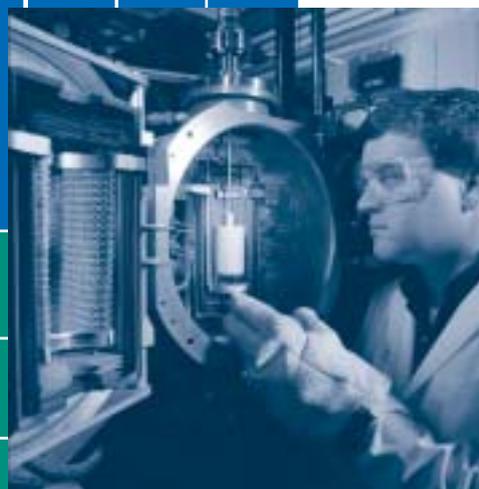
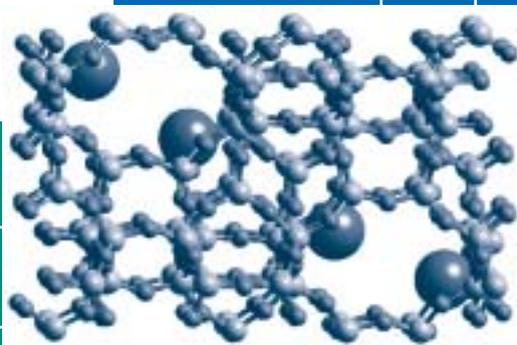


Chemical Technology Division

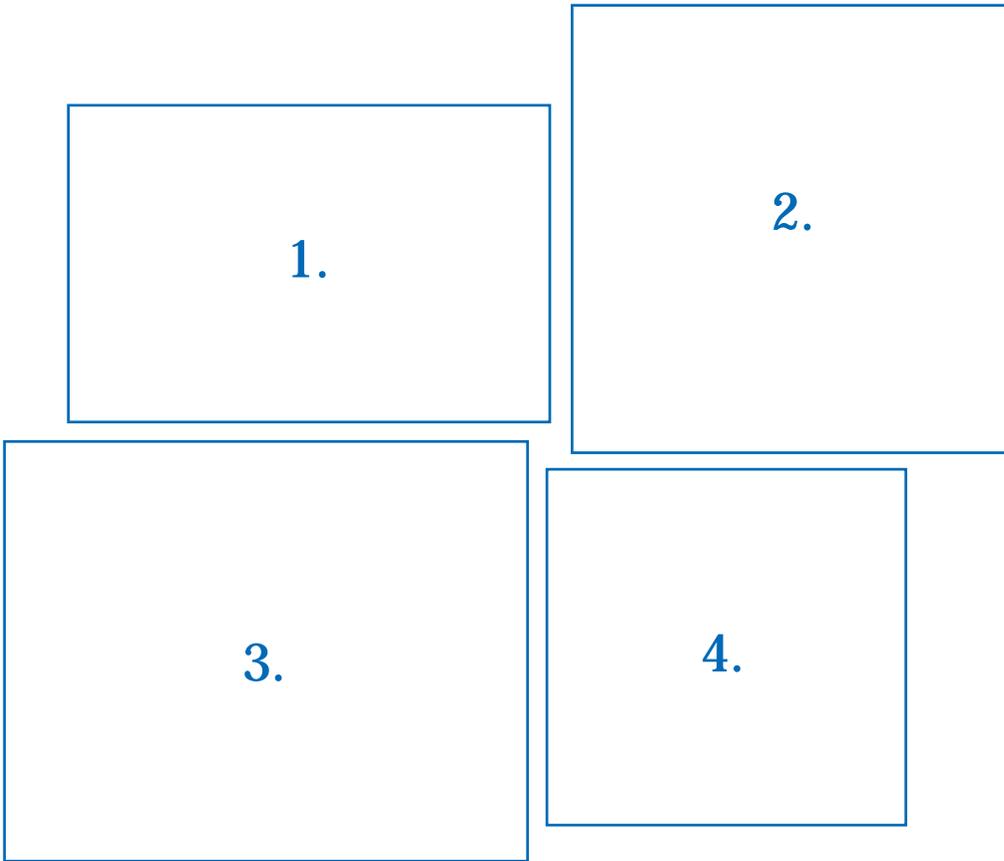
Annual Technical Report

2001

Applying Chemical Innovation to Energy and Environmental Problems



Argonne National Laboratory



Cover Description

1. A catalyst previously used in NO_x reduction chemistry, Cu-ZSM-5, is very promising for a one-step method for making phenol that CMT is developing.
2. A high-temperature materials research furnace is used by CMT to synthesize and test nuclear materials in a controlled atmosphere or vacuum environment.
3. The Fuel Cell Test Facility within CMT provides DOE and other sponsors with independent, standardized technology validation and analysis.
4. In CMT's Analytical Chemistry Laboratory, chemists conduct a wide range of analyses. Here, an analytical chemist measures carbon using a carbon analyzer.

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2001

Chemical Technology Division

Annual Technical Report

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May 2002

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2001

Chemical Technology Division

Annual Report

Introduction

The Chemical Technology Division (CMT) is one of eight engineering research divisions within Argonne National Laboratory, 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 by developing innovative technology and transferring it to industry.

CMT is a diverse early-stage engineering organization, specializing in the treatment of spent nuclear fuel, development of advanced electrochemical 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 Argonne's mission. Additionally, the Division operates the Analytical Chemistry Laboratory and Environment, Safety, and Health Analytical Chemistry services, which provide a broad range of analytical services to Argonne and other organizations.

The Division is multidisciplinary. 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:

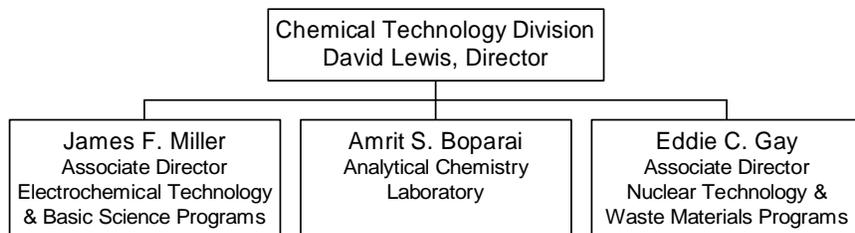
- Advanced lithium-ion and lithium-polymer batteries for transportation and other applications,
- Fuel cells, with an emphasis on the use of an oxidative reformer and gasoline as the fuel supply,
- Stable nuclear waste forms suitable for storage in a geological repository, and
- Electrochemical and pyrochemical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

A separate program in basic science is engaged in smaller research projects, such as catalysis and superconductivity, that have the potential to impact future energy systems.

The Division also serves as a source of technical support in process design and development for DOE programs in nuclear weapons materials, isotope separation, and other areas requiring specialized expertise.

During 2001, CMT had an annual operating budget of approximately \$38 million. Eighty-five percent of this funding came from DOE; the remainder was from other government agencies and private industry. The level of full-time staffing during the past year was 176 full-time, and 33 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 have become very popular as power sources for consumer electronic devices, because of their high energy density relative to nickel cadmium and nickel metal hydride batteries. Cellular telephones, digital cameras, camcorders, laptop computers, and other electronic devices currently employ high-energy lithium-ion batteries. Due to their success in these applications, they have been under development for other applications such as energy storage devices for electric vehicles, hybrid electric vehicles, and specialty battery applications, since the mid-1990s.

The Chemical Technology Division (CMT) has been involved in the development of advanced lithium batteries for transportation applications since 1994. Our early work was on lithium-polymer batteries, which employ metallic lithium negative electrodes, a polyethylene oxide solid electrolyte, and a metal oxide positive electrode. This technology was being developed for the electric vehicle (EV) application, under a cooperative R&D agreement with 3M Corporation and Hydro-Quebec. The U.S. Advanced Battery Consortium and the U.S. Department of Energy (DOE) sponsored this

research and development (R&D) from 1994 to 2001. Under this program, CMT provided technical support in three main areas: electrochemical characterization and modeling of advanced cell designs, testing and evaluation of prototype hardware, and the development of advanced electrode materials.

In 1998, CMT helped DOE to organize and initiate a new multi-laboratory R&D program on high-power lithium-ion batteries. Lithium-ion batteries employ a liquid or gel-polymer electrolyte and lithium insertion compounds in both the positive and negative electrodes. The development of high-power lithium-ion batteries was initiated as part of DOE's participation in the Partnership for a New Generation of Vehicles (PNGV) Program. This program is a federal government/U.S. auto industry partnership to develop low-emission full-size passenger vehicles with an 80-mile-per-gallon fuel economy. The program focuses on the development of hybrid electric vehicles (HEVs), which employ an energy storage device to level the load on the prime power source and recapture regenerative braking energy. The multilaboratory R&D

program, denoted the Advanced Technology Development (ATD) Program, was initiated to assist PNGV industrial developers of high-power lithium-ion batteries overcome the barriers of life, abuse tolerance, and cost for this promising technology. The ATD Program covers a broad range of R&D activities associated with understanding the mechanisms that limit life and abuse tolerance, as well as evaluating and developing advanced materials that are designed to overcome these limitations and simultaneously reduce material costs. It involves the development of novel approaches for reducing cell packaging costs.

Additionally, CMT receives support for longer-range, but focused, research on materials for lithium batteries. These longer-range research activities seek to develop novel new materials that can enhance the performance, life, and/or safety of advanced lithium batteries while reducing cost. In recent years, a new family of intermetallic negative electrode materials was discovered and efforts to develop optimal electrode compositions continue.

During the last year, CMT expanded its lithium battery R&D activities to include rechargeable lithium batteries for commercial and specialty applications.

Three different industrial battery developers selected CMT to work with them on Department of Commerce NIST/ATP projects. In all cases, CMT was assigned the responsibility for developing advanced electrode materials for these batteries. In one case we are responsible for developing principal and back-up advanced cell chemistries. The principal cell chemistry involves a new polymer electrolyte that possesses high ionic conductivity at room temperature, while the back-up employs a more conventional liquid electrolyte.

CMT operates the Electrochemical Analysis and Diagnostics Laboratory, which was established to study advanced battery systems for applications such as EV, HEV, and stationary energy storage applications. This facility has been cited as a valuable resource by battery users, developers, and program managers, who must evaluate and make choices regarding competing battery technologies and research directions. Since it was established more than two decades ago, the laboratory has tested more than 4000 cells and batteries, ranging from individual 4-Wh cells to 50-kWh batteries, representing 12 technologies and 18 battery developers. The test facility has expanded to include the test and evaluation of fuel cell stacks and fuel cell systems up to 50 kW.

Development of High-Power Lithium-Ion Batteries

Safer, longer-lived and less costly batteries for hybrid electric vehicles

Under the Partnership for a New Generation of Vehicles (PNGV) Program, the U.S. Department of Energy (DOE) is working with the U.S. auto industry to develop high-power lithium-ion batteries for use as energy storage devices in hybrid electric vehicles. Argonne's Chemical Technology Division (CMT) is working with four other DOE laboratories (Berkeley, Brookhaven, Idaho, and Sandia) to help the industrial battery developers of high-power lithium-ion batteries overcome the key barriers of calendar life, safety, and cost. The approach is to develop high-power cell chemistries, incorporate them into sealed cells, conduct well-defined thermal abuse and accelerated aging tests on the cells, and then employ a suite of diagnostic tools and techniques to identify the main factors that control their life and abuse tolerance. CMT has developed two high-power cell chemistries (see Table 1) for use in this program. Results to date indicate that the second-generation cell chemistry is more stable than the first-generation cell chemistry and we are identifying the reasons for the improvements.

2001 Research Highlights

During 2001, we completed diagnostic studies on first-generation cells, while second-generation cells were built and testing was initiated. Also, few new and aged second-generation cells underwent diagnostic evaluations.

The first- and second-generation cells were both capable of meeting the PNGV power requirements prior to aging. Under our accelerated aging tests, the first-generation

cells displayed a rapid loss of power. The second-generation cells are exhibiting a much slower rate of power fade, which indicates that the materials are inherently more stable.

The positive electrode was the major source of impedance rise in the first-generation cells, as measured on electrodes harvested from aged cells (see Fig. 1a). Figure 1b shows similar data for electrodes harvested from aged second-generation cells. For the later, the negative and positive electrode impedances are comparable, indicating that the positive electrode is much more stable than the one used in the first-generation cells. Gas analysis data from second-generation cells show that the total quantity of gas does not increase significantly after the first month of accelerated aging (at temperatures up to 55°C). Similarly, electrolyte analyses show that compositional changes occur only during the initial formation cycle and early in the aging process. Therefore, the diagnostic evaluations are confirming the greater stability of the second-generation cell chemistry. The accelerated aging and diagnostic evaluation studies continue, with the goal of quantifying the factors responsible for power fade in the second-generation cells.

Also, the diagnostic data are used in a CMT-led activity to develop advanced low-cost materials that are tailored to meet the performance, life, and safety requirements of this HEV application. During the past year, collaborations with Superior Graphite and the Army Research Laboratory led to the development of a low-cost natural graphite and a low-cost PC-based electrolyte

Table 1. Chemistries Used in ATD Program High-Power Cells

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

PVDF = polyvinylidene fluoride, EC = ethylene carbonate, DEC = diethyl carbonate, EMC = ethyl methyl carbonate

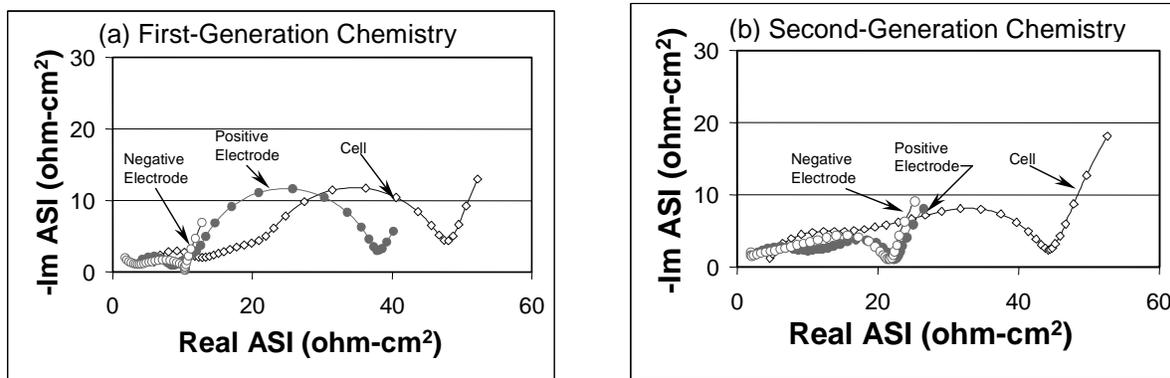


Fig. 1. AC impedance spectra of laboratory cells incorporating aged electrodes from (a) first- and (b) second-generation cells. Micro-reference electrodes were used to identify the individual ASI contributions from the positive and negative electrodes.

system, respectively. This graphite exhibits a reversible discharge capacity >300 mAh/g, while its round-edge particle morphology imparts enhanced safety. It is projected to cost $<\$10/\text{kg}$ in volume production. The 1.2M $\text{LiPF}_6/\text{EC}:\text{PC}:\text{EMC}$ (3:3:4) electrolyte, with 1% of CMT's VEC additive, possesses a low melting point (-32°C), high ionic conductivity, and a low flame propagation rate. Use of PC lowers the cost relative to other organic carbonate solvents.

This research is funded by the U.S. Department of Energy, Energy Efficiency

and Renewable Energy, Office of Advanced Automotive Technologies.

Research Participants

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Advanced Electrode Materials for Lithium-Ion Batteries

Developing safer, longer-lived battery electrodes

In recent years there has been a renewed interest in intermetallic negative electrodes as alternatives to graphite for lithium-ion batteries because of the inherent safety hazards of those carbon-based cells, particularly when subject to abuse or overcharge. Binary lithium-metal systems such as Li_xAl , Li_xSi and Li_xSn have not yet found practical application as negative electrodes because the expansion and contraction that occur during lithiation and delithiation are so large that the structural integrity and cycle life of the electrode are impaired. It has also been recognized that, to obtain high capacities and high rates, the particle size of these binary Li_xM electrodes should be as small as possible, preferably with nano-scale dimensions.

2001 Research Highlights

Because very small electrochemically active particles will be more prone to reaction with the organic-based electrolytes of lithium cells, a different approach has been adopted by the Chemical Technology Division in the search for new negative electrode materials. This approach has involved the identification of ternary systems in which a strong structural relationship exists between a parent binary intermetallic electrode, MM' , in which M and M' are different metal atoms, and a lithiated $\text{Li}_x\text{MM}'$ product. It was envisioned that if such systems existed, then lithium insertion reactions might be possible, which would circumvent the need to use intermetallic electrode particles of nano-size dimensions. In early investigations, it was discovered that such systems

did indeed exist, as exemplified by Cu_6Sn_5 and InSb . Lithium insertion into Cu_6Sn_5 is accompanied by the topotactic displacement of 50% of the Sn atoms, which induces a phase change from the nickel-arsenide-type structure of Cu_6Sn_5 to the lithiated zinc-blend-type structure of Li_2CuSn . The diffusion of Sn atoms within the host structure, however, compromises the kinetics of this reaction. Of greater significance was the observation that lithium insertion into InSb occurs with the concomitant extrusion of In, without disturbing the face-centered-cubic Sb array, which expands by only 4.4% on complete lithiation to form Li_3Sb . Although the electrochemical process is reversible, high-resolution transmission electron microscope studies of lithiated InSb electrodes have shown that the efficiency of the reaction is compromised by exaggerated grain growth of the extruded In metal.

The studies of Cu_6Sn_5 and InSb led to investigation of the copper-antimonide system, notably Cu_2Sb , which has shown significantly superior electrochemical properties. The typical voltage profile of a $\text{Li}/\text{Cu}_2\text{Sb}$ cell is shown in Figure 1. The excellent cycling behavior of these cells is shown in Figure 2, in which it can be seen that after one conditioning cycle, the Cu_2Sb electrode provides a steady rechargeable capacity of approximately 300 mAh/g; this practical specific capacity compares favorably with the theoretical capacity of graphite (372 mAh/g). With respect to volumetric capacity, the Cu_2Sb electrode provides 1914 mAh/ml (based on an average electrode density of 6.6 g/ml), which is

significantly superior to the theoretical volumetric capacity of graphite (818 mAh/ml). In-situ x-ray diffraction data obtained during the operation of Li/Cu₂Sb cells have provided structural information about the reaction mechanism that occurs at the Cu₂Sb electrode (Fig. 3). Analysis of the data has shown that lithium is inserted into Cu₂Sb with a concomitant extrusion of copper, which initiates a phase transition to a lithiated zinc-blend-type structure, Li_xCu_{2-y}Sb for 0 < x ≤ 2 and 0 ≤ y ≤ 1, yielding Li₂CuSb at x=2, y=1. Further lithiation results in displacement of the remaining copper to yield Li_{2+z}Cu_{1-z}Sb compositions (0 < z ≤ 1) with the end member Li₃Sb. The reactions occur predominantly between 1.0 and 0.6 V vs. Li⁰. The excellent electrochemical performance obtained from Cu₂Sb electrodes is attributed to the retention of a face-centered cubic Sb array throughout discharge and charge, despite a 42% expansion/contraction of the array that occurs during electrochemical cycling. Other factors that contribute to the good electrochemical properties of Cu₂Sb electrodes are the fast diffusion of both lithium and copper within the Sb array and the apparent lack of exaggerated crystal growth of the extruded copper.

This research is funded primarily by the U.S. Department of Energy, Office of Basic Energy Sciences, and Office of Advanced Automotive Technologies.

Research Participants

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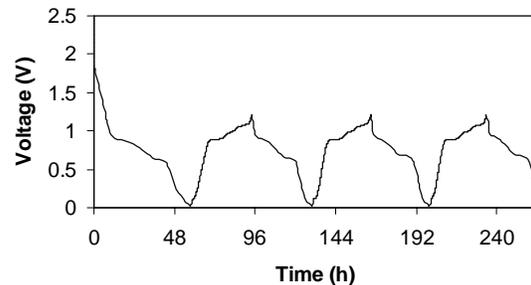


Fig. 1. Voltage profile for the first three cycles of a Li/Cu₂Sb cell.

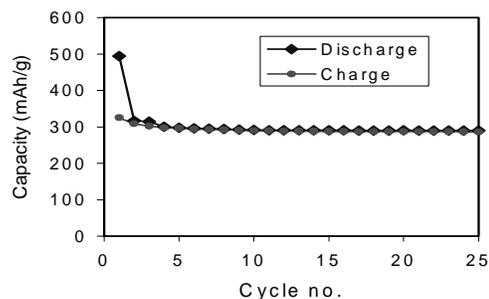


Fig. 2. Plot of capacity vs. cycle number for a Li/Cu₂Sb cell.

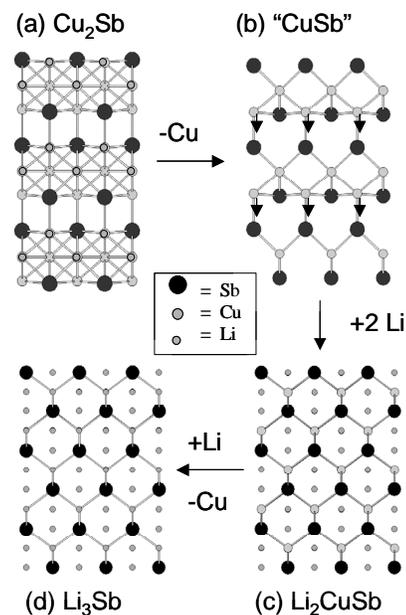


Fig. 3. Schematic illustrations of the structures formed during the electrochemical transformation of the Cu₂Sb to Li₃Sb: (a) Cu₂Sb [010] projection, (b) "CuSb" component of Cu₂Sb, (c) Li₂CuSb [110] projection, and (d) Li₃Sb [110] projection.

High-Energy Batteries for Commercial and Specialty Applications

Better batteries for biomedical, telecommunications, and transportation use

In 2001 the Chemical Technology Division (CMT) began work with three industrial firms—Quallion LLC, Ultralife, and PolyStor—on projects to develop batteries for a range of commercial uses. The project with Quallion consists of developing a long-life high-energy lithium battery, based on a new solid polymer electrolyte and an advanced cathode material. This battery would power injectable micro stimulators or “bions,” which could provide a variety of therapies ranging from diagnostic to rehabilitative and functional for conditions such as urge urinary incontinence, shoulder subluxation (following strokes), sleep apnea, and epilepsy. The Ultralife project is to develop an advanced high-energy/high-density cathode material that can be used in power sources for low-earth-orbit and geostationary (LEO and GEO) satellites for both military and civilian applications. With PolyStor, we are working to develop an advanced anode material that will enhance the energy and safety and extend the life of secondary gel-polymer lithium-ion batteries in commercial applications (discussed separately; see “Development of Advanced Electrode Materials for Lithium-Ion Batteries”).

2001 Research Highlights

High-Energy “Bion” Battery: Conventional lithium-ion batteries are candidates for powering miniature implantable medical devices. However, their limited calendar life and inherent safety limitations prevent them from being used in their current form. An alternative is a lithium-ion battery that uses

a solid polymer electrolyte. This chemically stable system should be very suitable for this application, where it operates at human body temperature (37°C). Working with Quallion and the University of Wisconsin, CMT has developed a new interpenetrating network (IPN) solid polymer electrolyte system that uses a poly(ethylene oxide) grafted siloxane polymer as its major ion-conducting phase. The system exhibits the highest polymer electrolyte ionic conductivity reported to date (see Fig. 1) and has a 6X higher transference number (0.3) than the PEO-based polymer (0.05) being used by HydroQuebec. Further, the system shows good mechanical strength, can be prepared easily, displays good cycleability at 37°C (see Fig. 2), and has outstanding safety characteristics. CMT also is developing an advanced cathode material, based on the olivine LiFePO_4 , for use in this new battery system. This olivine possesses greater stability in the presence of the electrolyte and better safety performance compared

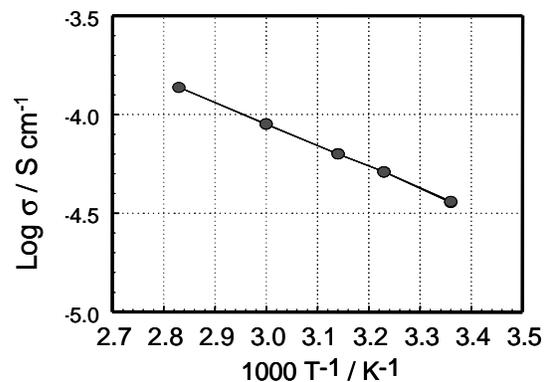


Fig. 1. Ionic conductivity of IPN solid polymer electrolyte.

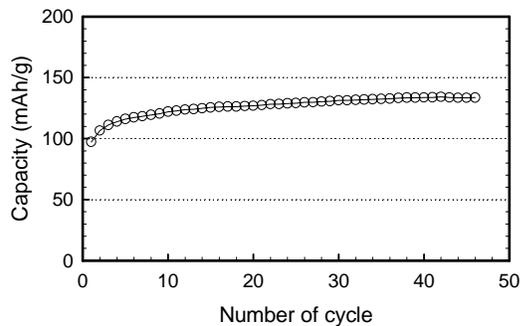


Fig. 2. Capacity as a function of cycles for a cell with IPN solid polymer electrolyte.

with the more conventional $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ system being used in the lithium-ion battery industry today.

Advanced Cathode Material for Commercial and Satellite Applications: Lithium-ion battery systems, based on the use of layered $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ as the positive electrode material have high energy density compared with other secondary batteries. However, this cathode material exhibits significant capacity fade because of its high surface reactivity with the non-aqueous electrolytes and the well known phenomenon of divalent nickel impurities displacing to the lithium sites, which affects cycleability. The displaced divalent nickel causes rapid capacity fade by blocking the path for lithium ions, preventing them from shuttling into and out of the cathode and resulting in a corresponding large, irreversible capacity loss. In its simplest form, this system is not suitable for either consumer electronics or satellite applications, where sustainable cycleability is very critical. Most of the lithium battery industry employs doped lithium nickel oxides to help stabilize the cathode. CMT, however, is addressing this issue by developing a new layered cathode material, based on $\text{LiNi}_{1-x}\text{Ti}_x\text{O}_2$, with titanium substitution. In this case, the titanium is tetravalent, which allows the unstable divalent nickel ions to remain in the

nickel layer and prevents transitions to the lithium sites. The material can be prepared easily by solid-state reaction, using LiOH , $\text{Ni}(\text{OH})_2$, and TiO_2 (anatase) powders as precursors. X-ray diffraction patterns of samples prepared by this method show a phase-pure layered structure with the integrated intensity ratio of $(R_{(003)} = I_{(003)}/I_{(104)} = 2.5)$. This value, which is twice as high as that observed in $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, clearly indicates a highly ordered structure (without any displacement). Figure 3 shows the cycle performance of $\text{LiNi}_{0.95}\text{Ti}_{0.05}\text{O}_2$ at the C/3 rate. The material exhibits high capacity densities (almost 200 mAh/g) and outstanding cycleability, with no fade for almost 30 cycles. With help from industrial partners, CMT succeeded in scaling up this material for potential application in satellite batteries, under the project with Ultralife Battery Corporation.

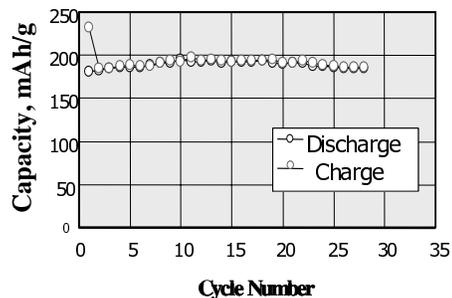


Fig. 3. Capacity as a function of cycles for a cell with $\text{LiNi}_{0.95}\text{Ti}_{0.05}\text{O}_2$ cathode material.

This research is funded by awards to industrial partners by the National Institute of Standards and Technology, Advanced Technology Program.

Research Participants

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Battery and Fuel Cell Testing and Evaluation

Independent, standardized testing for battery and fuel cell developers

The Chemical Technology Division's Electrochemical Analysis and Diagnostics Laboratory (EADL) is a large laboratory designed to test batteries and fuel cells designed within and outside of Argonne National Laboratory. Comprising the Battery Test Facility and the Fuel Cell Test Facility, the EADL provides DOE and battery and fuel cell developers with reliable, independent, and unbiased performance evaluations of their cells, modules, and battery packs of many types and sizes.

The EADL has the capabilities to conduct 120 concurrent advanced battery studies under conditions that simulate electric-vehicle (EV), electric-hybrid vehicle (HEV), utility load-leveling, and standby/uninterruptible power source applications.

A major portion of the EADL's testing is conducted on batteries and fuel cells intended for automotive applications. Many evaluations have been performed for DOE, the Partnership for the New Generation of Vehicles (PNGV), and the U.S. Advanced Battery Consortium (USABC).

2001 Research Highlights

In our work on EV batteries, we characterized and tested two 12-V, 95-Ah Ni/Metal-Hydride (Ni/MH) modules that were made by Yuasa Corporation to determine their thermal performance, power characteristics and cycle life. Several of Yuasa's specifications were obtained under conditions different from those used by the USABC. The rated peak power of 260 W/kg was obtained for 50% depth of discharge

(DOD) over 10 seconds rather than for 80% DOD over 30 seconds as specified by USABC. The life rating of 1000 cycles was based on charging at the C/10 rate and discharging at the C/5 rate, rather than 600 cycles and 80% dynamic stress test (DST) discharging for USABC. The principal goal of the testing at Argonne was to determine the performance of these modules in standard USABC tests. We characterized these modules in terms of DST cycle life, power capabilities and thermal performance. The modules completed 330–350 life cycles. The thermal performance experiments in the temperature range of -10 to $+50^{\circ}\text{C}$ show that DST and C/3 capacities and power capabilities are reduced by more than 12% at -10 and at $+50^{\circ}\text{C}$ (see Figs. 1 and 2, respectively). In life cycling studies, changing the charging algorithm from temperature compensated to simple 105% return decreased the capacity and power fade rates by almost a factor of 2.

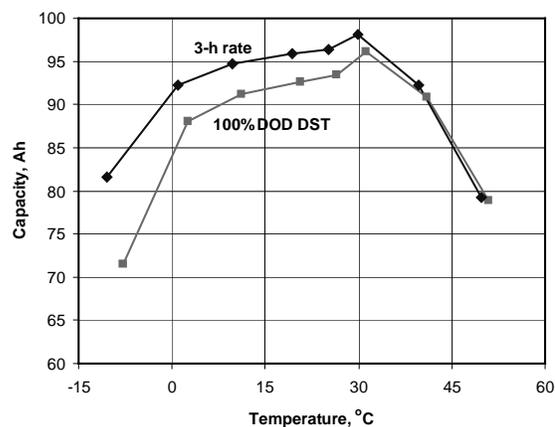


Fig. 1. 3-h rate and 100% DOD DST capacity as a function of temperature.

Batteries

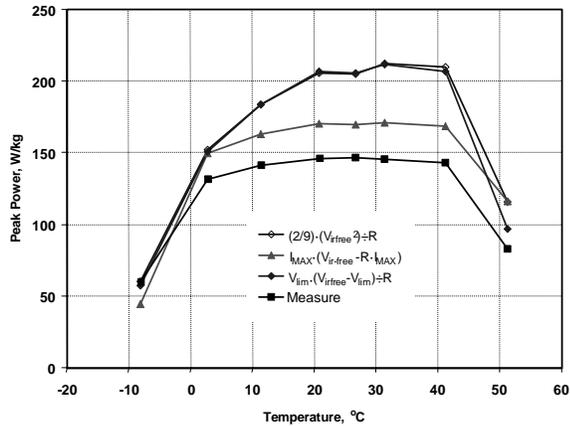


Fig. 2. Peak power vs. temperature.

In our HEV work with lithium-ion batteries, we characterized and tested prototype batteries made under DOE's Advanced Technology Development (ATD) Program. 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 better understand the effect of accelerated calendar life testing at four temperatures (40, 50, 60 and 70°C) and two states of charge (SOCs, 40 and 60%) on the performance of these batteries.

Useful cell life was strongly affected by temperature, time, and state-of-charge. Temperature accelerated cell performance degradation. The rates of area specific impedance (ASI) increase and power fade followed simple laws based on a power of time and Arrhenius kinetics. The data have been modeled using these two concepts and the calculated data agree well with the experimental values.

The calendar life ASI increase and power fade data follow $(\text{time})^{0.5}$ kinetics. This may be due to solid electrolyte interface layer growth. The model was then used to project the calendar life of these cells (see, for example, Fig. 3). The PNGV goals assume

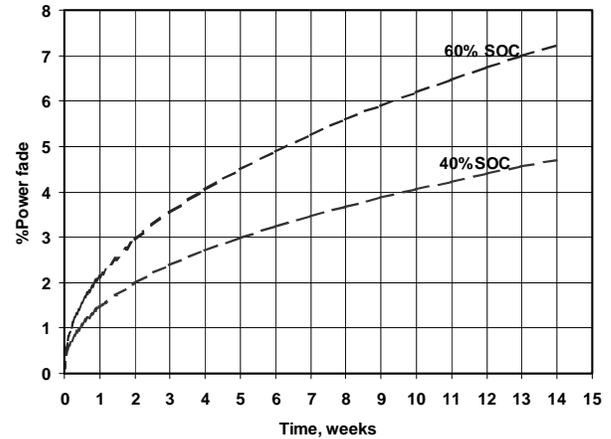


Fig. 3. Calculated power fade vs. time for ATD Li-ion cells at two states of charge.

that 24% power fade represents the end of life. Using this power fade value, the projected cell lives are 553 and 188.56 weeks for 40% and 60% SOC, respectively. These lifetimes do not meet the PNGV requirement of 15 years under our test conditions.

CMT's EADL was established in 1976 by the Department of Energy's Office of Advanced Automotive Technologies, within the Office of Energy Efficiency and Renewable Energy, Office of Transportation Technologies.

Research Participants

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Fuel Cells

Fuel cells continue to gain momentum as a clean and efficient potential future energy conversion technology. All the major automobile companies are spending substantial amounts of resources to develop polymer electrolyte fuel cell systems as a prime power source for passenger cars. Some insist on hydrogen stored on-board the vehicle, and others prefer gasoline as fuel, which then needs to be converted to a hydrogen-rich gas. The hydrogen camp counts on a future hydrogen infrastructure, but for the short term would generate hydrogen from natural gas at service stations.

Since internal combustion engines are being manufactured for less than \$30 per kilowatt, reducing the cost of fuel cell systems to a comparable level remains a major challenge. To that end, the use of fuel cells in stationary applications is viewed as a stepping stone. General Motors and several smaller companies have announced plans to market polymer electrolyte fuel cell systems for houses, cell-phone towers etc. These systems would operate on natural gas or propane fuel.

Another potential transportation application for fuel cells is the “auxiliary power unit”. Such units would not provide propulsion power but would generate electricity in a vehicle while the engine is turned off. A major application would be in heavy-duty vehicles for providing air conditioning during overnight idle periods. A leading candidate for this application is a low-temperature solid oxide fuel cell (SOFC).

The Department of Energy has established a major new initiative, the Solid State Energy Conversion Alliance, or SECA, to further the development of SOFCs.

The Chemical Technology Division is engaged in on-board fuel processing and in materials development for low-temperature SOFCs. We continue to lead the field in compact and efficient gasoline fuel processors, and we are developing a natural gas version for a private sponsor. In support of fuel processor development, we adapt and improve catalysts for the reforming and water-gas shift reactions. One of the reforming catalysts that was developed under this program has been licensed to

Süd-Chemie, Inc., of Louisville, Kentucky, and is widely used by the industry.

In materials development for SOFCs, we are exploring cathode materials, metallic bipolar plates, and sulfur-tolerant anodes. We also continue to model and analyze fuel cell systems as requested by the Department of Energy.

Fuel Processor Engineering

Making the transition to hydrogen-powered fuel cells

Fuel-cell-powered vehicles will find wide consumer acceptance if they can operate on widely available conventional fuels. The fuel processor will convert fuels such as gasoline to a hydrogen-rich reformat gas that can operate a fuel cell. Besides meeting stringent restrictions on the amount of carbon monoxide, sulfur, etc. that can be present in the reformat, the fuel processor should be energy-efficient, lightweight and compact enough to fit inside the hood of a vehicle without compromising performance.

The Chemical Technology Division's fuel processor is based on autothermal reforming. Development is occurring at three levels. The first is a study of the process fundamentals at the micro-reactor level (producing ~100 ml/min of H₂). At this level we study the effect of catalysts and operating conditions (temperature, space velocity, etc.) on performance (product yields, conversion efficiency). Second, conceptual reactor designs are modeled to specify the parameters (volume, surface area, etc.) that will result in the desired conversions and yields. Third, the engineering-scale reactor (capacity of 150 L/min H₂, or ~1/5th of full scale for light-duty vehicles) is fabricated and tested in the laboratory. These tests help validate the models and novel design features, and identify challenges and issues to related to the product design.

2001 Research Highlights

This year we demonstrated an engineering-scale integrated fuel processor (Fig. 1), which accepts room-temperature feeds of fuel, water, and air, and produces a

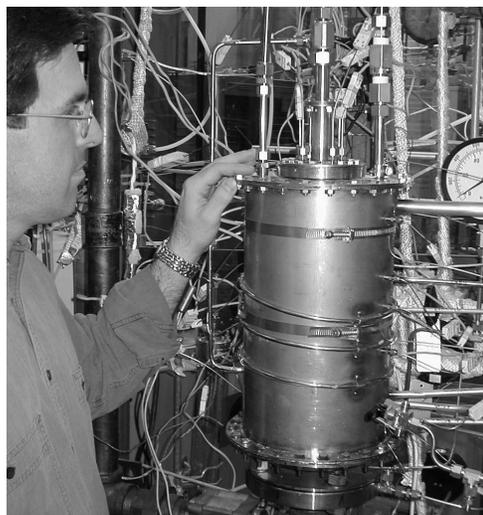


Fig. 1. The integrated fuel processor has been demonstrated to operate with gasoline.

reformat gas that contains ~40% (dry basis) H₂. After vaporization, the feeds are passed through the reformer where they undergo the autothermal reforming reaction, $C_nH_mO_p + x(O_2+3.76N_2) + (2n-2x-p)H_2O = nCO_2 + (2n-2x-p+m/2)H_2 + 3.76xN_2$.

In addition to hydrogen, carbon dioxide, and nitrogen, the reformat gas contains byproducts such as carbon monoxide, excess steam, hydrogen sulfide produced from the sulfur-containing organic species, and small amounts of light hydrocarbons (mostly methane). The reformat is first passed through a sulfur trap to reduce the sulfur level. This is followed by the water-gas shift reactor, where the majority of the CO is reacted with steam to produce CO₂ and additional H₂. The reformat leaving this unit contains ~1% CO and is further processed in the preferential oxidation unit, which reduces the CO level to 10-50 ppm.

The reactor shown in Figure 1 is 20 cm in diameter and 36 cm long, with a total volume of 11.3 liters. It has been designed to produce enough hydrogen to fuel a 10-kWe fuel cell system.

Figure 2 shows the product gas composition obtained from the conversion of iso-octane (used as a surrogate for gasoline). The fuel feed rate was gradually increased from 14 to 42 mL/min, equivalent to 25 to 75% of the rated power. The O₂/fuel molar ratio was varied between 3.0 and 3.5, and the average temperature in the reformer section was 750-800°C. The concentration of hydrogen varied from 38 to 43%, averaging 41%. Isooctane conversion was greater than 99%. The average CO₂, CO, and CH₄ concentrations were 17%, 4%, and 2%, respectively. The higher-than-expected CO concentration resulted from a non-optimal temperature profile in the water gas shift section.

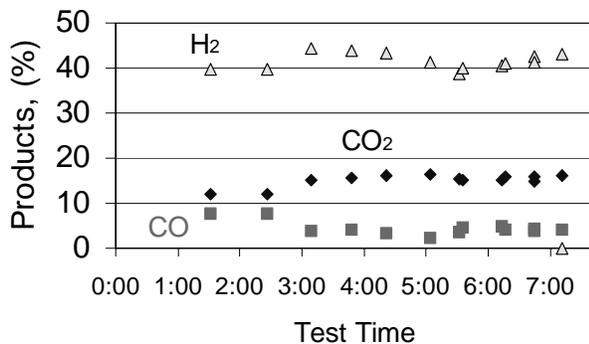


Fig. 2. Composition of the reformate gas produced from the conversion of iso-octane.

To meet the specifications of a polymer electrolyte fuel cell, the CO level needs to be reduced further. Los Alamos National Laboratory (LANL) has provided a stand-alone preferential oxidation unit that can be connected to the integrated unit. Ultimately, the preferential oxidation unit will be integrated into a hardware package.

A key criterion for a fuel cell vehicle will be rapid start-up. Our current effort is directed at examining the factors that limit rapid start, and on designing the reactor and devising start-up approaches that will enable the fuel cell system to generate power in 30 seconds or less.

Our fuel processor technology can be adapted to non-automotive applications (e.g., residential or portable). H2fuel Inc. (Spokane, Washington, and Mt. Prospect, Illinois) has established a cooperative research and development agreement with Argonne to apply our technology toward the development of a non-automotive fuel processor. In one year, this joint program has demonstrated the conversion of natural gas, ethanol, and gasoline in a compact fuel processor package capable of delivering enough hydrogen for a 6-kWe fuel cell system. The current-generation H2fuel package, which includes the Argonne fuel processor, the LANL preferential oxidation unit, and the control electronics, has delivered a reformat gas containing less than 5 ppm of CO.

This research is funded by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, Office of Advanced Automotive Technologies.

Research Participants

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Fuel Processor Catalysts

Fine-tuning catalysts to enable gasoline-powered fuel cells for vehicles

The development of fuel cell systems, in particular, the polymer electrolyte fuel cell (PEFC), for vehicle propulsion for transportation applications has seen remarkable progress in the past decade because of a need to improve energy efficiency and to address concerns about the environmental consequences of using fossil fuel. The lack of an infrastructure for producing and distributing H₂ has led to a research effort to develop on-board fuel processing technology for reforming gasoline and diesel fuels because of the existing infrastructure for producing and distributing these fuels for the internal combustion engine.

The development of new reforming catalysts has been crucial to the development of the fuel processor because of the unique operating modes the catalysts will experience in transportation applications—operation over a wide load range with only brief periods at full power, considerable time at 30-50% of the rated power, and relatively frequent shutoffs and restarts.

Argonne has developed and patented a reforming catalyst derived from solid oxide fuel cell technology, where a transition metal is supported on an oxide-ion-conducting substrate, such as ceria or zirconia, that is doped with a small amount of a non-reducible oxide, such as gadolinium or samarium, to improve its oxide ion conductivity and to increase the number of oxygen ion vacancies. Süd-Chemie, Inc., of Louisville, Kentucky, currently manufactures the Argonne catalyst under a licensing agreement.

2001 Research Highlights

A primary focus of our research this year has been to determine the activity of the Argonne catalyst at the high gas hourly space velocities (GHSV) required for transportation applications. Figure 1 shows that the product yields of H₂, CO, CO₂ and CH₄ obtained from reforming isooctane (2,2,4-trimethylpentane) are relatively independent of the GHSV up to 200,000 h⁻¹ for a Rh catalyst in powder form. The average H₂ yield of 10.2 moles of H₂ in the fuel gas per mole of isooctane in the feed agrees well with the predicted equilibrium value of 10.6 moles based on an exit temperature of 600°C. For transportation applications, a structured form of the catalyst, such as a monolith, is preferred over a pellet form in order to eliminate the degradation of the catalyst due to physical grinding that occurs with pellets as a result of vibrations during a normal drive cycle. Figure 2 shows the product yields of H₂, CO, CO₂ and CH₄ obtained from reforming isooctane at a GHSV of 11,000 h⁻¹ for the Rh catalyst supported on a cordierite monolith. Testing of the monoliths with more complex fuel mixtures such as commercial-grade gasoline is in progress.

This research is funded by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, Office of Advanced Automotive Technologies.

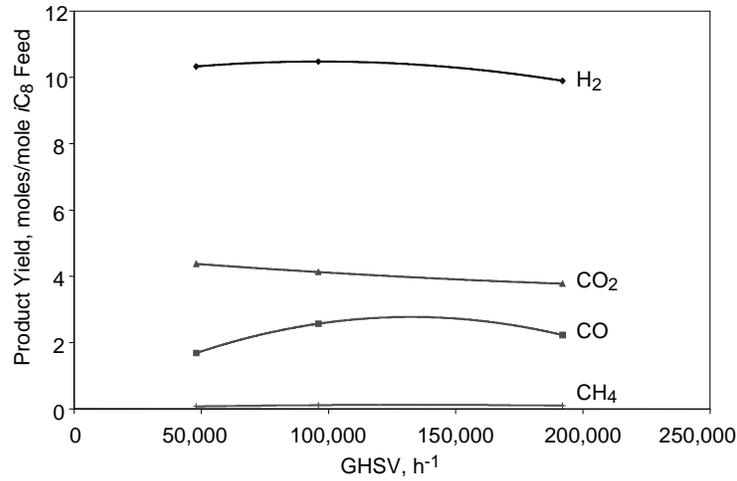


Fig. 1. Product yields of H₂, CO, CO₂, and CH₄ as a function of GHSV obtained from reforming isooctane using a Rh catalyst in powder form. The O₂:C ratio is 0.5 and the H₂O:C ratio is 1.1. The exit temperature of the catalyst is 600°C.

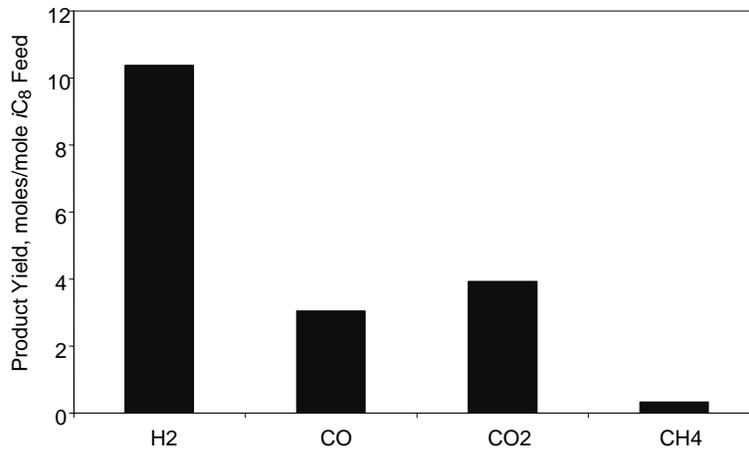


Fig. 2. Product yields of H₂, CO, CO₂, and CH₄ at a GHSV of 11,000 h⁻¹ obtained from reforming isooctane using a Rh catalyst supported on a cordierite monolith. The O₂:C ratio is 0.5 and the H₂O:C ratio is 1.1. The exit temperature of the catalyst is 730°C.

Research Participants

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Water-Gas Shift Catalysis

Finding catalysts that will work “under the hood”

Hydrocarbon fuel reformers are being developed for polymer electrolyte fuel cell (PEFC) systems for transportation, stationary, and portable power applications. The reforming of a carbonaceous fuel results in a product gas that contains hydrogen as a major component, along with carbon monoxide, carbon dioxide, water vapor, and trace amounts of other species. Depending on the fuel and the reforming process used, the CO content in the reformat may be as much as 16% by volume. The performance of the PEFC is severely degraded by as little as 100 parts per million (ppm) CO in the fuel gas. Therefore, it is necessary to decrease the CO concentration to trace levels. Current fuel processor designs employ a two-step catalytic process in which the CO concentration is reduced to ~1% using the water-gas shift (WGS) reaction, $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$, and then further reduced to <100 ppm using preferential oxidation (PrOx) of CO.

Two catalysts are currently used in the chemical process industry: iron-chrome oxide catalyst, which operates temperature of 300-450°C and is referred to as the high-temperature shift (HTS) catalyst, and a copper-zinc oxide catalyst, which operates at 160-250°C and is referred to as the low-temperature shift (LTS) catalyst. These catalysts have several shortcomings relative to transportation applications. For example, they must be reduced in H_2 prior to exposure to the fuel gas and must not be exposed to air in the reduced state. Due to the highly intermittent duty cycle and size/weight constraints of transportation systems, new WGS catalysts are required that (1) eliminate the need to activate the catalyst

in situ, (2) eliminate the need to sequester the catalyst during system shutdown, (3) increase tolerance to temperature excursions, and (4) reduce the size and weight of the shift reactors.

We are investigating bifunctional WGS catalysts where one component of the catalyst adsorbs or oxidizes CO and the other component dissociates water. Research is focusing on metal-support combinations to promote this bifunctional mechanism. The metallic component is chosen to adsorb CO at intermediate adsorption strengths (Pt, Ru, Pd, PtRu, PtCu, Co, Ag, Fe, Cu, and Mo). The support is chosen to adsorb and dissociate water, typically a mixed-valence oxide with redox properties or oxygen vacancies under the highly reducing conditions of the fuel gas.

2001 Research Highlights

This year we developed a copper/oxide catalyst with the same activity as the commercial copper-zinc oxide catalyst (Fig. 1). The Argonne copper/oxide catalyst, however, can operate above 250°C without deactivation and retains its activity after exposure to air at 230°C (Fig. 2). Its higher operating temperature range allows it to be used in both the HTS and LTS stages.

This catalyst also has higher water-gas shift activity than iron-chrome and so can dramatically reduce the size and weight of the HTS stage. The temperature stability of the copper/oxide catalyst allows the LTS stage to run at a higher inlet temperature (e.g., 300°C) than would be possible with copper/zinc oxide (200°C). The improved

kinetics afforded by a higher operating temperature will reduce the size and weight of the LTS. This year we also developed perovskite catalysts and catalysts consisting of cobalt supported on transition metal oxides. These catalysts are more active than commercial iron-chrome at 400°C and the activity is not affected by exposure to air at 400°C.

This research is funded by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, Office of Advanced Automotive Technologies.

Research Participants

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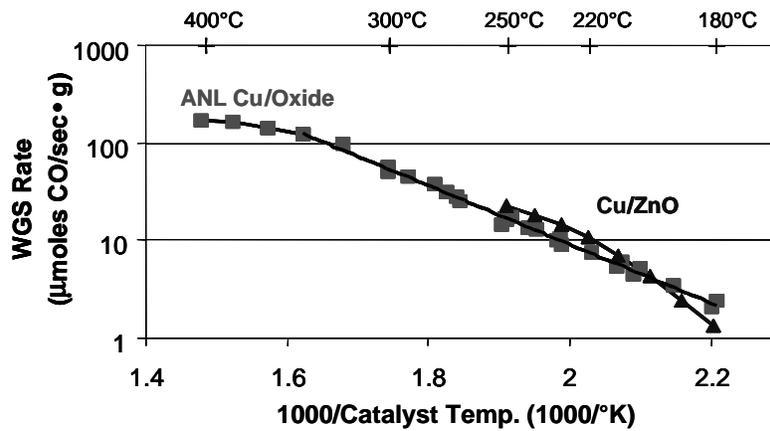


Fig. 1. Argonne’s copper/oxide catalyst has comparable activity to commercial copper/zinc oxide and is not limited to temperatures <250°C.

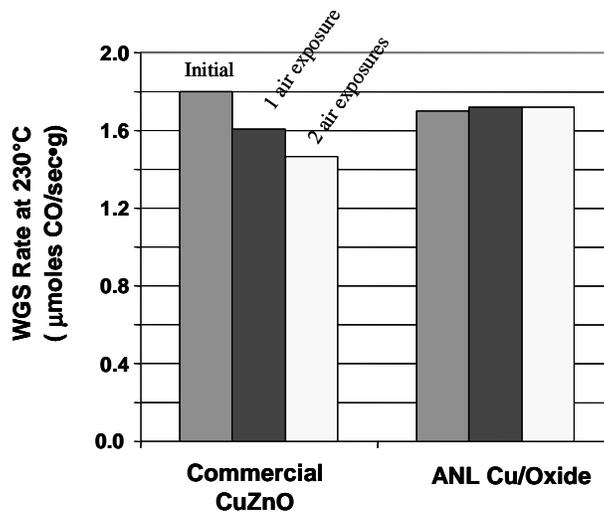


Fig. 2. Argonne’s copper/oxide catalyst retains activity when exposed to air at 230°C.

Fuel Cell Systems Analysis

Finding the right balance of efficiency, cost, and power density for automotive use

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. Work in the Chemical Technology Division is addressing design, performance, and cost issues, such as the influence of the various design and operating parameters and system configurations on the system's efficiency, transient response, and cost. These analyses are being used to identify the key improvements needed in component performance and the potential trade-offs in efficiency, cost, and power density to meet automotive requirements. For these analyses, we use the GCtool software package developed at Argonne.

2001 Research Highlights

During 2001, we developed reaction kinetics and reactor designs for fuel processor components, developed detailed multi-nodal transient models for radiators and condensers, analyzed the influence of the design operating pressure on the sizes of the major components in pressurized fuel cell systems, and quantified the effects of varying the design-point cell voltage on system efficiency and fuel cell stack size. The last two analyses are discussed briefly below.

Component Size versus Operating Pressure: We quantified the effects of different design operating pressures on the sizes of the fuel cell stack, the fuel processor, and the

radiator and condenser for a pressurized, gasoline-fueled polymer electrolyte fuel cell system. The original DOE guidelines specified a compressor discharge pressure of 3.2 atm; however, the compressor/expander hardware being developed appears more likely to offer somewhat lower discharge pressures. Our analyses (Fig. 1) showed that decreasing the design operating pressure from 3.2 atm to 2.0 atm would increase the sizes of all components, but by different amounts: fuel cell stack active area by ~5%, fuel processor volume by ~20%, and radiator and condenser masses by ~60%.

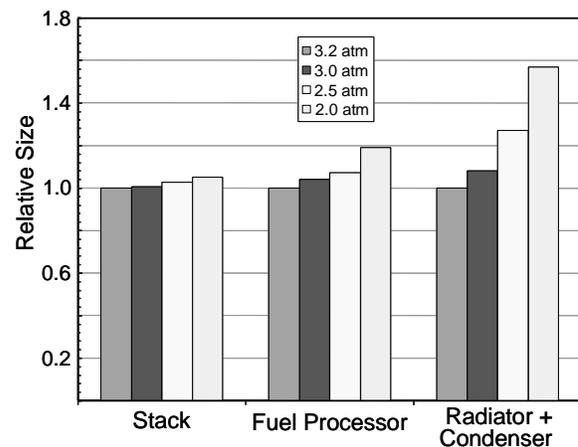


Fig. 1. Decreasing the design operating pressure (from 3.2 to 2.0 atm) increases the relative sizes of the fuel cell stack, fuel processor, and the major heat exchangers.

We have also analyzed gasoline-fueled atmospheric pressure systems, where waste heat rejection and water management have been identified as significant issues, particularly at high ambient temperatures. Developers are pursuing both pressurized and ambient pressure systems, and these analyses can help to provide a common

means of evaluating the relative merits of each.

Effect of Design-Point Cell Voltage: The fuel cell stack is the most expensive component of a fuel cell system. For a given power rating, it is possible to decrease the cell active area required (and hence, the cost of the fuel cell stack) by decreasing the cell voltage and increasing the current density at the design operating point. There is, however, a concomitant decrease in system efficiency. The results of these interactions are summarized in Figure 2, where the active cell area and the system efficiencies at full load and at 25% of full load are shown as a function of the cell voltage at the rated power point.

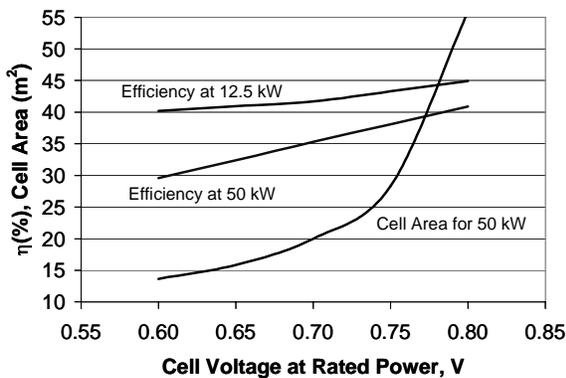


Fig. 2. Decreasing design-point cell voltage also decreases the required fuel cell stack active area and overall system efficiency, as shown here at the rated power and at 25% of the rated power.

As the design-point cell voltage is decreased from 0.8 V to 0.6 V, the required active fuel cell area decreases by a factor of ~3, from 55 m² to 14 m². At the same time, however, the system efficiency also decreases significantly, from 41% to 29% at full load, and from 45% to 40% at one-fourth of full load, for example.

In addition to these and other analyses of fuel cell systems, we are working with Arthur D. Little to define system configurations, environmental parameters, and component performances for that company's DOE-sponsored study of the manufacturing costs of automotive fuel cell systems, and to evaluate trade-offs in size, cost, and efficiency.

This research is funded by the U.S. Department of Energy, Energy Efficiency and Renewable Energy, Office of Advanced Automotive Technologies.

Research Participants

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Materials for Solid Oxide Fuel Cells

Reducing cost and improving performance in SOFCs

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

The overall goal of this research and development (R&D) is to reduce costs while improving performance, to make the fuel cells competitive with existing technologies. Much of the present effort is focused on developing SOFC materials for use at 800°C or lower, where alternative, potentially lower-cost, materials become applicable. Operating the SOFC at lower temperatures, however, increases significantly the performance requirements for the cell and stack components, such that new materials need to be developed.

2001 Research Highlights

The Chemical Technology Division is developing advanced cathodes for use at $\leq 800^\circ\text{C}$, sulfur-tolerant anodes (for SOFC operation on sulfur-containing fuels), and metallic interconnects.

Low-Temperature Cathode Materials: The cathode material used in today's SOFCs is a mixture of strontium-doped lanthanum manganite (LSM) and yttria-stabilized zirconia (YSZ). This material, however, has poor conductivity and performance at $< 900^\circ\text{C}$. We are exploring the options of replacing Mn in LSM by Co, Fe, or Ni, as well as using materials other than perovskites. We have found that ferrite-based perovskites display the best performance at all temperatures, and $\text{La}(\text{Sr})\text{FeO}_3$ (LSF) has proven to

be the most compatible and best performing cathode material, as indicated in Figure 1.

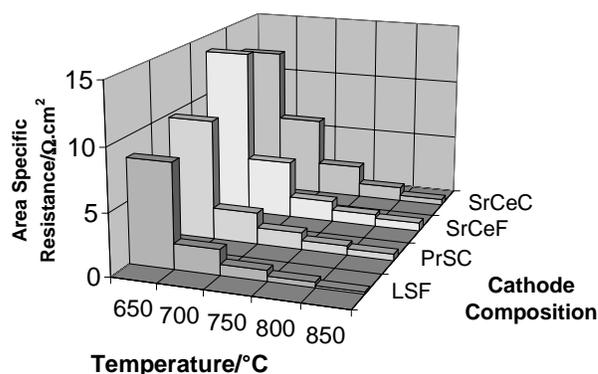


Fig. 1. Area-specific resistance of candidate cathode materials as a function of temperature (LSF - lanthanum strontium ferrite, PrSC - praseodymium strontium cobaltite, SrCeF - strontium cerium ferrite, SrCeC - strontium cerium cobaltite).

The LSF material improved with current-conditioning. Cathode overpotentials decreased with time over 15 days at $250\text{ mA}/\text{cm}^2$ and 800°C , as shown in Figure 2. The values for LSF at 800°C were similar to LSM at 950°C , showing that LSF is potentially a much superior cathode material to the presently used LSM. Full cell polarization curves confirmed this (Fig. 3).

Sulfur-Tolerant Anode Materials: Sulfur species are present as contaminants or additives in conventional fuels (~ 20 ppmv in natural gas, and 30 ppmw in future gasoline/diesel). The corresponding sulfur content in the reformat is 10–15 ppmv for natural gas and 3–5 ppmv for gasoline/diesel. Even at these low levels, sulfur degrades the performance of the conventional Ni-YSZ anodes.

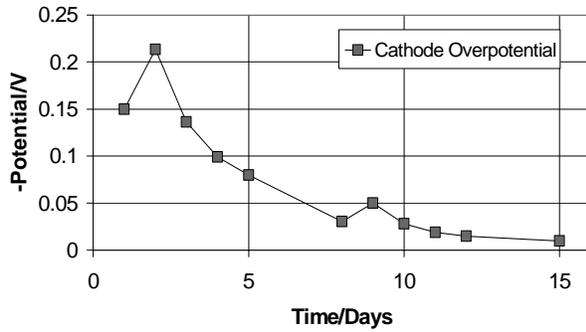


Fig. 2. Current conditioning is effective in reducing cathode overpotentials.

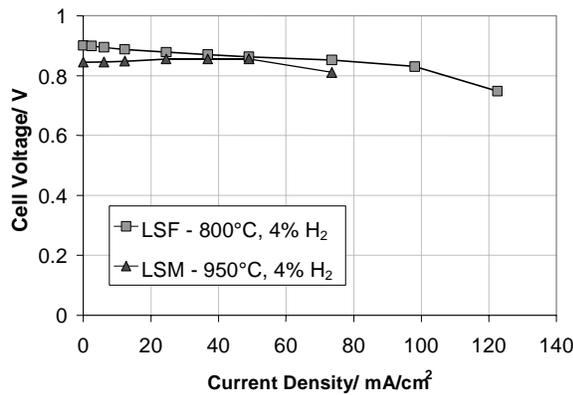


Fig. 3. Performance of LSF cathodes at 800°C is comparable to or better than that of LSM cathodes at 950°C.

We are developing sulfur-tolerant anode materials by one or more of the following approaches: (1) Modify the Ni-YSZ with an additive that has suitable redox chemistry, where the H₂S is captured by the additive in preference to Ni and is subsequently oxidized to SO₂. (2) Replace the Ni in Ni-YSZ with other metal or alloy that is active for electrooxidation of H₂ but resistant to poisoning by H₂S. (3) Investigate new classes of materials based on carbides and/or sulfides.

We have identified several candidate sulfur-tolerant anode materials based on thermodynamic considerations and prepared half cells using these materials. Shakedown tests of the experimental apparatus show severe poisoning of Ni-YSZ by H₂S at 5-30 ppm but no poisoning of Pt anodes (Fig. 4).

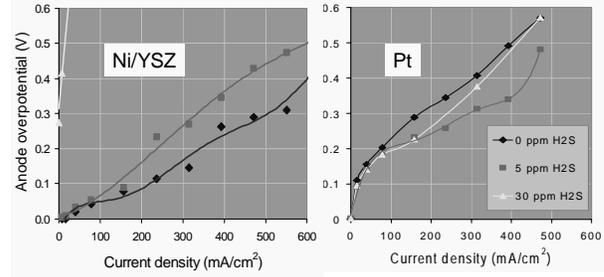


Fig. 4. The conventional Ni-YSZ anode is severely poisoned by H₂S at 5–30 ppm (left) while a Pt anode is unaffected (right).

Metallic Interconnect (Bipolar) Plates: We are investigating alloys similar to ferritic stainless steels but with reduced Cr and added constituents to improve properties and provide a protective scale. We have developed a novel processing technique that can yield almost any desired shape (see Fig. 5), with graded composition from one surface to the other, if desired.

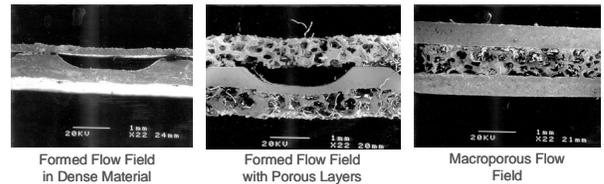


Fig. 5. Examples of different metallic shapes and structures that can be used as interconnects in SOFC stacks.

This research is funded by the U.S. Department of Energy, Office of Fossil Energy, through the National Energy Technology Laboratory, Morgantown, West Virginia, and Pittsburgh, Pennsylvania.

Research Participants

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Waste Materials Research

The Chemical Technology Division (CMT) conducts research on the treatment and disposal of nuclear wastes generated at Department of Energy sites and by commercial light water reactors. Our research falls into two primary areas: (1) the behavior of wastes already in or slated for disposal in geologic repositories, and (2) methods of separating wastes to reduce overall volume and allow further treatment.

Waste Form Behavior

Funded by the Department of Energy (DOE), this work is conducted on all the major waste forms intended for interment in repositories: spent nuclear fuel from DOE sites, spent fuel from commercial light water reactors, and the ceramic waste form that results from the electrometallurgical treatment of spent sodium-bonded fuel from Experimental Breeder Reactor-II at the Argonne-West site in Idaho Falls, Idaho.

Our work focuses on determining the release rate of radionuclides, qualifying the nature of the release, and the formation and character of colloids through chemical and

physical characterization, testing, and analysis.

Spent Nuclear Fuel From DOE Sites: DOE is the steward of about 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 behavior for long time periods under repository-relevant conditions must be understood.

DOE spent fuels have been divided into two groups to facilitate degradation testing—metallic uranium and mixed-oxide fuels. We are performing characterization and ground-water corrosion tests on both. A major finding this year was the observation of colloids in the leachate from both types of fuels. These particles are of significant concern because they could absorb radionuclides from the corroding fuels and transport them through the subsurface environment.

Spent Fuel from Commercial Reactors: 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 will be used to support the site recommendation regarding Yucca Mountain. Specifically, we have been selected to provide analysis and modeling reports on a variety of topics, including the corrosion rate of defense high-level waste glass, concentration limits for colloid-associated and mixed-phase dissolved radionuclides released through environmental degradation, and interaction between corroding fuel and the cladding in fuel rods.

CMT also supports the Yucca Mountain Project by characterizing and testing commercial spent fuel. The objective is to determine how spent fuel corrodes and releases radionuclides under the conditions to which it may be exposed in an unsaturated repository (one that will not at any relevant time have a significant probability of flooding with water). 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. This year's efforts have concentrated on the behavior of high-burnup and gadolinium-bearing fuels.

CMT 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. We are attempting to diversify the colloids work into non-nuclear applications.

Spent Sodium-Bonded Fuel: A glass-bonded sodalite waste form has been developed by CMT to immobilize salt wastes generated during the electrometallurgical treatment of EBR-II fuel. 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 are underway to demonstrate how the impact of these waste forms can be integrated into the DOE "Total System Performance Assessment" that will support the license application for the repository.

Waste Separation

Aqueous separations efforts focus on (1) substitution of low- for high-enriched uranium in the production of molybdenum-99, (2) use of centrifugal contactors to separate waste streams for the salt waste in tanks at the Savannah River Site, and (3) the accelerator transmutation of waste.

Use of Low-Enriched Uranium in Molybdenum-99 Production: 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 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 cooperative work with Argentina, we are modifying their current process to accept the new target.

Using Centrifugal Contactors to Separate Waste Streams: An alkaline-side solvent-extraction process for ^{137}Cs removal from alkaline tank waste was evaluated at CMT in cooperation with Oak Ridge National Laboratory, the Savannah River Technical Center, and the Savannah River Site (SRS). A week-long demonstration of the process in a 36-stage 2-cm centrifugal contactor has demonstrated decontamination factors significantly above those expected. This demonstration was a major reason this process was chosen for deployment at SRS to remove ^{137}Cs from all their tank waste solutions.

Separating Waste Streams: The Accelerator Transmutation of Waste (ATW) Program was created to address the disposal of commercial nuclear fuel and improve the performance of a long-term geological repository. The goal is to separate dissolved commercial fuel into three streams: (1) a transuranic (TRU) product stream that will be processed further, converted to ATW

fuel, and transmuted by fissioning to generate electrical power, (2) separate ^{99}Tc and ^{129}I streams that will be fabricated into targets for transmutation, and (3) a uranium product stream that will be disposed as low-level waste. Activities in 2001 were focused on the alternative aqueous front end and demonstrating its ability to meet processing goals. Tasks focused on developing and demonstrating the capabilities of the Uranium Extraction (UREX) flowsheet to generate the three product streams and developing the AMUSE (Argonne Model for Universal Solvent Extraction) code to design optimized flowsheets for the demonstration.

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.

Spinoff Research

In spinoff projects from nuclear waste form research, CMT is investigating the chemical durability of a dental glass-ceramic in collaboration with scientists at the University of Florida School of Dentistry. CMT is also studying the use of magnetic particles for the delivery of drugs in collaboration with Argonne's Energy Technology Division and the University of Chicago. We also are working with the Energy Technology Division on the development of its advanced ceramic material, Ceramicrete, for waste forms for the solidification of low-level waste at the Hanford and Savannah River sites. In addition, we are investigating the oxidation states of plutonium oxide and the generation of hydrogen using the heat stored in the coolant of a liquid metal reactor.

Waste Form Alteration Products

Understanding how the environment affects nuclear waste behavior

One challenge in evaluating the long-term behavior of nuclear waste is to understand how the environment affects the durability of various waste forms. One potential effect is the release of hazardous elements into groundwater; another is the incorporation into alteration products of elements released from the original waste form, effectively creating “secondary” waste forms that are more stable than the original ones.

The Chemical Technology Division (CMT) has conducted corrosion studies of waste forms exposed to various environmental conditions. Solids formed during these studies are analyzed by a variety of chemical and structural methods, providing detailed information on the roles that solids may play in the release of hazardous elements.

CMT discoveries this year led to the development of an alternative solubility model for neptunium-237 that may be useful in evaluating long-term performance of the repository at Yucca Mountain, Nevada.

2001 Research Highlights

The long half life (2.14 Ma) and potential mobility of neptunium-237 (^{237}Np) in oxidizing groundwater make it an important isotope for evaluating the long-term performance of a geologic repository for high-level nuclear waste. Current performance assessment models for Yucca Mountain indicate that the dose contribution from ^{237}Np may become significant after about 50,000 years. This is based in part on the assumption that dissolved concentrations of ^{237}Np in water emanating from a breached

waste package with spent fuel will be limited by the precipitation of neptunium pentoxide (Np_2O_5); however, crystalline Np_2O_5 has never been identified as an alteration product of corroded spent nuclear fuel. In our experiments examining oxidative dissolution of spent fuel under hydrologically unsaturated conditions, Np is released to solution congruently with uranium (U); however, a substantial amount of U derived from the dissolving fuel re-precipitates on the surface of the fuel, implying that a comparable fraction of Np also is being retained in precipitated solids. Furthermore, the concentrations of Np released to solution in drip experiments are well below Np concentrations that might be expected if Np_2O_5 were limiting dissolved Np concentrations. If concentrations of Np in solutions recovered from CMT drip tests are representative of concentrations likely to emanate from a breached waste container with commercial spent nuclear fuel, Np-related radiation doses to individuals near Yucca Mountain might be several orders of magnitude lower than current estimates.

Microstructural and chemical analyses of solid alteration products formed during corrosion of spent fuel in humid air revealed that the uranium(VI) oxyhydroxide *dehydrated schoepite* contained trace levels of ^{237}Np . Because U(VI) oxyhydroxides may persist for hundreds of thousands of years or more, they are potentially important long-term fission-product and actinide hosts that may help limit dissolved concentrations of radionuclides such as ^{237}Np , if those radionuclides can be incorporated into their structures.

CMT's discovery that low levels of Np (on the order of 0.4 wt %) are incorporated in dehydrated schoepite led to the hypothesis that dissolved Np concentrations in a breached waste package can be modeled by using Np-bearing schoepite as the solubility-limiting phase for both U and Np. Dissolved concentrations of Np estimated with this model agree qualitatively with those measured in solutions recovered from our experiments on spent fuel (Fig. 1). This model is now an important alternative solubility model for ^{237}Np for potential use in performance assessment evaluations of the potential repository at Yucca Mountain.

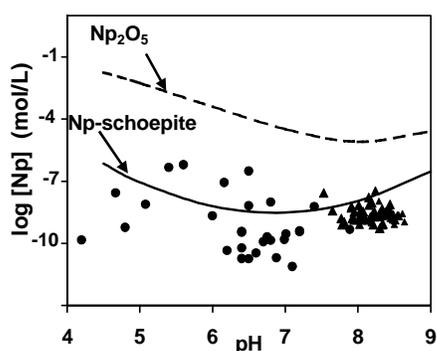


Fig. 1. Concentration of dissolved Np as a function of pH in groundwater based on Np_2O_5 as the solubility limiting solid (dashed line) compared with that calculated from the model based on Np-bearing schoepite developed by CMT (solid line).

Aqueous corrosion experiments of unirradiated Np-doped U oxides have shown that dehydrated schoepite can incorporate Np during humid air corrosion of Np-doped U_3O_8 at 150°C , corroborating our earlier findings, but under more carefully controlled conditions, and offering preliminary validation of our hypothesis. On the other hand, our results suggest that the ability of dehydrated schoepite to incorporate Np may decrease as temperature decreases, because the Np concentration in dehydrated schoepite formed at 150°C is approximately

five times greater than Np concentrations in dehydrated schoepite formed during fuel corrosion at 90°C .

We observed NpO_2 to crystallize at 90° and 150°C during corrosion of U_3O_8 with Np added (Np:U = 1:8) indicating that NpO_2 is a stable Np-bearing solid under nominally oxidizing conditions (Fig. 2). This is consistent with current thermodynamic data, and indicates that previous failures to precipitate NpO_2 from Np(V)-bearing solutions below 250°C reflect a kinetic barrier. We also found that Np_2O_5 crystallizes from altered Np-doped U_3O_8 during humid-air corrosion at 90°C , where it is approximately as abundant as the coexisting NpO_2 . Whether the coexistence of two Np oxides with Np in different oxidation states reflects thermodynamic or kinetic control is not yet known.

This research is funded by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Site Characterization Project.

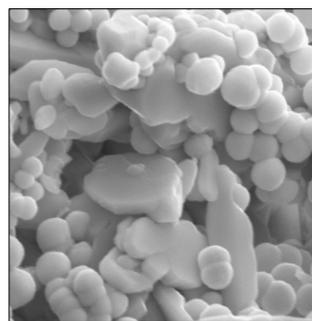


Fig. 2. Scanning electron image showing 1–3 micrometer spheres of NpO_2 with tabular crystals of dehydrated schoepite. Experiment at 150°C . Field of view is 0.03 mm across.

Research Participants

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Corrosion of High-Burnup and Gadolinium-Bearing Spent Fuels

Characterizing and testing commercial spent nuclear fuel

As of September 2000, 42,000 metric tons of spent fuel are being stored at U.S. power plants. By 2035, the amount could double if all currently operating plants complete their initial 40-year license period. The spent fuels include pressurized water (PWR) and boiling water (BWR) reactor fuels with a wide range of fuel burnup (20-70 MWd/kgU); some fuels contain gadolinium (Gd), a rare-earth element, added as a burnable neutron poison. Source term definition requires information on the release from different types of spent fuels under conditions expected at the Yucca Mountain repository.

The Yucca Mountain (YM) site consists of hydrologically unsaturated volcanic tuff beds in an oxidizing environment. Service condition tests that examine the behavior of light water reactor (LWR) fuels under similar hydrologically unsaturated and oxidizing conditions are in progress to determine radionuclide release rates. PWR fuels with burnups of 30 and 45 MWd/kgU have oxidized and formed uranyl alteration phases, which contain silicon, a major component of YM groundwater.

Because initial PWR tests do not examine the effect of very high burnup (70 MWd/kg U) or of the presence of gadolinium, their nuclide release rates may not be representative of those of the suite of fuels to be placed in a repository. Therefore, two high-burnup BWR fuels, one containing gadolinium, are being examined under similar test conditions. Of particular interest are the release behaviors of ^{99}Tc ,

the primary contributor to the dose rate at the YM site boundary at <50,000 years, and ^{237}Np , the primary contributor at >100,000 years.

2001 Research Highlights

Effect of Gadolinium on Nuclide Release Rates: The release rates of ^{99}Tc for the two BWR fuels are shown in Figure 1. For fuel that does not contain gadolinium (9A), the ^{99}Tc release rate is almost two orders of magnitude larger than for the gadolinium-containing fuel 9C. There is no difference in their ^{237}Np release rates. Two explanations for the differences in release behavior are possible. First, the suites of alteration phases that form when 2% gadolinium is present have smaller solubility products than those formed in gadolinium's absence. These former phases also incorporate ^{99}Tc , reducing its release rate. Second, the rate of fuel oxidation and dissolution may be reduced when gadolinium is present; this would also reduce the ^{99}Tc release rate. To

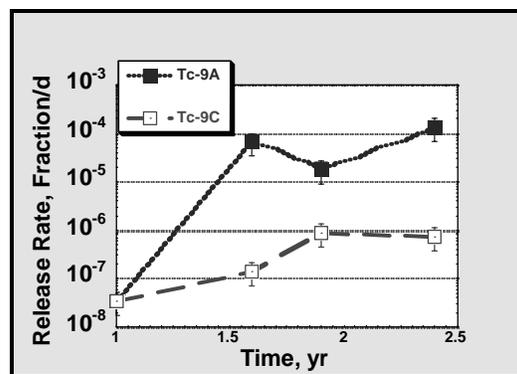


Fig. 1. ^{99}Tc mass fraction release rates for BWR fuels. The 9C fuel contains 2% gadolinium.

differentiate between the two possibilities, the alteration phases will be characterized. If ^{99}Tc retention can be assured when gadolinium is present, the use of gadolinium at YM could potentially reduce the ^{99}Tc source term.

Effect of High Burnup on Nuclide Release Rates: For PWR fuels, a general corrosion reaction occurs at the fuel surface. After the first year of reaction, uranyl alteration phases, which have formed on the fuel surface, control the solubility of the actinides and other nuclides that are co-precipitated. Release rates of nuclides with high dissolved concentrations under oxidizing conditions like ^{99}Tc and ^{129}I should be bounded by the fuel's reaction rate. Thus, their release rates can be used to compare the effect of different burnups on the rate of fuel reaction and dissolution. Nuclide release rates for ^{99}Tc and ^{129}I are shown in Figure 2 for the fuels with the highest and lowest burnup of those tested.

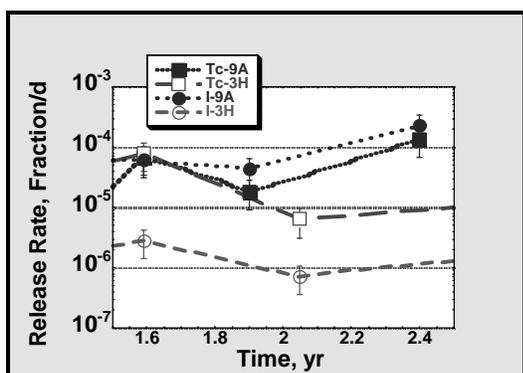


Fig. 2. ^{99}Tc and ^{129}I mass fraction release rates for BWR fuel, 9A (burnup of 71 MWd/kgU) and PWR fuel 3H (burnup of 30 MWd/kgU).

The ^{129}I release rate of the high-burnup 9A fuel is two orders of magnitude larger than that of the PWR fuel. The ^{99}Tc release rate of the 9A fuel is an order of magnitude larger than that of the PWR fuel. Having both the ^{129}I and ^{99}Tc release rates larger for the high-burnup fuel is consistent with a more rapid fuel oxidation and dissolution rate. The ^{99}Tc and ^{129}I release behavior of the high-burnup fuel must be confirmed at longer time intervals before these observations can be used to predict the reaction behavior of other fuels.

This study has shown that both the presence of 2% gadolinium and a very high burnup can affect the nuclide release rates of LWR fuels. The presence of gadolinium reduces the ^{99}Tc release rate by almost two orders of magnitude compared with the release rates of a fuel with a similar burnup. A very high-burnup (71 MWd/kgU) fuel, without gadolinium, has ^{99}Tc release rates an order of magnitude larger than those for a low-burnup fuel (30 MWd/kgU). The larger ^{99}Tc release rate and larger ^{129}I release rate are consistent with a higher fuel dissolution rate for high-burnup fuel.

This research is funded by the U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Yucca Mountain Site Characterization Project.

Research Participants

Patricia A. Finn, Robert J. Finch, Lester Morss, Yifen Tsai, and James C. Cunnane. For more information contact Robert Finch (630-252-9829, finch@cmt.anl.gov).

Colloid Characterization

Understanding the way radionuclides travel underground

Common household products such as milk, wine, and hand cream are colloidal suspensions whose shelf lives are determined by their rates of oxidation and the extent to which their suspended sub-micron-sized particles stick together, or agglomerate. Although nuclear waste bears little resemblance to such products, it generates colloidal materials as it corrodes in aqueous (water-based) solutions. As in household products, the stability of those colloids depends on their oxidation and agglomeration kinetics; in this case however, colloids can incorporate radionuclides, and are termed radiocolloids.

In the proposed Yucca Mountain repository for nuclear waste, radiocolloids are a major concern because they may provide a means for transporting radionuclides from a breached waste package through the subsurface environment to a potable water aquifer. Our programs examine waste form colloids to determine their stability, reactivity, and potential transportability. While we can utilize the chemical and mathematical theories and analysis methods more commonly applied to household product colloids, we also develop and modify methods specifically for radioactive materials at ultra-low concentrations.

This year we developed enhanced research methods that will aid us in predicting the subsurface transport of radiocolloids.

2001 Research Highlights

The most useful information for predicting the stability of a colloid includes its size, charge, mineral form, and association with

radionuclides and/or other colloids. Because no analytical technique is completely free of bias or artifacts, we employ an arsenal of specialized techniques. In that way, the potential biases of one technique can be checked or corrected by another. For example, anisotropic membrane ultrafilters enable the separation of colloidal particles from dissolved species. However, particle charge or shape can influence filtration efficiency and prevent unambiguous size determination. To provide scientific certainty, we determine particle size by additional unrelated methods, including photon correlation spectroscopy (PCS) (see Fig. 1) and transmission electron microscopy (TEM; see Fig. 2).

This year we added a new technique to our size-determination arsenal, small angle x-ray scattering (SAXS). Using highly energetic synchrotron radiation from the Advanced Photon Source, SAXS successfully determined particle dimensions and shapes for both natural and uranium-bearing colloids.

Determination of colloid concentration can also be challenging. While concentration estimates can be made from PCS intensities, the method depends on particle size and refractive index. For polydisperse mixtures or mixtures of different colloid substrates, concentration determination can become intractable. However, colloid filtration followed by inductively coupled plasma mass spectrometry (ICPMS) allows an independent determination of elemental (and isotopic) composition within each colloid size group. During the past year, we modified a new, tandem chromatography/mass spectrometry technique for

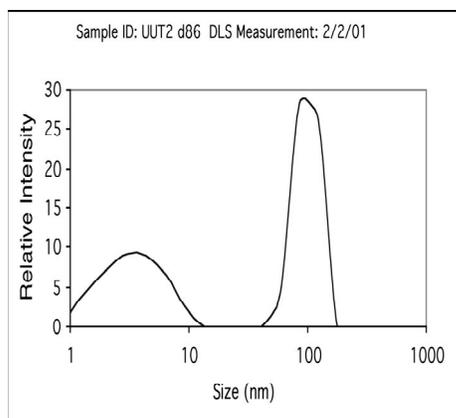


Fig. 1. Photon correlation spectroscopy is used to determine colloid size. The data here show the bimodal size distribution of colloids formed in the corrosion of metallic uranium fuel.

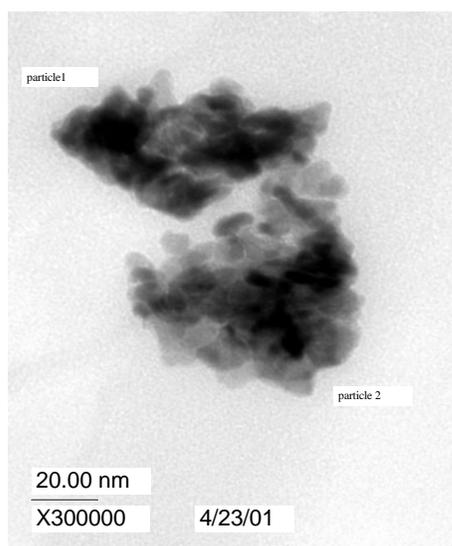


Fig. 2. This TEM image shows the size and agglomeration of uranium dioxide colloids generated during corrosion of metallic uranium fuel in groundwater.

determination of ultra-low concentrations of radiocolloids. This state-of-the-art technique, size exclusion chromatography-high resolution-ICPMS allows on-column size fractionation of microliter quantities of samples with sequential mass spec determination of fg/mL concentrations of elements within each size category.

This year we also upgraded our ability to determine colloidal surface charge and zeta potential. Using electrophoretic light scattering (ELS), we determined the pH and ionic strength regimes over which colloidal mineral substrates are stable (see Fig. 3). As this research continues, we will be able to determine sub-surface aquatic conditions that promote or hinder transport of radionuclide-associated colloids.

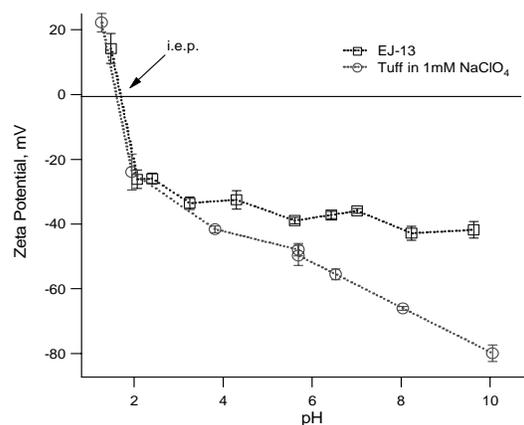


Fig. 3. This year CMT determined colloidal zeta potentials of tuff from Yucca Mountain in ground water (EJ13) and inert electrolyte (NaClO₄) by ELS. At zeta potentials between 0 and ± 30 mv, the colloids precipitate; only at $>|30|$ mv are they stable.

As we apply the suite of colloid characterization techniques to the problem of radiocolloids, we are able to determine the chemical and physical nature of the waste-form colloids, predict their reactivity, and ultimately predict their mobility in the aqueous environment.

This research is funded by the U.S. Department of Energy, National Spent Nuclear Fuel Program.

Research Participants

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Waste Form Qualification Program

Meeting requirements for high-level waste storage

Waste forms produced to immobilize high-level nuclear wastes must be qualified for disposal in the federal high-level waste repository to ensure that the disposal system will meet regulatory requirements.

Chemical Technology Division (CMT) scientists and engineers are conducting tests and analyses to support the qualification of several high-level radioactive waste forms, including commercial and defense spent nuclear fuels, high-level waste glasses, the pyrochlore ceramic for excess weapons plutonium, and the glass-bonded sodalite ceramic and metallic waste forms for electrometallurgically treated Experimental Breeder Reactor II spent sodium-bonded fuel.

Guidance for qualification requirements is from two primary sources. The first source is the Waste Acceptance System Requirement Document (WASRD), which provides requirements that address the chemical, physical, and radiological properties of the waste form and packaging materials. The WASRD was developed to define the interface between the U.S. Department of Energy (DOE) Office of Civilian Radioactive Waste Management, which is responsible for construction and operation of the federal high-level waste disposal system, and the DOE Offices of Environmental Management and Nuclear Energy, Science, and Technology, which are responsible for waste form production. The WASRD specifies limits on the radionuclide contents, dimensions, and weights of waste packages, the need to monitor product consistency, the required production records, package labeling, etc. For the most part, the WASRD

requirements are met by performing specific tests and analyses and by conforming waste package designs.

The second source used for guidance is the more subjective requirement that a waste form not compromise the capacity of the disposal system to satisfy regulatory requirements, such as groundwater contamination limits for hazardous and radioactive species. Total System Performance Assessment (TSPA) calculations are being performed by DOE to demonstrate that the disposal system is expected to meet regulations regarding the containment of radionuclides. Models are being developed to take into account the degradation of each type of waste form.

2001 Research Highlights

Most of the work being done in CMT to qualify waste forms is focused on (1) gaining an understanding the important degradation modes that lead to the release of radionuclides, (2) developing first a conceptual model and then a quantitative model, (3) measuring model parameter values, and (4) confirming that the model adequately represents the degradation behavior that will likely occur over geological times under evolving disposal conditions.

CMT staff are also working with scientists in the Yucca Mountain Project to integrate the waste form degradation models into TSPA and interface with other models used in TSPA, such as groundwater and colloid transport models.

A range of test and analytical methods are used by scientists in CMT to support

qualification of waste forms for disposal. Some tests highlight a particular aspect of corrosion behavior to characterize a specific corrosion mode or measure a particular model parameter value. Test conditions may differ significantly from the anticipated disposal environment, and the test conditions needed to highlight a corrosion mode may be different for different waste forms. For example, vapor hydration tests are conducted at temperatures and water vapor pressures that are much higher than those that can occur in the disposal system to promote the formation of thermodynamically stable alteration phases. These tests reduce the time required for the solution to become saturated with respect to alteration phases. The vapor hydration test may not have the same accelerating effect on other waste forms that corrode by mechanisms different from waste glasses. For example, vapor hydration tests have little or no accelerating influence on the corrosion rate of metallic waste forms, which is not sensitive to either the solution chemistry or the formation of alteration phases.

Other tests are designed to measure the corrosion response under conditions similar to those expected in the disposal system. Tests such as these are run initially to identify which corrosion modes should be modeled and again later to confirm model predictions. Since the environmental conditions (temperature, radiation field,

amount of groundwater, etc.) will change over time, tests must be conducted under a range conditions to measure the dependence of the corrosion behavior and response to environmental variables.

For most waste forms, the release rates of radionuclides are not measured directly for input into TSPA calculations. This may be because the release of a particular radionuclide from a waste form is too low to measure reliably in corrosion tests, but also because the release of several radionuclides that occur at different rates must be modeled using a single rate. Therefore, the release of radionuclides is usually bounded by the release of the most readily released element of the host matrix, such as the release of boron from borosilicate glass or uranium from the UO_2 matrix remaining in a spent fuel. Therefore, tests are required to first show the matrix degradation rate bounds the release of radionuclides and then quantify the rate of matrix degradation for use in TSPA.

This research is funded by the U.S. Department of Energy, Office of Nuclear Engineering.

Research Participants

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Caustic-Side Solvent Extraction (CSSX) Process Demonstration

Separating high-level waste for lower disposal cost and easier management

The Savannah River Site (SRS) in South Carolina has 34 million gallons of high-level waste (HLW), stored in underground tanks, that must be decontaminated. Less than 0.1% of the waste is in the form of harmful radionuclides, and separating this fraction can greatly reduce overall disposal cost while concentrating the hazard into a more manageable volume.

Scientists in Argonne's Chemical Technology Division have shown that the volume of high-level waste containing cesium-137 can be reduced 15-fold, and the cesium-137 can be removed with decontamination factors of 40,000 or higher. Further, these goals were met using a very low solvent-to-feed ratio, an achievement made possible by using multistage centrifugal contactors and a new, highly selective solvent.

The process, called CSSX (caustic-side solvent extraction), can separate the radioactive isotope cesium-137 from the extremely saline liquid present in the tanks. Once removed, the cesium can be incorporated into a glass waste form for disposal in a geologic repository.

Based on significant technical achievements, including the successful demonstrations of the CSSX process by Argonne, the Department of Energy has chosen the solvent extraction technology to process the highly radioactive salt waste at SRS. We are now working with our partners at SRS, the Savannah River Technical Center (SRTC), and Oak Ridge National Laboratory to

increase the robustness of the process and design a facility for the CSSX process at SRS.

The use of the Argonne-designed multistage centrifugal contactor in the demonstrations at Argonne and on real waste at SRTC is an important element in the success of this effort. The centrifugal contactor will also be used in the actual processing facility. This most recent application of the Argonne contactor technology is just one of many different uses in extraction processes developed for the treatment and disposal of radioactive waste.

2001 Research Highlights

Three proof-of-concept tests were performed in September and October 2000. In these tests, the CSSX process achieved both key process goals: (1) the cesium was removed from the waste with decontamination factors greater than 40,000, and (2) the recovered cesium was concentrated by a factor of 15 in dilute nitric acid.

As part of DOE's selection process, we were asked to demonstrate that the CSSX process could be operated around the clock for several days. Although these proof-of-concept tests were of brief duration (72 hours), the demonstration was a major undertaking. We used 1.4 L of solvent to process 180 L of SRS simulant, so that the solvent was recycled a total of 42 times.

The results for the decontamination factor, given in Figure 1, showed that we were able

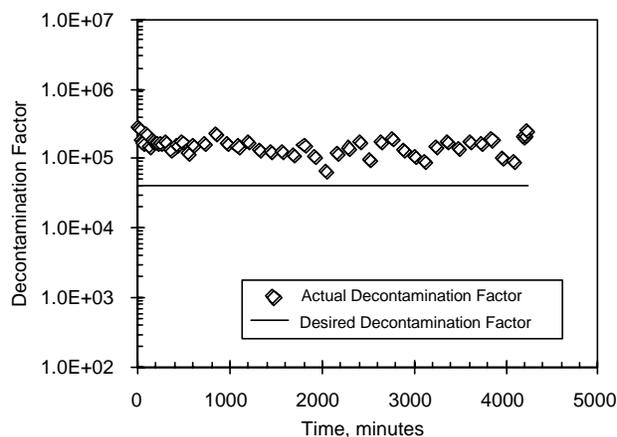


Fig. 1. The decontamination factor for the CSSX process remained above 40,000 throughout proof-of-concept tests.

to keep it above the 40,000 goal throughout the test. The average decontamination factor was $159,000 \pm 45,000$.

Figure 2 shows that we were able to bring the concentration factor quickly to 15 and keep it there throughout the test. After process startup, the average value of the concentration factor was 15 ± 1 , which meets the second process goal.

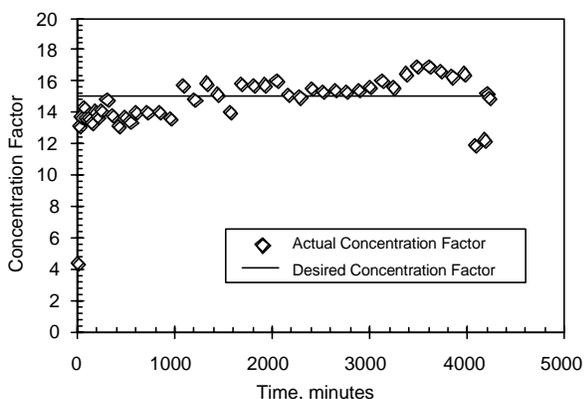


Fig. 2. The concentration factor quickly reached 15 and remained there through proof-of-principle tests.

The test was stopped twice due to a pump failure and the presence of solids. In both cases we were able to correct the problem and resume operation without jeopardizing the process, proving its robustness.

In addition to the Argonne demonstration, we designed and built 52 2-cm contactor stages, similar to those shown in Figure 3 for SRTC. This allowed SRTC personnel to test the CSSX process at their facility using real waste. After our successful 3-day test with SRS simulant, SRTC carried out a successful 2-day test with real waste.

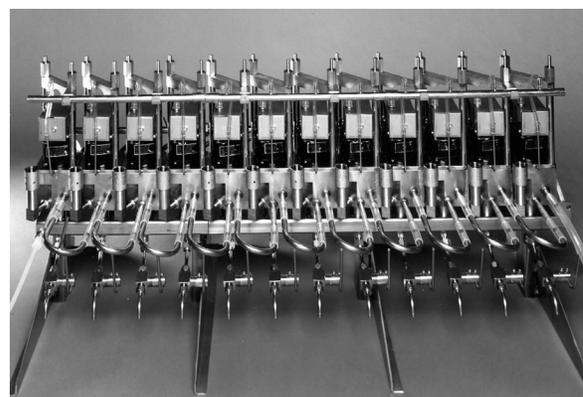


Fig. 3. Argonne built 52 of these 2-cm contactor stages for tests on real waste at the Savannah River Technical Center.

This research is funded by the U.S. Department of Energy, Office of Environmental Management.

Research Participants

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ATW Aqueous Front-End Development

Improved separations lead to safer long-term disposal of spent nuclear fuel

Transmutation of waste is a process in which long-lived radioisotopes are converted to short-lived radioisotopes. If technical issues could be overcome and accelerator transmutation of waste (ATW) technology successfully implemented, it would reduce the volume, toxicity, and fissile content of waste now requiring repository disposal; reduce materials that create proliferation and environmental risks; and support a simpler geologic repository.

One of the technical issues of ATW is the adequate separation of transuranic (TRU) long-lived fission product elements from spent fuel, and uranium. Research under the Department of Energy's ATW Program is addressing that issue by separating dissolved commercial fuel into three streams: (1) a transuranic (TRU) product stream that will be further processed, converted to ATW fuel, and transmuted by fissioning to generate electrical power, (2) separate ^{99}Tc and ^{129}I streams that will be fabricated into targets for transmutation to short-lived nuclides, significantly reducing the dose from the parent isotopes, and (3) a uranium product stream that will be disposed of as low-level waste.

Solvent extraction processes can provide the large-scale selective, efficient separations required for these three product streams. This year scientists in Argonne's Chemical Technology Division developed a process for uranium extraction (UREX). Development was aided by a computer model (AMUSE; see "Argonne Model for Universal Solvent Extraction" elsewhere in this section of the Annual Report).

2001 Research Highlights

Activities focused on the aqueous frontend and demonstrating its ability to meet processing goals. Tasks focused on developing and demonstrating the ability of the uranium extraction (UREX) process to generate the three product streams and on further developing AMUSE to optimize the UREX process for demonstration.

In the UREX process, $\geq 99.9\%$ of the uranium and $>95\%$ of technetium are separated from each other and the other fission products and actinides. The key is the addition of acetohydroxamic acid (AHA) to the extraction and scrub sections of the process. The addition of AHA greatly diminishes the extractability of plutonium and neptunium, providing greater proliferation resistance than with the plutonium extraction (PUREX) process, where uranium and plutonium are separated from the fission products and other actinides.

Figure 1 is the flowsheet for the UREX process as tested in a 49-stage 2-cm centrifugal contactor using simulated feed. In the extraction section of the process, uranium and technetium were extracted from the aqueous phase with minor amounts of the other feed components by solvent introduced into Stage 1. The feed was introduced into Stage 12 and flowed to Stage 1, countercurrent to the solvent flow.

The raffinate from Stage 1 contained all feed components but uranium and technetium. The U/Tc-loaded solvent passed from Stage 12 into the scrub section, where a solution of

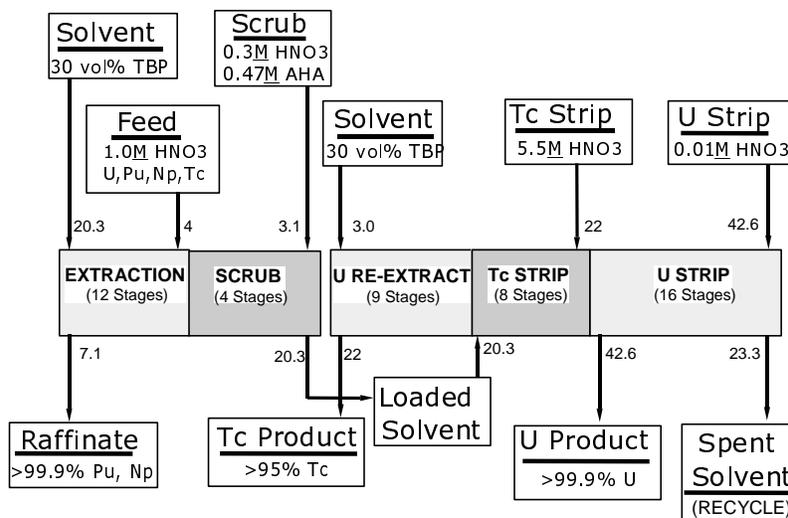


Fig.1. Countercurrent demonstration of UREX flowsheet designed by AMUSE and performed in a 49-stage 2-cm centrifugal contactor using a simulated feed containing U, Pu, Np, and Tc in 1 M nitric acid.

nitric acid and AHA scrubbed impurities from the solvent. The loaded solvent bypassed Stages 17-25 and entered the technetium strip section at Stage 26. As it passed from Stage 26 to 33, technetium was stripped from the solvent. The Tc-product solution then passed from Stage 25 to 17, where it was contacted with fresh solvent to remove uranium that was also stripped. Uranium was stripped from the solvent using dilute nitric acid in Stages 34 to 49.

The first 33 stages of the UREX process demonstration were run in a glove box (Figure 2). The remaining 16 stages (uranium-strip section) were run in a hood.

Demonstration results will be used to increase the accuracy of AMUSE and to prepare for a demonstration to be run during 2002 at the Savannah River Technology Center using feed from dissolved spent commercial fuel.

This research is funded by the U.S. Department of Energy, Office of Nuclear Energy.



Fig. 2. The first 33 stages of the UREX process demonstration were run in a glove box due to the high concentration of plutonium in the feed.

Research Participants

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Argonne Model for Universal Solvent Extraction

Optimizing solvent extraction processes through modeling

Transmutation of waste is a process in which long-lived radioisotopes are converted to short-lived radioisotopes. One of the technical issues involved is the separation of transuranic (TRU) long-lived fission product elements from spent fuel, and uranium. Research under the Department of Energy's Advanced Accelerator Applications Program is addressing that issue by separating dissolved commercial fuel into three streams: (1) a transuranic (TRU) product stream that will be further processed, converted to accelerator transmutation of waste (ATW) fuel, and transmuted by fissioning to generate electrical power, (2) separate ^{99}Tc and ^{129}I streams that will be fabricated into targets for transmutation to short-lived nuclides, significantly reducing the dose from the parent isotopes, and (3) a uranium product stream that will be disposed of as low-level waste.

As part of the Chemical Technology Division's research on Accelerator Transmutation of Waste, or ATW (described elsewhere in this section of the Annual Report), researchers and computer scientists are developing a computer model that can help optimize the processes used to separate these three product streams--the Argonne Model for Universal Solvent Extraction, or AMUSE.

2001 Research Highlights

Activities this year focused on further developing AMUSE to optimize the uranium extraction (UREX) process.

AMUSE, which is based on the Generic TRU EX Model (GTM), was developed to design feed-specific, goal-specific flowsheets for the transuranic extraction (TRUEX) process. Several key features of the GTM make it useful beyond its initial application. These features include the ability to calculate: (1) mass balances for multistage (≤ 256) countercurrent process flowsheets with up to 25 feed streams, with rerouting of section effluents, in a variety of contacting equipment; (2) complex aqueous-phase speciation, thermodynamic activities, and extraction behaviors in highly complex solutions containing a variety of cations and anions; and (3) space and cost associated with installing a solvent extraction process. Using Microsoft[®] Excel, we have written the model so that it is easy to add new features. For example, other anions and cations and aqueous-phase complexation equilibria can be added to speciation calculations, or new unit operations can be introduced to the space and cost calculations.

This year AMUSE was enhanced to add distribution ratio algorithms for the plutonium and uranium extraction (PUREX and UREX) processes.

Figure 1 is a flowchart for AMUSE calculations.

AMUSE comprises four computational elements:

- User input, where the compositions and flow rate of each feed, the number of sections, and the number of stages per section are selected by the user.

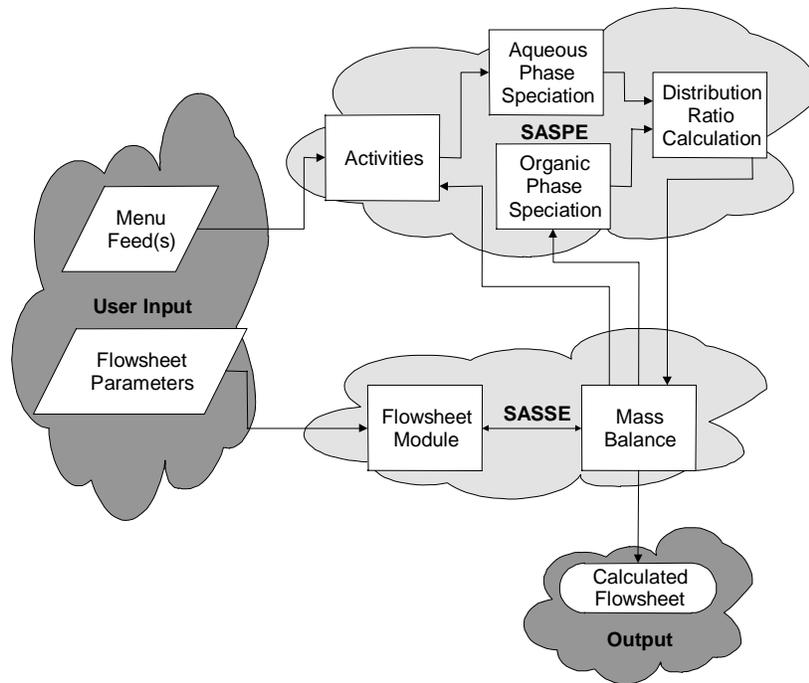


Fig. 1. How AMUSE calculations are performed.

- SASPE (spreadsheet algorithms for speciation and partitioning equilibria), where distribution ratios are calculated based on aqueous- and organic-phase compositions in each stage.
- SASSE (spreadsheet algorithms for stagewise solvent extraction), where a steady-state material balance is performed for all stages of the flowsheet.
- Output, where effluent and stagewise compositions and component behaviors are reported in tabular and graphical formats.

SASSE and SASPE calculations iterate until the compositions calculated by SASSE provide distribution ratios in SASPE that agree within 1% of its previous calculation.

Demonstration results will be used to increase the accuracy of AMUSE and to prepare for a demonstration to be run during 2002 at the Savannah River Technology Center using feed from dissolved spent commercial fuel.

This research is funded by the U.S. Department of Energy, Office of Nuclear Energy.

Research Participants

George F. Vandegrift, Jacqueline Copple, and Monica C. Regalbuto. For more information, contact George Vandegrift (630-252-4513, vandegrift@cmt.anl.gov).

IV

Nuclear Technology

The Chemical Technology Division (CMT) is developing pyrochemical technologies for the treatment of spent nuclear fuel discharged from several types of reactors, evaluating materials for use in pyroprocessing and nuclear systems, and exploring alternative fuel concepts for future nuclear systems. Technology development efforts range from laboratory-scale studies of new processing concepts such as the electrolytic reduction of spent light water reactor (LWR) oxide fuel to the engineering-scale demonstration of high-throughput uranium electrorefining. The objective of the work is to develop a viable set of technologies for partitioning the actinides contained in spent nuclear fuel for recycle into power-producing systems or storage and encapsulating the fission products in durable, leach-resistant waste forms for disposal thus reducing the amount and nature of the material destined for storage in a geologic repository. Although a number of fuel treatment concepts are being explored, the focus of the effort is on the treatment of spent LWR oxide fuel, recycle of metallic reactor fuel, and stabilization of “at risk” fuels in the DOE complex.

CMT has the lead role in developing pyroprocessing technologies for the Advanced Accelerator Applications (AAA) program, which is a multi-laboratory program aimed at demonstrating partitioning and transmutation (P&T) of actinides and long-lived fission products contained in commercial spent fuel. Several P&T scenarios were evaluated by the AAA program in 2001, including single-tier systems (accelerator-driven and fast-spectrum critical reactors) for actinide transmutation and multi-tier systems that incorporate actinide recycle in critical systems (thermal or fast spectrum) prior to ultimate disposition in a transmutation system. Process flowsheet concepts were developed and evaluated for each of the P&T scenarios studied by the AAA program. Beyond these flowsheet development activities, laboratory-scale testing of the newly developed electrolytic oxide reduction process continued as a priority, and electrorefining studies of non-fertile alloy fuel were initiated. Electrolysis was evaluated as an alternative to the liquid cadmium cathode for actinide recovery due to its suitability to high throughput rates and lower waste generation.

Materials development efforts centered on the development of inert anode materials for use in the electrolytic reduction and actinide recovery processes. Both processes require materials that are stable at moderately high temperature (~650°C) in an oxidizing environment and have acceptable electronic properties that allow for high current operation. Preliminary stability testing of candidate materials (e.g., Pt, Au, SnO₂, Li₂SnO₃) is complete. Polarization testing of the materials that passed the stability test will follow.

Liquid metal corrosion is another area in which CMT conducts materials research. The emphasis of the work is on elucidating the corrosion mechanism of various alloy materials in flowing-lead and lead-bismuth systems. Lead and lead-bismuth were recently proposed as alternatives to the sodium coolant used in advanced liquid metal cooled reactors. These coolants are less chemically reactive and offer a wider operating temperature range than sodium. However, the method to mitigate the corrosion of containment materials is not as mature as that for sodium because of the limited fundamental knowledge of the corrosion process.

CMT is also developing fuels for advanced nuclear systems. Cermet, a ceramic kernel encased in a metal matrix, fuel has the potential for high burnup, good irradiation stability, low stored energy and excellent thermal conductivity. Fabrication, including microsphere production and coating, of two cermet fuel types is being examined:

thoria / urania microspheres encased in zirconium metal and coated transuranic oxide microspheres encased in zirconium. Exceptional fuel performance is predicted for the cermet fuels based on established modeling techniques.

CMT continues to provide process improvements to the Spent Fuel Treatment program, which is stabilizing sodium-bonded spent fuel from the Experimental Breeder Reactor II at Argonne National Laboratory-West in Idaho Falls, Idaho. Highlights of the work completed during the past year comprise two major process enhancements--refinement of the pressureless consolidation process for ceramic waste form fabrication and advancement of high-throughput uranium electrorefining. The pressureless consolidation method for fabricating ceramic waste forms was validated at facilities on both Argonne sites (near Chicago and Idaho Falls, Idaho) during 2001 and accepted as the baseline process for fabricating the ceramic waste form. The product quality was equivalent to that produced by the hot isostatic press process but the fabrication process is less complex and more amenable to completion by remote operations. We made advances in high-throughput electrorefining by evaluating different anode designs, determining the effects of operating parameters on electrorefining rate and product density, and deducing the influence of cell design on product morphology. The insight gained from these studies is critical to the design and operation of high-throughput electrorefiners for spent LWR fuel treatment.

Pyrochemical Treatment Technologies for the Advanced Accelerator Applications Program

Conserving high-level-waste repository space

The Chemical Technology Division (CMT) Division is developing and demonstrating the chemical separation technologies required for the Advanced Accelerator Applications (AAA) Program. The AAA technology provides an alternative to the repository disposal of spent nuclear fuel by partitioning the transuranic elements and long-lived fission products contained in this waste and transmuting them into 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.

In October 1999, a DOE-directed roadmap identified the research and development requirements for the AAA system separations technology. The roadmap recommended a baseline chemical separations flowsheet that contained three processes (see Fig. 1): (1) UREX, an aqueous based solvent extraction process to separate uranium, technetium and iodine from a raffinate containing transuranics and other fission products in the spent fuel; (2) PYRO-A, a pyrochemical process that recovers transuranics from the UREX raffinate; and (3) PYRO-B, a pyrochemical process that separates the transuranics, technetium and iodine from the spent transmuter fuel. A molten-fluoride salt-based alternative to the UREX/PYRO-A processes, known as FLEX, was also selected for further evaluation.

2001 Research Highlights

This year we made significant advancements in the development of the PYRO-A, PYRO-B and FLEX process flowsheets and technologies. Highlights include the lab-scale evaluation of the direct electrolytic reduction of oxides for the PYRO-A application; commissioning of test facilities for the zirconia dissolution step of the FLEX process; and successful proof-of-concept testing of electrorefining for the baseline PYRO-B treatment of non-fertile metal alloy fuels.

The scope of the PYRO-B development was broadened to evaluate the treatment of different fuel types. Flowsheets were developed for the pyrochemical treatment of four non-fertile fuel types: (1) cercer (transuranic oxides dispersed in zirconium oxide matrix), (2) cermet (transuranic oxides dispersed in zirconium metal matrix), (3) nitride pellet (transuranic nitrides dispersed in zirconium nitride), and (4) particle (transuranic oxides with carbon based coating). For the most part, these flowsheets comprise individual technologies that have been developed for other applications (e.g. oxide reduction, electrorefining, electrolysis, chloride volatility, etc.).

Our present efforts are devoted to development work in the areas of direct electrolytic reduction of oxide fuels, electrorefining of metal alloy and nitride fuels, transuranic metal recovery by electrolysis, and process

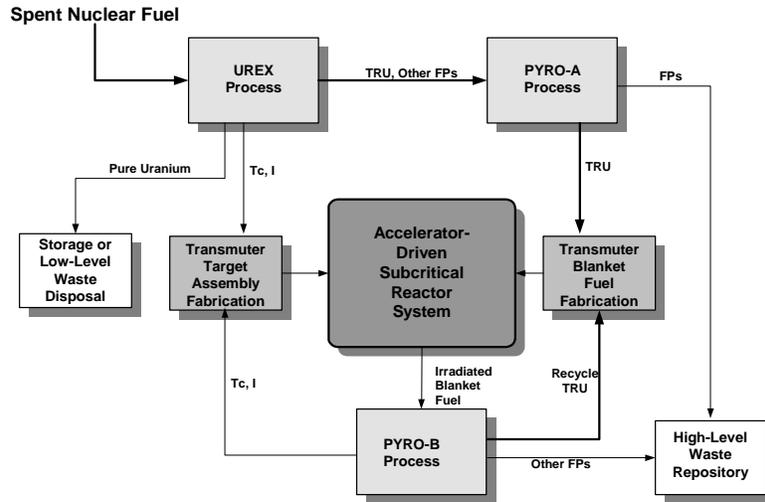


Fig. 1. Chemical separations flowsheet for the Advanced Accelerator Applications Program.

flowsheets for different transmuter fuel types. Experimental work for the program is conducted in gloveboxes in our plutonium facility.

This research is funded by the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology, Advanced Accelerator Applications Program.

Research Participants

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Materials Development Research for Nuclear Technology Applications

Understanding the behavior of materials in harsh chemical environments

Advanced pyrochemical processes and nuclear systems typically involve materials performance challenges due to harsh chemical environments and elevated temperatures. Materials development projects in the Chemical Technology Division (CMT) include advanced anode materials for light-water reactor (LWR) fuel processing, corrosion of heavy liquid metals, and the interaction of molten reactive metals with container materials. These projects reflect the growing diversity of our materials research and development activities.

2001 Research Highlights

Advanced Anode Materials for LWR Fuel Processing: The advanced pyrochemical process for treating spent LWR fuel involves the direct electrochemical reduction of oxides in a molten LiCl electrolyte at 650°C. Oxides are reduced to metal at the cathode while oxygen (and perhaps chlorine) is evolved at the anode. An advanced anode material is required for this process. We have selected non-consumable, inert anodes as having the best chance of success in this system.

We selected candidate anode materials using thermodynamic calculations, existing industrial solutions, and our experience. The candidates were screened using three methods: (1) immersion in LiCl-1 wt% Li₂O at 650°C, (2) measurement of electrical conductivity to 750°C, and (3) behavior evaluation in an electrochemical cell (Fig. 1). The first method provided gross screening, the second enabled relative ranking, and the third was a process-relevant performance test. Initial test results include the following:

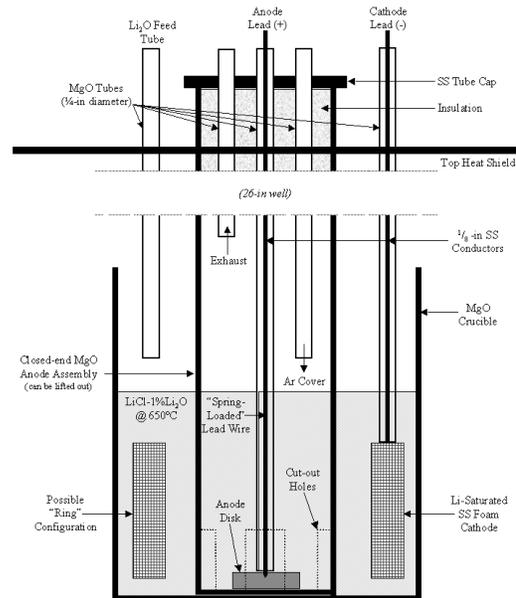


Fig. 1. Schematic of the test cell designed to evaluate ceramic anode materials.

- **Candidate materials:** Pt, Au, pure SnO₂, doped SnO₂, Li₂SnO₃, LiFeO₂, CoFe₂O₄, and BaCrO₄.
- **Eliminated by immersion test:** BaCrO₄.
- **Downgraded due to fabrication difficulties:** Li₂SnO₃ and pure SnO₂.

Additional electrochemical performance testing will be completed to select an anode material for use in scale-cell tests.

Heavy-Liquid-Metal Corrosion: A particular set of advanced nuclear reactor concepts use lead and lead-bismuth eutectic (LBE) coolants; these coolants are of interest where high coolant temperatures are required (e.g., hydrogen generation). Liquid-metal corrosion is a primary issue in the long-term

performance of reactor components in such systems.

We have installed a test system to expose candidate materials to flowing lead and lead-bismuth under a temperature gradient at a controlled oxygen potential. The gradient is essential for discerning preferential dissolution and transport of alloy components. Alloy samples are sealed within a quartz harp (Fig. 2), which is filled with molten metal; natural circulation induces liquid metal flow. Stainless steel alloys have been tested at 550°C/~400°C (hot leg/cold leg). Figure 3 shows an example of LBE corrosion in HT-9 with evident corrosion at defects on the sample surface. Future work will focus on advanced materials for hydrogen-generating nuclear systems using lead coolant at temperatures up to 800°C.

High-Temperature Materials Interfaces: The high-temperature durability of materials in aggressive environments is of paramount importance in advanced nuclear systems and processing methods. Many Generation IV (Gen IV) nuclear system concepts push the performance envelope by assuming improvements in high-temperature materials performance. One issue we are presently studying is the interaction of molten reactive metals (i.e., U and Zr alloys) with stable crucible materials.

We have been examining ceramic-metal interfaces generated in this crucible project to develop novel materials strategies. Advanced ceramics, coatings, and functional graded materials are all likely to find use in advanced nuclear technologies. The arenas of ceramic-metal brazing and, more generally, interfacial chemistry are therefore critical to the success of some Gen IV concepts. An example is shown in Figure 4, where molten zirconium was in contact with zirconium nitride.



Fig. 2. Quartz convection harp for heavy metal corrosion studies.

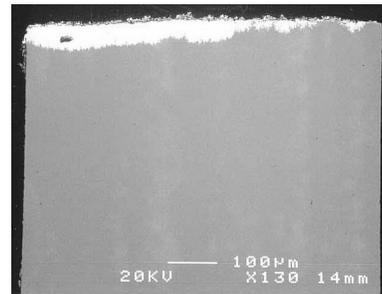


Fig. 3. Corrosion of HT-9 stainless steel in molten lead-bismuth eutectic liquid metal.

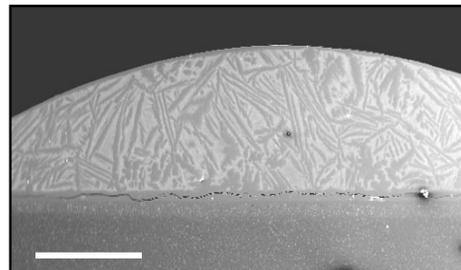


Fig. 4. Interface between molten Zr and ZrN at ~2000°C.

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Research Participants

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Development of Advanced Cermet Nuclear Fuels: Mixed Oxide Dispersions in a Metal Matrix

Improving the performance of nuclear fuels

Zirconium matrix cermet nuclear fuels are being developed by the Chemical Technology Division (CMT) in collaboration with Purdue University, Oak Ridge National Laboratory, Los Alamos National Laboratory, and other Argonne research divisions. Cermet fuels have demonstrated potential to enhance fuel performance because the high thermal conductivity of the matrix maintains low internal temperatures, which has beneficial performance and safety implications. We are presently working to develop two different cermet fuel concepts: (1) thorium-uranium oxide microspheres in a dense zirconium matrix, and (2) coated transuranic (TRU) actinide microspheres in a low density zirconium matrix.

2001 Research Highlights

Thorium-Uranium Oxide Cermet Fuel: This project, conceived in CMT, is a collaboration with Purdue University. The principal project goal is to demonstrate the feasibility of a metal-matrix dispersion, or cermet, fuel comprising (Th,U)O₂ microspheres in a zirconium matrix that can achieve high burnup and subsequently be directly disposed as nuclear waste. Potential benefits include high actinide burnup, inherent proliferation resistance, improved irradiation stability due to low internal fuel temperatures, low fuel failure rate, and minimal waste treatment.

The cermet fuel concept is shown in Figure 1. The fuel “meat” is composed of a fine dispersion of (Th,U)O₂ microspheres that have a theoretical density between 70 and 99% and a uranium enrichment below

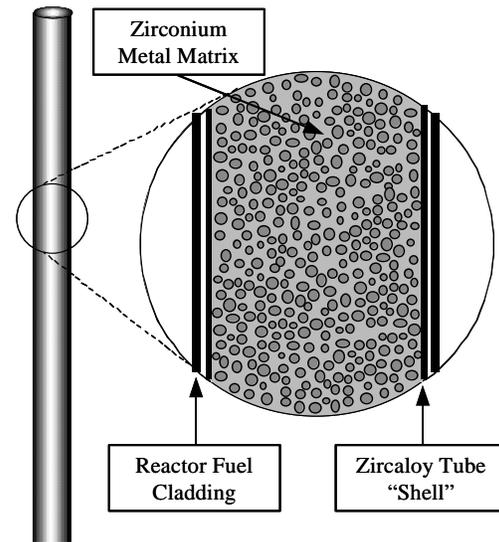


Fig. 1. Concept sketch for (Th,U)O₂ dispersion fuel pin.

20% U-235. Nominal values for the microsphere diameter, ThO₂-to-UO₂ ratio, fuel-to-matrix ratio, and U-235 enrichment were selected as ~50 μm, 50:50, 50:50, and ~19.5%, respectively, to provide guidance for calculations and experiments in the project.

This year there were several important project achievements:

- Development of the powder-in-tube method and equipment for the fabrication of cermet rods,
- Establishment of laboratory-scale fabrication equipment for (Th,U)O₂ microspheres by spray drying,
- Creation of a detailed thermal model to simulate the behavior of cermet fuel, and

- Design and simulation of nuclear reactor fuel cycle behavior and economics.

Initial computer simulations revealed excellent thermal behavior and beneficial neutronic properties with the zirconium matrix cermet. As a result of initial simulation, a boiling water reactor (BWR) core with a tight-pitch hexagonal lattice was selected, benchmarked, and studied. Using our nominal $(\text{Th,U})\text{O}_2$ cermet in a typical BWR, the moderator-to-fuel area was reduced and the conversion ratio increased from ~ 0.6 to more than 0.9, which resulted in a substantial increase in the fuel burnup. Work in this area is now focused on applying these unique advantages toward high-conversion reactor concepts, including boiling water, pressurized water, reduced-moderator water, and supercritical light water reactor systems.

As the lead organization for this project, CMT provides technical oversight in all areas, but we also have specific responsibility for the development of low-cost cermet fabrication methods. Figure 2 shows the hydraulic drawbench installed in a controlled area to enable the fabrication of cermet rods up to ~ 4 ft in length. We are developing methods for metal-ceramic powder mixing methods, particle coating, matrix densification, and cermet characterization.

Coated Actinide Cermet Fuel: Cermet fuels also have potential use within the Advanced Accelerator Applications (AAA) program, where fuel materials are being evaluated to contain TRU elements separated from commercial light-water reactor fuel. The

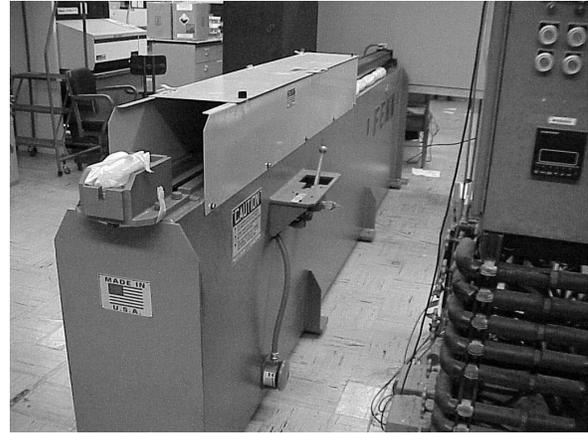


Fig. 2. Laboratory-scale hydraulic drawbench to fabricate $(\text{Th,U})\text{O}_2$ cermet fuel pins in CMT.

fuel materials will be highly radioactive, so remote fabrication is required. The role of CMT in the AAA fuels program is to develop methods for (1) coating the TRU microspheres to provide fission product containment and thermochemical stabilization in the zirconium matrix and (2) fabricating the cermet fuel containing the coated TRU microspheres. While this program is just underway, our experience with the NERI fuel described above provides a solid foundation for this project.

This research is funded by the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology, Nuclear Energy Research Initiative (NERI) Program.

Research Participants

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Pyrochemical Treatment of Spent Oxide Fuels

Developing methods to re-use spent reactor fuel

Commercial light-water nuclear reactors generate about 2000 metric tons initial heavy metal (MTIHM) of spent oxide fuel annually in the United States, adding to the current inventory of more than 44,000 MTIHM. The energy value of this spent fuel is enormous: as much as 870 MWye/MTIHM could potentially be recovered with advanced fast-reactor technology.

2001 Research Highlights

The Chemical Technology Division (CMT) is developing a pyrochemical process to recover the uranium and transuranic value of spent oxide fuels, as shown schematically in Figure 1. At the core of this process is a newly developed electrochemical technology for the reduction of oxide fuels to

metals. The direct electrolytic reduction process has been successfully demonstrated on a laboratory scale with uranium oxide feed. Samples from this demonstration are shown in Figure 2. The reduction process is versatile and can be extended to the extraction of other actinide and rare-earth metals from their oxides.

A simplified diagram of the direct electrolytic reduction cell is shown in Figure 3. In the reduction process, the oxide fuels are loaded into cathode baskets and reduced in-situ to metals. The cathodic reactions generate oxide ions that dissolve in the electrolyte and diffuse to the anode. Oxygen gas is evolved at the non-consumable anode. The cell is operated at 650°C with a molten LiCl/Li₂O salt electrolyte.

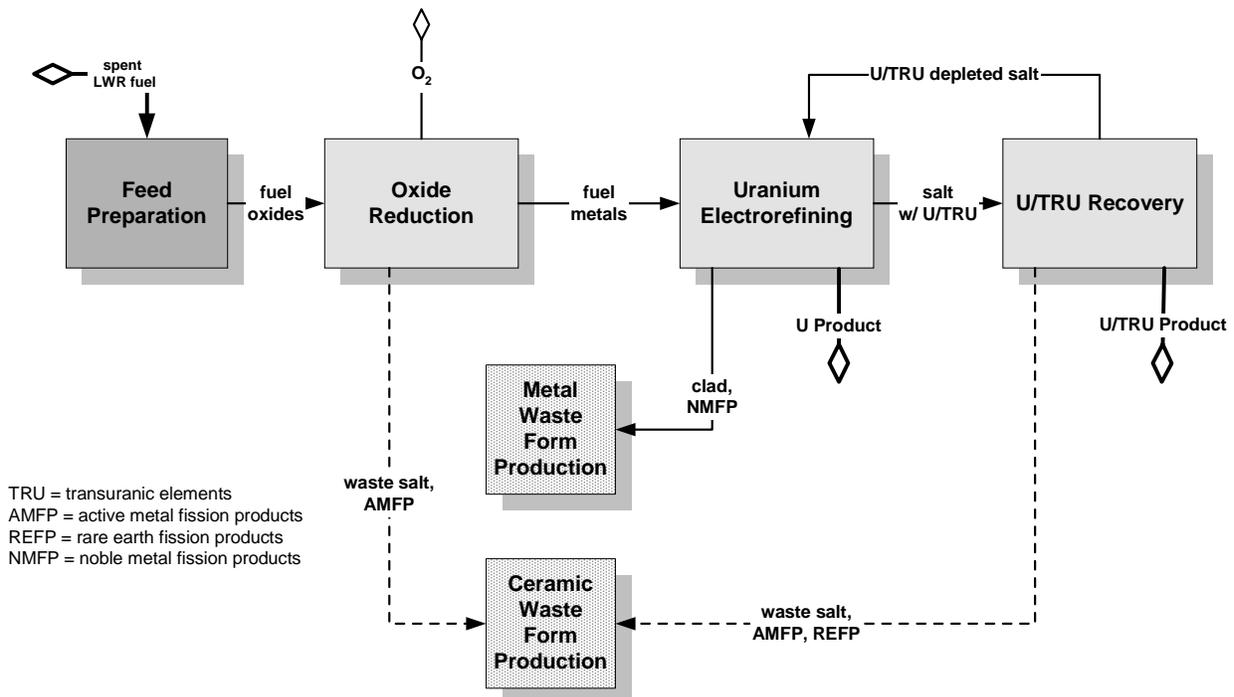


Fig. 1. Pyrochemical treatment of spent oxide fuels.

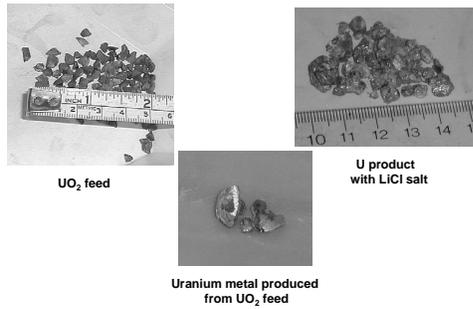


Fig. 2. Samples from direct electrolytic reduction tests with uranium oxide feed.

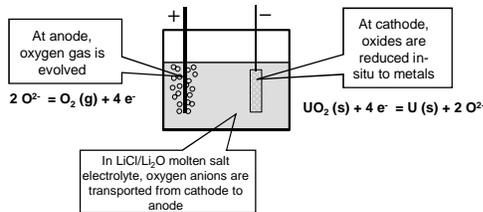


Fig. 3. Schematic of the electrolytic reduction cell concept.

In the integrated fuel treatment process, the mixed-metal product from the direct electrolytic reduction will be electrorefined to recover its uranium and transuranic metal content. The focus of the development work

on the reduction process has been to maximize rates and minimize the oxygen transferred (as unreduced oxides or residual oxides in retained salt) to the electrorefining step. To that end, a novel cell design has been invented and will be tested in the near future. Additional development efforts are concentrated on studying the cathode kinetics and reduction mechanisms, testing anode materials, developing on-line and analytical measurement tools, and defining cell design, scale-up and control.

This research is funded by the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology.

Research Participants

Mark A. Williamson, Karthick Gourishankar, Laszlo Redey, Diane J. Graziano, John P. Ackerman, Dennis W. Dees, David B. Chamberlain, Sean M. McDeavitt, Mark C. Hash, Andrew S. Hebden, Leonard Leibowitz, Dusan Lexa, Chris T. Snyder and Laurel A. Barnes. For further information, contact Mark Williamson (630-252-9627, williamson@cmt.anl.gov).

High Throughput Electrorefining

Recovering uranium from spent nuclear fuel

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. 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.

2001 Research Highlights

This year our efforts focused on evaluation of electrorefiner design features that will be incorporated into the next-generation high-throughput design. The next-generation electrorefiner will require an order of magnitude increase in throughput. Operating conditions and design elements such as anode geometry, cathode material, use of insulating materials, scraper design, anode rotation vs. agitation, and cathode current density were all evaluated with respect to their effect on electrorefining rate and morphology of the electrorefined uranium product.

Anode design proved to have a very significant influence on both throughput and product morphology, whereas scraper design, cathode material, cathode current density, and anode rotation vs. agitation had less or no effect on either throughput or product morphology.

An increased capacity anode was evaluated first. Although the increased anode loading

would reduce handling requirements, the design suffered from a significant increase in electrical resistance and was not able to perform at high electrorefining rates. However, the work with the increased-capacity anode did provide insight into the effect of anode design and operating conditions on product morphology.

After evaluating the increased capacity anode, our attention focused on optimizing the operation of the present Mk-V anode design to increase the bulk density of the product. Using the operating conditions optimized only for electrorefining rate, an electrorefining rate of >500 g/hr for each of the four anode-cathode modules was routinely achieved. A 400 g/hr rate was the minimum required to meet programmatic throughput goals. However, under the 500g/hr operating conditions, the bulk density of the product was low--only about 1.5 g/cm³. A photograph of the low-density product is shown in Figure 1. Although the electrorefining rate was high, the product collector had to be emptied frequently due to the low bulk density of the product and this extra handling effectively slowed down the overall process.

Evaluating the effect of operating conditions and anode design on product morphology, we determined that an increase in product bulk density could be achieved by decreasing the vertical flux of uranium in the region between the cathode and the anode baskets. Decreasing the vertical flux of uranium requires either decreasing the current or increasing the open cross-sectional area between the cathodes and the anode baskets. Because the cross sectional



Fig. 1. Low bulk density electrorefined uranium product.

area of the Mk-V anode/cathode module is fixed, we decreased the current and almost doubled the bulk density of the electrorefined uranium product. A photograph of the increased bulk density product is shown in Figure 2. This work highlighted the uranium vertical flux as a key parameter for our present efforts to scale up the present electrorefiner technology from 5 tons per year to 50 tons per year.



Fig. 2. High bulk density electrorefined uranium product.

This research is funded by the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology.

Research Participants

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V

Basic Science

The Chemical Technology Division (CMT) conducts forefront scientific studies of fundamental issues involving chemistry and materials functionality in systems that are relevant to emerging energy efficiency and clean air technologies. These studies embrace (1) the processing and characterization of ceramic oxide materials with high superconducting critical temperatures, (2) novel heterogeneous catalysts, (3) new vistas in homogeneous catalysis, and (4) the details of ion transport mechanisms in electrochemical devices. This research makes use of cutting-edge synchrotron x-ray and nuclear magnetic resonance facilities at Argonne National Laboratory.

Our investigations of high-temperature superconducting (HTS) ceramics have two main areas of emphasis, one directed at the optimization of processing conditions for the silver-sheathed $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (Ag/Bi-2223) composite superconductor, and the other at the characterization of HTS-coated conductor embodiments employing biaxially textured $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_7$ in thick-film form as the superconducting medium. During the past year we demonstrated an important connection between the volume

fraction of non-superconducting secondary phases at intermediate stages of the heat treatment process for Ag/Bi-2223 and the transport critical current capacity of the fully processed conductor. New heat treatment strategies for Ag/Bi-2223 are emerging from this research. Also, we have significantly stepped up our characterization efforts in the coated conductor area, where we have developed and demonstrated the utility of molecular spectroscopy and synchrotron x-ray methods for probing performance-limiting chemical and microstructural phenomena.

Our research on homogeneous catalysis continues to explore the utility of supercritical CO_2 as a solvent system for chemical synthesis. During the past year, the scope of this research has been extended in new directions that combine features of nanoscience, multiphase media approaches, and surfactant technology, with the goal of developing a new class of catalysts exhibiting the beneficial characteristics of homogeneously and heterogeneously induced chemical reactivity.

The conception and development of innovative NMR imaging methods for the study of ion transport processes remains an integral part of the basic science program in CMT, with more than a dozen patent applications generated in the past year. One of the new developments in this area involves a device that integrates the electrodes of a coin cell battery with the detector element of an NMR probe. This device can be used to monitor cation intercalation into electrode structures, the phases formed in conjunction with electrode reactions, and the factors that contribute to cell capacity fade.

The number and nature of the research activities in the heterogeneous catalysis program has expanded significantly in the

past year. Ongoing work currently includes the synthesis/development and characterization of catalyst materials for (1) reduction of NO_x in mobile source emissions, (2) the selective oxidation of aromatics, (3) reductive pyrolysis of methane to produce hydrogen, (4) biodesulfurization, (5) nanophase hydro-desulfurization, and (6) new Fischer Tropsch chemistries. Highlights in this report describe the progress made in the identification of a selective oxidation catalyst for the one-step conversion of benzene to phenol using combinatorial methods and the development of a new deactivation-resistant NO_x reduction catalyst. In the latter activity, forefront characterization measurements have been made using the Advanced Photon Source at Argonne National Laboratory.

Characterization of HTS Embodiments Using Molecular Spectroscopy

Studying how superconductor properties affect current-carrying capacity

The Chemical Technology Division is using spectroscopic methods to investigate the structural and chemical properties of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) coated conductor specimens fabricated using alternative methods, such as inclined substrate deposition (ISD) of seed layers, pulsed laser deposition of buffer and YBCO layers, and metal-organic deposition of YBCO. The purpose is to determine how interfacial and bulk properties influence the nucleation and propagation of biaxial texture, the development of strain from layer to layer (substrate through to superconductor), and, ultimately, the current-carrying capacity of the conductor. This reports summarizes examples of the application of Raman microscopy as a characterization tool for the YBCO layer. Raman microscopy is proving very useful for measuring a variety of coated conductor characteristics, including oxygen stoichiometry, cation disorder, spatial distribution of second phases, c-axis verticality, and relative strain levels. During the past year, we have used Raman microscopy to develop spatial maps that gauge the c-axis alignment of the grains in YBCO films grown on textured substrates.

2001 Research Highlights

As a result of the inherent differences in the polarization tensors for the Raman active phonons of YBCO, when the excitation laser strikes the sample surface in a direction perpendicular to the YBCO c axis, the out-of-phase O2/O3 mode of YBCO at ca. 340 cm^{-1} reaches maximum intensity, while the O4 mode at ca. 500 cm^{-1} reaches minimum

intensity. As the c axis tips with respect to the incident laser line, the I(500)/I(340) intensity ratio increases, thus providing a measure of the degree of YBCO c-axis tilt with respect to the incident laser. As long as the direction of propagation of the laser remains perpendicular to the substrate surface, the I(500)/I(340) intensity ratio provides a measure of the extent of c axis tilt relative to the substrate surface. An example of two common conditions that illustrate this effect is shown in Figure 1.

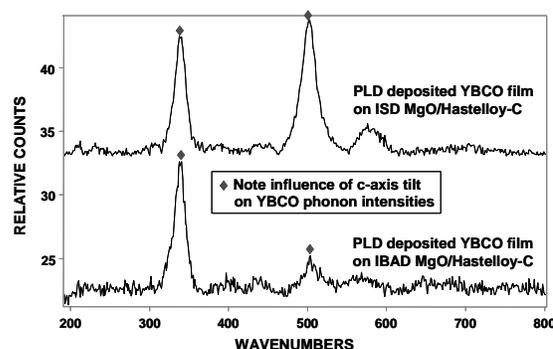


Fig. 1. Raman spectra of ISD- and IBAD-type coated conductors.

The top spectrum in Figure 1 is for a YBCO film deposited by pulse laser deposition (PLD) onto an MgO template layer applied to a Hastelloy-C substrate by ISD. The bottom spectrum is for the same embodiment except that the MgO template layer was applied by ion-beam-assisted deposition (IBAD). Both spectra were recorded with the propagation direction of the excitation laser perpendicular to the Hastelloy-C substrate surface. The enhanced intensity of the 500 cm^{-1} mode relative to the 340 cm^{-1} mode in the top spectrum evidences the tilt

of the YBCO grains caused by the inclination pitch of the ISD template. In the IBAD sample, the YBCO grains lie flat on the substrate surface (c-axis vertical), hence the intensity of the 500 cm^{-1} mode is near its minimum as expected. Current efforts are focused on correlating $I(500)/I(340)$ with measured values of the ISD inclination angle and with transport J_c .

The utility of Raman microscopy for probing the spatial variation of YBCO c-axis alignment is illustrated by the results of a mapping study (Fig. 2) of $I(500)/I(340)$ performed on an ISD-templated YBCO (PLD) film. The surface of evolution in Figure 2 was determined by creating a contour map of 11 systematically spaced measurements on a $3\text{ mm} \times 10\text{ mm}$ specimen.

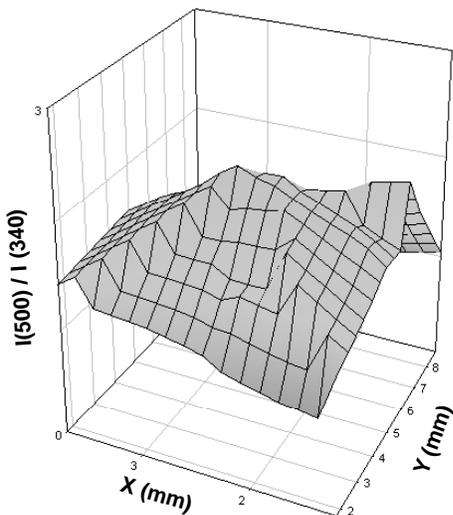


Fig. 2. C-axis contour map of an ISD-type coated conductor

For a perfectly textured ISD sample, this surface would be smooth, parallel to the x,y plane, and finite in value, depending on the ISD tilt angle. In the case of the particular sample chosen for the measurement in Figure 2, there is evidence of a finite tilt angle in all locations, but it is not uniform. We plan to record c-axis contour maps for a

series of ISD-type YBCO specimens to investigate their connection with specimen preparation method and performance.

Raman microspectroscopy is also proving useful for measuring relative strain in textured YBCO specimens. We have used this method to probe strain fields in YBCO grains adjacent to non-superconducting second-phase (NSP) crystallites. The results in Figure 3 illustrate the spatial dependence of the frequency of the YBCO O4 phonon in a melt texture YBCO specimen containing Y_2BaCuO_5 (211) precipitates of various sizes and shapes. As Figure 3 shows, the O4 phonon softens in the vicinity of NSPs, and the extent of this softening appears to depend on the shape and orientation of the NSP. Since the O4 phonon is purely a c axis mode, its softening implies that (1) the c axis of the YBCO grains is in greater tension near NSPs than in domains of pure YBCO and, consequently, (2) the a-b planes of YBCO are experiencing greater compression near NSPs than in the pure YBCO domains.

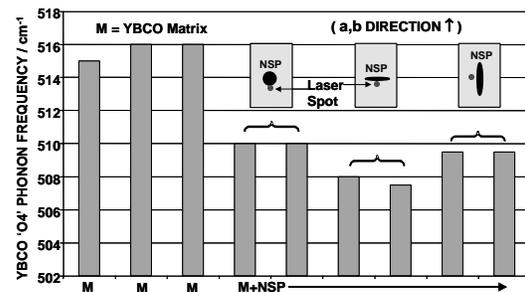


Fig. 3. Effect of proximity to NSPs on the O4 phonon of YBCO.

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New Catalyst Technology for Selective Oxidation of Aromatics

Finding a one-step method for making phenol

Catalytic chemical synthesis accounts for 60% of today's chemical products and 90% of the current chemical processes. Given this dominance, catalytic oxidation has been targeted by the Department of Energy as one of the most significant areas for advancement in the chemical industry (Energy Efficiency and Renewable Energy, Office of Industrial Technologies, Vision 2020 Chemical Industry of the Future). Catalytic oxidations are the lifeblood of the chemical industry. The products of oxidation are the required intermediates for many industrial chemicals and organic polymers. As such, selective oxidation is an important element for future development of the chemical industry.

The direct oxidation of benzene to phenol has been the focus of work by numerous investigators over the last thirty years. However, most of these investigations were exploratory in nature. To our knowledge, there is no known, one-step process using molecular oxygen that selectively converts benzene to phenol with high yield.

Currently, phenol is produced at a rate of about 4.5 billion (4.5×10^9) lb/yr in the U.S. and about 11 billion lb/yr worldwide. Phenol is used primarily to produce phenol-formaldehyde resins. The three-step cumene process produces about 95% of the phenol used in the world. Starting from benzene, the cumene process involves:

- Alkylation of benzene with propene to form cumene, catalyzed by phosphoric acid or aluminum chloride.

- Oxidation of cumene to cumene hydroperoxide using molecular oxygen.
- Cleavage of cumene hydroperoxide to phenol and acetone, catalyzed by sulfuric acid.

Argonne's Chemical Technology Division is conducting research aimed at finding a one-step method of producing phenol.

2001 Research Highlights

In the current project we are investigating a new process for manufacturing phenol from either benzene or toluene by a one-step, heterogeneous catalytic, selective oxidation reaction using molecular oxygen:



If successful, this one-step process would require much less energy and produce fewer wastes than the conventional process. The proposed process is also attractive in that, in principle, it produces no by-products. In the cumene process, phenol and acetone are produced in equimolar amounts, so the economics of the process depends on the marketability of acetone. This dependence could become a problem when the demand for phenol and acetone are quite different. Currently, the acetone market is over-supplied, and expectations are that it will not grow with the anticipated demand for phenol.

In a joint program with Engelhard Corporation, ABB Lummus, Reaction Design,

Northwestern University, and the University of Virginia we are working on new catalysts that will undergo reaction 1 without deep oxidation to carbon dioxide.

To aid in this work we are employing combinatorial techniques to screen a large number of potential candidates. This then gives us a database of promising candidates to test in more conventional plug flow reactors. The combinatorial reactor uses a series of glass plates into which a variety of homogeneous or heterogeneous catalyst candidates have been placed. A simple color change indicates a successful candidate (Fig. 1). Using this technique we have been able to screen an average of 20 catalysts per week. From these screenings, a number of candidates have shown promise for the direct oxidation of benzene to phenol.

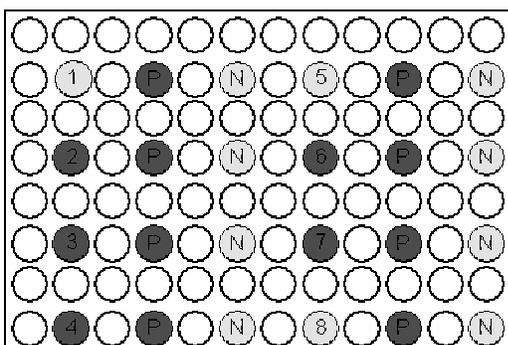


Fig. 1. A new technique developed by CMT allows promising catalysts for a one-step phenol production method to be identified by a simple color change.

Testing of the promising candidates has shown that a catalyst previously used in NO_x reduction chemistry has activity and selectivity for phenol production. Cu-ZSM-5 (Fig. 2) shows selectivity of better than 50% for phenol. The remaining products are mostly organic (not CO_2) and hence could potentially be converted into further phenol with the proper reactor configuration. In particular we are investigating the use of short contact time reactors, which give only primary products while minimizing the amount of unwanted side products.

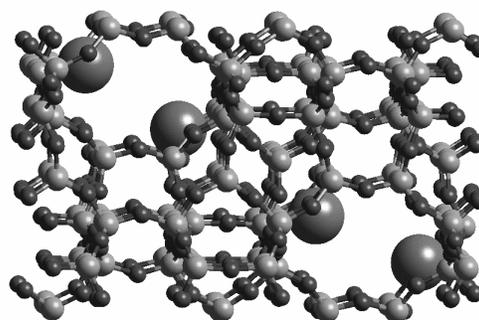


Fig. 2. A catalyst previously used in NO_x reduction chemistry, Cu-ZSM-5, is very promising for the one-step method, showing selectivity of >50% for phenol.

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Reducing NO_x Emissions

New catalyst eliminates water stability problem, improves activity

The oxide forms of nitrogen (NO, NO₂, and N₂O--collectively called NO_x) are some of the most difficult but important pollutants yet to be eliminated from exhaust streams. A key problem is that the most active commercial catalysts use ammonia to convert NO_x to nitrogen in the exhaust. Not only is ammonia difficult to store, but if conversion is not complete, ammonia can be released to the atmosphere--a problem worse than the release of NO_x. Catalysts are needed that will convert NO_x using a more readily available, more environmentally benign reductant.

One of the most promising is a metal-exchanged form of the zeolite ZSM-5. In the copper (Cu) exchanged form (Cu-ZSM-5) this catalyst shows a significant ability to reduce NO_x to N₂ using hydrocarbons such as propylene as the reductant. Many published studies have shown that Cu-ZSM-5 has high selectivity for NO_x conversion with very low hydrocarbon slippage. A major disadvantage to Cu-ZSM-5 is that it is effective only when the exhaust stream is dry. The addition of water (a common component in all exhaust streams) renders the catalyst inactive. For this reason, most commercial development of Cu-ZSM-5 has been stopped.

2001 Research Highlights

In our laboratory, we in the Chemical Technology Division have been working on new additives to extend the life of catalysts such as Cu-ZSM-5. One of these additives (patents applied for) has not only proven effective in eliminating the water stability

problem for Cu-ZSM-5, but actually improves its activity.

Figure 1 shows the activity of an unpromoted Cu-ZSM-5 for the reaction:

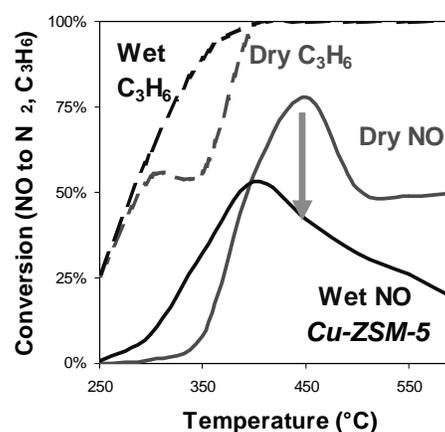
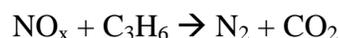


Fig. 1. Loss in activity with “unpromoted” Cu-ZSM-5.

The activity of the catalyst is significantly reduced in the presence of water. With the new additive (Fig. 3), however, the activity remains high. In addition, the selectivity of the catalyst remains high. With NO as the feed, the main product is N₂ with little NO₂ or N₂O being formed.

In situ x-ray absorption fine structure spectroscopy (EXAFS) and x-ray absorption near edge spectroscopy (XANES) (Fig. 3) show that the mechanism of this stabilization is a change in the reduction potential of the Cu in the zeolite. At left in Figure 2 (Cu-ZSM-5) we see the appearance of the Cu²⁺ (RT), Cu¹⁺ (200°C) and Cu⁰

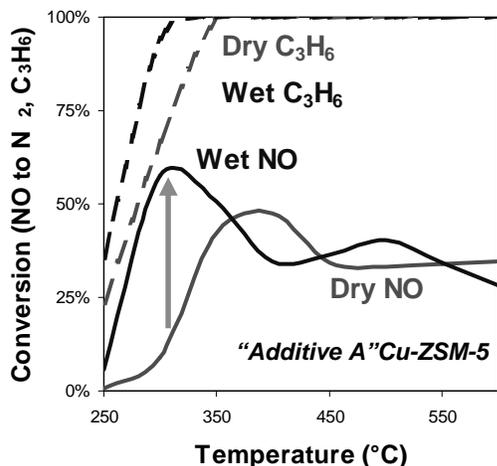


Fig. 2. With CMT's new additive, Cu-ZSM-5 catalyst activity and selectivity remain high or even improved in the presence of water.

(450°C). The second XANES spectrum, at right, shows that the additive lowers the temperature of the reduction from Cu²⁺ to Cu¹⁺ to 150°C and the Cu¹⁺ to Cu⁰ to 350°C.

The search for even better additives continues.

This work is being done in collaboration with BP Chemicals Company under a cooperative research and development agreement (CRADA). Further discussion regarding the use of this catalyst for controlling NO_x in diesel emissions is being investigated with a number of engine manufacturers.

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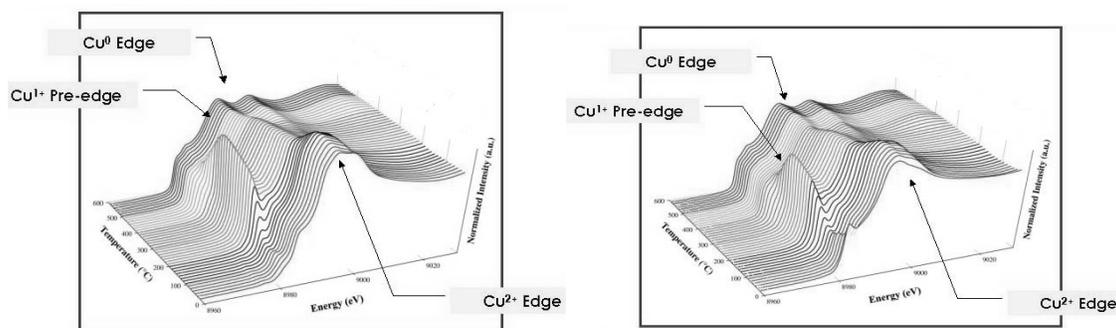


Fig. 3. The stabilization mechanism of the new CMT additive is change in the reduction potential of the Cu in the zeolite.

Gas Phase Micelles as Nanoreactors for Catalysis

Using nuclear magnetic resonance to better understand catalytic reactions

Homogeneous catalysts, which are of considerable commercial importance in the production of chemicals, are generally noted for selectivity and reactivity advantages. However, separating products in these systems often requires energy-intensive distillations. Attempts over the past three decades to facilitate product separation by anchoring homogeneous catalysts to insoluble support materials have met with limited success because the resultant supported catalysts typically exhibit reduced reactivity. Accordingly, a current industrial quest in hydrogenations, carbonylations, epoxidations, and hydroformylations is the development of biphasic reaction systems where an unencumbered homogeneous catalyst and the bulk of the reaction product reside in separate solvent phases. For example, Ruhrchemie produces more than 300,000 tons of n-butyraldehyde per year using an innovative aqueous-organic biphasic hydroformylation system.

2001 Research Highlights

Nanosized micellular reactors offer a new approach to this type of biphasic homogeneous catalyst system by increasing the interfacial surface area. Furthermore, the results of this investigation demonstrate that the nanoreactor approach could greatly improve the reactivity because the homogeneous catalysts should be concentrated within the electric double layer at the micellular interface.

In the Ruhrchemie process, all of the reaction chemistry occurs within the aqueous phase where the organic reactants and products have very low solubility. Mass

transport could be improved by employing surfactants to increase the interfacial surface area through the formation of emulsions or microemulsions. This approach is critically dependant on having control over the stability of the microemulsion. A supercritical fluid offers an advantage over conventional organic solvents in that it should be possible to evenly disperse the rhodium catalyst or alternatively to concentrate it at the bottom of the reactor through subtle changes in the pressure, as schematically indicated in Figure 1.

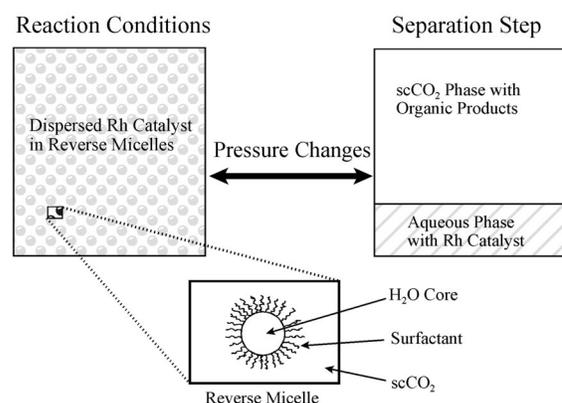


Fig. 1. Nanoreactor approach to olefin hydroformylation.

High-pressure nuclear magnetic resonance (NMR) spectroscopy was used for the first time to investigate micro-emulsions of water in supercritical carbon dioxide ($scCO_2$). The emulsions were formed using a family of anionic perfluoropolyether ammonium carboxylate surfactants. Systems of this type have been investigated by optical and scattering techniques. It was our goal to see if these systems were amenable to NMR investigation. High-pressure NMR techniques have proven to be quite valuable in

the investigation of catalytic mechanisms under industrial conditions.

An ionic guest compound with high water solubility was used to test for micelle formation. Typically, ionic compounds have low solubility in $scCO_2$. However, the ionic guest could be solubilized in $scCO_2$ by occupying the aqueous cores of a microemulsion. Ammonium hexafluorophosphate was chosen as the guest because it exhibits a highly characteristic doublet in a region of the ^{19}F NMR spectrum that is clear from surfactant resonances. Experiments were conducted to establish that the guest has no detectable solubility in $scCO_2$ in the absence of the surfactant, and that stable microemulsions were produced with or without stirring under a variety of pressure, temperature, and water-to-surfactant ratios. The PF_6^- guest was found to form concentrated 0.2M solutions within the aqueous micellar cores.

The PF_6^- guest was not detected in the absence of the surfactant. However, it was important to establish that the NMR resonances resulted from a uniformly dispersed microemulsion phase, and that these resonances were not coming from localized surface layers wetting the walls of the toroid NMR detector in response to the addition of the surfactant. This is a question that has consistently plagued the optical methods where wetting of the window material is difficult to experimentally rule out. Fortunately this question can be addressed by the imaging capability of the toroid cavity NMR detector, developed by Argonne's Chemical Technology Division. Under micelle-forming conditions, the PF_6^- guest, surfactant, and water were uniformly dispersed throughout the CO_2 phase. There was no evidence for surface wetting, as demonstrated by *in situ* NMR imaging.

The nuclear overhauser effect (NOE) was used to probe the micellar structure through dipole-dipole interactions between the PF_6^- anion and specific locations along the fluorinated backbone of the surfactant. A strong negative homonuclear NOE was observed between the PF_6^- guest and the fluorine moiety that is located directly adjacent to the surfactant's carboxylate head group. This highly specific negative NOE indicates an ordered arrangement, where the PF_6^- anion and carboxylate ion are located in close proximity to one another (e.g., generally less than 4 Å). This close association of two negatively charged ionic groups in an aqueous environment is unusual and suggests that the PF_6^- guest is concentrated within the electric double layer that forms at the micellar interface. This surprising finding has key relevance to catalysis. It suggests that ionic metal catalysts will be naturally concentrated at the micellar interface in these nanoreactor systems without the need to develop synthetic pathways to tether the surfactant to the catalyst's ligand system.

These gas phase micellar nanoreactors hold promise as a reaction medium for conducting homogeneous catalytic reactions within the aqueous micellar cores while, at the same time, exploiting the facile mass transfer properties of the supercritical fluid.

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Coin Cell NMR Detector

Testing sealed batteries faster and better

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful tools available for studying electrode materials, electrolytes, and chemical oxidation/reduction reactions in advanced rechargeable batteries like the coin cell batteries in watches and hearing aids. But if a battery is placed inside a commercial NMR detector and studied under test conditions, severe distortions in the NMR spectra occur. These distortions occur because the probing radio frequency field and the externally applied magnetic field are affected by the presence of the metallic electrodes.

2001 Research Highlights

We have invented a device that integrates the flat, circular disk electrodes of a coin cell battery with the detector element of an NMR probe. Because the NMR inductor also serves as a metal electrode, the battery does not distort the radiofrequency signals. Thus, the coin cell NMR detector can simultaneously analyze all of the components of a coin cell battery in place in a device, under test conditions.

Previously, test batteries were assembled in a conventional coin cell, identical to the button-size batteries used for watches and hearing aids, then cycled under different conditions of power drain and temperature. Each component (anode, cathode, electrolyte, separator) was then extracted from the cell and analyzed independently. These tasks were time-consuming and, more importantly, precluded analysis of the battery materials under real test conditions.

Our device integrates the flat, circular disk electrodes of a coin cell battery with the detector element of an NMR probe. Because the NMR inductor also serves as a metal electrode, the battery electrode does not distort the radiofrequency signals, allowing simultaneous analysis of all battery components in place in a device, under actual test conditions. Figure 1 illustrates the coin cell NMR detector and the central role it plays in coupling an electrochemical analyzer (potentiostat) and an NMR spectrometer.

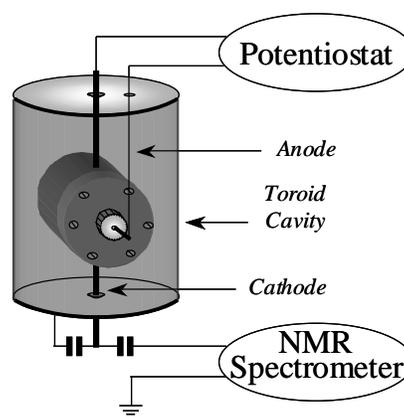


Fig. 1. The NMR coin cell detector was designed to accommodate the geometry and dimensions of the planar laminate electrodes used in commercial 2032-size coin cells like those in wrist watches and batteries.

The new probe conforms to the coin cell geometry, which maximizes NMR sensitivity for thin film samples. A toroid cavity (a cylindrical metallic container) houses the detector. The cavity provides a high surface area return path for electromagnetic radiofrequency currents that are conducted by the detector element during the NMR experiment, and serves to shield external sources of undesired alternating electromagnetic fields.

Active electrode materials of current interest, including various carbon materials for negative electrodes and metal oxides for positive electrodes used in lithium-ion batteries, are routinely prepared as flat laminates. We have studied several of these materials by analyzing wideline multi-nuclear NMR spectra that were recorded using the coin cell NMR detector. For example, for the first time, this device was used to study the reversible insertion and extraction of lithium ions in a carbon electrode *in situ* by ^7Li NMR spectroscopy. Figure 2 shows the ^7Li NMR spectrum of a lithium-ion battery following the insertion of lithium into the graphitic carbon electrode. The ^7Li -NMR spectrum is used to readily identify the speciation of lithium in the Li-ion battery. The peak at ~ 50 ppm in Figure 2 corresponds to the lithium ions intercalated between turbostratically disordered graphene planes. Inorganic and alkyl lithium signals occur near 0 ppm, and metallic lithium resonates near 275 ppm.

By recording a series of ^7Li -NMR spectra as a function of the battery potential we can follow the potential profile for the formation of lithium clusters in the nanopores of hard carbons; address the degradation of reversible lithium capacity with cycle number; and monitor the decomposition products of lithium salt electrolytes during cycling.

The coin cell NMR detector can analyze many different nuclei and therefore, can be used *in situ* to quantitatively characterize and monitor: the organic electrolyte components; the electrochemical reaction products formed at the surface and in the bulk electrode; and the electronic changes in the host carbon matrix. The broad capabilities of the coin cell NMR detector for analyzing all of the components in a sealed battery will make this novel device an

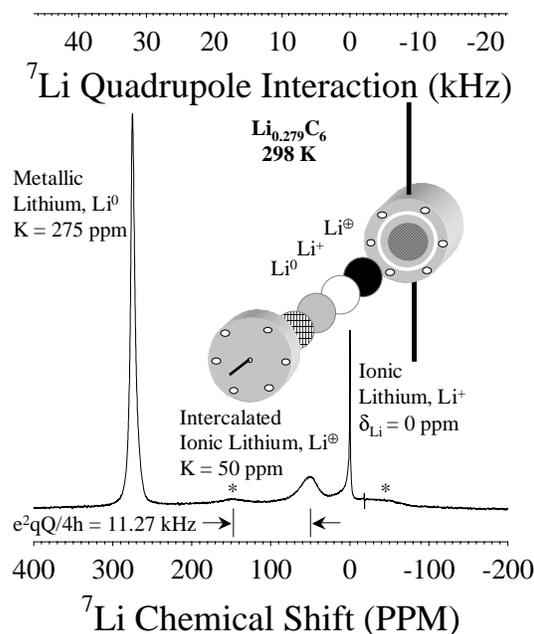


Fig. 2. *In situ* ^7Li -NMR spectrum of all the components in a sealed lithium-ion battery. The resonance peak at 275 ppm is the Knight shift signature for the lithium metal anode. The sharp resonance at 0 ppm represents the solvated lithium ions in the electrolyte. Chemically reacted lithium in the interphase between the electrolyte and the surfaces of the electrodes produces resonances in the range ± 6 ppm. The pattern of three resonances centered at ~ 50 ppm, with two satellite peaks (indicated by asterisks) is characteristic of an electric quadrupole powder pattern for ^7Li nuclei located between two graphite planes.

important tool in the development of new and improved rechargeable batteries.

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Hydrogen Production

Finding a “greener” way to produce hydrogen for energy

Hydrogen is a very efficient energy source that produces little or no pollution, particularly in fuel cell applications. Currently, fossil fuels provide about 80% of the world’s energy, but the resultant emissions (carbon monoxide, carbon dioxide, sulfur dioxide, nitrogen oxides, unburned hydrocarbons, and particulates) from fossil fuel combustion lead to environmental damage. A hydrogen-based energy system can meet energy demands while avoiding pollution.

The United States uses about 4 trillion cubic feet of hydrogen yearly and demand is growing at 5-10% per year. Almost all hydrogen now is produced by steam reforming of methane (SMR), which is the most efficient, economical, and widely used process. However, the process generates both carbon monoxide and carbon dioxide. Various methods have been proposed for reducing carbon dioxide release into the atmosphere, including deep-sea or salt-mine removal and isolation (sequestration) of the releases, and sorbent-enhanced reforming of natural gas.

The Chemical Technology Division (CMT) is studying an alternative method for producing hydrogen: direct-contact pyrolysis (DCP) of methane over a liquid metal using heat from nuclear reactors. Using DCP, only hydrogen and carbon are formed. No greenhouse gases are generated because there is no oxygen source and air and water are not involved in the process. The carbon can easily be removed from the surface of the liquid metal because of density differences. The recovered carbon can be burned for fuel, sequestered, or used to power a direct carbon conversion cell, a

promising new fuel cell that uses energy very efficiently (>70% thermodynamic efficiency). The DCP process is more energy-efficient than SMR because excess nuclear heat is used.

This year we showed that DCP with either methane or natural gas is possible, and the only gaseous product is hydrogen.

2001 Research Highlights

In proof-of-principle experiments we found that hydrogen (H₂) yields increase as flow rate decreases and temperature increases. No other gaseous products were observed. The pyrolysis products of natural gas are H₂ and C, and H₂ yields were greater with natural gas than with methane under the same conditions. Carbon (C) was segregated on the surface of the lead in the experiment apparatus).

Methane was bubbled through a horizontal quartz reactor that contained two “boats” filled with lead. The exit gas from the reactor was monitored by a mass spectrometer. The amount of hydrogen detected by the mass spectrometer increased as the methane flow rate decreased from 15 to 1 standard cubic centimeters per minute (sccm), as shown in Figure 1. The hydrogen partial pressures were proportional to the inverse of the flow rate at all temperatures investigated. Data from an 850°C run are shown in Figures 1 and 2. For a given flow rate, the amount of hydrogen that was produced varied exponentially with temperature. No gaseous product other than hydrogen was observed in any of the experiments conducted at 700-900°C. Data

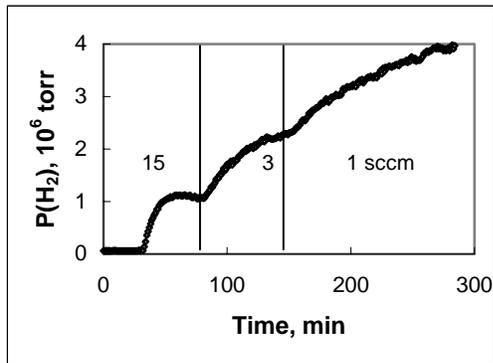


Fig. 1. More hydrogen was detected as methane flow decreased, as shown by the partial pressure of hydrogen at three methane flow rates at 850°C.

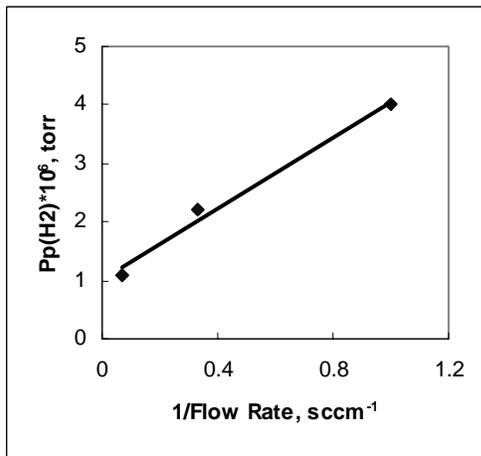


Fig. 2. Steady-state partial pressure of hydrogen at 850°C and three methane flow rates.

from the 900°C experiment are shown in Figure 3.

Carbon was found on the surface of the liquid lead and was not entrained in the metal. The formation of coke does not impede the pyrolysis reaction as it would if catalysts with active sites were involved.

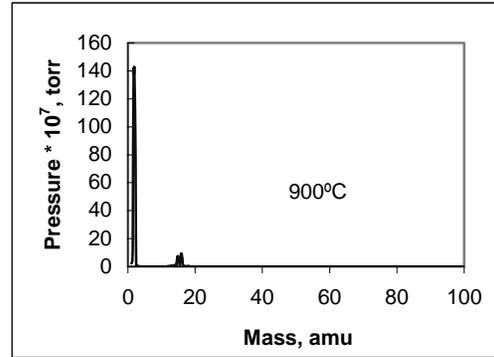


Fig. 3. Analog scans of exit gas from methane pyrolysis at 900°C.

Some experiments were also completed with natural gas. At 750°C, the amount of hydrogen produced from natural gas was about two times greater than that from pure methane. The natural gas contained about 96% methane and 4% ethane. Subsequent experiments showed that the ethane was preferentially pyrolyzed.

We have shown that DCP with either methane or natural gas is possible. The only gaseous product is hydrogen. The carbon is sequestered on the surface of the molten metal. The advantages of the DCP process over the more conventional SMR process are the elimination of greenhouse gases and greater energy efficiency with underutilized nuclear heat.

Research Participants

Christopher L. Marshall, Michele Lewis, Manuela Serban, Carl Udovich, and Richard Doctor (Energy Systems Division, Argonne National Laboratory). For more information, contact Christopher Marshall (630-252-4310, marshall@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 its mission also includes a complementary research and development component in analytical chemistry and its applications. Because of the diversity of research and development work at Argonne, the ACL handles a wide range of analytical problems in its technical support role. It is common for Argonne research and development 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.

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.

Organizationally, the ACL is lodged within Argonne's Chemical Technology Division (CMT). The ACL provides technical support not only for programs in CMT (its major client) but also for other technical divisions and programs at Argonne.

The ACL comprises three groups:

- Chemical Analysis
- Instrumental Analysis
- Organic Analysis

The skills and interests of staff members cross group lines, as do many projects within the ACL. The ACL receives about 1000 projects annually, many of which involve multiple 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. The group is also involved with chemical agent determination and the Waste Isolation Pilot Plant Head Space Gas Performance Demonstration Program.

Together, the ACL groups have a full range of analytical capabilities for performing inorganic, organic, and radiochemical analyses.

In addition to 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 those requiring 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 U.S. Department of Energy, the U.S. Environmental Protection Agency, the U.S. Army Corps of Engineers, and other organizations.

In this year's annual report, three ACL projects are highlighted: (1) Development of a method for the high-precision assay of lithium and aluminum within lithium aluminate ceramic pellets in support of a DOE program on tritium production, (2) preparation of simulated samples of headspace gas that will occur in the waste-bearing containers destined for disposal in the Waste Isolation Pilot Plant, and (3) participation in a plutonium metal exchange to ensuring that analytical determinations are valid.

Analysis of Simulated Headspace Gases for the Waste Isolation Pilot Plant

Helping to characterize transuranic wastes destined for disposal

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 cubic meters 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. One of the characterizations required for waste containers destined for WIPP is analysis of the gas in the space above the waste (headspace gas) for specified volatile organic compounds.

The National TRU Program Office of the Carlsbad Field Office of DOE has established the Performance Demonstration Program 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, and has been providing these support services to WIPP for more than a decade.

2001 Research Highlights

For the Cycle 15A (FY2001) Head Space Gas Performance Demonstration Program (HSGPDP), 13 sets of samples were prepared (Fig. 1). Each set consisted of five 6-L SUMMA canisters at 6 psig. Three sets of Performance Demonstration Program (PDP) samples were sent to Los Alamos National Laboratory and to Nuclear FilteTechnology, and one set was sent to each of the following: Rocky Flats Environmental Technology Site, Idaho National Engineering and Environmental Laboratory, TRU Tech, Inc., Westinghouse Savannah River Company, and Fluor Hanford. One set was used for verification analysis and one set was prepared as a backup sample.

Verification analyses were completed before sending out the HSGPDP samples. The verification data confirmed values for all

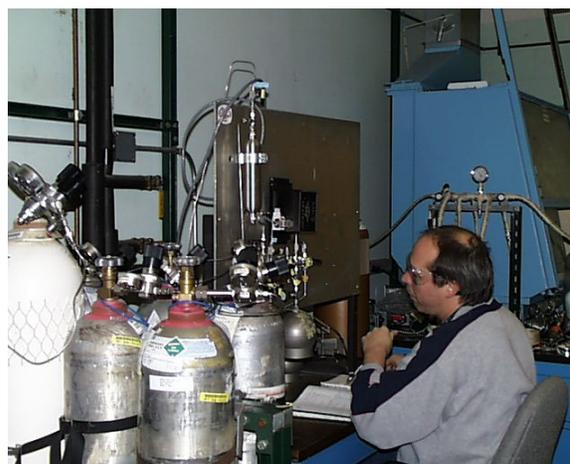


Fig. 1. CMT's Analytical Chemistry Laboratory prepares headspace gas samples for analysis.

Analytical Chemistry

compounds supplied by the vendor of the gas standards.

This work is funded by the U.S. Department of Energy, Carlsbad Field Office, National TRU Program Office.

Research Participants

Amrit S. Boparai, Michael J. Kalensky. For more information contact Amrit Boparai (630-252-4379, boparai@cmt.anl.gov).

Plutonium Metal Exchange Program

Checks and balances in measuring plutonium

With the closure of the Rocky Flats production site, the Department of Energy's National Nuclear Security Administration no longer has the ability to manufacture plutonium pits. Los Alamos National Laboratory (LANL) has been given the mission to duplicate, on a limited scale, the Rocky Flats facility at LANL's New Mexico site. LANL's Analytical Chemistry Group is responsible for various measurements on the pits and at several points in the production process. These measurements are vital due to the stringent quality requirements of the material.

As part of ensuring that analytical determinations are valid, LANL has asked several outside laboratories to participate in a plutonium metal exchange. The exchange entails sending small pieces of the same plutonium metal to be evaluated by each laboratory. The exchange is repeated two to three times per year using different plutonium material. Data from the participating laboratories are used to identify strengths and weaknesses of particular analytical procedures. The exchange program is also designed as an opportunity for the laboratories to collaborate and learn new techniques that are available at other organizations.

2001 Research Highlights

The Analytical Chemistry Laboratory in Argonne's Chemical Technology Division

was among the participants in the first rounds of the exchange. In 2001 we reported the results of our analysis of the first exchange samples and attended a meeting of participants at LANL to review the outcome of this initial exercise. We had determined the isotopic composition of the plutonium by thermal ionization mass spectrometry (TIMS) and assayed the metals for plutonium using TIMS measurements and the isotope dilution technique. We also analyzed the plutonium samples for metal impurities using chemical separation and inductively coupled plasma-atomic emission spectrometry (ICP-AES), and determined ^{241}Am using gamma spectrometry.

Our results from the first round were, in general, in good agreement with the other laboratories. The program, funded by LANL, is expected to continue with ANL's participation for several more years.

This work is funded by the U.S. Department of Energy, National Nuclear Security Administration.

Research Participants

Delbert Bowers, Florence Smith and Don Graczyk. For more information, contact Delbert Bowers (630-252-4354, bowers@cmt.anl.gov).

Tritium Target Qualification Project

Helping the Nation produce tritium

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. Each TPBAR contains columns of ^6Li -enriched lithium aluminate (LiAlO_2) ceramic pellets that generate tritium while maintaining criticality control in the reactor core.

The Tritium Target Qualification Project (TTQP) at Pacific Northwest National Laboratory (PNNL) is developing a national capability to mass-produce the needed LiAlO_2 pellets. The Analytical Chemistry Laboratory in Argonne's Chemical Technology Division is providing vital support by:

- Developing and validating modern methods for needed analytical chemistry measurements,
- Characterizing or preparing reference materials for method qualification and control,
- Transferring methods to a commercial analysis laboratory, and
- Providing analysis services for pellet manufacturing processes until a commercial capability is qualified.

2001 Research Highlights

Methods Development. Specifications for the LiAlO_2 pellets require determination of the ^6Li enrichment, lithium and aluminum content, and the Li/Al atom ratio. Also required are numerous impurities, including carbon, halides, and 24 cationic elements.

Our work on needed methods has produced several notable developments. Among these are a microwave-accelerated procedure for dissolving the highly refractory LiAlO_2 ceramic with acid; an exceptionally precise method using inductively coupled plasma-optical emission spectrometry (ICP-OES) for simultaneous measurement of lithium, aluminum, and the Li/Al ratio; a conventional ICP-OES procedure for simultaneous measurement of all 24 cation impurities using the same solution as the major-constituent determinations; and new methods for decomposing the ceramic to allow halide measurements with ion chromatography.

All of these methods have been reduced to standard practice, translated into detailed operating procedures, and validated for acceptable precision, bias, range, and sensitivity with program-specified test materials.

Standards for Method Qualification and Control. Because reference materials from nationally or internationally recognized agencies such as the National Institute of Standards and Technology (NIST) are not available for pertinent measurements, we were given responsibility for characterizing or preparing several working reference materials needed for system calibration, qualification of new laboratories, and tracking long-term continuity of results.

The "Highly Enriched Working Reference Material" (HEWRM) was extensively analyzed to establish its lithium content and isotopic composition. The HEWRM is a batch of 95% ^6Li enriched lithium carbonate that supplements NIST SRM 924a as a calibration standard for the high-precision

ICP-OES method. It is needed because the ICP-OES system shows different sensitivity for the ^6Li and ^7Li isotopes and must be calibrated for both to handle isotopic variation in the LiAlO_2 ceramics. Our ICP-OES assays for lithium in the HEWRM showed a relative standard deviation (RSD) of 0.065%. This statistic attests to homogeneity of the HEWRM as well as exceptional performance of the ICP-OES method.

A lithium aluminate powder produced by the TTQP as a laboratory control sample was also extensively characterized. A portion of this material is to be analyzed with every batch of pellet samples processed by a laboratory over the program's lifetime. Results contribute to the laboratory's quality control program and track consistency of results over time. Notable among our results is the precision of the lithium and aluminum assays. Both showed a 0.13% RSD over 50 samples that were separately weighed, dissolved with the microwave procedure, and analyzed by high-precision ICP-OES.

The TTQP was concerned that lithium isotopic reference materials available from recognized certifying agencies have either a low ^6Li enrichment (natural abundance at 7.59 at.% ^6Li) or a high enrichment (95.6 at.% ^6Li), while the tritium-target ceramics have enrichments in the range of 20 to 50 at.% ^6Li . This leaves some uncertainty about calibrating measurements in the actual range of interest. To address this concern, we prepared standards with 20, 30, 40, and 50 at.% enrichments following a plan that maintained traceability to the certified materials. We also made a set of check standards for testing laboratory performance in measuring lithium isotopes.

Another item that we prepared is a set of standards simulating the solution from the microwave-assisted dissolution of LiAlO_2 .

Made from best-available reference materials, these solutions are intended for use in testing a laboratory's ability to meet bias requirements at the ends of the calibration range for the ICP-OES method.

Technology Transfer. The ultimate goal of our support to the TTQP is to transfer our methods to a commercial laboratory that will analyze production lot pellets. This year a laboratory contracted by DOE completed an initial demonstration of capability. All the methods we developed for the TTQP were shown to be transferable to the commercial sector. The commercial laboratory expects to become qualified in the near future.

Measurements for Manufacturing-Process Development. Capabilities established as we developed methods for the TTQP have also allowed us to provide data to producers of the LiAlO_2 ceramics as they developed and scaled up processes for pellet production. We have analyzed a large number of samples related to powder precursors from which pellets are sintered and to the pellet-making process. Recently, we analyzed pellets from a production-size batch (several thousand pellets) that verified satisfactory process performance and marked a success milestone for the pellet maker. Analyzing these real-world samples has allowed us to improve our procedures and to encounter the kinds of problems that the commercial laboratory will face in its production support. This experience has been invaluable in our role as advisor to the commercial facility.

Research Participants

Donald Graczyk, Alice Essling, Susan Lopykinski, Florence Smith, and Frederic Martino. For further information contact Donald Graczyk (630-252-3489, graczyk@cmt.anl.gov).

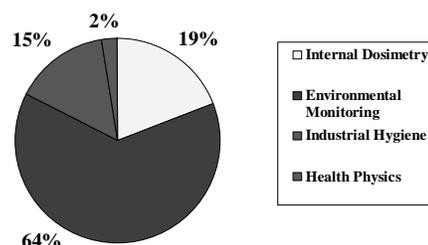
VII

Environment, Safety and Health Analytical Chemistry

Specialized capabilities to meet customized needs

In 2001, the Chemical Technology Division (CMT) acquired environment, safety, and health (ESH) analytical and technical support capabilities through a reorganization of the Laboratory's Environment, Safety, and Health Division. While residing administratively within CMT, the ESH Analytical Chemistry group (ESH-AC) provides analytical and technical support services for Argonne-wide environmental monitoring, industrial hygiene, and radiation protection programs, and similar services for non-Argonne organizations.

ESH-AC's experienced, diverse staff supports two integrated work units: low-level radiological analysis and chemical analysis. ESH-AC offers a full range of analytical capabilities for performing inorganic, organic, and low-level radiological analyses comprising a wide spectrum of analytes. The ESH-AC analyzes approximately 7000 samples annually. In 2001, for example, we analyzed 6002 (see chart at right above).



ESH-AC uses wet chemical and instrumental methods for elemental and compositional determinations as well as separation and measurement of organic compounds in solid and liquid samples. ESH-AC uses nuclear counting techniques to determine low-level radiochemical constituents in bioassay (urine, feces, and whole-body), environmental, and workplace monitoring samples.

In addition to the analytical capabilities listed above, the ESH-AC can provide other technical support. ESH-AC staff can perform quality assurance assessments; review, develop, and prepare standard operating procedures; review data packages;

prepare sampling plans; and conduct field-sampling tasks.

ESH-AC holds certifications for bioassay analysis with the Department of Energy Laboratory Accreditation Program (DOELAP) and workplace monitoring sample analysis (metals/organics on air filters/charcoal tubes) with the American Industrial Hygiene Association (AIHA). The ESH-AC participates in five blind inter-comparison sample programs to measure performance. We have maintained an exemplary record of satisfactory results for many years. Our experienced, dedicated staff maintains long-standing working relationships with clients. They strive to

understand client needs and to meet those needs by maintaining the highest standard of analytical service.

While the ESH-AC's primary mission is analytical and technical support, the group's expanded mission includes a complementary research and development element. With the reorganization fully implemented, the ESH-AC is looking forward to providing the specialized research that may be needed by its client organizations to meet their particular ESH analytical needs.

For more information, contact Theresa M. Davis (630-252-6077, davist@cmt.anl.gov).

VIII

Publications and Presentations—2001

The Division's publications and oral presentations for 2001 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.

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W. L. Ebert, M. A. Lewis, and S. G. Johnson

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Precipitation of Crystalline NpO_2 During Oxidative Corrosion of Neptunium-Bearing Uranium Oxides

R. J. Finch

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Neptunium Incorporation in Uranium(VI) Compounds Formed During the Aqueous Corrosion of Neptunium-Bearing Uranium Oxides

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M. Krumpelt

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C. Pereira

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

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Solvent Recovery from Aqueous Effluents Using a Centrifugal Contactor

H. A. Arafat and R. A. Leonard

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F. Gracia and E. E. Wolf

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

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M. D. Kaminski and L. Nunez

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A Bent Crystal Optic for Resolving Fluorescence X-Rays in Mixed Actinide Systems

A. J. Kropf

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R. A. Leonard, S. B. Aase, H. A. Arafat, D. B. Chamberlain, C. Conner,

M. C. Regalbuto, and G. F. Vandegrift

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V. A. Maroni

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V. A. Maroni, S. A. Johnson, K. T. Wu, and P. D. Maroni

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J. F. Miller

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L. Nunez, G. F. Vandegrift, D. L. Bowers, J. Sedlet, S. F. Wolf, and Y. Tsai

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J. P. Kopasz, M. A. Pacheco, S. Ahmed, X. Wang, and M. A. Márquez

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

Presented at the 4th World Congress on Oxidation Catalysis, Berlin, Germany, September 16–21, 2001

An *In Situ* X-Ray Absorption Spectroscopy Study of InSb Electrodes in Lithium Batteries

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

Presented at the 200th Meeting of the Electrochem. Soc., San Francisco, CA, September 2–7, 2001

Nondestructive Transmission X-ray Diffraction Analysis of the Silver-Sheathed Bi2223 Composite Superconductor

V. A. Maroni, K. Venkataraman, A. J. Kropf, Y. Huang, C. Segre

Presented at the 11th Users Meeting for the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, October 9–11, 2001

Colloids and U.S. DOE Fuels: Corrosion of Metallic Uranium Fuel

C. J. Mertz, M. D. Kaminski, S. F. Wolf, Y. Tsai, Y. Vojta, and J. L. Holly

Presented at the Eighth Int. Conf. on Chemistry and Migration Behavior of Actinides and Fission Products in Geosphere, Bregenz, Austria, September 16–21, 2001

Overview of Argonne's Battery and Fuel Cell Research

J. F. Miller

Presented at the Argonne/DOE/Community Leaders Round Table Meeting, Argonne National Laboratory, Argonne, IL, September 19, 2001

Aging and Life Analyses of Generation 2 Advanced Technology Development Lithium-Ion Cells

C. G. Motloch, J. P. Christophersen, R. B. Wright, and V. S. Battaglia

Presented at the 200th Meeting of the Electrochem. Soc., San Francisco, CA, September 2–7, 2001

Homogeneous Catalysis in Supercritical Fluids

J. W. Rathke, R. J. Klingler, M. J. Chen, R. E. Gerald II, and D. S. Hacker
Presented at Argonne National Laboratory, Argonne, IL, September 12, 2001

XANES/EXAFS Studies of Actinides in Environmental Samples

D. T. Reed, A. J. Kropf, R. J. Finch, L. R. Morss, S. B. Aase, C. Degueldre, L. A. Curtiss,
and B. E. Rittmann
Presented at the Eighth Int. Conf. On Chemistry and Migration Behaviour of
Actinides and Fission Products in the Geosphere, Bregenz, Austria,
September 16–21, 2001

Diffusional Transformations of InSb Electrodes in Lithium Cells

T. Sarakonsri, S. A. Hackney, C. S. Johnson, J. T. Vaughey and M. M. Thackeray
Presented at the 200th Meeting of the Electrochem. Soc. San Francisco, CA,
September 2–7, 2001

Biosorption of Neptunium (V) by Pseudomonas Fluorescens

W. Songkasiri, D. T. Reed, and B. E. Rittmann
Presented at the Eighth Int. Conf. on Chemistry and Migration Behaviour of
Actinides and Fission Products in the Geosphere, Bregens, Austria,
September 16–21, 2001

Phosphine-Modified Cobalt Catalysts for Hydroformylation in Supercritical CO₂

M. J. Chen, R. J. Klingler, and J. W. Rathke
Presented at the 10th Int. Symp. and Exhibition on Supercritical Fluid
Chromatography, Extraction, and Processing, Myrtle Beach, SC, August 19–22,
2001

NMR of SAMs on Electrode Surfaces

R. E. Gerald II, J. W. Rathke, and L. E. Iton
Presented at the NMR Symp. of the 43rd Rocky Mountain Conf. on Analytical
Chemistry, Denver, CO, July 29–August 2, 2001

Fuels Processing for Small Fuel Cell Systems

M. Krumpelt, S. Ahmed, T. R. Krause, R. Kumar, and J. P. Kopasz
Presented at the Am. Chem. Soc. 222nd National Meeting, Chicago, IL,
August 26–30, 2001

Advanced Nuclear Reactors: A Chemist's View

D. Lewis
Presented at the University of Florida, Department of Chemistry, Gainesville, FL,
August 3–4, 2001

An Apparatus for Simultaneous Differential Scanning Calorimetry/Powder X-ray Diffraction

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

Presented at the 56th Calorimetry Conf. Colorado Springs, CO, July 29–August 3, 2001

An Apparatus for Simultaneous Differential Scanning Calorimetry/Powder X-Ray Diffraction

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

Presented at the DEST Deutsches, Elektronen-Synchrotron, Hamburg, Germany, August 9, 2001

Infrared Thermography and EXAFS Studies of the Effects of Chlorine (Cl) during CO Oxidation on Pt Supported Catalysts

W. Li, F. Garcia, J. Kropf, J. Miller, and E. E. Wolf

Presented at the Am. Chem. Soc. 222nd National Meeting, Chicago, IL, August 26–30, 2001

An Investigation on the Catalytic Behavior of Modified Mesoporous Catalyst Supports for Hydrodesulfurization

C. L. Marshall

Presented at the ITT, Chemistry Department, Chicago, IL, September 19, 2001

Water-Gas Shift Catalysts with Improved Durability for Automotive Fuel Cell Applications

D. J. Myers, J. Krebs, T. R. Krause, and J. D. Carter

Presented at the 222nd Am. Chem. Soc. National Meeting, Chicago, IL August 26–30, 2001

Design Modeling of Lithium-Ion Battery Performance

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

Presented at the Workshop on Development of Advanced Battery Engineering Models, Washington, DC, August 14–16, 2001

Modeling Thermal Management of Lithium-Ion PNGV Batteries

P. A. Nelson, D. W. Dees, K. Amine, and G. L. Henriksen

Presented at the Workshop on Development of Advanced Battery Engineering Models, Washington, DC, August 14–16, 2001

In Situ EXAFS Characterization of the Reduction of Cu-ZSM-5

M. K. Neylon, C. L. Marshall, and A. J. Kropf

Presented at the 11th Users Meeting for the Advanced Photon Source, Argonne National Laboratory, Argonne, IL, October 9–11, 2001

Calendar-Life and Cycle-Life Studies of Advanced Technology Development Program
Generation 1 Lithium-Ion Batteries

R. B. Wright, C. G. Motloch, J. R. Belt, J. P. Christophersen, C. D. Ho, R. A. Richardson,
I. Bloom, S. A. Jones, V. S. Battaglia, G. L. Henriksen, T. Unkelhaeuser, D. Ingersoll,
H. L. Case, S. Rogers, and R. A. Sutula

Presented at the Workshop on Development of Advanced Battery Engineering
Models, Washington, DC, August 14–16, 2001

Gen 2 Cell Testing at Argonne National Laboratory

I. Bloom and S. A. Jones

Presented at the ATD Peer Review Meeting, Argonne National Laboratory,
Argonne, IL, August 7–8, 2001

Standards for the Design and Fabrication of Gloveboxes

A. A. Frigo

Presented at the Annual Conf. of the Am. Glovebox Soc., San Diego, CA,
July 16–18, 2001

Indirect Nuclear Spin-Spin Couplings in Supercritical CO₂ Solutions of Mercuric bis(n-
alkanethiolates)

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

Presented at the NMR Symp. of the 43rd Rocky Mountain Conf. on Analytical
Chemistry, Denver, CO, July 29–August 2, 2001

Technical Aspects of the Compression Coil Cell Battery Imager

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

Presented at the NMR Symp. of the 43rd Rocky Mountain Conf. on Analytical
Chemistry, Denver, CO, July 29–August 2, 2001

Analysis of Lithium Intercalants in Graphitic Synthetic Metals

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

Presented at Argonne National Laboratory, Argonne, IL, February 23, 2001

Applications for Large-Scale Toroid Cavity Detectors

C. R. Jones, Z. Dabi, R. E. Gerald II, L. Nuñez, R. J. Klingler, and J. W. Rathke

Presented at the NMR Symp. of the 43rd Rocky Mountain Conf. on Analytical
Chemistry, Denver, CO, July 29–August 2, 2001

Reformability of Fuels and Fuel Constituents

J. P. Kopasz

Presented at the IEA Annex XV Advanced Fuel Cell Meeting, Lucerne,
Switzerland, July 1–2, 2001

Development of Fuel Processors for Polymer Electrolyte Fuel Cell Systems at Argonne National Laboratory

J. P. Kopasz, R. K. Ahluwalia, S. Ahmed, J.-M. Bae, J. D. Carter, E. D. Doss, T. R. Krause, J. Krebs, M. Krumpelt, R. Kumar, S. H. D. Lee, D. J. Myers, C. Pereira, and X. Wang

Presented at the First European Polymer Electrolyte Fuel Cell Forum, Lucerne, Switzerland, July 2–6, 2001

ANL Aqueous-Processing Effort Progress and Needs

G. F. Vandegrift

Presented at the University of Nevada at Las Vegas, Las Vegas, NV, July 2, 2001

Lithium Insertion Reactions in Intermetallic Electrodes

J. T. Vaughey, C. S. Johnson, L. Fransson, A. J. Kropf, H. Tostmann, R. Benedek, and K. Edstrom

Presented at the Int. Conf. on Materials for Advanced Technologies (ICMAT), Singapore, July 1–6, 2001

RIDE'n RIPT—Compensating for Acoustic Ringing in Fast Rotating-Frame Diffusion Imaging

K. Woelk, P. Trautner, H. G. Niessen, and R. E. Gerald II

Presented at the NMR Symp. at the 43rd Rock Mountain Conf. on Analytical Chemistry, Denver, CO, July 29–August 2, 2001

Integrated Fuel Processor Development

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

Presented at the National Laboratory R&D Review, DOE Fuel Cells for Transportation Program, Oak Ridge, TN, June 6–8, 2001

Chemical Separations for Environmental Applications: Innovative Uses for Adsorption and Solvent Extraction

H. A. Arafat

Presented at Tuskegee University, Department of Engineering, Tuskegee, AL, June 12, 2001

Fuel Cell Power: What's Taking so Long?

J. D. Carter

Presented at the 25th Int. Precious Metals Conf., Tucson, AZ, June 9–12, 2001

Sulfur Removal from Reformate

J. D. Carter, T. R. Krause, J. R. Mawdsley, R. Kumar, and M. Krumpelt

Presented at the 2001 National Laboratory R&D Review DOE Fuel Cells for Transportation Program, Oak Ridge, TN, June 6–8, 2001

Novel Organoclay Designs for Nanocomposite Applications

D. J. Chaiko and A. A. Leyva

Presented at the Nanocomposites 2001 Conf., Baltimore, MD, June 4–5, 2001

Supercritical Ethane as a Reaction Medium for Preparation of Monodispersed Silver Nanoparticles

N. M. Dimitrijevic and C. D. Jonah

Presented at the Knowledge Foundation Inc. Nanostructured Materials 2001 Application and Commercialization Conf., Chicago, IL, June 21–22, 2001

Radioactive Colloids from Degradation of Metallic Uranium Reactor Fuel

J. Fortner, C. J. Mertz, M. M. Goldberg, and C. Shelton-Davis

Presented at the 75th Colloid and Surface Science Symposium, Carnegie-Mellon University, Pittsburgh, PA, June 10–13, 2001

A Combinational Method for the Fast Screening of Catalysts for the Oxidation of Benzene to Phenol

E. A. Gardner, C. L. Marshall, L. Iton, C. Hamilton, S. Alerasook, P. E. Mayurik, M. Neurock, P. C. Y. Yeh, F. M. Dautzenberg, R. Overbeek, D. H. Klipstein, and G. McRae

Presented at the 17th Meeting of the North American Catalysis Soc., the Westin Harbour Castle, Toronto, Ontario, Canada, June 3–8, 2001

Heterogeneous Catalysts for Selective Oxidation

E. A. Gardner, C. L. Marshall, L. Iton, and T. J. Pinnavaia

Presented at the University of Texas at El Paso, El Paso, TX, June 26, 2001

Near-Frictionless Carbon Films as Anodes for Lithium-Ion Batteries

R. E. Gerald II, J. Sanchez, R. J. Klinger, J. W. Rathke, A. Erdemir, G. R. Fenske, J. B. Woodford, L. A. Curtis, P. Zapol, and L. E. Iton

Presented at Argonne National Laboratory, Argonne, IL, June 6, 2001

Effects of Fuels and Contaminants on Performance of Reforming Catalysts

J. P. Kopasz, D. V. Applegate, X. Wang, L. E. Miller, S. Ahmed, and M. Krumpelt

Presented at the 2001 National Laboratory R&D Review, DOE Fuel Cells for Transportation Program, Oak Ridge, TN, Jun 6–8, 2001

Transition Metals on Oxide Ion Conducting Supports as Catalysts for Autothermal Reforming of Hydrocarbons

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

Presented at the 17th North Am. Catalysis Soc. Meeting, Toronto, Canada, June 3–8, 2001

Comparative Analysis of the Polymer Electrolyte and Solid Oxide Fuel Cells for Transportation Applications

R. Kumar

Presented at the Fuel Cells for Transportation National Conf., Chicago, IL,
July 16–17, 2001

Characterization of the Chemistry and Physics of Coated Conductor Embodiments by Molecular Spectroscopy and Synchrotron X-Ray Methods

V. A. Maroni, K. Venkataraman, M. Li, Y. Jee, B. Ma, H. You, J. H. Je, and
W. G. Cullen

Presented at the Fall Meeting of the Mater. Res. Soc., Boston, MA,
November 26–30, 2001

Colloid Stability in Corrosion Leachates of Unirradiated Uranium Metal Fuel

C. J. Mertz, S. F. Wolf, J. Fortner, M. D. Kaminski, and M. M. Goldberg

Presented at the 75th ACS Colloid and Surface Science Symp., Carnegie Mellon
University, Pittsburgh, PA, June 10–13, 2001

Alternative Water-Gas Shift Catalysts

D. J. Myers, J. Krebs, T. R. Krause, J. D. Carter, and M. Krumpelt

Presented at the 2001 DOE Annual National Laboratory R&D Review of Fuel
Cells for Transportation Program, Oak Ridge, TN, June 6–8, 2001

Evaluation of Potential Cathode Materials for SOFC Operation between 500–800°C

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

Presented at the 7th Int. Symp. on Solid Oxide Fuel Cells, Tsukuba, Japan, June 3–8, 2001

Supercritical Phosphine-Modified Hydroformylation Catalysis

J. W. Rathke, R. J. Klingler, M. J. Chen, and R. E. Gerald II

Presented at the Chemrawn XIV World Congress on Green Chemistry: Towards
Environmentally Benign Products and Processes, Boulder, CO, June 9–13, 2001

Gen 2 Cell Testing at ANL—An Update

I. Bloom and S. A. Jones

Presented at the ATD Quarterly Review Meeting, Idaho National Energy and
Environmental Laboratory, Idaho Falls, ID, May 8–9, 2001

XAFS Spectra of HREE in Synthetic Zircon

R. J. Finch, A. J. Kropf, and J. M. Hanchar

Presented at the 11th Annual Goldschmidt Conf., Roanoke, VA, May 20–24, 2001

A Combinational Method for the Fast Screening of Catalysts for the Oxidation of Benzene to Phenol

E. A. Gardner, L. Iton, C. L. Marshall

Presented at the 2001 Spring Symp., BP Research and Technology Conf. Center, Naperville, IL, May 22, 2001

Self-Assembled Monolayers as Models for Two-Dimensional Liquid Crystals

R. E. Gerald II and J. W. Rathke

Presented at the University of Illinois, Department of Chemistry, School of Chemical Sciences, Urbana-Champaign, IL, May 3, 2001

NMR Paradigms for the Electronic Environments and Mobilities of Lithium in Graphitic Nanoscale Structures

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

Presented at Argonne National Laboratory, Argonne, IL, May 2, 2001

New Electrode Materials for Rechargeable Lithium Batteries

C. S. Johnson

Presented at the Department of Environmental Chemistry and Technology, University of Wisconsin, Madison, WI, May 11, 2001

Layered $(1-x)\text{Li}_2\text{MnO}_3 \cdot x\text{LiMO}_2$ (M=Ni, Co, Cr. or Mn) Electrodes for Lithium Batteries

C. S. Johnson and M. M. Thackeray

Presented at the Lithium Battery Discussion Workshop (LiBD) Meeting, Institute for Chemistry on Condensed Materials of Bordeaux (CNRS), Bordeaux, Aracachon, France, May 27–June 1, 2001

Phosphine-Modified Hydroformylation in Green Solvent

R. J. Klingler, J. W. Rathke, M. J. Chen, and R. E. Gerald II

Presented at the 2001 Spring Symp. of the Catalysis Club of Chicago, BP Naperville Research and Technology Center, Naperville, IL, May 22, 2001

Challenges in Reforming Gasoline: All Components Are Not Created Equal

J. P. Kopasz, S. Ahmed, M. Krumpelt, and P. Devlin

Presented at the Soc. of Automotive Engineers Fuels and Lubricants Meeting, Orlando, FL, May 7–9, 2001

Proof-of-Concept Flowsheet Tests for Cesium Removal from Tank Waste by Caustic-Side Solvent Extraction

R. A. Leonard, S. B. Aase, H. A. Arafat, D. B. Chamberlain, C. Conner,

M. C. Regalbuto, and G. F. Vandegrift

Presented at the 25th Actinide Separation Conf., Boise, ID, May 14–18, 2001

Fundamental Studies of Ceramic/Metal Interfacial Reactions at Elevated Temperatures

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

Presented at the 6th Int. Conf. on Brazing, High Temperature Brazing and Diffusion Bonding, Aachen, Germany, May 8–10, 2001

Low Temperature Steam Reforming of Methanol over Layered Double Hydroxide-Derived Catalysts

S. R. Segal, K. B. Anderson, K. A. Carrado, and C. L. Marshall

Presented at the Catalysis Club of Chicago Meeting, Naperville, IL May 22, 2001

Demonstration of the UREX Process

G. F. Vandegrift, L. Nuñez, D. L. Bowers, J. Sedlet, and J. J. Laidler

Presented at the 25th Actinide Separations Conf., Boise, Idaho, May 14–18, 2001

The Role of Brannerite in the Corrosion of a Titanate Ceramic for Pu Disposition

A. J. Bakel, C. J. Mertz, D. B. Chamberlain, M. K. Nole, and J. K. Basco

Presented at the Am. Ceram. Soc. 103rd Annual Meeting and Exposition, Indianapolis, IN, April 22–25, 2001

The Corrosion of a Fluorocanastite-Glass Composite Dental Ceramic

A. J. Bakel, M. M. Siddiqui, E. C. Buck, J. L. Holly, and N.-Z. Zhang

Presented at the Am. Ceram. Soc. 103rd Annual Meeting and Exposition, Indianapolis, IN, April 22–25, 2001

An HLW Glass Degradation Model for TSPA-SR

W. L. Ebert and J. C. Cunnane

Presented at the 9th Int. High-Level Radioactive Waste Management Conf., Las Vegas, NV, April 29–May 3, 2001

Long-Term Corrosion Tests with Hanford Glasses

W. L. Ebert, M. A. Lewis, and N. L. Dietz

Presented at the Am. Ceram. Soc. 103rd Annual Meeting and Exposition, Indianapolis, IN, April 22–25, 2001

Modeling NP Concentrations in a Breached CSNF Waste Package

R. J. Finch and J. C. Cunnane

Presented at the 2001 Int. High-Level Radioactive Waste Management Conf., Am. Nucl. Soc., Las Vegas, NV, 2001

Modeling Neptunium Concentrations in a Breached Waste Package with Commercial Spent Nuclear Fuel

R. J. Finch, and J. C. Cunnane

Presented at the 9th Int. High-Level Radioactive Waste Management Conf., Am. Nucl. Soc., Las Vegas, NV, April 29–May, 3, 2001

¹²⁹I Release Fractions in Unsaturated Tests with Fast-Flux MOX Fuels

P. A. Finn, Y. Tsai, and M. M. Goldberg

Presented at the 9th Int. High-Level Radioactive Waste Management Conf.,
April 29–May 3, 2001, Las Vegas, NV

Corrosive Alteration of N-Reactor Fuel Exposed to Unsaturated Conditions Using Simulated Groundwater

J. Fortner, C. J. Mertz, and M. M. Goldberg

Presented at the Proc. of the 2001 Int. High-Level Radioactive Waste
Management Conference, Las Vegas, NV, April 29–May 3, 2001

Macroscopic SAMs of Mercury Thiolates Investigated by NMR Spectroscopy and Imaging

R. E. Gerald II, J. W. Rathke, and L. E. Iton

Presented at the Fundamentals and Applications of Mesoscopic Self-Assembly
Workshop, Materials Research Science and Engineering Center, The University
of Chicago, Chicago, IL, April 20, 2001

In Situ NMR of Incipient Thin Films of Synthetic Metals

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

Presented at the NMR Symp. of the 43rd Rocky Mountain Conf. on Analytical
Chemistry, Denver, CO, July 29–August 2, 2001

Combinatorial Screening for the Direct Catalytic Oxidation of Benzene to Phenol

C. Hamilton, E. A. Gardner, C. L. Marshall, L. Iton

Presented at the ACS Spring Symp., April 1–5, 2001

Towards a Better Understanding of Rare Earth Element Partition Coefficients in Zircon

J. M. Hanchar, R. J. Finch, E. B. Watson, and P. W. O. Hoskin

Presented at the 11th Annual Meeting of the European Union of Geochemistry,
Strasbourg, France, April 8–12, 2001

Gen 1 Cell Development and Calendar Life Study

G. L. Henriksen, I. Bloom, and K. Amine

Presented at the METI/LIBES DOE/USABC Meeting, Honolulu, HI, April 10–
11, 2001

Corrosion of Breached Aluminide Fuel under Potential Repository Conditions

M. D. Kaminski and M. M. Goldberg

Presented at the 2001 Int. High Level Radioactive Waste Management Conf.,
Las Vegas, NV, April 29–May 3, 2001

Overview of Autothermal Reforming Catalyst Development at ANL

T. R. Krause

Presented at Argonne National Laboratory, Argonne, IL, April 16, 2001

Environmental Considerations of Transmutation

J. J. Laidler

Presented at the NERAC Subcommittee Meeting, Washington, DC, April 18, 2001

Technical Progress: Separations Technologies

J. J. Laidler

Presented at the NERAC Subcommittee Meeting, Washington, DC, April 18, 2001

Proliferation Implications of Waste Transmutation

J. J. Laidler

Presented at the NERAC Subcommittee Meeting, Washington, DC, April 18, 2001

Monitoring Consistency of Ceramic Waste Form

M. A. Lewis and W. L. Ebert

Presented at the 103rd Am. Ceram. Soc. Annual Meeting and Exposition, Indianapolis, IN, April 22–25, 2001

Determination of K_d Values in the Base-Side Processing of Mo-99 Separation from Leu Irradiation Targets

J. H. Meiser, G. F. Vandegrift, H. Cols, C. Conner, and S. B. Aase

Presented to the Am. Nucl. Soc. National Meeting, San Diego, CA, April 1–5, 2001

Release of Plutonium from the EBR-II Ceramic Waste Form

L. R. Morss, E. C. Buck, C. J. Mertz, and W. L. Ebert

Presented at the Am. Ceram. Soc. 103rd Annual Meeting, Indianapolis, IN, April 22–25, 2001

Qualification Testing of Glass-Bonded Sodalite, A Ceramic Waste Form for Disposition of Sodium-Bonded Spent Reactor Fuel

L. R. Morss, W. L. Ebert, and C. J. Mertz

Presented at the Am. Chem. Soc. Meeting, San Diego, CA, April 1–5, 2001

Bifunctional Catalysts for Selective Catalytic Reduction of NO_x

M. K. Neylon, C. L. Marshall, L. C. Satek, M. E. Carrera

Presented at the ACS Spring Symp., San Diego, CA, April 1–5, 2001

Fuel Cells for Buildings Program

W. M. Swift and R. Fiskum

Presented at the Institute of Electrical and Electronics Engineers Power Energy Soc. Summer Power Meeting, Vancouver, British Columbia, Canada, July 15–19, 2001

Recent Advances in Electrode Materials for Lithium Batteries

M. M. Thackeray, J. T. Vaughey, and C. S. Johnson

Presented at the 221st Meeting of the Am. Chem. Soc., San Diego, CA, April 1–5, 2001

The Role of Fuel Processing in (Commercialization of) Fuel Cell Electric Vehicles

S. Ahmed, J.-M. Bae, J. P. Kopasz, M. Krumpelt

Presented at the Int. Symp. in Future Fuels for Advanced Vehicles, PDVSA-INTEVEP, Caracas, Venezuela, March 21, 2001

Test Bench Results of Yuasa Ni/MH Batteries

I. Bloom, B. W. Cole, A. F. Tummillo, and W. H. DeLuca

Presented at the SAE World Congress, Detroit, MI, March 5–8, 2001

Having A Science Career and Having a Life

J. M. Copple

Presented at the Science Careers in Search of Women Conf., Argonne National Laboratory, Argonne, IL, March 16, 2001

Nuclear Materials in a Geologic Repository: The Chemistry of Everything

J. Fortner

Presented at Argonne National Laboratory, Argonne, IL, February 19, 2001

What Does a Lab Manager Do and How Do They Do It?

D. W. Green

Presented at Pittcon 2001: Symp. on Laboratory Management, New Orleans, LA, March 4–9, 2001

Stabilization of Transition Metal Oxides for Lithium Batteries

A. J. Kahaian, C. S. Johnson, M. M. Thackeray, and K. D. Kepler

Presented at the Int. Battery Association (IBA) Symp. Conf., Kwa-Maritane, Pilansberg National Park, South Africa, March 11–14, 2001

An *In-Situ* X-Ray Absorption Spectroscopy Study of InSb Electrodes in Lithium Batteries

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

Presented at the MRCAT Advisory Committee, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, March 2001

U. S. DOE Sponsored Study on SOFC Applications in the Transportation Industry

M. Krumpelt and J. H. Hirschenhofer

Presented at the Second Solid State Energy Conversion Alliance Workshop, Arlington, VA, March 29–30, 2001

Solid Oxide Fuel Cell Research at Argonne National Laboratory

R. Kumar, R. Ahluwalia, T. A. Cruse, J. M. Ralph, X. Wang, and M. Krumpelt
Presented at the 2nd Solid State Energy Conversion Alliance Workshop,
Arlington, VA, March 29–30, 2001

Developing Catalytic Reformers for Use in Fuel Cells

C. L. Marshall
Presented at the MSI Workshop on New Technologies: Accelerate the R&D of
Fuel Cell and Battery Technologies, Windsor, CT, March 1, 2001

Solid Phase Microextraction (SPME) Screening for Chemical Warfare Agents

J. F. Schneider, A. S. Boparai, and L. L. Reed
Presented at PITTCONN 2001, New Orleans, LA, March 4–9, 2001

Intermetallic Electrodes for Lithium Batteries: The Significance of Face-Centered-Cubic Structures

M. M. Thackeray, J. T. Vaughey, C. S. Johnson, R. Benedek, L. Fransson, E. K. Edstrom,
and J. O. Thomas
Presented at the 18th Int. Seminar and Exhibit on Primary and Secondary
Batteries, Ft. Lauderdale, FL, March 2001

Gen 2 Cell Testing at ANL—An Update

I. Bloom and S. A. Jones
Presented at the ATD Quarterly Review Meeting, Lawrence Berkeley National
Laboratory, Berkeley, CA, February 8–9, 2001

Compact Fuel Cell Power Source

M. Krumpelt
Presented at the DOE NN-20 Power Source Workshop, Santa Barbara, CA,
February 6–8, 2001

Automotive Fuel Cell Systems Modeling and Analysis

R. Kumar, R. Ahluwalia, E. Doss, H. Geyer, and M. Krumpelt
Presented at the 2001 Annual National Laboratory R&D Meeting DOE Meeting,
DOE Fuel Cells for Transportation Program, Oak Ridge, TN, June 6–8, 2001

Pyrochemical Processing

J. J. Laidler
Presented at the Fifth Accelerator and Transmutation Technology Workshop,
Korean Atomic Energy Research Institute (KAERI), Taejon, Korea, February 6,
2001

Publications and Presentations

Status of Fuel Cell Testing at Argonne National Laboratory

E. G. Polzin and I. Bloom

Presented at the DOE Program Review, Argonne National Laboratory,
Argonne, IL, February 22, 2001

Corrosion of a Fluorocanite Dental Glass-Ceramic

A. J. Bakel, M. M. Siddiqui, N.-Z. Zhang, K. J. Anusavice, J. L. Holly, and Y. Tsai

Presented at the 25th Annual Int. Conf. on Advanced Ceramics and Composites,
January 21–26, 2001

Salt Processing Project: CSSX Flowsheet Test Results

R. A. Leonard

Presented at the Salt Processing Vendor Forum, Augusta, GA, January 30, 2001

Corrosion Testing of Structural Steels in Lead-Based Coolants in Support of ANL Advanced Reactor Concepts

S. M. McDevitt

Presented at Argonne National Laboratory, Argonne, IL, January 26, 2001

Characterization of Oxidation Products on a ZrFe₂-Type Laves Intermetallic Exposed to 200°C Steam

D. P. Abraham, N. Dietz, and N. Finnegan

Presented at the Corrosion 2001 Conf., Houston, TX, March 11–16, 2001

Toroid Cavity NMR Imaging Detector—High Resolution, In-Situ Chemical Analysis of High-Pressure, High-Temperature Industrial Catalysis Processes

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

Presented at the Gordon Research Conference on Chemistry of Hydrocarbon Resources, Ventura, CA, January 12, 2001

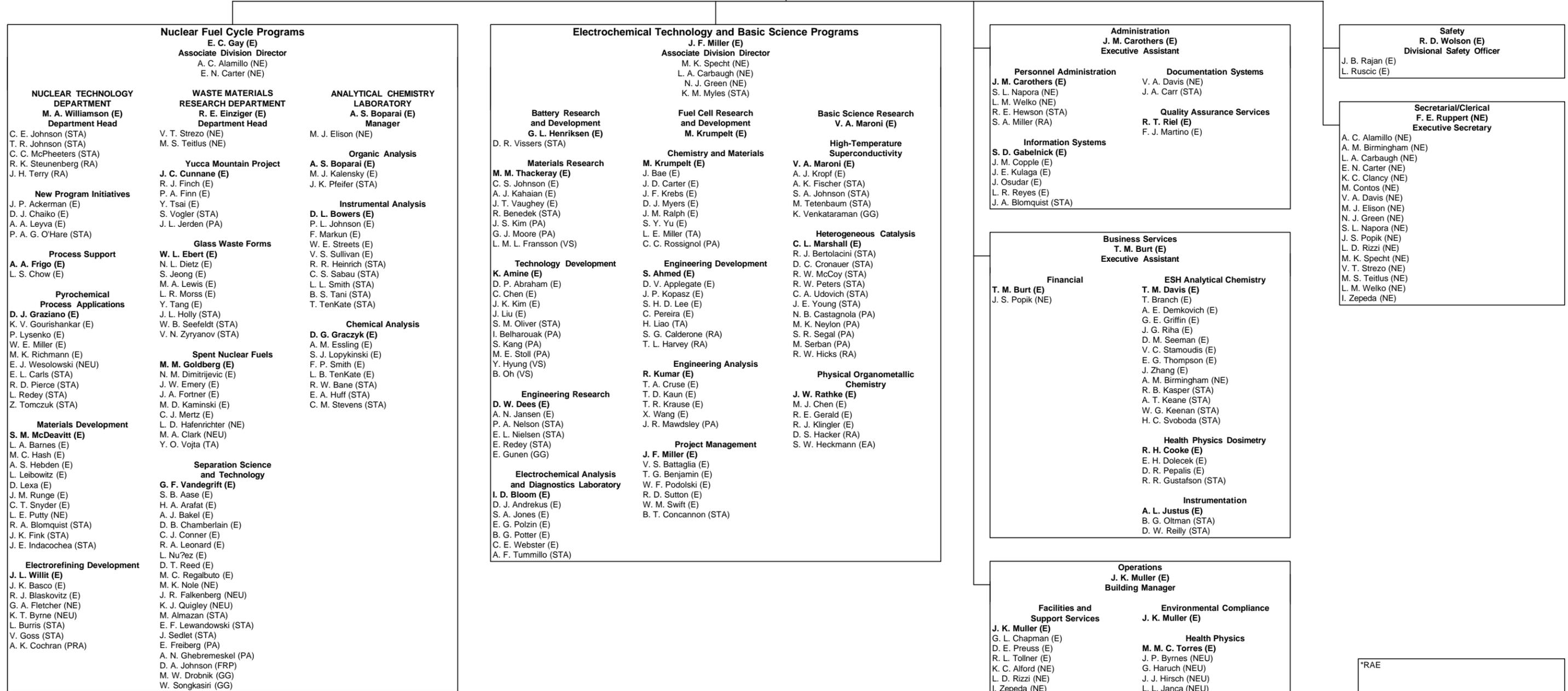
Characterization of Uranium Corrosion Product Colloids by Dynamic Light Scattering

C. J. Mertz, D. L. Bowers, M. M. Goldberg, and C. Shelton-Davis

Presented at the 2001 Int. High-Level Waste Management Conf., Las Vegas, NV,
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