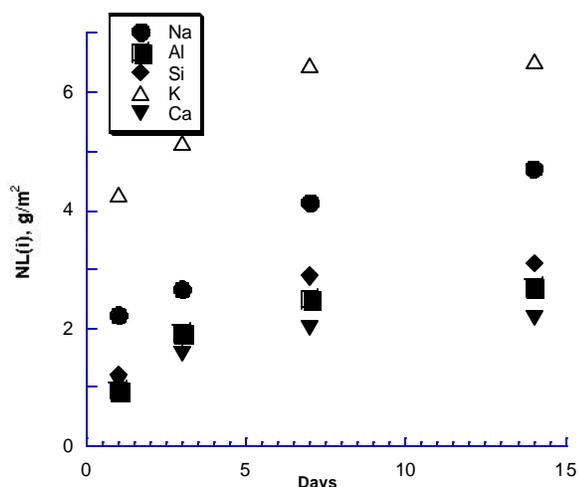


Fig. III-12. Normalized Mass Losses for Several Elements as a Function of Reaction Time for Fluorocanassite Dental Ceramic

The corrosion rates based on Si, Al, and Ca were similar and are lower than those based on Na and K. Because any calcium released was from dissolution of canasite, the corrosion rate based on calcium [0.15 g/(m²·day)] represents the corrosion of canasite. On the other hand, the glass contains much more potassium than does the canasite, so the corrosion rate based on potassium [0.8 g/(m²·day)] represents the corrosion of the glass. The release of Na⁺ and K⁺ as well as an increased pH resulted from an ion-exchange reaction between the cations in the glass for H⁺ in the solution. Therefore, the corrosion of the glass was faster than the corrosion of the canasite crystals.

Microscopic examination of a reacted monolith of the dental ceramic gave further evidence of the preferential glass corrosion. The dark, pitted region (area C in Fig. III-13) is reacted glass, and the “top” of another glass-rich region (area D in Fig. II-13) results from glass corrosion.

The glass phase near the cast edges of the dental ceramic monoliths was most affected

by the corrosion. An ion exchange of H⁺ from the solution with K⁺ and Na⁺ from the glass increased the pH and the concentrations of K⁺ and Na⁺. The rate of the ion exchange reaction in the glass is high, about 0.8 g/(m²·day). The rate of canasite dissolution is quite low, about 0.15 g/(m²·day). An improvement in the corrosion behavior of this dental ceramic might result from changes in the fabrication procedure that would reduce the amount of glass regions near the edges of the monolith.

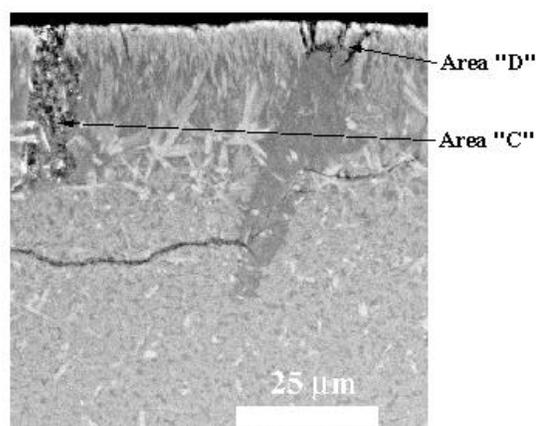


Fig. III-13. Scanning Electron Micrograph of a Reacted Fluorocanassite Dental Ceramic

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Low-Enriched Uranium Foil Targets for the Production of ^{99}Mo

To reduce nuclear-proliferation concerns, the U.S. Reduced Enrichment for Research and Test Reactors (RERTR) Program is working to curtail the world-wide use of high-enriched uranium (HEU) by substituting low-enriched uranium (LEU) for fuel and targets. Low-enriched uranium contains $<20\%$ ^{235}U . Currently, most of the world's supply of ^{99}Mo is produced by fissioning the ^{235}U in HEU targets, generally enriched to 93% ^{235}U . After irradiation, the ^{99}Mo is separated from the uranium and activation and fission products. The RERTR program is cooperating with several international partners in their conversion goals. Researchers in CMT led the target development and chemical recovery activities. We have developed a target that will allow the facile transition from HEU to LEU. In fact, our target has been so successful that many producers have completed feasibility studies and moved into planning for their conversion to LEU.

To yield equivalent amounts of ^{99}Mo , an LEU target must contain five times more uranium than an HEU target. Therefore, a denser form of uranium is required to keep the target geometry the same when changing from HEU to LEU. To this end we developed a highly efficient, cost-effective, annular-style target using LEU metal foil. In the annular target a piece of uranium foil is wrapped around a

tube. This uranium-wrapped tube is then slid inside of another tube. The inner tube is mechanically expanded to create good thermal contact of the uranium foil with target tubes. Finally, the two ends are welded closed.

Fissioning of the ^{235}U generates a large quantity of heat in the uranium foil, up to 200 W/cm^2 . This heat must be dissipated to the reactor coolant. The annular design allows coolant to flow over the outside and through the inside of the target during irradiation. This effectively doubles the heat transfer surface of a non-annular style target, allowing for more efficient cooling. A sketch of a target insertion rig with target is shown in Fig. III-14.

After irradiation, the target is removed from the target insertion rig, the welded ends are cut off, and a longitudinal cut is made along the outside of the target. The inner tube can then be slid out and the uranium foil recovered from the target (see Fig. III-15). Once recovered, the uranium foil is dissolved in acid or digested in caustic, which releases the ^{99}Mo from the irradiated uranium. The ^{99}Mo is then recovered and purified to a very high degree.

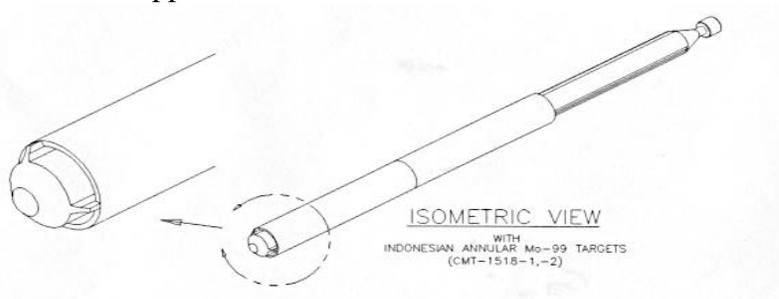


Fig. III-14. Target Insertion Rig with Annular Target

During several test irradiations, we had difficulty recovering the foil from the target tubes. The uranium foil had bonded to the target tubes during irradiation. This occurred because high-energy fission fragments from the surface of the foil flew out and struck the target tubes. Where these fission fragments hit the tubes, they essentially created a tiny spot weld. To prevent the formation of these spot welds, we added fission-recoil barriers to the uranium foil. These barriers stop the fission fragments before they hit target tubes, thus preventing the foil from bonding to the target tubes. The fission recoil barriers are typically 10-25 μm thick. We have developed a method to electrodeposit either nickel or zinc barriers onto the uranium foil. The foil can also be wrapped in thin foils of nickel, zinc, or aluminum. The addition of fission recoil barriers has proven to be very successful in preventing the bonding of the uranium foil to the target tubes.

During irradiation, the uranium grains in the metal foil can grow. This growth is anisotropic, causing the grains to grow in an uneven pattern. This uneven growth can tear the fission recoil barriers, allowing the uranium to bond to the target tubes. To prevent this, we developed a heat treatment that produces a fine, randomly oriented grain structure in the metal foil (see Fig. III-16).

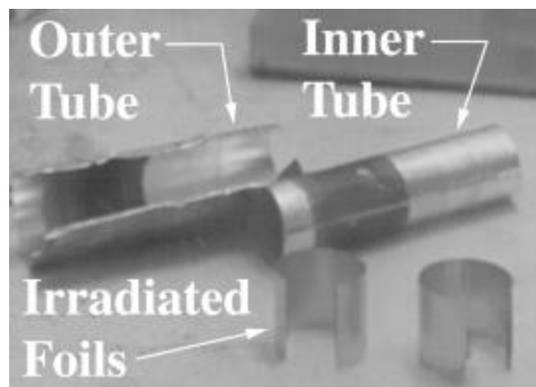


Fig. III-15. Irradiated LEU Annular Target

This treatment minimizes the effects of anisotropic grain growth and has been very successful in preventing the tearing of the fission recoil barriers.

Several annular targets containing LEU foil have been successfully irradiated in Indonesia's RSG-GAS reactor. After irradiation the targets were cut open, and the uranium foil was recovered and successfully processed to produce highly pure ^{99}Mo . Targets have also been fabricated and successfully irradiated in Argentina's RA-3 reactor. These targets were also successfully processed to produce highly pure ^{99}Mo . Finally, LEU metal foil targets fabricated by the Australian Nuclear Science and Technology Organisation based on CMT technology were successfully irradiated in Australia's HIFAR reactor.

Our work has shown that targets using LEU metal foils are a viable substitute for HEU targets. We are currently working with producers of ^{99}Mo to convert their current production processes to the use of LEU targets.

ANL Participants

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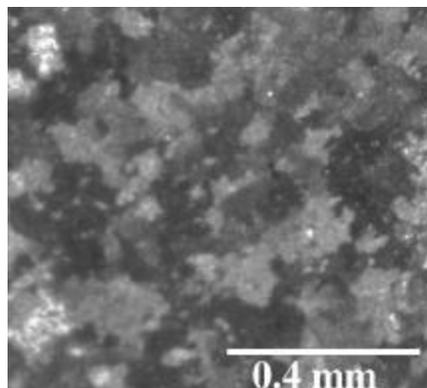


Fig. III-16. Grain Structure of Heat-Treated Uranium Foil

Removal of Cesium from Tank Waste

Savannah River Site (SRS) has 34 million gallons of high-level waste in 48 tanks that needs to be cleaned up. The cesium in this waste is to be removed from the supernate liquid. Subsequently, the cesium will be vitrified for disposal, and the liquid will be immobilized in low-level grout. The initial method chosen by DOE for cesium removal was precipitation with tetraphenylborate; however, this method failed on plant startup. Three new methods are now being developed and evaluated, one of which is caustic-side solvent extraction (CSSX). Because of our many years of experience in solvent extraction, we have been given the responsibility of demonstrating the CSSX process in a pilot-plant centrifugal contactor.

In preparation for this demonstration, we modified our laboratory-scale contactors (2-cm dia rotors) so that they achieved the desired stage efficiency of $\geq 80\%$ (Fig. III-17). We also added eight contactor stages to the existing unit of 24 stages and designed a flowsheet for testing the CSSX process in the modified 32-stage unit. Calculations indicated that this flowsheet should meet the process goals of (1) cesium decontamination by a factor of 40,000 and (2) cesium concentration in the strip effluent by 15 times.

Proof-of-concept tests have now been completed in this pilot plant facility. The results demonstrated a cesium decontamination factor of greater than 40,000 (Fig. III-18), as well as cesium concentration in the aqueous strip effluent by a factor of 15. Successful attainment of both process goals was essential to continued interest in solvent extraction as a method for removing cesium from the SRS high-level waste. In the next year, a five-day flowsheet test will be

carried out to further evaluate the CSSX process. One of the three final processes will be selected by DOE before the end of FY2001.

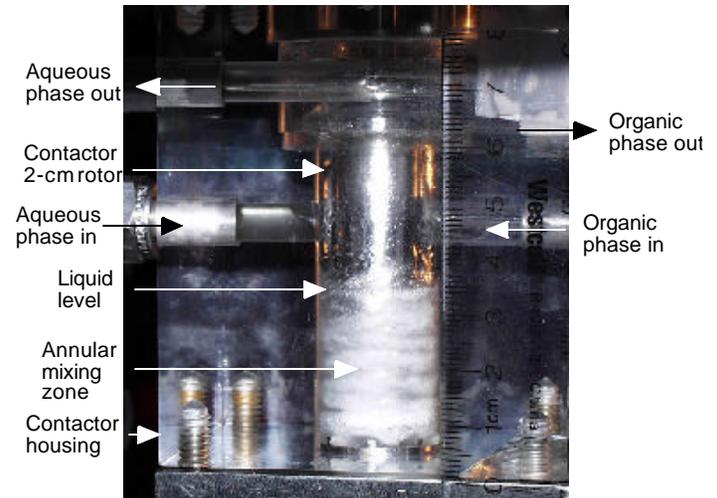


Fig. III-17. Annular Region of 2-cm Contactor during Testing. Intense mixing and a high liquid level in the annular region of each stage are required for efficiencies of 85 to 90%.

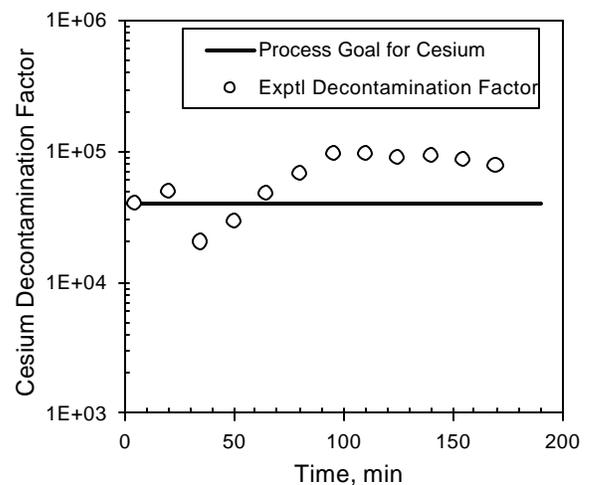


Fig. III-18. Cesium Decontamination Factor during Testing of the CSSX Flowsheet. The cesium decontamination factor quickly reaches the required goal of =40,000.

ANL Participants

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A Cleaning and Decommissioning Process Based on Organo-phosphonic Acid

Many of the more than 100 aging nuclear reactors in the U.S. will be retired from service within the next 40 years. The estimated cost for the decontamination and decommissioning (D&D) of these nuclear facilities is in the billions of dollars. Due to the limited number of disposal sites around the country, high costs, and the liability associated with handling radioactive materials, nuclear utilities have a strong incentive to make use of efficient cleaning and D&D processes for coolant pipes, steam generators, evaporators, tanks, etc.

The current D&D processes are ineffective at removing the oxide scales that form on component surfaces. We have developed a novel chemical cleaning process based on 1-hydroxyethane-1,1-diphosphonic acid (HEDPA), which selectively dissolves metal oxides from metallic surfaces and minimizes radioactive waste streams. The HEDPA process consists of multiple stages: dissolution, concentration/recycle, liquor processing, and preparation of the final waste form. The HEDPA-based process has several advantages over traditional methods: lower operation temperatures, shorter cleaning times, and fewer toxic products resulting in the reduction of waste products.

According to the fundamental rate equation, increased dissolution of iron oxide can be attained by increased reduction of Fe^{3+} , increased acidity, and increased Fe^{3+} chelation. The HEDPA process has all three desirable characteristics. Minerals such as magnetite, hematite, ferrite, and other iron-rich spinel phases can be dissolved while the base-metal substrate is unaffected. The HEDPA molecule thermally decomposes into innocuous species—a metal phosphate

phase, CO_2 , and H_2O . Similarly, the reducing agent we have found that works with HEDPA, sodium formaldehyde sulfoxylate (SFS), decomposes to NaOH , SO_2 , and H_2O . This leads to minimal waste generation from the spent solutions.

The HEDPA process was tested with contaminated samples from a pressurized water reactor (PWR). The ability of the HEDPA process to decontaminate stainless steel was demonstrated by the cleanup of the oxide layer that formed on pieces of the PWR primary vessel (A) and the control drive housing (B). The oxide layers were strongly adherent and could not be removed by mild scrubbing.

Figure III-19 illustrates the complete removal of the brown/black oxide scale achieved with piece A. It is evident that the piece has been completely decontaminated of the surface oxides. The decontamination factors (total activity before decontamination divided by that after decontamination) for suspected surface radionuclides were 7.8 for Eu-152, 70 for Sn-113, 79 for Sb-125, 36 for Ag-110m, 111 for Co-58, and 16 for Mn-54.

To better illustrate the contrast between a cleaned and original surface, only half of Piece B was submerged in the HEDPA/SFS solution. The result is presented in Fig. III-20. One can easily discern the interface line between the submerged and non-submerged fraction.

A pilot-scale reactor has been constructed to provide further testing of the dissolution, concentration/recycle, and waste preparation stages, and we continue optimizing the

process for different applications. Compared with available alternatives, this process can provide significant cost savings in the cleaning and D&D of equipment such as evaporators, heat exchangers, and steam generators.

ANL Participants

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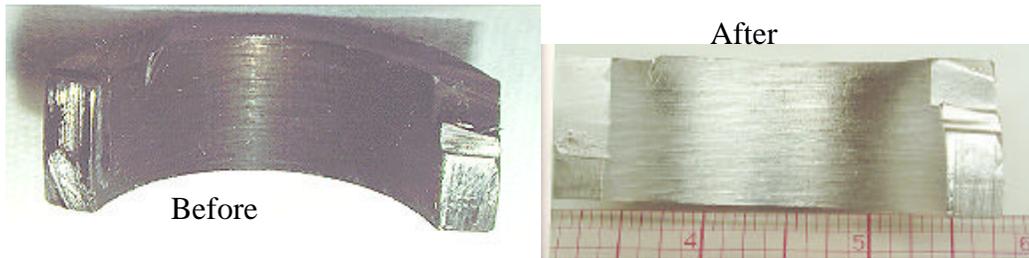


Fig. III-19. Piece A before and after HEDPA/SFS Treatment. The oxide scale has been completely removed. The ruler indicates inches.

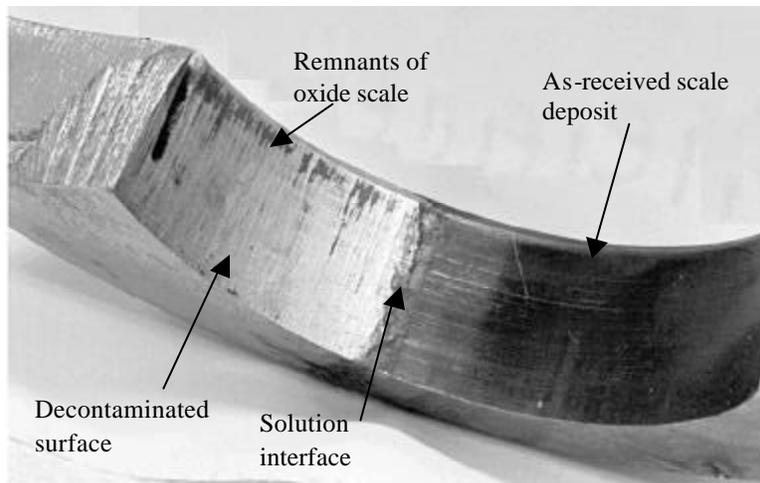


Fig. III-20. Piece B after HEDPA/SFS Decontamination of One-half the Piece for 2 Days

IV

Nuclear Technology

The CMT Division has developed an innovative electrometallurgical process for treatment of spent nuclear fuels for disposal in a geological repository. It is capable of handling most types of spent fuel and is especially intended for fuels at risk of chemical reaction with the groundwater in the repository. These “at risk” spent fuels include metal fuels with various cladding and matrix materials, reactive compounds, and highly enriched fuels. The process uses an electrorefining technique to separate uranium, inert materials, and fission products plus transuranic elements from spent nuclear fuel, greatly reducing the volume of high-level waste and placing disposal costs within the range of practicality. The process is being developed for application to all constituents of the DOE-owned spent nuclear fuel inventory, which amounts to over 2,700 metric tons of uranium and transuranic elements contained in over 150 fuel types.

The process developed by CMT is now being used for treatment of irradiated driver fuel and blanket assemblies discharged from the Experimental Breeder Reactor-II in Idaho and is a candidate technology for treatment of N-Reactor fuel, oxide fuels,

aluminum-based research and test reactor fuels, naval reactor fuels, and molten-salt reactor fuel.

The central feature of the electrometallurgical treatment is electrorefining of the spent fuel in a molten salt electrolyte at 500°C (773 K). The LiCl-KCl eutectic electrolyte is formulated to contain about 2 mol% UCl_3 . A potential is applied between a solid cathode and anodic dissolution baskets containing chopped segments of spent fuel in the molten salt. Uranium, active fission products, and transuranic elements dissolve at the anode, while pure uranium product is deposited on the solid cathode. The fission products and transuranic elements are left behind to accumulate, either in the anodic dissolution baskets (the more-noble fission products) or in the molten salt electrolyte (active fission products and transuranic elements).

The transuranic elements and more active fission products may be extracted by passing the molten salt through anhydrous zeolite. The loaded zeolite may then be combined with a suitable glass frit and hot pressed to make a stable waste form for repository disposal. Fuel cladding, assembly hardware,

and the noble metal fission products left in the anodic dissolution basket are melted together to form a Zr-Fe-based metal waste form for repository disposal.

All the electrorefining process steps were developed in laboratory-scale experiments, and most have been demonstrated at the engineering scale (10- to 150-kg batch size). Recent work has concentrated on developing acceptable metal and ceramic waste forms for the waste products from the electrorefining and on improving the electrorefiner throughput.

The CMT Division also has a lead role in a new multilaboratory DOE project (Accelerator Transmutation of Waste) with the overall goal of using accelerator-driven technology to transmute the spent fuel from commercial reactors into more benign, stable waste forms. For this project, we are investigating solvent extraction and pyrochemical processes that will separate the fission products and actinides in the waste. Subsequently, the fission products are prepared for disposal, the uranium can be either reused or prepared for disposal, and the transuranics are transferred to a waste burner, where they are fissioned into materials that pose mostly short-lived hazards.

Disposition of Plutonium in Waste Forms Produced from Electrometallurgical Treatment of Spent Fuel

Sodalite/glass composite waste forms, pioneered in CMT, are being developed for disposal of radioactive fission elements in salt form from the electrometallurgical treatment of spent nuclear fuel from the Experimental Breeder Reactor-II. The salt waste from the electrometallurgical process consists primarily of an LiCl-KCl eutectic salt loaded with various other fission-product chloride salts. In addition, this salt contains up to 2 mol% actinide chlorides, namely, uranium, plutonium, and neptunium chlorides. The salt from the treatment process is sorbed by zeolite 4A, which has an aluminosilicate cage structure of nominal composition $\text{Na}_{12}(\text{AlSiO}_4)_{12}$ and is known for its ability to contain or “occlude” other species within the cage structure. The zeolite 4A, with its occluded fission-element salts, is mixed with glass and heated to high temperatures and pressures to convert the zeolite to a more thermodynamically stable sodalite form and consolidate the waste form.

Primary considerations in this process are (1) questions of reactivity of the various salts with the zeolite structure as raised by thermodynamic calculations and (2) the fate of the fission elements in the resulting waste form. The objective of this work is to determine the fate of plutonium in this waste form via extended X-ray absorption fine structure spectroscopy (EXAFS) and X-ray absorption near-edge spectroscopy (XANES) synchrotron techniques under conditions that rule out the use of conventional scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The question we sought to answer is whether plutonium will reside within the sodalite or zeolite lattice. To that end, we fabricated simulated waste form samples that contain plutonium and LiCl-KCl salt, with and without fission products present. These samples were then analyzed by EXAFS and XANES to determine the location, size, oxidation state, and form of the plutonium.

In the non-fission-product case, plutonium was found to segregate as Pu(IV) oxide with a crystallite size (mean) of 2.5 nm. With fission products present, the crystallite size was at least 1.3 nm. No plutonium was observed within the sodalite in a sample made from the plutonium-loaded salt without fission products. Less than 15% of the plutonium in a sample made from the plutonium-loaded salt with fission products was segregated with a heavy element nearest neighbor other than plutonium, with inclusion into the sodalite lattice being a possibility as well. We concluded from these results that the plutonium was tied up within the simulated waste sample as a leach-resistant species, as desired.

Figure IV-1 shows the EXAFS-derived spectra for the samples with and without fission products, as well as a plutonium dioxide standard. The peaks for the standards and test samples are essentially identical except for the amplitudes, indicating that the plutonium in the waste form must be at least 95% PuO_2 .

The utility of the EXAFS/XANES technique is clearly evident in unusual systems like the salt-loaded zeolites, where atoms may be

occluded within the latticework of the zeolite molecule and hidden from direct observation by more conventional SEM and TEM techniques. The XANES/EXAFS technique also provides a broad three-dimensional view of the material, whereas SEM and TEM techniques are limited to sampling small areas. In the larger picture, XANES/EXAFS and SEM/TEM techniques act to give us both sides of the same coin and provide a powerful means of characterizing waste form materials.

ANL Participants

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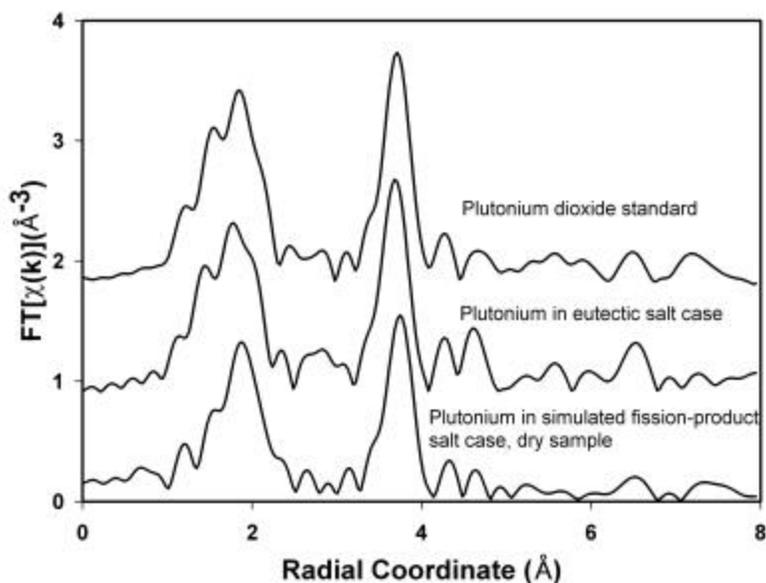


Fig. IV-1. Radial Distribution Data from Fourier Transform (FT) of EXAFS Scaled Oscillations for the Two Types of Experimental Samples and the Matching Pu(IV) Dioxide Standard

Development and Testing of Metal Waste Forms

Metal waste forms have been developed at CMT for the disposal of the metallic waste resulting from the electrometallurgical treatment of spent nuclear fuel. This metallic waste includes cladding hulls and assembly hardware from the treated spent fuel, along with small amounts of noble-metal fission products and actinides. The waste is consolidated by melting at 1600°C under an argon atmosphere and cast into ingots.

The waste form composition differs depending on the type of spent fuel. Stainless steel-15 wt% zirconium (SS-15Zr) waste forms were developed for stainless steel-clad fuels, such as the spent fuel from Experimental Breeder Reactor-II (EBR-II) currently being treated at Argonne-West in Idaho. Zirconium-8 wt% stainless steel (Zr-8SS) waste forms were developed for Zircaloy-clad fuels (e.g., N-Reactor fuel) or zirconium-based fuels, such as the proposed fuel for treatment by the accelerator-driven transmutation of waste. Other metallic waste forms, such as stainless steel-molybdenum alloys for Mo-rich spent nuclear fuels (e.g., Fermi reactor fuel), are also being developed and evaluated.

For disposal in a geologic repository, waste forms in general must meet certain guidelines with respect to physical characteristics and consistency, and they must demonstrate acceptable corrosion behavior. Over the past several years, CMT has played an active role in characterizing the processing-microstructure-property relationships of the metal waste forms. Important achievements of past years include the following:

- the determination of process parameters for ingot production,

- characterization of microstructures, including the distribution of fission product and actinide elements,
- studies of corrosion behavior,
- measurements of mechanical and thermophysical properties, and
- assessment of phase stability with the waste form alloys.

The data for the SS-15Zr waste forms were documented in a handbook to meet the goals established for the EBR-II Spent Fuel Treatment Demonstration.

Our recent experiments have been focused on supporting the qualification of the SS-15Zr waste form for disposal. This work has included the generation of data needed for repository performance assessment and for a model of waste form corrosion. Corrosion experiments have been conducted with SS-15Zr waste form alloys to determine

- uniform and localized corrosion behavior (e.g., pitting and crevice corrosion), and
- corrosion mechanisms that delineate the pathways of radionuclide release from the waste forms.

Results of immersion corrosion tests (based on a standard procedure of the American Society for Testing and Materials, ASTM C1220) have shown that SS-15Zr alloys are very resistant to corrosion in repository-relevant solutions. Figure IV-2 shows the typical alloy dissolution data in J-13 solution, which represents the groundwater at the Yucca Mountain geologic repository. The corrosion resistance of the SS-15Zr alloys after 40 days is believed to arise from

the formation of oxide layers that passivate the metal surface.

Corrosion layers have been observed on SS-15Zr alloys during immersion corrosion tests (90 to 200°C), air-oxidation tests (200 to 700°C), and steam-oxidation tests (200°C). Alloy corrosion behavior under these experimental conditions is governed by the corrosion behavior of the iron-based solid solutions (ferrite and austenite) and ZrFe₂-type intermetallics present in the microstructure (see Fig. IV-3).

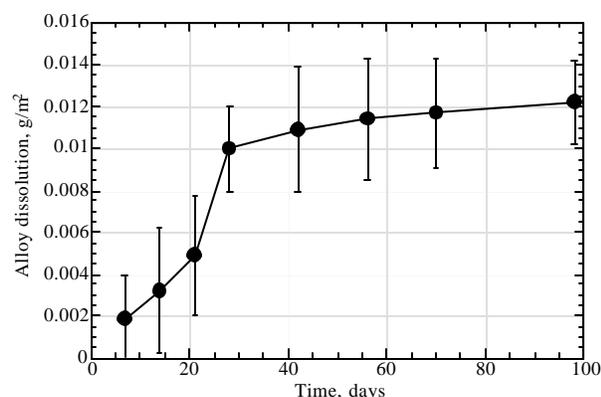


Fig. IV-2. Dissolution of SS-15Zr Alloy in J-13 Solution at 90°C in J-13 Groundwater

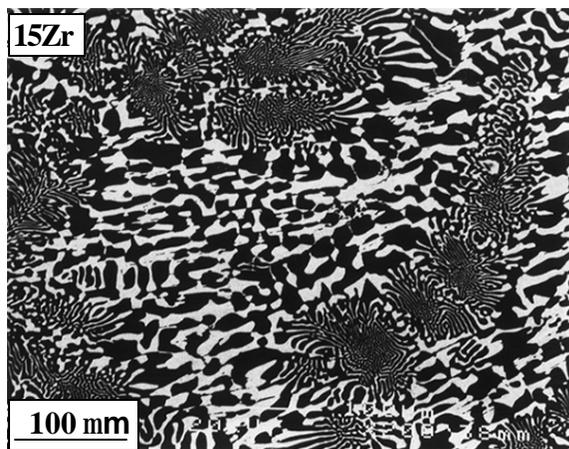


Fig. IV-3. Typical Microstructure of a SS-15Zr Alloy. The dark phase is mainly ferrite (an iron-based solid solution), and the bright phase is ZrFe₂-type intermetallics.

The corrosion layers that form on the various phases are being studied by Auger electron spectroscopy, analytical electron microscopy, and X-ray diffraction. A typical transmission electron microscopy image from a ZrFe₂-type intermetallic sample that was oxidized in 200°C steam showed a multi-layered oxide (see Fig. IV-4).

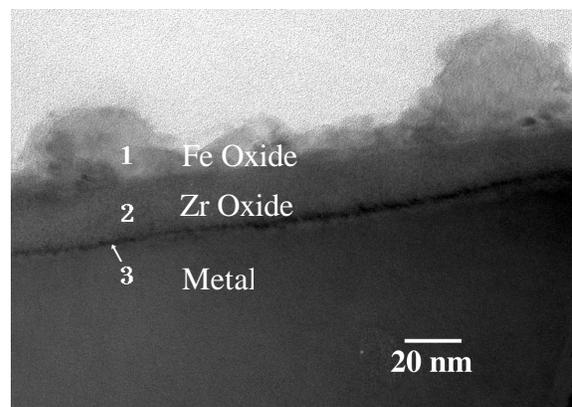


Fig. IV-4. Corrosion Layers on a ZrFe₂-Type Intermetallic Tested in 200°C Steam

The layer adjacent to the metal was dense, adherent, and amorphous and is believed to be a sub-stoichiometric Zr oxide. Above the Zr oxide layer was a porous, crystalline Fe-oxide layer. A qualitative mechanism has been formulated to describe the corrosion layer formation. These mechanistic understandings will be incorporated into models being developed to quantify waste form corrosion over geologic time frames.

ANL Participants

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Development of Fabrication Process for Ceramic Waste Form

A ceramic waste form has been developed in CMT to immobilize salt-borne wastes from the electrometallurgical treatment of spent nuclear fuel from Experimental Breeder Reactor-II (EBR-II). The objective of this CMT effort is development of a full-scale fabrication process for the ceramic waste form.

The electrometallurgical treatment process includes a set of operations designed to break down spent nuclear fuel, recover refined uranium metal, and segregate the radioactive waste constituents into two waste forms: a glass-ceramic composite and a metallic alloy. The key operation is the electrorefining of uranium metal in a molten salt electrolyte (LiCl-KCl eutectic) at 500°C. During electrorefining, transuranics (e.g., Pu, Np, and Am) and other fission products (e.g., Cs, Sr, and Ce) are oxidized to form soluble chlorides in the electrolyte. This electrolyte salt must be disposed of from time to time for any of several reasons, including the buildup of radionuclides. At that point, these salt-borne wastes are immobilized by ion exchange in zeolite 4A, an aluminosilicate mineral with a cage-like crystal structure. The salt-loaded zeolite is a loose granulated powder that is mixed with 25 wt% glass frit, and that mixture is consolidated into a monolithic waste form. The zeolite transforms into sodalite, another aluminosilicate mineral, at processing temperatures greater than 600°C.

Hot isostatic pressing (HIP) was developed in CMT as the primary fabrication method for the ceramic waste form, and it has been demonstrated at sample sizes up to ~140 kg for simulated ceramic waste forms and up to ~2 kg for EBR-II salt-borne wastes.

However, significant safety and other issues make the full-scale (250 kg) implementation of the HIP method undesirable.

Over the last three years, CMT has developed an alternative to the HIP process, designated as “pressureless consolidation.” In this method, the salt-loaded zeolite and glass materials are processed at ambient pressure to provide a strong monolithic sodalite-glass composite waste form; the baseline thermal profile has been set at 915°C and 16 h. Densification is possible without HIP pressure because of the wetting and infiltration behavior of the near-molten glass into the sodalite granules. Figure IV-5 shows a 10-kg sample fabricated with pressureless consolidation.



Fig. IV-5. Prototypic 10-kg Ceramic Waste Form Made by Pressureless Consolidation

An intense multi-divisional development effort, coordinated by CMT, came to a climax in May 2000 when pressureless consolidation was selected by a review committee over HIP as the reference method for full-scale implementation of ceramic waste form processing. Work continues on

Nuclear Technology

evaluation of the densification mechanism and optimization of processing parameters.

ANL Participants

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Electrorefining Throughput Studies

Electrorefining is a metallurgical separation technique that has been used to recover uranium from fission products and other components of spent fuel from the Experimental Breeder Reactor-II (EBR-II), as well as to purify impure plutonium metal. The technique is well suited to this application because the separation is based on changes in oxidation state and is accomplished by the addition or removal of electrons at electrodes rather than the use of chemical oxidizing or reducing agents, which can significantly increase the volume of waste generated.

For the last six years, we have mounted a significant effort to increase the throughput of this process as it is applied to the treatment of spent EBR-II fuel. In that time we have moved from a small prototype device to a working unit that was demonstrated successfully at a throughput of 150 kg uranium/month with actual spent fuel in the Fuel Cycle Facility at ANL-West. The throughput still needs to be substantially increased, however, to handle the large inventory of EBR-II blanket fuel and other spent metal fuels at DOE sites. The basic electrochemistry of the process is now well understood and optimized. Consequently, increasing the throughput has focused primarily on improving the engineering of the process.

In the high-throughput electrorefiner design, uranium is loaded into anode baskets that rotate in a channel between cathode tubes. The anode assembly and the cathode tubes are submersed in a molten LiCl-KCl eutectic. The salt also contains 5 to 7 wt% uranium cations. Uranium and the elements in the fuel that are less noble than uranium are oxidized at the anode and form cationic

species that dissolve in the molten salt. Uranium cations are then reduced at the cathode, and the reduced uranium metal deposits on the cathode surface. Scrapers mounted on the rotating anode basket assembly dislodge the electrodeposited uranium, which then falls to the bottom of the unit where it is collected.

Figure IV-6 presents a cross-sectional rendering of the high-throughput concept. This drawing shows 12 anode baskets with attached scrapers in the unit. Four cathode tubes form three channels within which the anode baskets rotate. After being scraped off the cathode tubes, the uranium product is collected in a basket attached to the bottom of the outer cathode tube. Figure IV-7 is a photograph of the cathode and anode baskets for a high-throughput unit (Mark V) built at CMT.

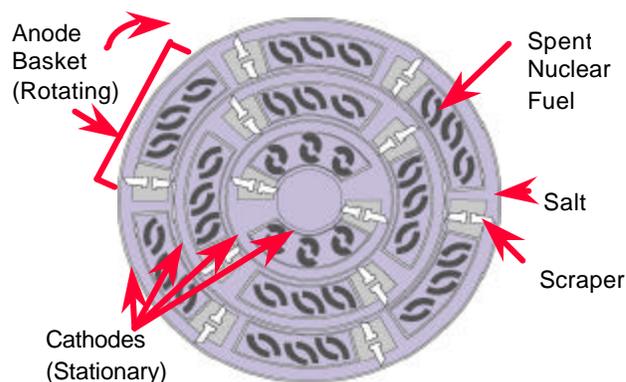


Fig. IV-6. Cross-Sectional View of High-Throughput Electrorefiner Design

An operating profile has been identified that makes it possible for a single high-throughput module, with 10-in. (25-cm) diameter, to recover uranium from spent EBR-II fuel at an average rate of nearly half a kilogram per hour. In the Fuel Cycle

Facility at ANL-West, four of these units are operated in a single process vessel. One of the key steps in the operating profile is a periodic reversal of the current to remove a dense layer of uranium that builds up on the surface of the cathode and is not dislodged by the scrapers.

Operating parameters that have been optimized include anode rotation rate, amount of charge passed between periodic current reversals, current levels, and voltage limits.

The operating experience gained with the high-throughput modules at ANL-West, as well as further tests at CMT, have contributed to the design of a next-generation high-throughput electrorefiner that should be capable of treating as much as 20 metric tons of uranium per year.

This new design features a peripherally driven anode assembly, independent

removal of the product collector, and electrically isolated stripper rods located between the anode baskets. The stripper rods prevent the buildup of a dense uranium layer on the cathode tubes, which was observed in earlier tests to cause the anode drive to stall. Simplified handling is a key design feature of this next-generation design. Remote operation of such a device in a hot cell places some demanding requirements on the design that are not typically encountered in other engineering development efforts.

Some of the key design aspects of this next-generation electrorefiner will soon be tested in small-scale version.

ANL Participants

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Fig. IV-7. Cathode (left) and Anode Basket (right) Assembly for High-Throughput Electrorefiner (Mark V)

Pyrochemical Treatment Technologies for the Accelerator-Driven Transmutation of Waste Program

The CMT Division is developing and demonstrating the chemical separation technologies required for the Accelerator-Driven Transmutation of Waste (ATW) Program. The ATW technology provides an alternative to the direct disposition of spent nuclear fuel by converting the transuranic elements and long-lived fission products contained in this waste to stable or short-lived fission products. Applying this treatment to the nation's spent nuclear fuel would increase the capability of the planned high-level waste repository at Yucca Mountain and, perhaps, eliminate the need for an additional repository. At the heart of the ATW concept is a high-power proton accelerator that produces spallation neutrons which cause the transuranics, contained in fuel assemblies in a subcritical nuclear system, to fission and produce additional neutrons for fission or transmutation reactions. Developing and demonstrating efficient separation technologies for the transuranics and long-lived fission products in spent fuel are paramount to the successful development of the ATW technology.

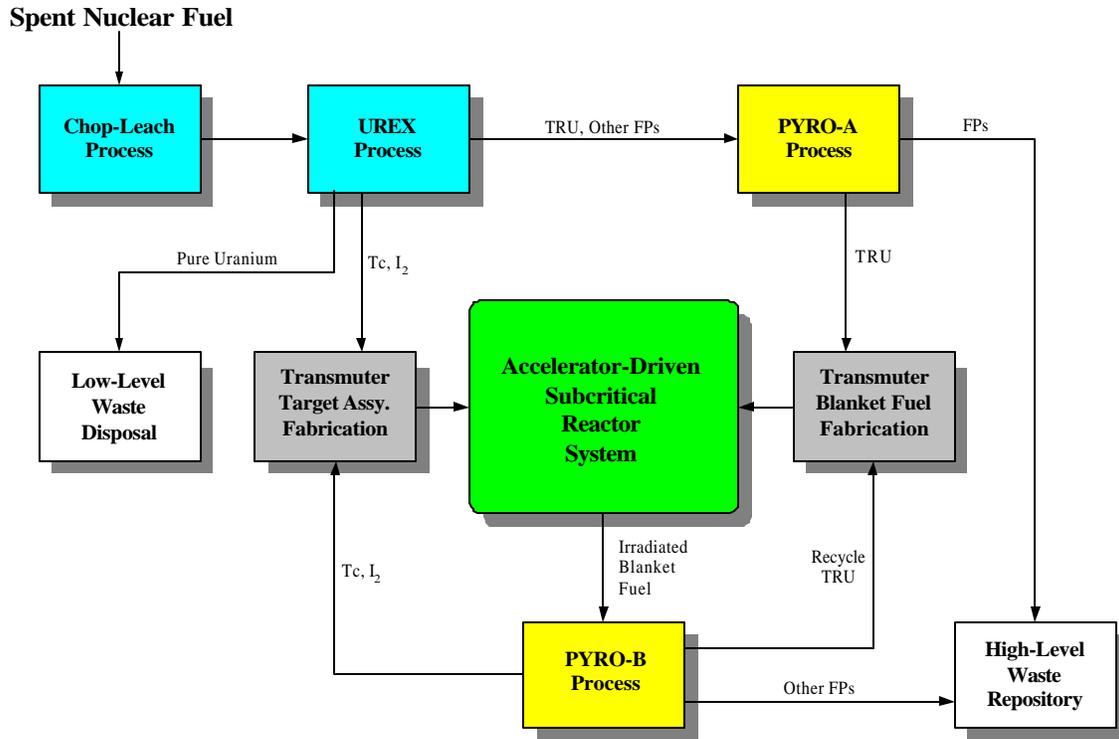
In October 1999, a DOE-directed roadmap identified the research and development requirements for the ATW technology. The roadmap recommended a baseline chemical separations flowsheet that contained three processes (Fig. IV-8): UREX, a solvent extraction process similar to PUREX that separates uranium, technetium, and iodine from the transuranics and other fission products contained in spent fuel; PYRO-A, a pyrochemical process that partitions the transuranics, contained in the UREX product, from the fission products; and

PYRO-B, a pyrochemical process that separates the transuranics and newly generated Tc and I₂, contained in spent ATW fuel, from the fission products for recycle. The CMT Division is evaluating the proposed process options, developing alternative technologies that eliminate problem areas that were identified in the evaluation process, and experimentally demonstrating important process steps. Figure IV-9 shows one of CMT's employees preparing for a test of pyrochemical process viability.

Our present efforts are devoted to investigating the direct electrochemical reduction of oxide fuels, the use of fluoride-based molten salts as processing solvents, methods of chloride volatility separation, and high-efficiency separation technology for minor actinides and lanthanides.

ANL Participants

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FPs = fission products
 TRU = transuranic element

Fig. IV-8. Chemical Separations Flowsheet Developed for the ATW System



Fig. IV-9. Glovebox Facility Used in Pyrochemical Experiments for the ATW Program

V

Basic Science

Basic chemistry research in CMT is being pursued on fundamental issues that relate to the preparation of ceramic oxide materials with high superconducting temperatures, heterogeneous catalysis, homogeneous catalysis, and ion transport mechanisms in lithium batteries. As part of the last two efforts, we are developing and exploiting novel means of nuclear magnetic resonance (NMR) imaging to better understand complex chemical processes.

Our research on superconducting materials focuses on the development of a silver-sheathed $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Ag/Bi-2223) conductor. The aim of this work is to explore novel processing methods that lead to improved performance in terms of current-carrying capacity under conductor operating conditions that prevail in electric power devices. In a collaborative effort with American Superconductor, we have demonstrated a new heat-treatment method for producing Bi-2223 in a silver sheath with fewer impurities and a more uniform microstructure of the type required to obtain high critical current densities in long-length wire.

In the heterogeneous catalysis research, fundamental analysis methods are being integrated with reactor studies to improve the general understanding of solid catalyst systems. The systems being investigated are of fundamental interest to the petroleum, chemical, and transportation industries. Special emphasis is placed on developing and applying new tools (such as synchrotron X-ray techniques) for analyzing catalysts *in situ* under realistic conditions with regard to temperature, pressure, and feed composition.

One of our major projects in heterogeneous catalysis involves developing more robust, higher-activity catalysts for reducing the sulfur content of crude oil by hydrodesulfurization, a crucial component of petroleum refining. Careful control of pore diameters of the catalyst supports to match feed characteristics has allowed us to develop catalysts that are more selective for sulfur removal.

Advances in the homogeneous catalysis research in CMT have led to the discovery of new catalytic processes for converting petroleum-based hydrocarbon feedstocks into alcohols and aldehydes that can be used

as industrial solvents (for example, plasticizers), detergents, and agricultural chemicals. This research centers on modifying the commercial oxo processes used for the hydroformylation of olefins, a family of hydrocarbons. The modifications replace conventional separation of the catalytic products by distillation steps with more energy-efficient separations that use CO₂ supercritical fluid. They also make the oxo processes more environmentally benign by achieving cleaner separations and by replacing liquid solvents with relatively nontoxic, nonflammable, and easily recycled CO₂ gas. For the basic research into ion transport mechanisms in lithium-polymer battery materials, we earlier developed an *in situ* NMR imager. This device is able to follow fast kinetic processes that occur on or near a working electrode by rapidly collecting repetitive NMR images. Significantly, this method achieves the same distance resolution, 2 : m, as the original rotating frame imaging method, yet on a much faster (millisecond) time scale. Our recent work on the NMR imager has expanded its capabilities to work at pressures as high as 30,000 psi (207 MPa) so that it can now be used to study the effects of stress on materials such as polymers.

High Temperature Superconductivity Research

Members of the CMT Division have been engaged in research on high-critical-temperature superconducting (HTS) ceramics since shortly after their discovery in 1986. Unlike earlier materials, which were superconductive only up to a temperature of 10 K, these oxides show superconductivity at temperatures exceeding 100 K. This means that they could find practical application in devices cooled by liquid nitrogen, which is widely used in industry for cryogenic purposes.

Most of this research at CMT has focused on the development of the silver-sheathed $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ composite conductor (Ag/Bi-2223) prepared by the powder-in-tube (PIT) processing technique. This technique involves packing a precursor oxide powder in a silver billet, drawing the billet to a fine wire, rolling the wire to a flat ribbon, and heat treating the ribbon to produce nearly phase pure Bi-2223 with an extended grain colony microstructure that is conducive to the flow of supercurrent through the composite wire. The Bi-2223 formation reaction has been studied extensively by the CMT staff involved in this project over the past ten years. In the course of this research we elucidated many important details of the phase formation and grain growth mechanisms, including

- the connected influence of temperature, oxygen partial pressure, and time on the evolution of superconducting and non-superconducting phases,
- the importance of the Pb dopant on the Bi site in effecting liquid phase formation and grain growth, and

- demonstration/quantification of (1) the reaction-induced texturing mechanism that controls Bi-2223 grain alignment and (2) the texture-directing influence of the silver sheath.

More recently, our work has been focused on exploring new heat treatment strategies based on the concept of controlled thermodynamic states, wherein processing parameters are synchronously adjusted to dissipate nonsuperconducting second phases (NSPs) without perturbing the Bi-2223 formation and grain growth processes. The result of this effort has been the identification of a front-end heat treatment that produces Ag/Bi-2223 composites with better intergrain connectivity and an NSP particle size distribution that is shifted to an appreciably smaller dimensional range (Fig. V-1). The wires subjected to this treatment are superior to conventional PIT-type Ag/Bi-2223 wires in terms of their ability to retain intergranular connectivity during the final deformation and finishing heat treatment of the wire manufacturing process. All of our work on the development of the Ag/Bi-2223 composite conductor has been done in collaboration with American Superconductor under a Collaborative Research and Development Agreement (Fig. V-2). Also participating in this research have been the ANL Materials Science and Energy Technology Divisions.

ANL Participants

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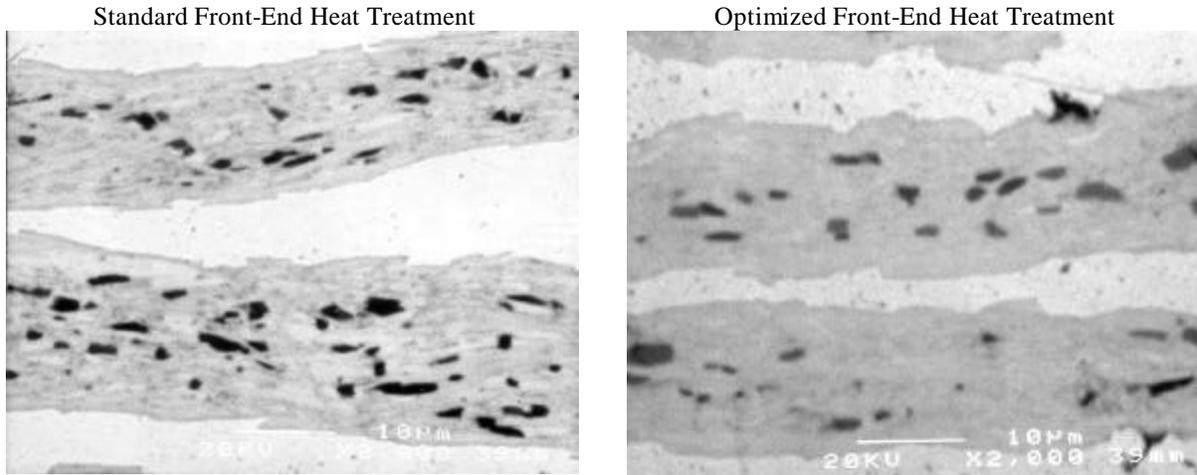


Fig. V-1. Micrographs of Specimens Prepared by Different Heat Treatments. Specimens processed using the optimized front-end heat treatment (right) show less than half as many nonsuperconducting second-phase particles (black phases) as do specimens (left) given a standard front-end heat treatment.



Fig. V-2. High-Temperature Superconducting Motor (1000 horsepower) Produced with Ag/Bi-2223 Wire Made by American Superconductor

New Supports for the Catalytic Removal of Sulfur from Heavy Oils

Hydrodesulfurization (HDS) represents a crucial component of current petroleum refining operations in terms of both environmental and economic considerations. At the same time that crude oils are becoming heavier with increasing amounts of sulfur, product regulations are becoming more stringent. Therefore, new support materials and new active phases for high-performance HDS catalysts are needed.

Because of the large size of the organic molecules in the heavy oil fractions, HDS catalyst supports contain primarily mesopores and macropores. Typical HDS catalysts consist of Co-Mo or Ni-Mo sulfides on an alumina support material. At present, intensive effort is being devoted to the development of new support materials with pore diameters optimized for desulfurization of heavy oil molecules.

One support material, MCM-41, has been shown to be very effective for the removal of sulfur from diesel fuels. This semi-crystalline material was originally developed by Mobil Oil. The constrained pores of MCM-41 increase the effective number of collisions between the sulfur-containing species and the Co-Mo catalyst on the surface of the support. In addition, catalysts with this support are more selective to adding hydrogen directly to the sulfur while not hydrogenating side rings.

Table V-1 compares the performance of MCM-41 with a commercial catalyst (Crosfield 465) tested with a high-sulfur diesel feed of dibenzothiophene in hexadecane. These results show that the CoMo/MCM-41 catalyst has a comparable activity and superior selectivity to the commercial catalyst.

Table V-1. Performance of Hydrodesulfurization Catalyst/Supports at 400°C and 27 atm

Catalyst	Conversion (%)	Selectivity (%)
CoMo/MCM-41	70	84
CoMo/Commercial	77	61

Recent work in CMT has demonstrated that MCM-41 is also effective in removing sulfur from heavy oils, such as slurry oil (Fig. V-3). At 370°C the catalyst works by first reducing the linked sulfur-containing species to small aromatic molecules. These species then enter into the pores, where they are selectively desulfurized by the catalyst. After 3 hours at 370°C, this catalyst had reduced the amount of sulfur in the oil by 50%.

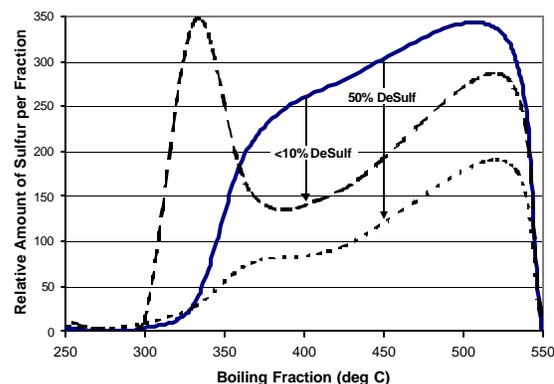


Fig. V-3. Sulfur Concentrations in Slurry Oil from Conoco Inc. (1.25 wt% sulfur) before and after Treatment with CoMo/MCM-41 Catalyst. Solid curve, before treatment; dashed curve, after batch processing for 1 h at 370°C; dotted curve, after batch processing for 3 h at 370°C.

Basic Science

Future work will concentrate on optimizing these catalysts for accomplishing desulfurization of heavy oils and deep desulfurization of gasoline without loss in valuable octane.

ANL Participants

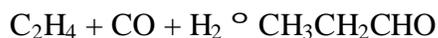
Christopher L. Marshall, Lillian Ruscic, Di Wei, Langqiu Xu, and Kathleen A. Carrado. For further information contact Christopher Marshall at (630) 252-4310 or marshall@cmt.anl.gov.

Catalytic Chemistry in Supercritical Fluids

Over 90% of industrial chemical processes entail the use of catalysts, and nearly half of these are homogeneous catalytic processes in which the catalyst is dissolved in a fluid. We have pioneered in research investigating catalytic reactions in supercritical fluids.

Supercritical fluids such as CO₂ and water offer inexpensive and environmentally benign alternatives to the toxic organic solvents that are commonly used in homogeneous catalysis. An additional advantage is the elimination of energy-intensive distillations necessary for product separations and catalyst recovery from organic solvents. Our recent research has focused on the development of phosphine-modified cobalt catalysts for the hydroformylation of olefins in supercritical CO₂.

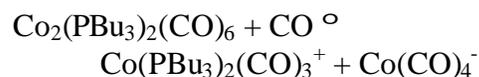
The hydroformylation of olefins, also known as the oxo reaction, is the largest industrial process that is catalyzed by homogeneous catalysts. This process, which is usually conducted in organic media, converts olefins to aldehydes, as exemplified with ethylene:



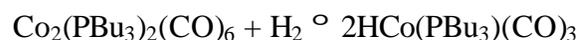
While rhodium catalysts account for most of the C₄ hydroformylation products, oxo reactions producing C₅ and higher products are dominated by cobalt over rhodium catalysts by a ratio of 9 to 1. The primary advantage of cobalt catalysts is their higher reactivity toward internal olefins. The phosphine-modified cobalt catalyst process, which was discovered and is used exclusively by Shell Chemical Co., differs from the unmodified cobalt carbonyl catalyst Co₂(CO)₈ in that the presence of a tertiary phosphine improves the selectivity

toward the linear products. Our interest in Shell's hydroformylation process stems from its industrial importance and the fact that the phosphine ligand provides for easy modification to produce cobalt catalysts that are soluble in supercritical CO₂.

In our earlier study of Shell's phosphine-modified cobalt catalyst system with tributylphosphine in organic solvents, we discovered that [Co(PBu₃)₂(CO)₃][Co(CO)₄] was produced under the oxo reaction conditions according to



The reaction reduces the concentration of Co₂(PBu₃)₂(CO)₆, and, therefore, the concentration of the key hydride intermediate, HCo(PBu₃)(CO)₃. This intermediate species is generated from Co₂(PBu₃)₂(CO)₆ as follows:



This salt formation presented a particular challenge for the development of supercritical CO₂ as a solvent for the phosphine-modified hydroformylation reaction since this supercritical fluid is known to be a poor solvent for salts. We found that all of the cobalt species precipitated from supercritical CO₂ using highly basic phosphines, such as PBu₃.

We approached this problem by fine tuning the phosphine ligand to decrease the basicity with the goal of reducing the driving force for salt formation. Furthermore, the use of fluorine substituents had the additional advantage of enhancing the solubility of the cobalt complexes in supercritical CO₂.

Accordingly, we have synthesized $\text{Co}_2[\text{P}(\text{C}_6\text{H}_4\text{CF}_3)_3]_2(\text{CO})_6$ and showed that it catalyzes the hydroformylation of ethylene (see first reaction above) in supercritical CO_2 with a rate comparable to that of the unsubstituted cobalt carbonyl catalyst. A great surprise was the discovery that with a 1:1 ratio of CO/H_2 gas, this catalyst continued to function until all the CO/H_2 was consumed, as shown by the curve so labeled in Fig. V-4. For comparison, Fig. V-4 also shows the curve obtained for the consumption of H_2 with the unsubstituted $\text{Co}_2(\text{CO})_8$ under similar conditions. This reaction stopped when the CO pressure (the same as H_2) reached 4.5 atm, because of decomposition of the catalyst. The presence of the $\text{P}(\text{C}_6\text{H}_4\text{CF}_3)_3$ ligand apparently stabilizes the catalyst at 100°C without the need of a CO pressure.

We have thus shown that $\text{P}(\text{C}_6\text{H}_4\text{CF}_3)_3$ -substituted cobalt carbonyl catalyst is active in catalyzing the hydroformylation of ethylene. The results further show that the hydroformylation reaction may be carried out at atmospheric pressure. For practical consideration, it is desirable to carry out the reaction at moderate pressures to reduce capital equipment costs. The main advantage for this catalyst is that the reaction may be carried out until all the CO and H_2 are used up, eliminating the need to recycle these gaseous reactants. At the end of the reaction, all that is required is to isolate the products from supercritical CO_2 , a very simple process.

ANL Participants

Michael J. Chen, Robert J. Klingler, and Jerome W. Rathke. For further information, contact Michael Chen at (630) 252-5258 or chenm@cmt.anl.gov.

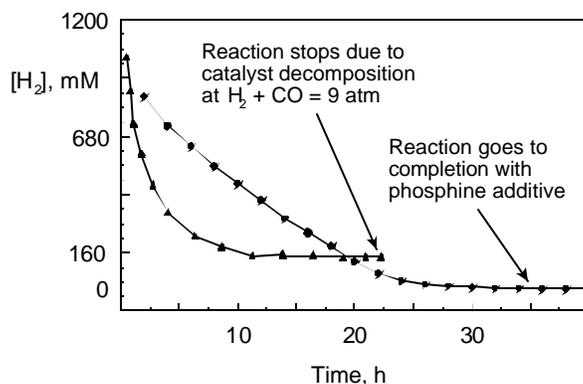


Fig. V-4. Rate Plots for the Hydroformylation of Ethylene with and without Phosphine Additive

Test conditions: 100°C , $[\text{H}_2] = [\text{CO}] = 1.1 \text{ M}$, $[\text{C}_2\text{H}_4] = 2.0 \text{ M}$, and CO_2 partial pressure = 119 atm. Triangles indicate $[\text{Co}_2(\text{CO})_8] = 4.1 \text{ mM}$; circles, $[\text{Co}_2(\text{CO})_6\text{L}_2] = 4.1 \text{ mM}$ and $\text{P}(\text{C}_6\text{H}_4\text{CF}_3)_3 = 74 \text{ mM}$.

Rotational Exchange Gradient Imager Invention

Nuclear magnetic resonance (NMR) analysis is one of the most powerful tools available for the determination of chemical structures and reaction dynamics in homogeneous catalysis. We have invented a rotational exchange gradient imager that extends the capabilities of NMR to the study of heterogeneous catalytic reactions and the development of new materials and processes to make these reactions more efficient. This imager has diverse potential applications, including the development of improved fuel cells and processes for the petroleum and chemical industries.

The rotational exchange gradient imager makes use of magic angle spinning to narrow the broad NMR signals observed for solid samples. Other researchers have used magic angle spinning NMR to study heterogeneous catalyzed reactions at elevated pressures. Several technical problems, however, limit the use of this technique. For flow-through reactions, which include most industrial processes, the need for rotating seals limits attainable pressures to ~80 psi (~5.5 kPa). Glass, plastic, or ceramic pressure vessels are brittle and further limit pressures to less than 100 psi (6.9 kPa). Metal containers are thus necessary for the high pressures used in industrial applications, but they require that a radiofrequency (RF) detector coil be positioned inside the container. Enclosing the RF coil in a metal container complicates the apparatus significantly because the electromagnetic field generated by the RF coil strongly interacts with the electronically conductive surfaces. This electromagnetic interaction reduces the sensitivity of the detector. The device we have invented utilizes a metallic toroid cavity that

circumvents the problem by combining the functions of the high-pressure container (up to 50,000 psi or 345 MPa) and the RF coil into one device.

Figure V-5 illustrates the operation of the rotational exchange gradient imager. The catalyst sample is contained in a ceramic rotor, which is propelled by a jet of gas containing the reactant(s), and rotated around the egress tube at a rate of 1-50 kHz. The stator is a toroid cavity resonator with the egress tube serving as its central conductor. A bleed-off valve and regulator maintain a reduced pressure in the egress tube and draw off the products of the reaction for analysis by gas chromatography, mass spectrometry, or other methods. The circulator pump drives the rotor and produces very high pressures.

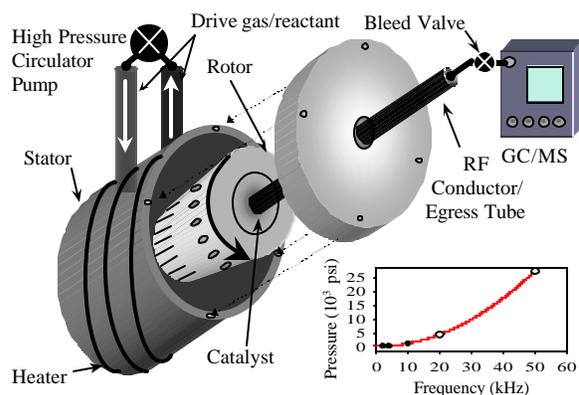


Fig. V-5. Schematic of the Rotational Exchange Gradient Imager. High-pressure carrier gas doped with reactant gases circulates in a closed loop and causes the turbine to rotate at up to 50 kHz. The axis of rotation is inclined at the magic angle (54.74°) with respect to the direction of a static external magnetic field.

The stator and central conductor tube generate the RF magnetic field for the NMR analysis. This design avoids the problem of a metal container interfering with the RF field because the container itself generates the RF field. This geometry has two other significant advantages over a conventional solenoid coil. First, the RF magnetic field is contained within the cavity, so that it can be generated more efficiently. The high efficiency increases the sensitivity of the imager. Second, the strength of the RF field decreases with distance from the center of the stator. As a result, the imager has the capability to record high-resolution NMR spectra for heterogeneous samples as a function of distance on a microscopic scale.

Figure V-6 illustrates the ability of the imager to narrow NMR signals in a sample of poly(isoprene) for easy identification of the hydrocarbon species present. The broad spectrum observed for the static sample is narrowed and shifted upon rotation of the sample at 2.3 kHz. We were thus able to resolve two distinct peaks, corresponding to the alkyl (methyl and methylene) protons at 1.9 ppm and the olefinic protons at 5.4 ppm, in the approximate ratio of 7:1. The enhanced resolution of the different proton signals makes it possible to detect subtle changes in the conformations, dynamics, and packing of molecules subjected to large compressing forces.

The imager has application in tribology and rheology because of its ability to generate stresses in solids and semisolids via centrifugal forces. The centrifugal forces in our device can produce the pressures plotted in Fig. V-5 (lower right), which were calculated for a 100- μm -thick annular shell of a polymer. As shown by the solid circles in Fig. V-5, our prototype apparatus can attain pressures of 200-1000 psi (1.4-6.9 MPa). The open circles project that stresses from

pressures as high as 30,000 psi (207 MPa) can be obtained by using existing commercial rotors. Since stress inside the sample varies with distance from the center of rotation, a radial image of the NMR spectrum maps changes in the sample with respect to stress. A larger variation in stress can be obtained by increasing the rotation rate. In support of a program on development of a lithium-polymer battery, we plan to investigate the effect of polymer deformation for the range of stresses obtainable with our device.

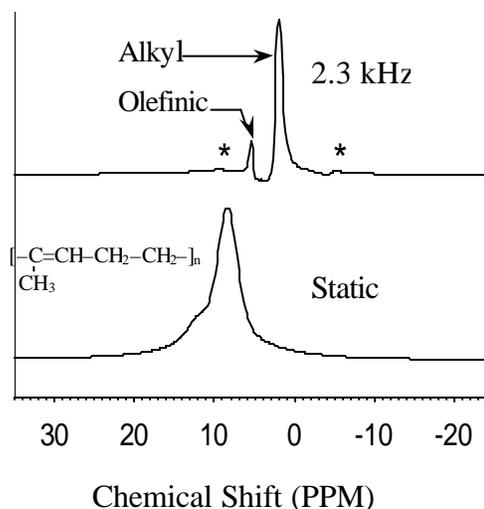


Fig. V-6. Proton NMR Spectra of Polymer Obtained with the Rotational Exchange Gradient Imager at a Spin Rate of 0.0 and 2.3 kHz. The asterisks (*) indicate the location of spinning side bands.

ANL Participants

Rex E. Gerald II, Robert J. Klingler, and Jerome W. Rathke. For further information contact Rex E. Gerald II at (630) 252-4214 or gerald@cmt.anl.gov.

VI

Analytical Chemistry Laboratory

The Analytical Chemistry Laboratory (ACL) operates in the Argonne system as a full-cost-recovery service center, but it has a mission that includes a complementary research and development component in analytical chemistry and its applications. Because of the diversity of research and development work at ANL, the ACL handles a wide range of analytical problems in its technical support role. Some routine or standard analyses are done, but the ACL usually works with commercial laboratories if high-volume, production analyses are required by its clients. It is common for the Argonne R&D programs to generate unique problems that require significant development of methods and adaptation of techniques to obtain useful analytical data. Thus, much of the support work done by the ACL is very similar to applied research in analytical chemistry.

The ACL is administratively within CMT, its principal ANL client, but it provides technical support for many of the other technical divisions and programs at ANL.

The ACL has three groups—Chemical Analysis, Instrumental Analysis, and

Organic Analysis, which together include about 20 staff members. Talents and interests of staff members cross group lines, as do many projects within the ACL. The ACL receives about 1000 jobs annually—many of which involve several samples.

The Chemical Analysis Group uses wet-chemical and instrumental methods for elemental, compositional, and isotopic determinations in solid, liquid, and gaseous samples and provides specialized analytical services. The Instrumental Analysis Group uses nuclear counting techniques to determine the radiochemical constituents in a wide range of sample types, from environmental samples with low radioactivity to samples with high radioactivity that require containment. The Organic Analysis Group uses a number of complementary techniques to separate organic compounds and measure them at trace levels and has performed development work in sensors, chemometrics, and detectors. Together, the ACL groups have a full range of analytical capabilities for performing inorganic, organic, and radiological analyses.

Besides a wide spectrum of advanced analytical instruments, the ACL has a sample-receiving system that allows efficient processing of environmental samples and hazardous and mixed-waste samples, including chain-of-custody procedures. The ACL also has quality assurance and control systems in place to produce analytical data packages that meet the reporting requirements of the Department of Energy (DOE), the U.S. Environmental Protection Agency (EPA), the U.S. Army Corps of Engineers (USACE), and other organizations.

The ACL projects highlighted in this report include

- Method development for the high-precision assay of lithium and aluminum within lithium aluminate ceramic pellets in support of a DOE program on tritium production.
- Preparation of simulated samples of solidified waste and the headspace gas that will occur in the waste-bearing containers destined for disposal in the Waste Isolation Pilot Plant.
- Radioactive waste analysis for various waste sites being remediated under the auspices of the EPA (Region V) and USACE.
- Development of databases accessible through the web in support of a national DOE program to assess the ability of analytical labs to produce high quality data for use in making environmental management decisions.

Modernizing Methods for Chemical Analysis of Lithium Aluminate Ceramics

The Department of Energy has selected light water reactor irradiation of Tritium Producing Burnable Absorber Rods (TPBARs) as its preferred option for tritium production over the next 40 years. The TPBAR assemblies consist of columns of ^6Li -enriched lithium aluminate ceramic pellets that serve a dual purpose of generating tritium and maintaining criticality in the reactor core. A very important aspect of fabricating the assemblies is assuring that the chemical composition and impurity levels of the ceramic pellets are within specified values. Consequently, reliable methods for the chemical analysis of lithium aluminate are required for the program.

The Analytical Chemistry Laboratory (ACL) in CMT first established analytical methods for lithium aluminate when this material was developed at Argonne around 1980 for fuel-cell components and provided analytical chemistry data to DOE contractors when ^6Li -enriched ceramics were subsequently being developed as tritium targets. In 1997, ACL provided analysis support to the Tritium Target Qualification Project (TTQP) at Pacific Northwest National Laboratory, which is assisting DOE in developing systems and capabilities for production-scale manufacture of TPBAR assemblies. We analyzed developmental ceramics and later carried out production lot analyses for a demonstration assembly after a multi-laboratory evaluation exercise failed to identify any other laboratories with acceptable capabilities for determining the major constituents (Li and Al).

The methods currently in place are laborious, time-consuming, and require special apparatus or skills not readily

available in private-sector laboratories. To lower cost, enhance throughput, and allow commercial availability of analytical chemistry for the TPBAR ceramics, we have been investigating alternative methods to replace the wet-chemical methods previously used. One new method developed for dissolving the ceramic involves a microwave-accelerated acid dissolution that exploits recently available commercial technology (Fig. VI-1). A new method being employed for determining Li and Al content is based on inductively coupled plasma-optical emission spectrometry (ICP-OES) and was adopted from the National Institute of Standards and Technology (NIST). Efficient methods for measuring impurities such as carbon, halides, and metals have also been developed.



Fig. VI-1. MARS-5 Microwave System (CEM Corp., Matthews, SC)

Performance of the microwave method was tested by filtering solutions from several ceramics having different process histories and weighing the residues. Filters were 0.2-micron polycarbonate membranes. The method averaged 99.98% dissolution and met our goal of >99.9%. We also met the

analytical goals for major constituents and impurities (see Tables VI-1 and -2).

Efforts are in progress to transfer our new methods to commercial laboratories contracted by the TTQP. Meanwhile, we are using the methods to provide analysis support to ceramic manufacturers developing production-scale techniques for pellet fabrication and to characterize materials DOE intends to use for laboratory quality control during the production decades. The investment made by DOE to

modernize the methods available for analyzing lithium aluminate will return substantial dividends over the program's life.

ANL Participants

Donald Graczyk, Alice Essling, Florence Smith, Susan Lopykinski, Fredric Martino, Doris Huff, and Christine Snyder. For further information contact Don Graczyk at (630) 252-3489 or graczyk@cmt.anl.gov.

Table VI-1. Required Precision and Allowed Bias in Analysis of TPBAR Assemblies for Major Constituents and Impurities

	Measured	Precision, %RSD	Allowed Bias, %
Li Isotopes	6/7 Ratio	0.45	0.40
Li Assay	wt% Li	0.45	0.40
Al Assay	wt% Al	0.45	0.40
Carbon	wt% C	20	25
Halides	F, Cl, Br, I	20	25
Cations & Neutron Poisons	23 Metals	20	25

Table VI-2. Results summary from Li and Al assays of five samples with ICP-OES. The pooled relative standard deviations (precision) are 0.06% for Li and 0.02% for Al. The average percent differences (allowed bias) are -0.03% for Li and -0.06% for Al. These results greatly exceed the goals specified in the above table.

Sample No.	1	2	3	4	5
at.% ⁶Li	7.5	20	30	40	95
Li Assay RSD, %	0.07	0.08	0.04	0.06	0.05
% Diff. from Known	-0.04	-0.09	-0.08	-0.10	+0.07
Al Assay RSD, %	0.01	0.02	0.02	0.03	0.03
%Diff. from Known	-0.03	-0.06	-0.08	-0.10	-0.01

Support for the Waste Isolation Pilot Plant Project

Over the past decade, the Analytical Chemistry Laboratory has provided extensive support to the Waste Isolation Pilot Plant (WIPP) project for (1) development of analytical methods for determining volatile organic compounds in headspace gases and (2) the preparation of simulated samples of headspace gases and solidified wastes.

The Waste Isolation Pilot Plant is a DOE installation located in southeastern New Mexico. It is designed to permanently dispose of transuranic (TRU) radioactive waste left from the research and production of nuclear weapons at the various DOE sites. The WIPP site consists of large interconnecting rooms hollowed out of a salt vein approximately 600 m underground. This facility has a maximum capacity of 175,000 m³ and began to receive waste on March 26, 1999. Over the next 35 years, WIPP is expected to receive about 37,000 shipments of waste.

Before being shipped to the WIPP site, wastes must be characterized to identify the presence of any hazardous materials in addition to the radioactivity. Among other characterizations of the waste containers destined for WIPP, analysis of the headspace gas for specified volatile organic compounds is required. The National TRU Program Office of the Carlsbad Field Office of DOE has established a performance demonstration program (PDP) for laboratories that will participate in the analysis of headspace gas in these containers. The Carlsbad Field Office grants approval only to those laboratories that are successful in analyzing blind audit samples. The ACL was selected as the laboratory to

prepare, analyze, and distribute simulated headspace-gas samples in specially designed stainless steel containers.

During FY2000, the ACL prepared eleven sets of headspace-gas samples (as part of Cycle 14A). Each set consisted of 6-L canisters containing low and high concentrations of analytes, as well as special and duplicate mixtures. A blank containing "ultra zero" grade air was also included in each set.

During the past year, nine sets of ACL-prepared samples were sent for analysis to the participating laboratories: TRUgas, NFT Inc., Idaho Engineering and Environmental National Laboratory (two sets), Rocky Flats Environmental Technology Site, Los Alamos National Laboratory, Savannah River Site, Environmental Protection Agency (at Research Triangle Park), and Fluor Hanford. Of the remaining two sets, one was used for verification analysis, while the other was archived if needed to be sent to a laboratory. The verification analyses involved determination of 29 volatile organic compounds.

Solidified waste (sludge) destined for WIPP must also be characterized for the presence of organic and inorganic hazardous materials, in addition to the radioactivity. As part of the WIPP waste characterization, a performance demonstration program was established in 1995 for analysis of solidified wastes containing hazardous constituents as specified by the Resource Conservation and Recovery Act (RCRA).

The purpose of this ACL effort is to assist in testing the performance of laboratories

seeking to participate in the analysis of solidified transuranic-bearing waste samples for specified metal, semivolatile and volatile organic compounds, and polychlorinated biphenyls. The Carlsbad Field Office approves laboratories for analysis of solid waste samples destined for WIPP, as demonstrated by their ability to successfully analyze blind audit samples.

During FY2000 the ACL prepared approximately 2 kg each of uncemented and cemented samples of simulated "Type 1" solidified waste (the solidified sludge resulting from treatment of waste waters to recover TRU elements). The waste matrix was then supplied to a contractor selected by the PDP coordinator for spiking with metal analytes. The contractor also provided blind audit samples containing semivolatile and volatile organic compounds to participating laboratories. These samples will be added to a suitable matrix, such as sand, for determination of test analytes.

ANL Participants

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Support for Work-for-Others Projects

Since its establishment in 1971 as an analytical chemistry laboratory intended to serve the scientific community at Argonne National Laboratory, the Analytical Chemistry Laboratory (ACL) has been called upon to provide analyses in support of a number of Argonne projects.

Fifteen years ago the ACL was asked to provide analytical expertise as a participating member of the DOE Superfund Environmental Survey Program. The ACL participation in such Work-for-Others (WFO) programs has since grown to include those for other DOE laboratories, the U.S. Environmental Protection Agency (EPA), the U.S. Army Corps of Engineers (USACE), and the National Institute of Standards and Technology. The ACL has also participated in projects for non-government agencies, such as the 3M Company.

The WFO experience with these organizations has been synergistic in that the uniqueness of some of these projects has helped the ACL become a more diversified, experienced, and proficient analytical laboratory. In meeting client needs, the ACL has developed some unique analytical capabilities and laboratory facilities.

Two of the more ambitious efforts in recent years are separate programs involving remediation of waste sites under the auspices of different federal agencies: (1) the EPA Region 5 Office Special Analytical Services (SAS) and (2) the USACE Formerly Utilized Site Remedial Action Program (FUSRAP). Both agencies require a certified/validated organization to serve as a quality assurance laboratory following standardized and defensible methodology;

conveniently located and readily accessible; and having facilities and experienced personnel capable of processing hazardous and radioactive mixed waste of potentially unusual matrices.

The SAS program focuses on the EPA need for a provider of on-call analytical services, with quick turnaround to allow for real-time results contributing to problem solving and site remediation. This work primarily involves the analysis of mixed waste samples submitted to the ACL as part of EPA remediation programs initiated at three sites: Ottawa, Illinois; Belding and Benton Harbor, Michigan; and Chicago, Illinois.

Ottawa was the site of a company that applied luminescent paint containing ^{226}Ra to clock dials. The soil and groundwater samples analyzed by the ACL had been taken from the area of what was the building foundation and surrounding grounds, as well as local hot spots in area landfills where material from the site had been dumped. The samples were analyzed for $^{226/228}\text{Ra}$ by gamma spectroscopy and for isotopic UTh by alpha spectroscopy.

Surplus metal from the Belding and Benton Harbor sites had been sold to an Arkansas foundry and later discovered to be radioactive. The material was tracked to a warehouse that had contained nearly 35,000 radium-painted airplane gauges, compasses, switches, etc., dating from World War II. The waste materials had been shredded, mixed, and packed in one-gallon paint cans, whose geometry posed an analytical challenge in instrument calibration and determination of ^{226}Ra content. The ACL provided accurate gamma spectroscopy results within 24 hours.

The Lindsay Light site was used to manufacture thorium lantern mantles in the Chicago downtown area. As part of the EPA's remediation plan, the ACL analyzed soil samples by gamma spectroscopy and identified ^{226}Ra "hot spots."

The USACE FUSRAP program is a more long-term approach to remediation, with ongoing periodic sampling of FUSRAP sites to determine their environmental status. The ACL involvement covered two USACE districts: Buffalo and Baltimore.

The Buffalo district is responsible for several FUSRAP sites in New York (two in Ashland and one in Niagara Falls), along with a site in Luckey, Ohio. The ACL served the Buffalo district as a quality assurance laboratory for the analysis of ambient matrix samples (e.g., soil, sediment, ground, or surface water) from the remediation sites. These sites are the object of remediation efforts requiring analytical data for making decisions.

The ACL also analyzed samples received through the Baltimore district of the USACE from the site of a former electroplating facility and manufacturer of components from uranium and thorium (in Colonie, New York). Our data for this site helped the Baltimore district ensure the quality of the data previously received from production laboratories analyzing samples taken from the same contaminated site.

The ACL has been successful in meeting the needs of agencies like the EPA and FUSRAP and continues to provide these services as a part of its WFO programs.

ANL Participants

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Lopykinski, and Michael J. Kalensky. For further information contact David W. Green at (630) 252-4379 or green@cmt.anl.gov.

Support for the National Analytical Management Program

Analytical chemistry measurements play a key role in the DOE cleanup efforts. The DOE National Analytical Management Program (NAMP) is charged with assessing the ability of environmental analytical laboratories to provide high-quality analytical data for use in making environmental management decisions. The Analytical Chemistry Laboratory (ACL) has supported the development and implementation of NAMP since 1991.

Starting in 1991, the ACL has developed and implemented the Integrated Performance Evaluation Program (IPEP), which uses information from national performance evaluation programs as a cost-effective indicator of the performance of all analytical laboratories providing data to DOE's environmental management programs. Owing to the success with IPEP, the NAMP work at Argonne National Laboratory expanded to other areas in 1997. In this expanded role, the ACL has developed the NAMP Laboratory Informational Network (NAMPnet), a centralized web-based system that allows personnel within the DOE complex to share pertinent information about the quality initiatives administered by DOE's Office of Environmental Management (DOE-EM). The NAMPnet provides a web interface for users to input and access information about DOE-EM contacts at each site, costs of analyses, laboratory contracts, and audits, as well as individual laboratory performance in national performance evaluation programs. As part of NAMPnet, the ACL maintains *The U.S. Department of Energy Methods Compendium*, a compilation of methods used at DOE sites for analyzing radioactive and mixed waste samples.

The ACL has also provided technical and advisory support to NAMP for two multi-agency efforts. In the first, the ACL has contributed chapters to the *Multi-Agency Radiation Laboratory Protocols Manual*, which provides guidance on the development of new radioanalytical methods and the incorporation of Performance-Based Measurement Systems (PBMS) approaches and planning processes. In the second, the ACL is advising the multi-agency Methods and Data Comparability Board on the design and development of the National Environmental Methods Index, a web-accessible database that allows comparison of methods for determining water quality. This methods index is being developed to support PBMS implementation.

ANL Participants

W. Elane Streets, David W. Green, Jacqueline M. Copple, Anthony E. Scandora, Joseph E. Kulaga, and Ronald R. Kroll. For more information contact W. Elane Streets at (630) 252-4460 or streets@cmt.anl.gov.

VII

Publications and Presentations—2000

The Division's publications and oral presentations for 2000 were entered into a bibliographic database. The pages that follow are a printout of this information sorted into five categories: (1) patents, (2) journal articles, books, and book chapters, (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., and (5) oral presentations at scientific meetings and seminars not referenced in the fourth category.

Patents

Method for the Removal of Ultrafine Particulates from an Aqueous Suspension

D. J. Chaiko, J. P. Kopasz, and A. J. G. Ellison

Patent No. 6,153,103, issued November 28, 2000

Consolidation Process for Producing Ceramic Waste Forms

H. C. Hash and M. C. Hash

Patent No. 6,143,944, issued November 7, 2000

Partial Oxidation Catalyst

M. Krumpelt, S. Ahmed, R. Kumar, and R. Doshi

Patent No. 6,110,861, issued August 29, 2000

Near-Electrode Imager

J. W. Rathke, R. J. Klingler, K. Woelk, and R. E. Gerald

Patent No. 6,046,592, issued April 4, 2000

Journal Articles, Books, and Book Chapters

Development of High-Power Lithium Ion Batteries for Hybrid Vehicle Application

K. Amine and J. Liu

ITE Letters **1**(1), B39 (2000)

Olivine LiCoPO_4 as 4.8 V Electrode Material for Lithium Batteries

K. Amine, H. Yasuda, and M. Yamachi

Electrochem. Solid-State Lett. **3**(4), 178 (2000)

Density Functional Calculations on CO Attached to $\text{Pt}_n\text{Ru}_{(10-n)}$ ($n = 6-10$) Clusters

R. C. Binning, M.-S. Liao, C. R. Cabrera, Y. Ishikawa, H. Iddir, R. Liu, E. S. Smotkin, A. J. Aldykiewicz, and D. J. Myers

Int. J. Quantum Chem. **77**, 589–598 (2000)

A Robust Alkaline-Side CSEX Solvent Suitable for Removing Cesium from Savannah River High Level Waste

P. V. Bonnesen, L. H. Delmau, B. A. Moyer, and R. A. Leonard

Solvent Extr. and Ion Exch. **18**(6), 1079–1107 (2000)

Challenges for Fuel Cells in Transport Applications

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Abstracts, DOE Workshop on Interfaces, Phenomena, and Nanostructures in Lithium Batteries, Argonne National Laboratory, Argonne, IL, December 11–13, 2000, p. 25 (2000)

Mechanistic and In-situ X-ray Studies of Intermetallic Electrodes for Lithium-Ion Batteries

J. T. Vaughey, C. S. Johnson, R. Benedek, M. M. Thackeray, L. Fransson, K. Edstrom, and J. Thomas

Abstracts, 198th Meeting of the Electrochem. Soc., Phoenix, AZ, October 22–27, 2000, Vol 2000–2, No. 123 (2000)

Structural and Mechanistic Studies of Intermetallic Electrodes

J. T. Vaughey, C. S. Johnson, R. Benedek, M. M. Thackeray, L. Fransson, K. Edstrom, and J. Thomas

Abstracts, Tenth Int. Meeting on Lithium Batteries, Como, Italy May 28–June 2, 2000, No. 119 (2000)

Intermetallic Insertion Electrodes for Lithium Batteries

J. T. Vaughey, K. Kepler, C. S. Johnson, T. Sarakonsri, R. Benedek, J. O'Hara, S. Hackney, and M. M. Thackeray

Proc. of the 196th Meeting of Electrochem. Soc., Honolulu, HI, October 17–22, 1999, Vol. 99–24, pp. 280–289 (2000)

Papers Presented at Scientific Meetings

Corrosion of Structural Materials by Lead-Based Reactor Coolants

D. P. Abraham, L. Leibowitz, V. A. Maroni, S. M. McDeavitt, and A. G. Raraz

Presented at the IAEA Technical Committee Meeting on Core Physics and Engineering Aspects of Emerging Nuclear Energy Systems for Energy Generation and Transmutation, Argonne National Laboratory, Argonne, IL, November 28–December 1, 2000

Fuel Processor Development at Argonne National Laboratory

S. Ahmed, D. V. Applegate, J.-M. Bae, B. Bergin, J. D. Carter, J. P. Kopasz, T. R. Krause, J. Krebs, S. H. D. Lee, D. J. Myers, C. Pereira, L. Ruscic, and M. Krumpelt

Presented at the Army Research Office Workshop on Fuel Processing for Polymer Electrolyte Fuel Cells, Romulus, MI, June 19–21, 2000

Integrated Fuel Processor Development

S. Ahmed, S. H. D. Lee, E. Doss, C. Pereira, D. Colombo, and M. Krumpelt

Presented at the Annual National Laboratory R&D Meeting of the DOE Fuel Cells for Trans. Prog., Pacific Northwest National Laboratory, Richland WA, June 7–8, 2000

Fuel Processing for Fuel Cells

S. Ahmed, C. Pereira, J.-M. Bae, and M. Krumpelt

Presented to the DOD Diesel Fuel Reforming Coordination Meeting, Fort Belvoir, VA, April 18, 2000

Source of Impedance Rise in Lithium-Ion High Power Batteries

K. Amine

Presented at the Battery Workshop, Rome, Italy, June 5–6, 2000

Publications and Presentations

Development of High Power Batteries

K. Amine, G. L. Henriksen, S. Rogers, and R. Sutula

Presented at the Power Source Meeting, Cherry Hill, NJ, June 11–15, 2000

Surface Phenomena Responsible for Impedance Rise in Lithium-Ion High-Power Batteries

K. Amine, J. Luo, J. Liu, C. Chen, and D. R. Vissers

Presented at the Workshop on Interfaces, Phenomena, and Nano Structures in Lithium Batteries, Argonne National Laboratory, Argonne, IL, December 11–13, 2000

Batteries and Fuel Cells for Hybrid and Electric Vehicles

V. S. Battaglia

Presented at the 2nd 2015 Future Threat Technologies Panel, CIA Headquarters, McLean, VA, August 4, 2000

Histographic Analysis of the Microstructure of Ag/Bi-2223 Composite Conductors

R. M. Baurceanu, N. N. Merchant, A. K. Fischer, V. A. Maroni, and R. D. Parella

Presented at the Min., Met. and Mater. Soc. Annual Meeting and Exhibition, Nashville, TN, March 12–16, 2000

First Principles Calculations for InSb-Li Battery Anodes

R. Benedek, M. M. Thackeray, L. H. Yang, and R. Prasad

Presented at the 103rd Annual Meeting of the Am. Ceram. Soc., San Francisco, CA, September 6–9, 2000

Intermetallic Anode Materials for Li Batteries

R. Benedek, J. T. Vaughey, M. M. Thackeray, L. H. Yang, and R. Prasad

Presented at the 102nd Annual Meeting of the Am. Ceram. Soc., St. Louis, MO, April 30–May 3, 2000

Accelerated Calendar Life Studies of Gen 1 Cells

I. Bloom, C. Motloch, and T. Unkelhaeuser

Presented at the DOE Advanced Technology Development Program Peer Review, Washington, DC, May 2–3, 2000

Analysis for Chemical Agents to Support the U.S. EPA's Region 5 Emergency Response Branch

A. S. Boparai, J. F. Schneider, and L. L. Reed

Presented at the Eighth Int. Conf. On-Site Analysis Meeting, Lake Las Vegas, NV, January 23–26, 2000

The Impact of Brannerite on the Release of Plutonium and Gadolinium during the Corrosion of Zirconolite-Rich Titanate Ceramics

D. B. Chamberlain, A. J. Bakel, E. C. Buck, M. C. Hash, C. J. Mertz, M. K. Nole, J. K. Basco, and S. F. Wolf

Presented at the Am. Nuclear Soc. Meeting, San Diego, CA, June 5–9, 2000

Lithium Conductivity of a Perovskite-Type Li-Sr-Ta-Zr-O Solid Electrolyte

C. H. Chen, K. Amine, E. Sperling, and G. L. Henriksen

Presented at the Materials Research Soc. Meeting, Boston, November 27–December 1, 2000

Production of Mo-99 from LEU Targets Acid-Side Processing

C. Conner, J. Sedlet, T. C. Wiencek, D. J. McGann, G. L. Hofman, and G. F. Vandegrift

Presented at the Meeting on Reduced Enrichment for Research and Test Reactors, Las Vegas, NV, October 1–6, 2000

Technical Presentations

J. C. Cunnane, P. A. Finn, S. F. Wolf, W. L. Ebert, J. Fortner, C. J. Mertz, and R. J. Finch

Presented at the U.S. Nuclear Regulatory Commission, DOE-NV/OQA Quality Assurance Audit, Argonne National Laboratory, Argonne, IL, October 24–26, 2000

Challenges Facing Air Management for Fuel Cell Systems

P. B. Davis, R. D. Sutton, and F. W. Wagner

Presented at the Int. Symp. on Automotive Technology and Automation, Dublin, Ireland, September 26, 2000

The U. S. Department of Energy Fuel Cells for Transportation Program

P. R. Devlin and W. F. Podolski

Presented to the Japan Electric Vehicle Association, Tokyo, Japan, September 13, 2000

The U. S. Department of Energy Fuel Cells for Transportation Program

P. R. Devlin and W. F. Podolski

Presented at the Fuel Cell Commercialization Policy Meeting, Ministry for Int. Trade and Industry, Tokyo, Japan, September 12, 2000

The U. S. Department of Energy Fuel Cells for Transportation Program

P. R. Devlin and W. F. Podolski

Presented to the Japan Automotive Research Institute, Tsukuba City, Japan, September 12, 2000

Automotive Fuel Cell System Design Points, Efficiency Targets, and Tradeoffs to Achieve PNGV Goal 3

E. D. Doss, R. Ahluwalia, R. Kumar, and M. Krumpelt

Presented at the Fuel Cell Targets Workshop, Arlington, VA, April 5–6, 2000

Transportation Fuel Cell Systems Modeling and Analysis

E. Doss, R. K. Ahluwalia, H. K. Geyer, R. Kumar, and M. Krumpelt

Presented at the Annual National Laboratory R&D Meeting of the DOE Fuel Cells for Transportation Program, Pacific Northwest National Laboratory, Richland, WA, June 7–8, 2000

Fuel-Flexible Automotive Fuel Cell Power System

W. E. Ernst, J. R. Boyer, D. L. Ho, and W. F. Podolski

Presented at the Future Car Congress, Arlington, VA, April 2–6, 2000

Microwave-Accelerated Acid Dissolution of Lithium Aluminate

A. M. Essling and D. G. Graczyk

Presented at the Pittcon Conf., Sci. for the 21st Century, New Orleans, LA, March 12–17, 2000

Publications and Presentations

Degradation Modeling of the ANL Ceramic Waste Form

T. H. Fanning and L. R. Morss

Presented at the Topical Meeting on DOE Spent Nuclear Fuel and Fissile Materials Management Meeting, San Diego, CA, June 4–8, 2000

Mineralogy of Nuclear-Waste Disposal: Comparing Experiments and Nature

R. J. Finch

Presented at University of Missouri-Rolla, Rolla, MO, March 15, 2000

Uranium: Mineralogy, Geochemistry and the Environment

R. J. Finch

Presented at Purdue University, Lafayette, IN, February 24, 2000

Actinide and Lanthanide Host Phases Formed during the Corrosion of Nuclear-Waste Form

R. J. Finch, E. C. Buck, J. Fortner, C. J. Mertz, S. F. Wolf, P. A. Finn, W. L. Ebert, and J. C. Cunnane

Presented at the Am. Chem. Soc. Meeting, San Francisco, CA, March 26–30, 2000

Accessory Minerals and Alteration of Nuclear Waste Forms: Insights and Comparisons

R. J. Finch, E. C. Buck, J. Fortner, and S. F. Wolf

Presented at the American Geophysical Union Spring Meeting, Washington, DC, May 30–June 3, 2000

Small Angle X-ray Scattering from Synthetic Yucca Mountain Groundwater Colloids

J. Fortner, C. J. Mertz, and E. C. Buck

Presented at the Geol. Soc. Am. Conf., Reno, NV, November 9–18, 2000

Determination of Transmutation Effects in Crystalline Waste Forms

J. Fortner, D. T. Reed, R. E. Gerald, and A. J. Kropf

Presented at the Environmental Management Science Program National Workshop, Atlanta, GA, April 24–28, 2000

Standard Practice for the Design and Fabrication of Gloveboxes for the Containment of Materials that Emit Low-Penetrating Ionizing Radiation

A. A. Frigo

Presented at the 14th Annual Conf. and Exposition of the Am. Glovebox Soc., New Orleans, LA, August 21–23, 2000

The ACT External HEPA Push-Through Filter Assembly

A. A. Frigo, S. G. Wiedmeyer, D. E. Preuss, E. F. Bielick, and R. F. Malecha

Presented at the 14th Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc., New Orleans, LA, August 21–23, 2000

Nuclear Magnetic Resonance of Nano-Structures by Levitation in Supercritical Fluids

R. E. Gerald

Presented at the First Meeting on Emerging Nanotechnologies, Kraft Foods, Inc., Skokie, IL, January 17–18, 2000

The Excitement and Process of Inventing

R. E. Gerald

Presented at the Summer 2000 Community College Internship, Argonne National Laboratory, Argonne, IL, July 26, 2000

Passively Shimmied Toroid Cavity Detectors

R. E. Gerald, E. Growney, and J. W. Rathke

Presented at the University of Bonn, Institute of Physical and Theoretical Chemistry, Bonn, Germany, December 15, 2000

Application of the Near Electrode Imager to Lithium Polymer Electrolyte Battery Systems

R. E. Gerald, R. J. Klingler, and J. W. Rathke

Presented at the Structure, Dynamics and Charge Transport in Polymeric Materials Theory Workshop, Argonne National Laboratory, Argonne, IL, June 19–23, 2000

Disclosure of the Rotational Exchange Gradient Imager

R. E. Gerald, R. J. Klingler, and J. W. Rathke

Presented at the 42nd Rocky Mountain Conf. on Analytical Chemistry, Denver, CO, July 30–August 2, 2000

Fundamental NMR Investigations of Conduction Ions in Anode and Electrolyte Materials Using the Near Electrode Imager

R. E. Gerald, R. J. Klingler, and J. W. Rathke

Presented at the 50th Am. Crystallographic Association Conf., St. Paul, MN, June 22–27, 2000

Introduction to Toroid Cavity NMR Imagers

R. E. Gerald, R. J. Klingler, and J. W. Rathke

Presented at the Department of Chemistry, Northeastern Illinois University, Chicago, IL, November 1, 2000

New TCD Inventions for NMR Investigations at Electrode Surfaces

R. E. Gerald, R. J. Klingler, and J. W. Rathke

Presented at the University of Bonn, Institute of Physical and Theoretical Chemistry, Bonn, Germany, December 16, 2000

A New NMR Detector for Investigation of SAMs

R. E. Gerald and J. W. Rathke

Presented at the University of Bonn, Institute of Physical and Theoretical Chemistry, Bonn, Germany, December 19, 2000

In-situ Multinuclear NMR Studies of Lithium Batteries

R. E. Gerald, J. Sanchez, R. J. Klingler, and J. W. Rathke

Presented at the Workshop on Interfaces, Phenomenon, and Nanostructures in Lithium Batteries, Argonne National Laboratory, Argonne, IL, December 11–13, 2000

Publications and Presentations

Coin-Cell Battery NMR Imager

R. E. Gerald, J. Sanchez, R. J. Klingler, and J. W. Rathke

Presented at the University of Bonn, Institute of Physical and Theoretical Chemistry, Bonn, Germany, December 21, 2000

Corrosion Testing of Spent Nuclear Fuel Performed at Argonne National Laboratory for Repository Acceptance

M. M. Goldberg

Presented at the Min., Met. and Mater. Soc. Meeting, St. Louis, MO, October 8–12, 2000

Role of Analytical Laboratories within EM

D. W. Green

Presented at the NAMP 2K Conf., National Initiatives towards Analytical Excellence, Gaithersburg, MD, June 6–8, 2000

Role of Analytical Laboratories within EM

D. W. Green

Presented at the 18th Meeting of the DOE Analytical Managers Group, Denver, CO, August 14–17, 2000

New Catalyst Technology for the Direct Oxidation of Benzene to Phenol

C. Hamilton, E. A. Gardner, L. Iton, C. L. Marshall, S. Alerasool, P.E. Mayuririk, P. C. Y. Yeh, F. M. Dautzenberg, R. Overbeek, G. McRae, E. Meeks, M. Neurock, H. H. Kung, and K. Popp

Presented at the National Laboratory Catalysis Research Conf. Argonne National Laboratory, Argonne, IL, October 12–13, 2000

Test and Diagnostic Methods Used to Study Interface Phenomena in High-Power Lithium-Ion Cells

G. L. Henriksen

Presented at the Workshop on Interfaces, Phenomena, and Nanostructures in Lithium Batteries, Argonne National Laboratory, Argonne, IL, December 11–13, 2000

Diagnostic Studies on High-Power Lithium-Ion Cells for Hybrid Electric Vehicle Energy Storage

J.-S. Hong, J. Liu, A. Newman, and K. Amine

Presented at 198th Meeting of the Electrochem. Soc., Phoenix, AZ, October 22–27, 2000

High-Precision Determination of Lithium and Aluminum by Inductively Coupled Plasma-Atomic Emission Spectrometry

D. R. Huff, D. G. Graczyk, and S. J. Lopykinski

Presented at the Pittcon Conf., Sci. for the 21st Century, New Orleans, LA, March 12–17, 2000

8-fluoro-8methyl-calix[4]pyrole: An NMR Study of Neutral Anion Receptor

C. R. Jones, R. E. Gerald, M. J. Chen, R. J. Klingler, J. W. Rathke, M. Marquez, and R. D. Kraft

Presented at the SMASH NMR Symp., Argonne National Laboratory, Argonne, IL, July 16–19, 2000

Fuel Cell Technology for Navy Shipboard Application

E. J. Karell

Presented at the Naval Engineering Workshop, Washington, DC, February 13, 2000

The Effect of Actinides on the Microstructural Development in a Metallic High-Level Nuclear Waste Form

D. D. Keiser, W. Sinkler, D. P. Abraham, J. W. Richardson, and S. M. McDevitt

Presented at the Miner., Met., and Mater. Soc. Meeting, Nashville, TN, March 12–16, 2000

The Effect of Substitution of $\text{LiNi}_{1-x}\text{M}_x\text{O}_2$ System for High Power Application

J. Kim and K. Amine

Presented at the 198th Meeting of the Electrochem. Soc., Phoenix, AZ, October 22–27, 2000

Polymerizing Clusters in the Solid State: Structure and Bonding in Sr_3Sn_5

M. Klem, J. Harp, J. T. Vaughey, and J. D. Corbett

Presented at the Gordon Conf. on Solid State Chemistry, Colby-Sawyer College, New London, NH, July–August 2000

High-Pressure NMR Characterization of Micellar Systems for Catalysis

R. J. Klingler, D. Fremgen, R. E. Gerald, and J. W. Rathke

Presented at the National Laboratory Catalysis Conf., Argonne National Laboratory, Argonne, IL, October 12–13, 2000

NMR Imaging of Fuel Cell and Battery Components

R. J. Klingler, R. E. Gerald, and J. W. Rathke

Presented at the University of Chicago Review of the Chemical Technology Division, Argonne National Laboratory, Argonne, IL, September 13, 2000

Fuel Issues for Fuel-Cell Vehicles

J. P. Kopasz

Presented at the CMT Technical Seminar, Argonne National Laboratory, Argonne, IL, July 28, 2000

Effects of Gasoline Components on Fuel Processing and Implications for Fuel Cell Fuels

J. P. Kopasz, D. V. Applegate, L. Ruscic, and S. Ahmed

Presented at the Fuel Cell Seminar, Portland, OR, October 29–November 2, 2000

Effect of Fuels/Contaminants on Reforming Catalyst Performance and Durability

J. Kopasz, D. V. Applegate, L. Ruscic, S. Ahmed, and M. Krumpelt

Presented at the Annual National Laboratory Meeting of DOE's Fuel Cells for Transportation Progress, Richland, WA, June 7–8, 2000

Development of New Catalysts for Reforming Hydrocarbon Feedstocks

T. R. Krause, J. D. Carter, J. P. Kopasz, J.-M. Bae, S. Ahmed, and M. Krumpelt

Presented at the National Laboratory Catalysis Research Conf., Argonne National Laboratory, Argonne, IL, October 12–13, 2000

Publications and Presentations

Gasoline—How its Composition Affects Reforming and the Implication for Developing New Catalysts for On-Board Reforming for Fuel Cell Vehicles

T. R. Krause, J. P. Kopasz, S. Ahmed, and M. Krumpelt

Presented at the Am. Inst. of Chem. Eng. Meeting, Los Angeles, CA, November 12–17, 2000

Sulfur Removal from Reformate

T. R. Krause, R. Kumar, and M. Krumpelt

Presented at the R&D Meeting of the DOE Fuel Cells for Transportation Program, Pacific Northwest National Laboratory, Richland, WA, June 7–8, 2000

In-Situ XAFS of Intermetallic Insertion Electrodes for Lithium-Ion Batteries: A Study of Li_xInSb

A. J. Kropf, C. S. Johnson, M. M. Thackeray, J. T. Vaughey, and H. Tostmann

Presented at the Tenth Users Meeting for the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, May 2–4, 2000

The Role of Cobalt in (Co)MoS₂ Hydrodesulfurization Catalysts

A. J. Kropf and C. L. Marshall

Presented at the National Laboratory Catalysis Conf., BP Amoco Research Center, Naperville, IL, October 12–13, 2000

EXAFS of (Co)MoS₂ Hydrodesulfurization Catalysts

A. J. Kropf, C. L. Marshall, J. T. Miller, and K. A. Kunz

Presented at the Catalysis Club of Chicago, Chicago, IL, May 11, 2000

Difference Analysis of the EXAFS of (Co)MoS₂ Hydrosulfurization Catalysts

A. J. Kropf, C. L. Marshall, D. Wei, J. T. Miller, and K. Kunz

Presented at the Tenth Users Meeting for the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, May 2–4, 2000

Catalytic Autothermal Reforming for Fuel Cell Systems

M. Krumpelt, J. D. Carter, R. Wilkenhoener, S. H. D. Lee, J-M. Bae, and S. Ahmed

Presented at the Fuel Cell Seminar, Portland, OR, October 30–November 2, 2000

Catalytic Autothermal Reforming

M. Krumpelt, T. Krause, J. Kopasz, R. Wilkenhoener, and S. Ahmed

Presented at the Annual National Laboratory Meeting of DOE's Fuel Cells for Transportation Progress, Richland, WA, June 7–8, 2000

Fuel Processing Considerations: Cold Start, Transients, Coking, and Related Issues

R. Kumar

Presented at the National Research Council/Fuel Cell Meeting, USCAR, Southfield, MI, January 12, 2000

Catalysts in Automotive Fuel Cell Systems

R. Kumar

Presented at the Int. Conf. on Elementary Processes in Molecule-Metal Surface Interactions, San Juan, Puerto Rico, November 11–15, 2000

Separations Technologies Supporting the Development of a Deployable ATW System

J. J. Laidler

Presented at Waste Management 2000, Tucson, AZ, February 28–March 2, 2000

Pyrochemical Separations Technologies Envisioned for the U.S. Accelerator Transmutation of Waste System

J. J. Laidler

Presented at the Pyrochemical Workshop, Avignon, France, March 14–15, 2000

Chemical Separations Technologies for the U.S. Accelerator Transmutation of Waste Program

J. J. Laidler

Presented at the IAEA Technical Committee Meeting on Core Physics and Engineering Aspects of Emerging Nuclear Energy Systems for Energy Generation and Transmutation, Argonne National Laboratory, Argonne, IL, November 29, 2000

Pyrochemical Processing of Irradiated Transmuter Fuel

J. J. Laidler

Presented at OECD-NEA 6th Information Exchange Meeting on Actinide and Fission Production Partitioning and Transmutation, Madrid, Spain, December 11–15, 2000

Developing Separations Technologies and Waste Forms for the Accelerator Transmutation of Waste (ATW)

J. J. Laidler, S. M. McDeavitt, M. A. Williamson, J. L. Willit, D. P. Abraham, and K. V. Gourishankar

Presented at the Min., Met. and Mat. Soc. Meeting, St. Louis, MO, October, 8–12, 2000

Fuel-Flexible Fuel Processor for Reforming Hydrocarbon Fuels

S. H. D. Lee, C. Pereira, S. Ahmed, and M. Krumpelt

Presented at Am. Inst. of Chem. Eng., Los Angeles, CA, November 12–17, 2000

Interaction of Molten Chloride Salts and Zeolite 4A: Nature, Thermodynamics, and Application to Nuclear Waste Treatment and Disposal

D. Lexa, L. Leibowitz, A. J. Kropf, and I. Johnson

Presented at the Austrian Research Center-Seibersdorf, Vienna, Austria, April 14, 2000

Interaction of Molten Chloride Salts and Zeolite 4A: Nature, Thermodynamics, and Application to Nuclear Waste Treatment and Disposal

D. Lexa, L. Leibowitz, A. J. Kropf, and I. Johnson

Presented at the Tenth Int. IUPAC Conf. on High Temperature Materials Chemistry, Jülich, Germany, April 10, 2000

Analysis and Modeling of Microscopic Radiation Effects on Nuclear Waste Forms

G. K. Liu, J. Luo, H. Z. Zhuang, J. Beitz, V. Zhorin, and V. Williams

Presented at the DOE EMSP Workshop, Atlanta, GA, April 25–27, 2000

Publications and Presentations

Specialized Cell and HRTEM Studies Elucidate Impedance Rise in High-Power Lithium-Ion Cells

J. Liu, C. H. Chen, J. S. Luo, G. L. Henriksen, and K. Amine

Presented at 198th Meeting of the Electrochem. Soc., Phoenix, AZ,
October 22–27, 2000

Microstructural Characterization of Halite Inclusions in a Glass-Bonded Ceramic Waste Form

J. S. Luo and W. L. Ebert

Presented at the 102nd Am. Chem. Soc. Meeting, St. Louis, MO,
April 30–May 3, 2000

Microstructural Characterization of a Surrogate Glass-Bonded Ceramic Waste Form

J. S. Luo, V. N. Zyryanov, and W. L. Ebert

Presented at the 102nd Am. Ceram. Soc. Meeting, St. Louis, MO,
April 30–May 3, 2000

Nanophase Support Materials as Catalysts for Ultra-Deep Sulfur Removal from Crude Oil and Transportation Fuels

D. Mahajan and C. L. Marshall

Presented at the National Laboratory Catalysis Research Conf., Argonne National
Laboratory, Argonne, IL, October 12–13, 2000

The Evolution of CMT Gloveboxes

R. F. Malecha, A. A. Frigo, and D. E. Preuss

Presented at the Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc.,
New Orleans, LA, August 21–23, 2000

Discussion on the Use of Matrix Diffusion Model after a Multidisciplinary Study of a Granitic Boulder Sample

N. Marcos, M. Siitari-Kauppi, J. Suksi, K. Rasilainen, R. J. Finch, E. Flitsyan, and
K.-H. Hellmuth

Presented at the 24th Symp. on the Scientific Basis for Nucl. Waste Management, Sydney,
Australia, August 26–31, 2000

Phase Chemistry Considerations in the Processing of State-of-the-Art Ag/Bi-2223 Composite Conductor

V. A. Maroni, R. M. Baurceanu, N. N. Merchant, A. K. Fischer, and R. D. Parrella

Presented at the Thermec 2000 Int. Conf. on Processing and Manufacturing of Advanced
Materials, Las Vegas, NV, December 4–8, 2000

Characterization of Coated Conductor Phase Purity, Oxygen Stoichiometry, Defect Structures, and In-Plane Texture by Spectroscopic and Synchrotron X-ray Methods

V. A. Maroni, A. K. Fischer, A. J. Kropf, H. You, Y. Jee, K. T. Wu, M. W. Rupich,
Q. Li, C. Thieme, and W. Zhang

Presented at the Fall Meeting of Materials Research Soc., Boston, MA,
November 27–December 1, 2000

The Investigation of Phase Evolution in Composite Ceramic Superconductors Using Raman Microscopy Techniques

V. A. Maroni, A. K. Fischer, and K. T. Wu

Presented at the Sixth Int. Conf. on Materials and Mechanisms of Superconductivity and
High Temperature Superconductors, Houston, TX, February 20–25, 2000

New Mesoporous Supports for the Desulfurization of Diesel and Heavy Oils

C. L. Marshall

Presented at the Chicago Section, American Chemical Soc., Chicago, IL,
February 25, 2000

Combinational Catalyst Testing

C. L. Marshall

Presented at the Great Lakes Chinese Chemical Society Meeting, Arlington Heights, IL,
August 19, 2000

Catalysis Research at Argonne National Laboratory

C. L. Marshall

Presented at the C1 Upgrading Meeting, Hedgesville, WV, August 1, 2000

Ab Initio Investigation of the Hydrodesulfurization Process

C. L. Marshall, J. R. Brenner, J. L. Tilson, M. Palmer, and A. Dutoi

Presented at the Catalysis Club of Chicago, Chicago, IL, May 11, 2000

The Pyrolysis of Methane over Liquid Metal to Form Hydrogen and Carbon

C. L. Marshall, M. A. Lewis, L. Leibowitz, and D. Lewis

Presented at the First Information Meeting on Nuclear Production of Hydrogen, Paris,
France, October 2–3, 2000

New Supports for the Desulfurization of Diesel and Heavy Oils

C. L. Marshall, L. Ruscic, D. Wei, L. Xu, K. A. Carradao, and D. Banerjee

Presented at the National Petroleum Technology Office Program Review, Denver, CO,
June 29, 2000

Hydrodesulfurization Activity and Selectivity of MCM-41 Supported Catalysts

C. L. Marshall, D. Wei, L. Ruscic, L. Xu, and K. A. Carrado

Presented at the National Laboratory Catalysis Research Conf., Argonne National
Laboratory, Argonne, IL, October 12–13, 2000

Materials Research for Nuclear Energy Applications

S. M. McDeavitt

Presented at the Graduate Seminar, University of Cincinnati, Cincinnati, Ohio,
May 12, 2000

Fuel for a Once-Through Cycle-(Th,U)O₂ in a Metal Matrix

S. M. McDeavitt

Presented at the Center for Reactor Information, Argonne National Laboratory, Argonne,
IL, September 29, 2000

Reactive Wetting in Refractory Metal/Ceramic Oxide Systems

S. M. McDeavitt, G. W. Billings, and J. E. Indacochea

Presented at the Miner., Met. and Mater. Soc. Meeting, St. Louis, MO, October 8–
12, 2000

Publications and Presentations

The Development, Processing and Qualification of Ceramic and Metal Waste Forms from the Electrometallurgical Treatment of Spent Nuclear Fuel

S. M. McDeavitt, K. M. Goff, D. P. Abraham, W. L. Ebert, M. C. Hash, S. G. Johnson, D. D. Keiser, D. Lexa, T. P. O'Holleran, M. K. Richmann, M. F. Simpson, and B. R. Westphal
Presented at the Miner., Met., and Mater. Soc. Meeting, St. Louis, MO,
October 8–12, 2000

Colloids Generated from Metallic Uranium Fuel

C. J. Mertz, J. Fortner, M. M. Goldberg, and C. Shelton-Davis
Presented at the Miner., Met., and Mater. Soc. Meeting, St. Louis, MO,
October 8–12, 2000

Structural Studies of Bulk and Powder-in-Tube Bi-1212 by Transmission Electron Microscopy

D. J. Miller, Z. P. Luo, N. M. Murphy, S. E. Dorris, V. A. Maroni, and H. Claus
Presented at the 102nd Annual Meeting of the Am. Ceram. Soc., St. Louis, MO,
April 30–May 3, 2000

Ternary Oxides of the Actinides with Alkali and Alkaline Earth Elements: Stability and Acid-Base Relationships

L. R. Morss
Presented at the Symp. in Honor of P. A. G. O'Hare, 16th IUPAC Conf. on Chemical Thermodynamics, Halifax, Nova Scotia, Canada, August 6–11, 2000

Uranium and Plutonium Release from Glass-Bonded Sodalite

L. R. Morss, W. L. Ebert, L. D. Hafenrichter, M. C. Hash, M. A. Lewis, D. Lexa, J. S. Luo, C. J. Mertz, L. E. Putty, M. K. Richmann, M. K. Nole, and V. N. Zyryanov
Presented at the Am. Chem. Soc. Meeting, San Francisco, CA,
March 26–30, 2000

Corrosion Rates of Sodalite and Glass-Bonded Sodalite, A Nuclear Waste Form, as Function of pH and Temperature

L. R. Morss, R. Miles, M. Stanley, and C. D. Tatko
Presented at the 10th Int. Symp. on Thermodynamics of Nuclear Materials and 16th IUPAC Conf. on Chemical Thermodynamics, Halifax, Nova Scotia, Canada,
August 6–11, 2000

Phase Formation and Superconductivity in PIT-Type (Bi,Pb)-1212

N. M. Murphy, S. E. Dorris, D. J. Miller, Z. P. Luo, H. Claus, and V. A. Maroni
Presented at the Sixth Int. Conf. on Materials and Mechanisms of Superconductivity and High-Temperature Superconductivity, Houston, TX,
February 20–25, 2000

Design and Modeling of Cylindrical and Flat Wound $\text{LiN}_{0.8}\text{Co}_{0.2}\text{O}_2/\text{C}$ Lithium Ion Cells for PNGV Application

P. A. Nelson, G. L. Henriksen, and K. Amine
Presented at the 198th Meeting of the Electrochem. Soc., Phoenix, AZ, October 22–27, 2000

Study of Battery State-of-Charge Control for HEVs by Means of Vehicle Simulation

P. A. Nelson, G. L. Henriksen, and K. Amine

Presented at the 198th Meeting of the Electrochem. Soc., Phoenix, AZ,
October 22–27, 2000

Commuter Simulation of Lithium-Ion Battery Performance in Hybrid Electric Vehicles

P. A. Nelson, G. L. Henriksen, and K. Amine

Presented at the 198th Electrochemical Society Meeting, Phoenix, AZ,
October 22–27, 2000

Differential Scanning Calorimetry Study: Kinetics and Thermodynamics of Electrode Reactivity for Lithium-Ion Cells

A. E. Newman, C. H. Brubaker, G. L. Henriksen, and K. Amine

Presented at the 197th Electrochem. Soc. Meeting, Toronto, Canada, May 14–18, 2000

Bifunctional Catalysts for Selective NO_x Reduction

M. K. Neylon and C. L. Marshall

Presented at the 2000 National Laboratory Catalysis Research Conf., Argonne National
Laboratory, Argonne, IL, October 12–13, 2000

Liquid Fuel Reformer Development

C. Pereira, S. Ahmed, J.-M. Bae, and M. Krumpelt

Presented at the Annual Meeting of DOE's Hydrogen Program, San Ramon, CA,
May 9–11, 2000

Catalytic Reforming of Gasoline and Diesel Fuel

C. Pereira, R. Wilkenhoener, S. Ahmed, and M. Krumpelt

Presented at the Am. Inst. Chem. Eng. Meeting, Atlanta, GA, March 5–9, 2000

A Vertical Transfer Lock for Large Gloveboxes

D. E. Preuss, A. A. Frigo, and R. F. Malecha

Presented at the 13th Annual Conf. and Equipment Exhibit of the Am. Glovebox Soc.,
New Orleans, LA, August 21–23, 2000

Medium Temperature Cathode Materials for Solid Oxide Fuel Cells

J. M. Ralph, J. T. Vaughey, and M. Krumpelt

Presented at the Fuel Cell Seminar, Portland, OR, October 30–November 2, 2000

High-Pressure NMR Studies of Methane Hydrate

J. W. Rathke, R. J. Klinger, M. J. Chen, and R. E. Gerald

Presented at the National Methane Hydrate Workshop, Argonne National Laboratory,
Argonne, IL, September 13, 2000

Supercritical Carbonylation Catalysis

J. W. Rathke, R. J. Klinger, M. J. Chen, and L. M. Wojcinski

Presented at the Am. Chem. Soc. Meeting, San Francisco, CA, March 26–31, 2000

Publications and Presentations

High-Pressure NMR Studies of Supercritical Carbonylation Catalysis

J. W. Rathke, R. J. Klingler, M. J. Chen, and L. M. Wojcinski

Presented at the 2000 National Laboratory Catalysis Conf., Argonne National Laboratory, Argonne, IL, October 12–13, 2000

Oxidation/Reduction of Multivalent Actinides in the Subsurface

D. T. Reed, S. B. Aase, A. J. Kropf, and B. E. Rittmann

Presented at the Plutonium Futures Conf., Sante Fe, NM, July 10–13, 2000

Subsurface Actinide Microbiological Interactions: Effects on Actinide Speciation

D. T. Reed, S. B. Aase, T. Marks, B. Rittmann, J. Banaszak, A. Hermes, and W. Songkasiri

Presented at the MIT Seminar, Boston, MA, November 9, 2000

Plutonium and Uranium Disposition in a Sodalite/Glass Composite Waste Form via XAFS

M. K. Richmann, A. J. Kropf, D. T. Reed, S. B. Aase, M. C. Hash, L. Putty, and D. Lexa

Presented at the Plutonium Futures—Sci. Topical Conf., Santa Fe, NM, July 10–13, 2000

Large Sample MAS NMR Spectroscopy of Gas Hydrates

J. S. Schuetz, C. R. Jones, R. E. Gerald, R. J. Klinger, J. W. Rathke, V. Thieu, and Y. Halpern

Presented at the SMASH NMR Symp., Argonne National Laboratory, Argonne, IL, July 16–29, 2000

Stability of Spinel, Orthorhombic and Layered Lithium Manganese Oxides

Y. Shao-Horn, S. A. Hackney, C. S. Johnson, A. J. Kahaian, K. D. Kepler, E. Skinner, J. T. Vaughey, and M. M. Thackeray

Presented at Int. Battery Assoc. Manganese Oxide Symposium, Argonne National Laboratory, Argonne, IL, May 10–12, 2000

Modeling Inhibition and Toxicity of Uranium in the Citrate-*Pseudomonas* System

W. Songkasiri, D. T. Reed, and B. E. Rittmann

Presented at the 220th Am. Chem. Soc. National Meeting, Washington, DC, August 20–24, 2000

EXAFS Investigation of Dissolved and Absorbed Pt Complexes Derived from CPA

W. A. Spieker, J. R. Regalbuto, A. J. Kropf, and J. T. Miller

Presented at the Tenth Users Meeting for the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, May 2–4, 2000

Status of Development of NAMP Information Systems

W. E. Streets, A. E. Scandora, J. S. Morton, and S. Woolf

Presented at the NAMP Database Working Group Meeting, Salt Lake City, UT, February 3, 2000

The National Analytical Management Program's Laboratory Informational Network: NAMPnet

W. E. Streets, A. E. Scandora, J.S. Morton, and S. Woolf

Presented at the NAMP 2K, National Initiatives towards Analytical Excellence, Gaithersburg, MD, June 6–8, 2000

Fuel Cell Issues for Fuel Cell Systems

R. D. Sutton

Presented at the Ninth Biennial Bioenergy 2000 Conf., Buffalo, NY, October 17, 2000

DOE Fuels for Fuel Cells Research and Development

R. D. Sutton and P. Devlin

Presented at the Fuel Cells 2000 Conf., Palm Springs, CA, May 23, 2000

On Understanding the Effect of Hydrogen Interaction on Tritium Release from Lithium Ceramics Breeder Materials

S.-W. Tam, A. Sutjianto, and R. Pandey

Presented at the 9th Int. Workshop, Hydrogen Isotope Recycling at Plasma-Facing Materials in Fusion Reactors, Argonne National Laboratory, Argonne, IL, September 20–22, 2000

Toroid Cavity NMR Detector for Operation at 600 MHz

M. A. ter Horst, R. E. Gerald, R. J. Klinger, and J. W. Rathke

Presented at the 41st Experimental NMR Conference, Pacific Grove, CA, April 9–14, 2000

Phase Stability Domains of the (Bi,Pb-2223): Data Sources, Correlation, and Assessment

M. Tetenbaum, N. M. Murphy, S. E. Dorris, and V. A. Maroni

Presented at the Sixth Int. Conf. on Materials and Mechanisms of Superconductivity and High Temperature Superconductors, Houston, TX, February 20–25, 2000

From Gems to Lithium Battery Electrodes: The Significance of the Diamond, Ruby (Sapphire), Spinel and Peridot Structures

M. M. Thackeray

Presented at the 10th Inter. Meeting on Lithium Batteries, Como, Italy, May 28–June 2, 2000

The Reduction of UCl_3 , PuCl_3 , and Select Rare Earth Chlorides by Li-Al

Z. Tomczuk, E. J. Wesolowski, I. Johnson, and W. E. Miller

Presented at the 24th Actinide Separations Conference, Las Vegas, NV, May 22–25, 2000

A New Class of Negative Electrodes for Lithium Batteries

J. T. Vaughey

Presented at the CMT Divisional Seminar, Argonne National Laboratory, Argonne, IL, April 28, 2000

A New Class of Intermetallic Electrodes for Lithium-Ion Batteries

J. T. Vaughey, C. S. Johnson, M. M. Thackeray, H. Tostmann, A. J. Kropf, T. Sarakonsri, and S. A. Hackney

Presented at the Gordon Conf. on Solid State Chemistry, Colby-Sawyer College, New London, NH, July/August 2000

Publications and Presentations

Application of ICPMS for the Characterization of Solutions Generated from Durability Testing of Spent Nuclear Fuel

S. F. Wolf

Presented at the Analytical Chemistry in Nuclear Technology Symp., Am. Chem. Soc. Meeting, Washington, DC, August 20–25, 2000

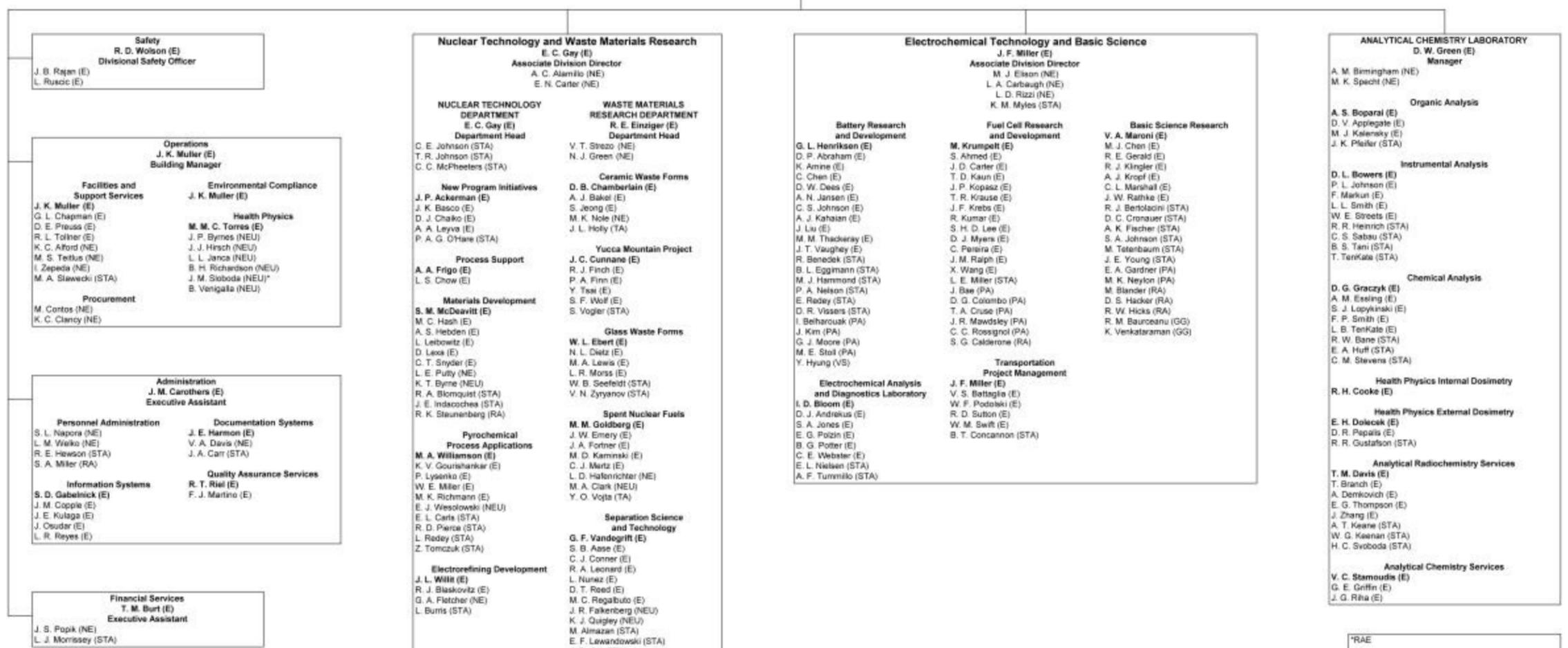
Analysis of High Burnup Spent Nuclear Fuel using HPLC-ICPMS

S. F. Wolf and D. L. Bowers

Presented at the Analytical Chemistry in Nuclear Technology Symp., Am. Chem. Soc. Meeting, Washington, DC, August 20–25, 2000

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