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CHEMICAL TECHNOLOGY DIVISION
ANNUAL TECHNICAL REPORT
1985

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CHEMICAL TECHNOLOGY DIVISION
ANNUAL TECHNICAL REPORT
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ABSTRACT

Highlights of the Chemical Technology (CMT) Division's activities during 1985 are presented. In this period, CMT conducted research and development in areas that include the following: (1) advanced batteries--mainly lithium-alloy/metal sulfide and sodium/sulfur; (2) advanced fuel cells with molten carbonate or solid oxide electrolytes; (3) corrosion-protective coatings for high-strength steel; (4) coal utilization, including the heat and seed recovery technology for coal-fired magnetohydrodynamics plants and the technology for fluidized-bed combustion; (5) methodologies for recovery of energy from municipal waste; (6) nuclear technology related to waste management, the recovery processes for discharged fuel and the uranium blanket in a sodium-cooled fast reactor, and proof of breeding in a light water breeder reactor; and (7) physical chemistry of selected materials in environments simulating those of fission and fusion energy systems. The Division also has a program in basic chemistry research in the areas of catalytic hydrogenation and catalytic oxidation; materials chemistry for associated and ordered solutions at high temperatures; interfacial processes of importance to corrosion science, surface science, and catalysis; the thermochemistry of zeolites and related silicates; and the geochemical processes responsible for trace-element migration within the earth's crust. The Division continued to be the major user of the technical support provided by the Analytical Chemistry Laboratory at ANL.

SUMMARY

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

1. Battery Research

Research is being conducted at ANL with the objective of attaining major improvements in the performance of rechargeable batteries. The principal batteries under investigation are sodium/sulfur with a glass electrolyte and lithium-alloy/metal sulfide with a molten-salt electrolyte. The intended applications for these batteries are electric-vehicle propulsion, utility energy storage, and military uses. The research effort involves basic laboratory studies, operation of small experimental cells, and analytical and engineering support of battery development programs.

Research on sodium-ion-conducting glasses has led to the development of an attractive family of glasses suitable for use as the electrolyte in sodium/sulfur batteries. The resistivities of these glasses are considerably lower than those of conventional glass electrolytes (~100 Ω-cm vs. 1000 to 20,000 Ω-cm). These glasses could permit the development of secondary batteries having unprecedented specific power (2000 W/kg) combined with a high
specific energy (200 Wh/kg). Alternatively, higher specific energy
(-300 Wh/kg) can be achieved at more moderate specific powers (-300 W/kg).

Research on the Li-Al/FeS₂ battery indicated that improved performance could be attained by use of LiCl-LiBr-KBr electrolyte (rather than the usual LiCl-KCl) and the limiting of discharge to the upper-plateau voltage. Experimental cells demonstrated a 50% increase in performance and essentially no capacity loss after 300 cycles (tests still in progress).

A joint program between ANL and the Gould Research Center is underway to develop the lithium-alloy/FeS battery for testing in an electric van. The emphasis in 1985 was on the design, fabrication, and testing of two Li-alloy/FeS modules (12 V, 300 Ah). In simulated driving profile tests, one of the modules attained a specific energy of 104 Wh/kg, which is acceptable for electric-van propulsion. Future effort will be concentrated on the design and testing of a full-size (36 V) battery.

Research on materials for sulfur-electrode containment and current collection in sodium/sulfur cells was concentrated on the evaluation of corrosion-resistant alloys. In static corrosion tests of aluminum-magnesium alloys and high-chromium alloys with Mo, W, Al, Ti, Y, or Zr added, no overall suitable alloy that had low corrosion in both a sulfur and Na₂S₃ environment was found. The corrosion protection provided by amorphous chromium electrodeposited onto steel substrates from aqueous or molten-salt solutions is under investigation.

In 1985, the Division provided the Department of Energy (DOE) with technical management of industrial contracts for development of lead-acid batteries (Johnson Controls, Inc.) and nickel/iron batteries (Eagle-Picher Industries, Inc.) and also conducted support research on these aqueous batteries.

An electrochemical performance model was developed in CMT for predicting the energy and power capabilities of nickel/iron battery designs. Model predictions were verified by comparing them with data from available cell tests. In addition, a thermal model, developed earlier in CMT, was used to investigate the temperature rise with discharge of lead-acid batteries having different designs.

A statistical analysis was completed on performance data from six lead-acid modules that had been tested with simulated driving profiles having different peak powers. The results indicated that the module power capability could be correlated with confidence levels higher than 99% to four factors: the depth of discharge, the number of charge-discharge cycles accumulated, the peak power demand of the driving profile, and the rest period. Analysis of the capacity data for the 36 individual cells contained in these six modules showed good correlation with the number of charge/discharge cycles completed, the peak power demand of the driving profile, and cell location within the module.

A study was also performed to select the most promising battery types for application in hybrid (battery/heat engine) vehicles. Results of the study showed that the most promising candidates for meeting the hybrid-vehicle application are lead-acid, Li-Al/FeS, Ni/Fe, Ni/Cd, and Na/S batteries.
In basic research studies on concentrated aqueous potassium hydroxide (the electrolyte of nickel/zinc cells), Raman studies provided evidence that only one dominant zinc species is present over a wide range of \( \text{Zn}^{2+} \) and \( \text{OH}^- \) concentrations. The studies further indicated that the dominant species is most likely \([\text{Zn(OH)}_4]^{2-}\).

2. Battery Test and Evaluation

The Division operates the National Battery Test Laboratory (NBTL), which continues to play a leading role in the testing and evaluation of various battery technologies. Since 1978, NBTL has tested almost 1700 cells, primarily in the form of three- to six-cell modules and full-size batteries, supplied by 17 domestic and foreign battery developers. During 1985, testing at NBTL was initiated on sodium/sulfur cells from Ford Aerospace & Communications Corp., Li-Al/FeS modules from Gould Inc., a zinc-bromine battery (30 kWh) from Exxon, tubular plate lead-acid modules from Lucas Chloride EV Systems of England, nickel/iron modules from Societe des Accumulateurs Fixe et de Traction of France, and nickel/cadmium modules from Energy Research Corp.

Charge/discharge studies were completed on an improved lead-acid battery fabricated by Johnson Controls for the electric-vehicle application. The optimum overcharge required was found to drop from 8% under 75 to 100% depth-of-discharge (DOD) conditions to only about 4% under 25 to 50% DOD conditions. The test data provided information for improved battery charger designs, which should lead to reduced water consumption and greater efficiency for the lead-acid battery. Internal impedance studies of nickel/iron modules fabricated by Eagle-Picher for the electric-vehicle application showed that the internal resistance is nearly constant with discharge and that the battery voltage (free of internal IR drop) can be used as a measure of DOD. In a separate study on the effect of temperature on discharge capacity of the nickel/iron battery, the optimum temperature was found to be 25°C, with decreased capacity exhibited at 0°C and 50°C.

A methodology was developed to predict battery discharge times for almost any load profile. This methodology uses the Ragone curve (specific energy vs. power demand) and the curve for peak power vs. depth of discharge. From the calculated discharge times, vehicle ranges during a single discharge of the battery can be easily calculated. Good agreement was found between ranges projected by this new methodology and NBTL results.

In addition to battery testing and evaluation, physical and chemical analyses of batteries are performed after termination of testing in the NBTL and other facilities. In 1985, post-test analyses were conducted on lead-acid and nickel/iron modules and sodium/sulfur cells.

The primary cause of capacity decline for the lead-acid modules was generally found to be corrosion of the positive electrode grid, combined with loss of positive-electrode active material. For nickel/iron modules, the migration of iron to the nickel electrode was found to cause loss of active material utilization and a decline in capacity. Future research will be directed at minimizing this iron transport and its detrimental effects on the nickel electrode. The post-test analyses of the sodium-sulfur cells (load-leveling application) indicated that the sulfur electrode develops two reaction zones when charged or discharged. One is a semicontinuous ring of sulfur near
the β"-alumina electrolyte; the second sulfur ring is located near the cell container wall. In addition, corrosion products from the container were found to migrate through the electrode and precipitate onto the electrolyte. Electrolyte fractures during freeze-thaw cycles were also discovered and appear to be caused by stresses produced by voids or sodium polysulfide buildup in the sulfur electrode.

3. Advanced Fuel Cell Development

The advanced fuel cells under development at ANL have electrolytes of molten carbonate and solid oxide.

The major technical problems in development of the molten carbonate cell are electrolyte management, cathode degradation, anode creep, corrosion of the bipolar separator sheet used to connect adjacent cells, and cross leakage of electrode gases. The CMT research emphasizes the development of an alternative cathode material to NiO, which had been found to have a long-term stability problem. The activities during 1985 were concentrated on improving the electronic conductivity of LiFeO$_2$, which, in earlier work, had been shown to be stable in the cathode environment. Magnesium, copper, and manganese were investigated as possible dopants to the LiFeO$_2$. Doping was found to be very effective in improving the conductivity of LiFeO$_2$, with each dopant having its particular advantages and disadvantages. Future work will focus on gaining a better understanding of the oxygen dependence of cathode materials, thus indirectly providing insight into the doping effects.

During 1985, ANL continued to provide technical support for the molten carbonate fuel cell program of the DOE Morgantown Energy Technology Center. This support took the form of program planning, systems analysis, technical monitoring of contractor efforts, and preparation of work statements.

Technical support was also provided to the DOE program in solid oxide fuel cells. This technical support included testing contractor cells, investigating fundamental cell phenomena, and providing technical insight as required to direct the efforts of Westinghouse Electric Co. (DOE's major contractor in the solid oxide fuel cell program). These technical support efforts were terminated at our request at the end of FY 1985 because of potential conflicts of interest. The Division's work on solid oxide fuel cells is being concentrated on development of the "monolithic fuel cell."

The monolithic fuel cell, which ANL is developing for the Department of Defense, employs the same thin, ceramic layer components of existing solid oxide fuel cells in a strong, lightweight honeycomb structure of small cells and is expected to yield very high power per unit mass or volume. This new design takes advantage of the ability to fabricate the solid electrolyte and other fuel cell components in shapes that cannot be achieved in liquid electrolyte systems. In 1985, the first cells of the monolithic design were built and operated. These cells were a three-layer composite of cathode/electrolyte/anode produced through sequential tape casting. The cells were operated at high current densities (2.2 A/cm$^2$), nearly four times higher than the design goal, with no fundamental limitation encountered.

A new system analysis and cost assessment project was initiated in 1985 for DOE. The project's purpose is to assess the benefit projections made
by fuel cell developers and to define R&D priorities. The first analysis has been nearly completed for the utility baseload application. This analysis projected the costs for electricity for both phosphoric-acid and molten-carbonate fuel cell systems, a combined-cycle (gas and steam turbines) combustion plant, and a pulverized-coal combustion plant. The projected costs for electricity for the two fuel cell systems were close to those for the two competing systems, confirming that fuel cells have potential in the baseload application.

4. Advanced Research Projects in Electrochemical Technology

Our advanced research projects in electrochemical technology include investigation into (1) the cadmium coating of high-strength steel for corrosion protection and (2) an electrochemical application for a new photochemical complex synthesized by ANL's Chemistry Division.

For decades, cadmium electrodeposits on steel substrates have been obtained by cadmium plating from alkaline cyanide electrolyte. However, codeposition of hydrogen during cadmium electroplating from this aqueous electrolyte is common; the hydrogen migrates to regions of high stress and weakens the metal's strength. In work done in CMT, it was found that cadmium, free of hydrogen, can be plated under DC pulse currents from a fluoroborate-based electrolyte. The coatings were free of voids and showed good adhesion. An electrolyte flow cell for improved pulse-current plating of the coating was developed. With this new cell, plating rates were increased and heat-generation problems were greatly reduced.

In the other effort, basic electrochemical studies are being conducted on a molecular complex that mimics the "reaction center" (i.e., the site where the transduction of light to chemical energy occurs) in photosynthetic systems. This complex has three distinct molecular entities that are covalently bonded together: a porphyrin, a triptycenenaphthoquinone, and a 2-(N,N-dimethylamino)triptycene. The overall objective of this effort is to develop the technology needed to collect the energy from the cation-anion radical pair formed upon illumination of the complex. In 1985, cyclic voltammetry studies were begun to investigate the molecular-complex constituents, and techniques were explored to immobilize the complex on metal and graphite electrode surfaces.

5. Fossil Fuel and Municipal Waste Utilization

The Division has programs on the utilization of coal and municipal solid waste.

The program in municipal solid waste (MSW) utilization centers on the pyrolysis of MSW to form fuel-like liquid and gaseous products that are storable and transportable. The basic mechanisms of the thermokinetic degradation of MSW are being investigated with a thermogravimetric analyzer (TGA) and a bench-scale reactor. The data obtained from these experiments will be used to derive a kinetic model of the pyrolysis mechanisms associated with gasification, liquefaction, and charring of MSW components. Two additional organizations, managed by CMT, are involved in the effort to determine the basic mechanisms of MSW pyrolysis: the Solar Energy Research Institute and the University of Arizona. The catalytic upgrading of the pyrolysis liquids to remove oxygen is also being
investigated at CMT. Testing of a nickel-molybdenum catalyst with model compounds (e.g., eugenol, furans) in a high-pressure microreactor indicated a large degree of hydrodeoxygenation.

The CMT program in coal utilization is focused on developing the hot-gas cleanup technology for pressurized fluidized-bed combustion (PBC), the heat and seed recovery technology for coal-fired magnetohydrodynamics (MHD), and methods for the cleaning of high-sulfur coal.

When gas turbines are directly operated with hot flue gas from the FBC of coal, particulates of ash and condensed alkali metal compounds in the flue gas cause erosion, corrosion, and fouling of the gas turbine blades and hardware. For several years, CMT has investigated the use of sorbents for the removal of the alkali vapor from the hot flue gas. After laboratory studies indicated that activated bauxite would be an effective sorbent, a granular-bed sorber was designed and fabricated, and its effectiveness will soon be tested on the pressurized fluidized-bed combustor in CMT. Also under way is the determination of the reliability of materials for in-bed air heaters in several atmospheric FBC cogeneration schemes.

The CMT Division is the lead laboratory in a multidivisional effort that is directed toward developing the technology required for the design of components in the MHD bottoming cycle. Experiments are under way to determine the capability of sootblowers to remove the seed-ash deposits that will form in the convective section of MHD boilers. At gas temperatures near 1340 K, the tube deposits were powdery and readily removed by sootblowing. At temperatures of ~1550 K, the deposits began to sinter and harden, and deposit removal by sootblowing became more difficult and, eventually, impossible. Although the combustion gas entering the radiant boiler of the MHD bottoming cycle will contain excessive nitric oxide, a chemical kinetics model developed at ANL predicts that the NO concentration in the exit of the boiler will be below emission standards, provided that the gas is not cooled too rapidly. Experimental data obtained at the University of Tennessee Space Institute agree with predictions from the chemical kinetics model. Work has been initiated to identify the severity of potential problems related to NOx control and back-wall burnout in interfacing the MHD diffuser and the radiant boiler.

The CMT Division is also participating in two joint projects with the Chemistry Division. The objective of one of these projects is to develop a method for the removal of organic sulfur from coal. This has been achieved by treatment of high-sulfur coal with aqueous cupric salts at 250°C. The objective of the other project is to develop a high-throughput method of separating the macerals in high-sulfur coal. In the past year, coal macerals have been obtained by use of a continuous magnetic field gradient. The petrographic characteristics and liquefaction reactivity of the macerals are being determined.

6. Nuclear Technology

Reaction of Glass with Water. Investigation of the volcanic tuff beds of Yucca Mountain, Nevada, as a potential location for a high-level radioactive waste repository is a function of the Nevada Nuclear Waste and Storage Investigations (NNWSI) project. For this project, CMT has developed and demonstrated a test method that measures the release of radionuclides from
the high-level waste package under conditions that simulate thousands of years of storage. Test results have been shown to be reliable and can be incorporated into models used to predict repository behavior.

In work related to the NNWSI project, CMT has investigated the glass, water, and air interactions that occur in a gamma-radiation field. These tests simulate events that may occur in the repository but are of low probability. Results suggest that the reaction of glass with water under these circumstances is a dynamic balance between glass dissolution and nitric acid generation, and that current methods used to accelerate reactions in a gamma-radiation field likely provide data that are not relevant to repository conditions.

Separations Science and Technology. The Division is participating in a project to develop a solvent extraction process that will remove and concentrate transuranic elements from waste generated by the plutonium finishing plant (PFP) of Rockwell Hanford Operations. A flowsheet for the TRUEX process (TRansUranic EXtraction), developed in cooperation with the Chemistry Division, was tested with a simulated PFP waste solution containing U, Pu, and Am. The TRUEX process results in a liquid raffinate which, after volume reduction by evaporation, may be incorporated into a suitable waste form (e.g., concrete) having a sufficiently low concentration of actinide elements to be rated as nonTRU waste. Under properly selected conditions, the TRUEX process should yield an americium product stream containing >99.9% americium and a plutonium product stream containing >99.9% plutonium. It was found that hydrolytic and radiolytic damage to the solvent would be of no consequence for periods equivalent to several years of processing typical PFP wastes.

In another project, a 16-stage centrifugal contactor was designed and fabricated for solvent extraction processing of concentrated HCl/brine waste streams. A process to separate actinides from the chloride salt wastes will be tested in 1986.

The Integral Fast Reactor Concept. An advanced fast reactor concept being developed by ANL is the Integral Fast Reactor (IFR)—a pool-type fast reactor fueled with a metal alloy fuel and equipped with a close-coupled fuel cycle facility. The CMT Division has the responsibility for developing the recovery processes for the discharged fuel and uranium blanket. Pyrometallurgical processes that directly yield metal products suitable for refabrication into new fuel elements have been chosen. There are two major process steps: electrorefining for separating cladding and fission products from the fuel, and halide slagging for enriching the plutonium in the blanket to a level such that it can be used to replenish the plutonium consumed by the core. In the electrorefining step, the uranium and plutonium are transported electrochemically from an anode to a cathode in a liquid cadmium/molten-salt system at about 500°C. Halide slagging involves the extraction of plutonium from liquid uranium by a molten salt at a temperature of 1250-1300°C.

Uranium electrorefining experiments on a small scale (300 g) demonstrated over 99% recovery of the uranium along with fission-product removals that were consistent with theoretical predictions. The electrorefining of plutonium and uranium-plutonium mixtures (30 g) was also demonstrated. Over 90% recovery of plutonium from uranium was achieved in halide-slagging experiments. Other activities included basic electrochemical studies of uranium and plutonium redox reactions, considerations of various methods for the disposal
of radioactive process wastes, and the development of flowsheets and process equipment concepts for economic studies.

**LWBR Proof-of-Breeding Analytical Support Project.** As part of a program for developing the technology of breeding with the $^{233}$U/$^{232}$Th nuclear fuel cycle, the Bettis Atomic Power Laboratory (BAPL) plans to estimate the fissionable content of the end-of-life (EOL) core in a light water breeder reactor (LWBR) that had been operated for five years. A statistical sample, comprising 500 core fuel rods, will be selected for assay by BAPL using a nondestructive delayed-neutron device. A comparison of the beginning-of-life core with the EOL core will establish the extent of breeding.

The role of ANL in this program is to carry out destructive chemical, physical, and radiometric analyses of LWBR fuel rods, which will provide BAPL with calibration and correction factors for its production irradiated-fuel assay gauge. In 1985, the processing of 17 full-length LWBR rods as part of the EOL campaign was completed. The processing involved precision shearing of the rods into segments, dissolution of each segment, and sampling and analysis of the dissolver solutions for uranium isotopes and selected fission products ($^{137}$Cs, $^{144}$Ce, and $^{95}$Zr). Mass spectrometric isotopic dilution and alpha and gamma spectroscopy were used for these analyses. Results from the destructive analysis of each fuel rod have been reported to BAPL, along with uncertainty estimates for each result. The dissolver solution is being disposed of by conversion to a cement waste form and removal to an approved site away from ANL. Dismantling of the cells and disposal of all waste are expected to require a year and are scheduled for FY 1987.

7. **Applied Physical Chemistry**

**Fission Product Chemistry.** The Division is engaged in three experimental efforts to investigate fission product release and transport under accident conditions in a light water reactor (LWR).

In the first effort, the chemical form and rate of release of fission products from a defected LWR fuel pin are being determined by quadrupole mass spectrometry. In the past year, experiments were run with an irradiated fuel sample contained in a nickel Knudsen cell at temperatures up to 1410 K. The fission-gas release rate was found to be $10^3$ times lower than previously reported. In addition, leaking oxygen into the cell at temperatures of 1190-1440 K indicated that oxidation of the fuel sample increases fission gas release.

During an accident, fission products released from defected fuel pins are likely to form aerosols that can be transported out of the reactor. Thus, in the second experimental effort, fission product solutions (CsI, CsOH, CsI/CsOH, Te/CsI/CsOH) were injected into superheated steam flowing through a stainless steel transport duct containing an aerosol sampling system. The runs with CsI and CsOH alone showed that fission product deposition on the duct walls occurs when the wall temperature is reduced to the saturation temperature of the fission product species in the steam. However, in the CsI/CsOH run, the CsI in the mixture deposited farther downstream than anticipated based on the run with CsI alone. This behavior was explained by postulating the formation of a CsI-CsOH reaction product that exhibits significantly different deposition behavior. The deposit formed from the CsOH/CsI/Te run was thought to be $\text{Cs}_2\text{TeO}_3$. 
In the third experimental effort, a transpiration technique is being used to study the release of three volatile fission products (LaO, BaO, SrO) from a core-concrete melt. The measured fractional release values for these fission products were found to follow the sequence Ba>La>Sr.

Metal Fuel Properties. An assessment of the data available on the thermophysical properties of metal fuel and blanket materials for the IFR revealed some important gaps. The properties for which data are most urgently needed are thermal conductivity, thermal expansion, and solidus and liquidus temperatures. The work in 1985 was concentrated on thermal conductivity measurements for the U-Zr alloy (11.36 wt % Zr) at temperatures of 535-800 K. The results of the measurements were in good agreement with estimated values based upon the work of others. Preparation is under way to make the thermal conductivity measurements at higher temperatures.

Experiments were also carried out to determine the feasibility of preparing UCl₃ (for use in the halide-slagging step for IFR reprocessing) by oxidation of uranium metal with CdCl₃. Small-scale tests (~40 g uranium) resulted in a 90% yield of UCl₃.

Fusion-Related Research. A crucial element in the development of fusion reactors is the blanket for breeding tritium fuel. Several studies are under way with the objective of determining the feasibility of employing lithium-containing ceramics as breeder material. The Division is also conducting design studies of methods for improving fusion reactor performance and neutron dosimetry and damage analyses of fusion materials in neutron facilities.

A computational study was completed to assess the tritium release achieved by applying a protium-purge gas stream (in the form of H₂ and H₂O) to three ceramic materials (LiAlO₂, Li₂O, and Li₄SiO₄) at temperatures of 900 and 1300 K and H₂O:H₂ ratios of 100:1 and 1:100. The calculations indicated that, at either H₂O:H₂ ratio, Li₂O and LiAlO₂ release more tritium at 900 K than at 1300 K, but that Li₄SiO₄ releases slightly more tritium at 1300 K than at 900 K for both H₂O:H₂ ratios. The predicted tritium release of the candidate breeder materials under protium purge was ranked as LiAlO₂>Li₂O>Li₄SiO₄.

An important observation from an earlier tritium release experiment (TRIO) was that the presence of a small amount of H₂ gas (1000 ppm) in a helium carrier gas significantly improved tritium release from LiAlO₂ breeder material. Bulk diffusion and surface processes are believed responsible for the tritium transport and release from γ-LiAlO₂. A plot has been constructed that allows one to assess the relative importance of bulk diffusion and surface processes as a function of temperature and hydrogen concentration. This plot indicates that, within the temperature regime of TRIO (773-973 K), diffusion is the rate-limiting step at lower temperatures, whereas neither process is dominant at higher temperatures. In another effort, a new configuration for the current sphere-pac breeder design was developed, and calculations indicated that it would lead to a 22-30% thermal conductivity improvement at 700-1300 K.

For fusion to be attractive as an energy source, an order of magnitude improvement in the total reactor cost per kilowatt-hour is needed. Thus, the Division is undertaking design studies to determine which concepts have the potential to achieve a significant performance improvement without an increase in costs. Two design concepts were assessed this year: (1) the use of polarized fuels and (2) the use of high-temperature, high-pressure helium as a heat...
transfer medium. Neither concept was found to provide a significant reactor performance improvement.

In neutron dosimetry and damage analysis, neutron facilities are being characterized in terms of neutron flux and energy spectrum, which can be used to calculate atomic displacements and transmutations. These damage parameters can then be used to correlate property changes between facilities and to predict materials performance in fusion reactors. Furthermore, attention is being given to determining the cross sections of selected nuclides because of their possible use in measuring plasma ion temperatures in fusion reactors. To date, cross sections have been determined for the \((n,2n)\) reactions on \(^{27}\text{Al}\) and \(^{54}\text{Fe}\) to form \(^{26}\text{Al}\) and \(^{53}\text{Mn}\) and the \(^{94}\text{Mo}(n,p)\) reaction to form \(^{94}\text{Nb}\).

8. **Basic Chemistry Research**

**Fluid Catalysis.** Fundamental studies in catalysis are being conducted in the areas of catalytic hydrogenation and oxidation chemistry.

The hydrogenation research resulted in identification of the mechanism for methanol formation from a soluble organometallic formate. This mechanism includes a preequilibrium process that equilibrates trimethylsilyl formate with hexamethyldisiloxane, carbon dioxide, and methyl formate at 250°C. After the initial preequilibration, methanol is produced by decarbonylation of methyl formate. Isotope labeling studies, using \((\text{CH}_3)_3\text{SiO}_2\text{CD}\), confirmed that methanol and methyl formate arise solely from the formate moiety on silicon, and not from appended methyl groups. A catalyst (zinc phthalocyanine) for the formate disproportionation and a related carbon monoxide hydrogenation was identified.

Research in the area of catalytic oxidation chemistry indicated that the catalytically activated organic bases are potential oxygen carriers. A collaboration with the National Institute for Petroleum Energy Research resulted in the first measurement of the N-O bond energy in an amine-N-oxide. The value for pyridine-N-oxide, 70 kcal/mol, indicates that reversible aerobic oxidation of amines is thermodynamically possible. A catalyst system in which trimethylamine appears to function as an oxygen carrier in the aerobic oxidation of an olefin was also identified.

**High-Temperature Materials Chemistry.** Our work on high-temperature materials chemistry involves theoretical and experimental investigations of associated and ordered solutions such as chloroaluminates, silicates, and "ionic" alloys. Quantum mechanical computations have provided information on the energetics, structures, and vibrational frequencies of molten-salt species such as \(\text{Mg}_2\text{O}_2^+\) and \(\text{AlCl}_4^–\); these computations are an important adjunct to experimental studies. Our studies of ordered alloys (e.g., Li-Pb, Na-Pb, K-Pb) led to the discovery of an unexpected phenomenon—ordering at more than one composition of an alloy. A solution theory we developed for dilute solutes in multicomponent solvents yielded predictions of solution properties of oxygen in the ternary Ag-Sn-Cu alloy at 1473 K. Our calculations with this theory were much more accurate than those of prior theories. Studies of submerged arc welding suggested that electrochemical reactions are important in understanding the factors governing welding chemistry.
Work has continued on the extraction of transition metals from land- based and deep ocean minerals by using pyrochemical media. Considerable success was achieved in lixiviating cobalt and manganese from Pacific Ocean nodules; nearly complete recovery of both metals was achieved with MgCl₂-KCl-NaCl eutectic. There is good reason to expect that our approach could be adopted to the recovery of other metals such as chromium and copper.

Interfacial Materials Chemistry. Research on interfacial materials chemistry is focused on scientific issues related to high-temperature aqueous corrosion, catalysis by synthetic zeolites, and mechanisms of chemical reactions on surfaces. Facilities for the performance of spectroscopic and transient electrochemical measurements on metals in aqueous media to 300°C and 10 MPa have been developed and tested and are now operating. Emphasis of studies done with these facilities is on charge transfer and structural properties of interfacial species involved in the aqueous corrosion of iron, nickel, and their alloys. Considerable progress has been made in the experimental work and in a parallel theoretical effort aimed at elucidating the charge transfer mechanism involved in the Fe²⁺/Fe³⁺ redox reaction. In work on zeolite catalysis, in situ diffuse reflectance infrared spectroscopy has been used to probe the relative catalytic activity of protonated sites in selected synthetic zeolites (i.e., ZSM-5 and offretite) as a function of temperature and organic reactant. Our determinations of the O-H and C-H stretching vibrations revealed several new details concerning the functional aspects of the zeolite during the intra-zeolite reactions that are involved in hydrocarbon reforming. In work on electrocatalysis by macrocyclic ligand complexes, iron protoporphyrin IX was found to be more stable but less active toward O₂ reduction than iron phthalocyanine. Ab initio quantum mechanical calculations for small metal clusters adsorbed on surfaces are being done and should serve as a means of modeling differences in surface chemistry between clusters and bulk metal. In the case of beryllium clusters (Beₙ-OH₂, n = 1-5), the calculated interaction energy of the cluster with a water molecule increased dramatically as the cluster size increased from one atom to three atoms but then leveled off for cluster sizes greater than three atoms.

Thermochemistry. Rock-water interactions play an essential role in many geochemical processes of both practical and theoretical interest. These reactions can be better understood with a knowledge of the thermodynamic properties of the product and reactant minerals, as well as the brine solutions. As a contribution to the understanding of such interactions, this CMT effort involves determining the thermodynamic properties of zeolites and related silicates. During the past year, calorimetric measurements were made on a natural sample of zeolite mordenite and on its dehydrated form. The results indicated that the water in zeolites is more strongly bound than in inorganic hydrates. Calorimetric measurements made on silicalite indicated that this material is not as stable as had been previously believed.

Trace-Element Migration. The redistribution of elements in active geothermal systems is being investigated through analytical studies of drill cores and thermal water from Yellowstone National Park, Wyoming. In 1985, determination was made of the content of a large group of elements in 30 samples from two drill cores (Y-7 and Y-8) in the Biscuit Basin Rhyolite Flow. The data for one of the cores were consistent with a model of single-stage uranium addition involving water/rock mass ratios as high as 10⁵ or more; data for the other core suggested much less uranium mobility. Equations were derived for ²³⁸U-series evolution in open geological systems.
9. **Analytical Chemistry Laboratory**

The Analytical Chemistry Laboratory (ACL) is administratively within CMT, the principal user, but serves most of the technical divisions and many of the programs at ANL as a full-cost-recovery service center. In addition, the ACL conducts a research program in analytical chemistry and provides analytical services for governmental, educational, and industrial organizations. The ACL has three technical groups—Chemical Analysis, Instrumental Analysis, and Organic Analysis.

The single project requiring the largest effort by ACL staff was the Proof-of-Breeding Project in CMT. Seventeen end-of-life fuel rods were destructively assayed for this project in FY 1985. The ACL role was to analyze dissolver solutions and gas samples for fission gases, including krypton and xenon isotopes, obtained during the processing of 152 segments sheared from the fuel rods. More than 1000 aliquots of dissolver solution were prepared and analyzed for uranium content and isotopic composition by thermal ionization mass spectrometry, and an additional 550 aliquots were analyzed for $^{137}$Cs, $^{144}$Ce, and $^{95}$Zr by gamma spectrometry. Project requirements for precision on the individual analyses were met or exceeded in every case.

Highlights of the ACL efforts for 1985 include analysis of the liquid produced from thermal degreasing of cellulose, the salt and product samples from the pyrometallurgical experiments of the IFR project, extractants from the TRUEX solvent extraction process, crystalline materials from electrochemical cells, alkali vapors in the flue gas from pressurized fluidized-bed combustion of coal, polyethylene pipe, samples of limestone and marble, and spent fuel from a pressurized water reactor. In addition, a study was completed on the utility of a light pipe compared with matrix isolation as gas chromatography/mass spectrometry interfaces.

10. **Computer Applications**

The Computer Applications Group assists CMT staff in many aspects of computer-related activities, including laboratory data acquisition and control, computer modeling and simulation studies, analysis of experimental results, graphics, information management and data-base development, computer networking, procurement of automatic data processing equipment, and advisory and consulting services. The disk storage capacity for the major component of the CMT computing system, a VAX 11/780, was increased from 1600 to 2000 megabytes, and memory was increased from 8 to 16 megabytes. In 1986, the Division plans to upgrade the VAX to a model 11/785, which will increase capacity by 50-70% to better accommodate its increased usage.
I. BATTERY RESEARCH

The CMT Division is engaged in research efforts on advanced and aqueous batteries whose primary application is vehicle propulsion.

The advanced-battery effort includes (1) exploratory research on stable sodium-conducting glasses for sodium/sulfur cells, (2) research and development of molten-salt cells and electrode materials for them, and (3) development of a positive-electrode current collector and container usable for more than five years in cells of high sulfur activity. In addition, a cooperative effort is under way with Gould Research Center to develop Li-Al/FeS batteries for electric-van propulsion.

The aqueous-battery effort includes (1) management of industrial contracts for development of improved lead-acid and nickel/iron batteries, (2) research in support of aqueous battery development, and (3) assessment of battery systems for hybrid-vehicle (internal combustion/electric) applications.

A. Glass-Electrolyte Development for Na/S Cell

Glass electrolytes are a potential alternative to the ceramic electrolyte (sodium α’-alu’-na) that is currently being used in Na/S cells. The objective of our research is the development of a glass that will have low resistivity (~100 Q-cm at 300°C), will be stable in the hostile Na/S cell environment, and can be easily fabricable at low cost. Soda-rich glasses in the soda-alumina-zirconia-silica system were selected for in-depth study based on our earlier experiments, thermodynamic calculations, and review of the literature.

1. Physical and Chemical Properties

Twenty-five glasses in the soda-alumina-zirconia-silica system were prepared and characterized in terms of their resistivity ($\rho$), activation energy for conduction ($E_a$), and glass transition temperature ($T_g$). The composition of these glasses and the data for $\rho$, $E_a$, and $T_g$ are given in Table I-1. We analyzed these data by multiple linear regression using a cubic polynomial in the form appropriate for a mixture of four components (four linear, six quadratic, and ten cubic terms). This twenty-term "simplex" polynomial was derived by Scheffé.\(^1\) A computer search found the best fit using the fewest possible terms, with the condition that the linear term for each component must always be included. The $\rho$ and $E_a$ data required the linear terms and five additional terms (two quadratic and three cubic) for squared correlation coefficients of 0.97 and 0.95, respectively. The $T_g$ data were fit with the linear terms and four additional terms (one quadratic and three cubic) for a squared correlation coefficient of 0.98. From the equations, we generated pseudoternary phase diagrams. Such diagrams are useful in making projections for the properties of new glasses in the region where experimental data have been collected (up to 46 mol % Na$_2$O, up to 25 mol % Al$_2$O$_3$, and up to 13 mol % ZrO$_2$); beyond these regions, the projections are not expected to be very accurate.

---

Table I-1.  Experimental Data from Glasses in the Soda-Alumina-Zirconia-Silica System

<table>
<thead>
<tr>
<th>Glass Code</th>
<th>Composition, mol %</th>
<th>Glass Transition Temp., °C</th>
<th>Resistivity, ρ-cm</th>
<th>Activ. Energy, eV</th>
<th>Weight Change, b mg/cm²</th>
<th>Na²⁺</th>
<th>Na₂S₄⁻</th>
<th>S</th>
<th>Na₂S₃⁻</th>
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<td>77.3</td>
<td>468</td>
<td>475</td>
<td>3704</td>
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<td>526</td>
<td>697</td>
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<td>479</td>
<td>479</td>
<td>312</td>
<td>0.582</td>
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</table>

| quartz     | 100.0             | 1024                     | 1058             |                  |                        |      |        |      |        |
| β²-alumina |                   |                          |                  |                  |                        |      |        |      |        |
| Dow Glass  |                   |                          |                  |                  |                        |      |        |      |        |


*At 300°C.

b At 400°C for 1000 h.
The thermal expansion of selected high-soda glasses (X, P, R, T, and RF3) was determined in a collaborative effort with ANL's Materials Science and Technology Division. In each experiment, the expansion of the sample was measured against an NBS standard alumina rod from room temperature to 400°C. The data indicate that the high-soda glasses have high thermal expansion coefficients (16 to 18.6 x 10^{-6}/°C).

The glasses were also subjected to chemical-stability tests in high-purity Na, Na2S3, and S at 400°C for 1000 h. Data from these tests are given in Table I-1; the borate glass2 of Dow Chemical and the β"-alumina of Ceramatec Inc. are also included to serve as a basis for comparison. Among the ANL glasses, the high-soda glasses showed the smallest weight change after exposure to the three media. The glasses that showed acceptable stability were X, IB6, P, R, T, RF5, and RF3. Further testing in Na2S3 was performed on eight quaternary glasses; the weight-change results are also given in Table I-1. The quaternary glasses that showed acceptable chemical stability in Na2S3 were IB51 (P glass made with quartz), RF1, RF2, RF2S, RF4, and T.

Based on these results, an ANL glass electrolyte was selected for testing in Na/S cells. This electrolyte has a composition (in mol %) of 42 Na2,0-8 Al2O3,5 ZrO2,45 SiO2. Moreover, it has an ionic conductivity of 7.1 x 10^{-3}/Ω-cm at 300°C, an activation energy for conduction of 0.53 eV, a glass transition temperature of 534°C, and a thermal expansion coefficient of 16 x 10^{-6}/°C. Its chemical stability in the cell environment is comparable to that of the Dow glass and β"-alumina: the ANL glass exhibited weight changes of 0.7, -0.5, -0.3, and 0.4 mg/cm² after 1000 hours at 400°C in Na, Na2S3, Na2S4, and S, respectively. A report on cell performance with this electrolyte will be given in the next annual report.

2. Preliminary Cell Designs

Preliminary designs were devised for cells employing tubes of the ANL glass electrolyte; a schematic of a 150-Ah cell is given in Fig. I-1. Calculations modeling performance of a cell with this design indicated that the major controlling parameter for performance is the electrolyte tube diameter. With a small-diameter tube (1.5-mm OD), the cell will contain about 4000 tubes and will yield a specific power of about 2000 W/kg and a specific energy of about 200 Wh/kg. With a larger-diameter tube (6-mm OD), the cell will contain about 100 tubes and will yield a somewhat higher specific energy (about 300 Wh/kg) at a moderate specific power (about 300 W/kg). These modeling results illustrate the system's design versatility and its excellent combination of energy and power.

B. Molten-Electrolyte Cell Research

Molten-electrolyte cells have, in addition to a molten-salt electrolyte, negative electrodes of lithium alloy and positive electrodes of transition-metal sulfide. The Li-Al/FeS cell with an LiCl-KCl electrolyte is capable of achieving a specific energy of 100 Wh/kg at the 4-h discharge rate and a specific power of 100 W/kg at 80% depth of discharge (DOD). The objective of this research project is to bring about innovations in the current technology

that will yield a specific energy of 200 Wh/kg at a 4-h discharge rate, a specific power of 200 W/kg at 80% DOD, and a cycle life of 1000 cycles. As reported later, an Li-Al/FeS₂ cell with LiCl-LiBr-KBr electrolyte promises to achieve these performance and cycle-life goals.³

1. Characterization of Electrode Materials

During this period, we investigated the performance of iron and nickel sulfides, and their mixtures, in half-cell experiments to determine their potential for application as positive electrode materials. In these studies, we tested molten-salt electrolytes having compositions (mol %) of 22 LiF-31 LiCl-47 LiBr (Electrolyte A) and 33 LiCl-30 LiBr-37 KBr (Electrolyte B). The melting points for these electrolytes are 430°C and 310°C, respectively. An intermittent galvanostatic cycling technique was used to measure the ohmic resistance, electrochemical impedance of the electrode bed, and active-material utilization. The peak power and power-sustaining capability of the electrodes were determined by a technique that measures area-specific impedance (mΩ·cm²) as a function of duration of high-intensity current pulses.

The most favorable values for area-specific impedance were obtained with the iron sulfide and nickel sulfide mixture (FeSₓ-NiSₓ, where x ≤ 2) in a

1:1 mole ratio. Tests also showed that the addition of Li$_2$S to the electrolyte in a quantity that assured saturation at any cycling condition substantially improved both active-material utilization and power capability.

The combination of Li$_2$S-saturated electrolyte (A or B) and mixed-sulfide active material showed uniformly low area-specific impedance over the entire range of the charge and discharge. This favorable area-specific resistance was not found for the FeS$_x$ and NiS$_x$ electrodes.

Figure I-2 plots the area-specific impedances of the (FeNi)S$_x$ electrode in Electrolytes A and B measured during sustained 50-s current pulses of 1 A/cm$^2$ at 10, 30, and 71% depth of discharge. These DOD values were chosen because they are at approximately the middle of each of the three voltage plateaus in the discharge curve (voltage vs. discharge capacity). As can be deduced from Fig. I-2, 10% DOD yields the highest and 30% DOD the lowest power capability in both electrolytes. In spite of the higher resistances, Electrolyte B is more favorable than Electrolyte A because of its lower melting temperature and wider operating-temperature range. The impedance values indicate acceptable power even in the 370-380°C range with this electrolyte.

The following three conclusions were reached from the half-cell experiments. First, during the entire charge and discharge, the ohmic resistance of the electrode bed is relatively low compared with its electrochemical impedance. Consequently, it is the electrochemical processes that control
electrode performance. Second, the active-material utilization for the mixed-
sulfide electrode in Li$_2$S-saturated electrolyte is very good, >95% of theoreti-
cal capacity, in contrast to the typically <70% utilizations observed for FeS$_x$
or NiS$_x$ electrodes when cycled under the same conditions. Third, elec-
trochemical impedance and active-material utilization are more favorable at higher
temperatures; e.g., the area-specific impedances determined after a 15-s poten-
tial relaxation for the mixed-sulfide electrode decreased from 2.0 to 0.5 $\Omega$-cm$^2$
when the temperature was increased from 370 to 470$^{\circ}$C in Electrolyte B.

Future work will focus on the power performance as a function of
pulse time, electrode and electrolyte composition, and operating temperature
for the metal sulfide electrode.

2. Development of High-Performance Cell

Careful attention to cell design and operation is needed if we are
to meet the performance goals of 200 Wh/kg and 200 W/kg and the cell lifetime
of 1000 cycles.

Our calculations indicated that improved energy density (Wh/cm$^3$)
would be achieved if the FeS$_2$ electrode were operated only on the upper of the
two plateaus in the voltage vs. discharge capacity curves. An added advantage
of this mode of operation is a 0.3-V increase in cell voltage (to about 1.65 V
vs. Li-Al) at 80% DOD. Upper-plateau operation takes advantage of the high
density of the discharge product of the FeS$_2$ upper-plateau reaction, Li$_2$FeS$_4$.

We also explored the use of lithium-alloy negative electrodes other
than Li-Al to increase cell energy density. Analysis of several alloys
(Li-Al, Li-Si, and Li-Al-Si) indicated that their capacity densities (within
acceptable voltage limits) are quite similar: 1.25 $\pm$ 0.05 Ah/cm$^3$. Hence, we
sought to increase the average lithium activity of the alloy without
sacrificing cell voltage at 80% DOD. Our analysis indicated that this might
be achieved by use of Li-Al alloy with 53 at. % Li, rather than the usual
48 at. % Li.

A survey of molten-salt compositions uncovered an electrolyte,
25 mol % LiCl-37 mol % LiBr-38 mol % KBr (mp, 310$^{\circ}$C), having higher lithium
content and lower melting point than the 58 mol % LiCl-42 mol % KCl (mp,
352$^{\circ}$C) eutectic electrolyte, which was used in earlier cells. This new
electrolyte permits use of a lower cell operating temperature. The lower
operating temperature is expected to slow the loss of sulfur from the FeS$_2$
electrode, which had caused an unacceptable rate of capacity decline with
cycling in earlier cells.$^4$

3. Testing of High-Performance Cell

Two intermediate-size "bicells" (i.e., central positive electrode
and two facing negative electrodes), one with twice the capacity of the other,
were employed in evaluating the performance of the Li-Al/LiCl-LiBr-KBr/FeS$_2$

$^4$P. A. Nelson et al., High-Performance Batteries for Stationary Energy
Storage and Electric Vehicle Propulsion, Progress Report for the Period
system. The electrodes (8.7 cm high by 6.3 cm wide) were contained behind perforated-sheet current collectors—molybdenum for the central FeS₂ electrode, and Type 1008 steel for the two Li-Al electrodes. The positive electrode contained FeS₂ with 15 mol % CoS₂ additive and had a theoretical capacity of either 24 or 48 Ah on the upper voltage plateau. The slurry-formed negative electrodes contained 53 at. % Li-Al alloy and had theoretical capacities of either 35 or 70 Ah. Cycle-life testing at an 8-h charge rate (25 or 50 mA/cm²) and 4-h discharge rate (50 or 100 mA/cm²) was controlled between voltage cutoffs of 2.10 and 1.25 V, respectively. The cell operating temperature was 388-427°C. An Ni/Ni₃S₄ reference electrode was used to determine working-electrode potentials during the deep-discharge cycling.

Testing of the upper-plateau FeS₂ cells at 397°C showed that they had 50% higher energy and power density than did Li-Al/LiCl-KCl/FeS₂ cells operated on both voltage plateaus at 427°C. The voltage vs. capacity curves of these two types of Li-Al/FeS₂ cell (both with 24-Ah capacities) are plotted in Fig. I-3. Energy density at a discharge current density of 50 mA/cm² was enhanced as a result of a 50% higher utilization of the capacity and a 10% higher average discharge voltage. The energy density at higher discharge current densities (100 and 150 mA/cm²) was also improved— with the utilization of theoretical capacity ranging from 65 to 85% (see Fig. I-4). The capacity utilization vs. current density curve for the 48-Ah cell matched that of the 24-Ah cell.

![Figure I-3: Voltage vs. Capacity Curves at a Discharge Current Density of 50 mA/cm² for Li-Al/FeS₂ Cells (24-Ah capacity)](image)

The improved power and energy density of the upper-plateau FeS₂ cell are believed to be caused by two factors: improved electronic conductivity of the electrode and increased liquidus range of the LiCl-LiBr-KBr electrolyte.

The active-material utilization for the high-performance cell has been constant at about 89% of the theoretical capacity (at 50-mA/cm² current density) through more than 300 cycles (4000 h), and the cell voltage vs. capacity curve has remained unchanged (Fig. I-3) during this time. Electrode potentials (vs. the Ni/Ni₃S₄ reference electrode) indicate that both electrodes, Li-Al and FeS₂, mutually attain full charge. The discharge capacity
is limited by the upper-plateau capacity of the positive electrode. With LiCl-KCl electrolyte, the Li-Al/FeS$_2$ cell would have lost 30% of its capacity in the first 200 cycles.

Based on the improved performance, a 250-Ah multiplate cell is expected to achieve 175 Wh/kg at a 4-h rate and 200 W/kg at 80% DOD. The specific energy value does not quite meet our performance goal. However, an advanced design (bipolar) has a projected performance of 200 Wh/kg at a 1-h rate and 600 W/kg at 80% DOD, and a bipolar cell specifically designed for continuous high-power output is projected to provide greater than 2000 W/kg.

Our results warrant continued research in a number of areas. For example, an investigation of the FeS$_2$ electrochemistry in LiCl-LiBr-KBr electrolyte should yield understanding of the reasons for the capacity stability. Furthermore, limits to operating temperature and current density for this new cell design need to be established.

C. Engineering Development of Lithium-Alloy/Iron Monosulfide Batteries

A program is under way at ANL and Gould Research Center to develop the lithium-alloy/FeS battery for electric van propulsion. The program is jointly funded by the Electric Power Research Institute (EPRI), the Department of Energy (DOE), and the Tennessee Valley Authority (TVA). The emphasis during 1985 was on the design, fabrication, and testing of 12-V modules fabricated by Gould Research Center. The modules have nine Li-alloy/FeS cells that weigh approximately 2.8 kg each and have a theoretical capacity of about 300 Ah. The modules were tested in the National Battery Test Laboratory (NBTL) located in CMT (see Section II).
The specific energy of these modules is plotted in Fig. I-5. Improvement in the performance of module 2 was achieved by changing the negative-to-positive capacity ratio, which improved the power attained at high DOD, and by decreasing the weight of module hardware. At a constant current of 60 A, module 2 delivered 2.78 kWh, which is equivalent to a specific energy of 110 Wh/kg based on the weight of the cells. Under a power regime dictated by a simulated driving profile (SAE J227a/D), this module achieved 2.62 kWh, which is equivalent to a specific energy of 104 Wh/kg (cell-weight basis).

![Graph](image.png)

**Fig. I-5. Specific Energy of Lithium-Alloy/Iron Monosulfide Modules**

The results from the module-2 tests have been applied to projecting the performance and specifications of a full-scale Li-alloy/FeS battery designed to power a Chrysler T-van. The 1986 effort will emphasize the design and testing of a 36-V battery at NBTL and in an electric van at the TVA Electric Vehicle Test Facility, as well as the start of development of full-scale battery components. We project that the 36-V module being designed for the TVA test will have an energy output of about 100 Wh/kg (module-weight basis) when tested under the SAE J227a/D driving profile.

D. Materials for Polysulfide Containment

The objective of this task is the development of materials for containment and current collection in cells (e.g., Na/S and Li/FeS₂) that have high sulfur activity and high electrical potential at the positive electrode. The principal approach has been to gain a basic understanding of corrosion fundamentals and the effects of alloying additions on corrosion mechanisms so that a rational effort on alloy development can be undertaken. Efforts are also directed toward the development of a process for the electrochemical deposition of microcrystalline chromium coatings onto metal substrates for corrosion protection.
1. Corrosion-Resistant Alloys

Previous results\(^5\) revealed several alloys with good corrosion resistance (i.e., low corrosion rates) in sulfur and \(\text{Na}_2\text{S}_3\) at 350°C: high-chromium iron and nickel-based alloys and aluminum-magnesium alloys.

During the past year, we examined the corrosion behavior of commercial high-chromium-content alloys, E-Brite (Fe-26Cr-1Mo) alloys modified by the addition of various secondary alloying elements, and binary aluminum-magnesium alloys. Tests of these alloys were done in sulfur and \(\text{Na}_2\text{S}_3\) at 350°C for up to 2500 h.

Examination of the high-chromium alloys after testing showed that the morphology and composition of the corrosion scale were similar for all the alloys; significant differences were found, however, in the corrosion rates, as indicated in Fig. I-6. The conclusion drawn from the data is that in sulfur the corrosion penetration increases with an increasing chromium concentration in the alloy, whereas in \(\text{Na}_2\text{S}_3\) an increasing chromium concentration causes a decrease in the corrosion penetration. The beneficial effects of adding molybdenum and tungsten can also be deduced from Fig. I-6.

To test the effects of other secondary alloying elements, we prepared a series of alloys in which 3 wt % additions of Al, Mo, Ti, Y, or Zr were made to E-Brite-26-1 (Fe-26Cr-1Mo). In sulfur all these alloys showed corrosion rates lower than those of pure chromium; the best corrosion resistance was found with the aluminum-containing E-Brite alloy, which had a corrosion penetration after 2500 h about one order of magnitude lower than that of pure chromium. In Na$_2$S$_3$, all of the alloys had corrosion rates higher than that of pure chromium; the worst corrosion resistance was exhibited by the aluminum-containing E-Brite alloy, which had a corrosion penetration over one order of magnitude higher than that of the pure chromium. For reducing corrosion, the best overall additives were molybdenum and yttrium. Work on preparing and testing additional high-chromium alloys is in progress.

Last year we reported that a protective MgS film was formed on Al-9.6 wt % Mg tested in Na$_2$S$_3$: this film effectively prevented further corrosion after about the first 100 h of exposure. We have now determined corrosion rates for Al-Mg alloys with 1 to 9.6 wt % magnesium. In sulfur at 350°C, all of these alloys showed very low corrosion rates. Initially, all of the alloys tested in Na$_2$S$_3$ had corrosion rates higher than those for pure aluminum. As testing continued, however, the corrosion rates all became lower than the rate for pure aluminum, although the alloy containing 9.6 wt % Mg was the only one in which the corrosion rate was effectively reduced to zero after about 100 h.

Preliminary results indicate that the protective MgS film is not electrically passivating, and the electrical properties of the corrosion scale are being further investigated by using in situ electrochemical polarization techniques and in situ conductivity measurements on doped, synthetic MgS. Work is also planned on developing new alloys that make full use of the protective and conductive properties of the MgS films.

2. Microcrystalline Chromium Coatings

Reports in the published literature suggest that the amorphous or glassy phase of a metal offers greater resistance to corrosion than does the polycrystalline phase of the same metal. The metallic glasses lack long-range order but do possess short-range order and, hence, are considered to be "microcrystalline." The work reported here was designed to investigate the technical feasibility of depositing thin-layer coatings of amorphous/microcrystalline chromium coatings on metallic substrates for corrosion protection in the molten Na$_2$S$_x$/S electrolyte of an Na/S battery.

We demonstrated that amorphous/microcrystalline chromium can be electrodeposited from aqueous chromic acid-based electrolytes using high current densities (up to 5 A/m$^2$). However, our results from preliminary corrosion tests suggested that amorphous chromium electrodeposited from aqueous solution does not provide any distinct improvement over the corrosion protection provided by polycrystalline chromium or E-Brite alloy. The observed poor corrosion resistance of the electrodeposited in 0.1 M H$_2$SO$_4$ was

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attributed to hydrogen incorporation in the film and the presence of stressed regions.

We also investigated the technical feasibility of electrodepositing amorphous/microcrystalline chromium on steel substrate from a molten-salt solution containing 58 mol % LiCl-42 mol % KCl eutectic plus CrCl\textsubscript{2}. The electrodeposition from the molten salt was achieved by using a nucleating pulse followed by potentiostatic growth. The CrCl\textsubscript{2} concentration was kept below 2.2 mol/dm\textsuperscript{3} in order to produce strongly adhering, pore-free, fine-grained, and dense coatings. The cross section of a 40-mm-thick chromium layer electrodeposited on Type 304 stainless steel shown in Fig. I-7 indicates strong adherence of the chromium. Preliminary testing has shown that the corrosion protection provided by these coatings is similar to that of state-of-the-art coatings used on current collectors for Na/S cells.

![Fig. I-7. X-Ray Imaging of Chromium across the Substrate (304 Stainless Steel)-Electrodeposit Cross Section](image)

The electrodeposition of microcrystalline chromium from LiCl-KCl-CrCl\textsubscript{2} melts at <450°C is being pursued further. Current efforts are also directed toward achieving an understanding of the electrochemical aspects of electrodepositing amorphous/microcrystalline chromium from molten salts.

E. Aqueous Battery R&D

Argonne is a key laboratory for DOE's activities associated with aqueous battery systems for electric and hybrid vehicles. In this capacity, CMT provides technical management of industrial contracts for development of aqueous battery technology for electric vehicles, as well as in-house technical support for DOE. In a project funded by EPRI, CMT is performing a statistical analysis of test data for lead-acid batteries.
1. Battery R&D by Contractors

For the past several years, CMT has provided technical management of two major industrial contracts: one with Johnson Controls, Inc. (formerly named Globe Battery) for the development of advanced lead-acid batteries, and the other with Eagle-Picher Industries, Inc. for development of nickel/iron batteries. The technical support includes assistance in program planning, systems analysis, and preparation of work statements for new work.

The work at Johnson Controls is focused on research and development of an advanced lead-acid battery based on the forced flow of electrolyte through the porous lead and lead dioxide electrodes, which was expected to yield better utilization of the active materials. A schematic drawing that illustrates the flow-through concept is shown in Fig. I-8. A full-size proof-of-concept cell with flow-through electrolyte was fabricated in 1985 and delivered to NBTL for testing and evaluation. This first-of-a-kind experimental cell demonstrated the viability of the flow-through concept by achieving very high levels of active-material utilization (85% greater than that obtained in commercially available lead-acid batteries); this dramatic increase in utilization should yield a 40% increase in the specific energy of lead-acid batteries.

![Schematic of Electrolyte Flow-Through Concept for Lead-Acid Battery](image)

The Eagle-Picher effort on advanced nickel/iron batteries continues to be focused on the development of nickel electrodes up to twice as thick as in prior technology and having the desired porosity and strength required for
good performance and long life. Cell designs based upon thick-electrode technology are projected to significantly reduce battery costs and to improve battery specific energy. The latest nickel/iron technology developed during FY 1985 demonstrated a specific energy of 53 Wh/kg at the 3-h discharge rate (13% greater than in prior technology). Meanwhile, laboratory and in-vehicle field tests continued to confirm the ruggedness and long life of nickel/iron batteries developed under this effort. At the NBTL, 1050 charge/discharge cycles in simulated electric-van driving, equivalent to over 55,000 miles of vehicle operation, were obtained for an Eagle-Picher nickel/iron multicell module. At the TVA Electric Vehicle Test Facility, an Eagle-Picher nickel/iron battery has powered an electric vehicle for over 20,000 actual miles of operation to date. The Eagle-Picher nickel/iron batteries also continue to perform well after four years in commercial fleet operation at the Northrop Corp. and at the GTE Service Co. The problem of electrolyte leakage, which had been encountered early in the field evaluations, was eliminated by a change in battery case material. Both the Eagle-Picher and Johnson Controls efforts are planned to be continued during 1986.

2. Electrochemical and Thermal Modeling

In 1985, we performed studies in which the electrochemical and thermal performance of aqueous batteries was modeled.

In the electrochemical performance model, the energy and power of a battery are related to battery design parameters by a set of differential equations. These equations are derived based on fundamental principles of electrochemistry and chemical engineering. The model takes into account the effects of reversible potential, ohmic resistances, and reaction and diffusion polarizations on the current distribution and cell voltage. The effects of the porous electrode structure and current-collector design are also included in model calculations, thus allowing direct comparison of calculated results with experimental data from cycled cells.

The Eagle-Picher nickel/iron battery was chosen for electrochemical model development and verification. Based on the physical and chemical properties of the battery, the model predictions of the specific energy and peak power for five different cell designs agreed well with NBTL test results. The model was used to evaluate the energy and power capability of the nickel/iron battery for hybrid-vehicle propulsion. The effects of nickel electrode thickness, electrode plaque porosity, and active-material loading density on battery performance were also studied.

Figure I-9 shows the model prediction of trade-offs of specific energy and peak power as a function of nickel electrode thickness for the Eagle-Picher nickel/iron battery. This information allows one to select an optimal electrode thickness for specific propulsion requirements. Other information provided by the model includes the makeup of total cell voltage loss in terms of the losses due to each component (positive grid, negative grid, separator, etc.). The results indicate that, under peak power discharge, a large percentage of voltage loss (39%) is due to the resistance of the current collector in the nickel electrode. Therefore, an improvement in current collector design is necessary to achieve the high-power capability required for hybrid-vehicle application. In the future, the electrochemical model will be used to analyze the performance of sodium/sulfur and tubular
lead-acid battery designs. The model can also be extended for studying the performance degradation mechanism of a battery under various operating conditions.

In the thermal modeling effort, the generic thermal model previously derived at ANL\(^8\) was used to evaluate the temperature behavior of the EV-2300 lead-acid battery (the flooded-electrolyte battery developed by Johnson Controls). It was found that the temperature rise per unit energy delivered for a starved-electrolyte battery (electrolyte completely absorbed in the pores of the separator and electrodes) is about 50% greater than that for an equivalent flooded-electrolyte battery such as EV-2300. This is due to the smaller heat capacity, greater heat generation rate, and poorer heat conduction of the starved-electrolyte battery.

3. Statistical Analysis of Test Data

In a battery testing and development program for EPRI, six EV-2300 lead-acid modules (fabricated by Johnson Controls) were tested at the NBTL to determine the effects of electric-vehicle operating parameters on the performance and cycle life of the battery. These parameters include the DOD (0-80%), peak power demand of the driving profile (35-57 W/kg), the battery resting period (8-h open-circuit period after charge or discharge), and the method of recharge (constant current/constant voltage or three-step constant current). The ampere-hour capacity and power capability (peak power for 30-s

pulse) obtained from these tests were analyzed by the multiple regression method to determine the statistical significance of the test results and to quantify the effect of each individual parameter.

The results of the analysis on the EV-2300 module data showed that the module power capability is correlated with only four factors: the DOD, the number of charge/discharge cycles accumulated, the peak power demand of the driving profile, and the resting period. The regression coefficients of all four factors have confidence levels higher than 99%. The effect of charge method on module power capability was found to have no statistical significance. The squared correlation coefficient of the regression, 0.95, also indicated that 95% of the variation in power capability can be explained by these four factors. Among these factors, DOD and number of accumulated charge/discharge cycles account for 88% of the changes in module power, whereas the peak power demand for the driving profile accounts for 5.5%, and the resting period a mere 1.5%. The regression coefficient also shows that the driving profile with the 57-W/kg peak power degrades the module power capability about 0.1 W/kg more rapidly with each charge/discharge cycle than does the driving profile with the 35-W/kg peak power. In Fig. I-10, the observed power capability for the six modules determined for various operating parameters was plotted against the module power predicted from the regression equation. The straight line indicates a very good agreement over the entire test range.

A similar technique was also used to analyze the ampere-hour capacity data for the EV-2300 lead-acid modules. The results indicate that

![Figure I-10. Observed and Predicted Power Capability for EV-2300 Lead-Acid Battery. (The numbers indicate the number of overlapping points; the asterisks indicate a single point.)](image-url)
module capacity is correlated with only the number of charge/discharge cycles and the peak power demand of the driving profile. A minor effect of charge method on capacity was detected (65% confidence level). The resting period was found to have no statistical significance. From the capacity data of 36 individual cells, we concluded that the capacity is strongly related to the cell location in the module. Those cells located near the positive terminal of the module consistently showed lower capacity than other cells. Further investigation will be made by post-test analysis of the EV-2300 modules.

F. Hybrid-Vehicle Battery Studies

This CMT project is part of the DOE Hybrid Vehicle Propulsion Technology Program. The hybrid vehicle will probably be powered by both a heat engine and a battery. The objectives for this project are to select the most promising battery types and designs for application in hybrid vehicles and to provide recommendations to DOE on the future R&D needed to fully develop these batteries. It is anticipated that R&D would be carried out in future years by selected battery contractors.

The first task in this project was to define a preliminary set of battery requirements for hybrid vehicles. This was accomplished by collecting information available from previous studies and also by contacting potential hybrid-vehicle developers worldwide and asking for their recommendations. One of the conclusions from this study was that, as compared with the electric-vehicle battery, the hybrid-vehicle battery must have higher power capability and will, on the average, be discharged at higher rates. The requirements for the hybrid-vehicle battery obtained from our study are given in Table I-2.

Based upon these preliminary battery requirements, we next assessed many different technologies proposed for hybrid-vehicle application. Key information for the study was obtained from a survey of 25 battery developers, who provided information on battery design concepts and approaches that would satisfy the hybrid-vehicle requirements.

<table>
<thead>
<tr>
<th>Table I-2. Preliminary Battery Requirements for Hybrid Vehicles</th>
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<tr>
<td>Battery Size</td>
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<tr>
<td>Specific Power&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Power Density&lt;sup&gt;a&lt;/sup&gt;</td>
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<tr>
<td>Specific Energy&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Energy Density&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Amortized Battery Cost&lt;sup&gt;c&lt;/sup&gt;</td>
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</table>

<sup>a</sup>Power at 20% state-of-charge.

<sup>b</sup>Energy deliverable under the Federal Urban Driving Schedule.

<sup>c</sup>Cost for total delivered throughput energy during lifetime.
The proposed battery design concepts were then evaluated by CMT. The electrochemical battery model (see Sec. I.E.2) was used to make a quantitative technical evaluation of the most promising design approaches. With this model, one can determine the power losses associated with each component in the battery and thus evaluate the effect of battery design changes on battery power capability and associated trade-offs in battery specific energy, cycle life, and cost. This analysis has shown that several battery types are potential candidates for meeting the hybrid-vehicle application; these include bipolar designs (for lead-acid and Li/FeS batteries), alkaline batteries (Ni/Fe, Ni/Cd), and Na/S batteries (small-cell or glass-electrolyte approaches). Zinc/halogen (Zn/Br, Zn/Cl) and metal/air (Al/air, Fe/air, Zn/air) batteries do not appear to be good candidates for two reasons: they have limited power capability and a high cost when designed for high power, and they do not scale down well to the 10-20 kWh size required for hybrid vehicles. We are preparing a report that will present conclusions resulting from the study and identify battery development needs for hybrid propulsion.

G. Spectroscopic Studies of Zincate Solutions

The purpose of this research project was to investigate the coordination chemistry of Zn\(^{2+}\) ions in concentrated aqueous potassium hydroxide—the electrolyte of Ni/Zn cells. Laser Raman and \(^{67}\)Zn nuclear magnetic resonance (NMR) spectroscopic techniques were used to study solutions having a wide range of Zn\(^{2+}\) and OH\(^-\) concentrations.

The Raman studies gave evidence that there is only one dominant Zn\(^{2+}\) complex in aqueous Zn\(^{2+}\)/KOH media. This finding applies equally to solutions having a large excess of hydroxyl or just enough hydroxyl to hold the dissolved Zn\(^{2+}\) in solution. Raman spectra typifying the results obtained under each of these conditions are shown in Fig. I-11. The upper and lower curves in Figs. I-11a and -11b show the effect of rotation of the plane of polarization for the exciting line. The polarized band at 465 cm\(^{-1}\) and the depolarized one at ~415 cm\(^{-1}\) only appear in Zn\(^{2+}\)-containing solutions. The polarized band at ~265 cm\(^{-1}\) is not due to the presence of Zn\(^{2+}\) since it appears in the spectrum of aqueous KOH and its intensity relative to the 465 cm\(^{-1}\) band is most sensitive to the amount of OH\(^-\) in solution, not Zn\(^{2+}\), as the insets in the upper right-hand corners of Figs. I-11a and -11b show. Furthermore, the large polarization of the 465 cm\(^{-1}\) band indicates that the Zn\(^{2+}\) species have a highly symmetrical structure. When these same experiments were conducted using D\(_2\)O instead of H\(_2\)O, the 465 cm\(^{-1}\) band shifted to lower frequency by ~13 cm\(^{-1}\). This is essentially the predicted shift for the totally symmetric stretching mode of a uniformly complexed Zn(OH)\(_2\)\(^{2-}\) species when the OH\(^-\) ligands (group mass = 17 amu) are substituted by OD\(^-\) ligands (group mass = 18 amu); thus, the presence in solution of Zn\(^{2+}\)/hydroxyl complexes (as opposed to ZnO\(_3\)\(^{2-}\) ions) is established.

The \(^{67}\)Zn NMR investigations were performed on zincate solutions of varying OH\(^-\)/Zn\(^{2+}\) ratio and a solution of 1.5 M Zn\(^{2+}\) (90% enriched in \(^{67}\)Zn) in 1 M HClO\(_4\) as a reference. Typical results are shown in Fig. I-12. The resonance for the octahedral Zn(H\(_2\)O)\(_5\))\(^{2+}\) complex in 1.5 M Zn\(^{2+}\)/HClO\(_4\) was observed
Parallel (||) and Perpendicular (__) Polarized Raman Spectra of ZnO Solutions in Aqueous KOH. Insets in the upper right-hand corner show the difference spectra (||-__)_. Set (a) is for 2.8 M ZnO in 18 M KOH; set (b) is for 0.8 M ZnO in 11 M KOH.

at the expected NMR frequency based on published results; its half-width was ~30 Hz, which is also consistent with prior work. In the 0.6 M Zn\(^{2+}\)/KOH solution (90% enriched in \(^{67}\)Zn), a shift in resonance signal of +221 ppm relative to 1.5 M Zn\(^{2+}\)/HClO\(_4\) was observed, and the half-width of the resonance signal increased to ~280 Hz. The more concentrated Zn\(^{2+}\) solution in aqueous KOH (~20% enriched in \(^{67}\)Zn) showed an even broader resonance signal, but this signal narrowed and converged to the peak frequency in curve b of Fig. I-12 as progressive dilutions were made (by addition of water). In previous studies of tetrahedral \([ZnX_4]^{2+q}\) complexes (where \(X = Cl^-, Br^-, CN^-, and NH_3\), and q = the charge on the ligand) in aqueous media, similar chemical shifts (150 to 300 ppm) relative to Zn\(^{2+}\) in HClO\(_4\) were observed, and the conclusion was drawn that the chemical shift is due to a transformation from a coordination number of six (in HClO\(_4\)) to four (in \([ZnX_4]^{2+4q}\)). The large increase in half-width, however, is unprecedented for 0.5 + 2.0 M Zn\(^{2+}\) in any coordination environment and suggests that the Zn\(^{2+}\) cations may have a short interaction distance, perhaps due to hydrolytic aggregation into \([Zn(OH)_2]^{2-}\)\(_n\) units.

In conclusion, the Raman studies show that there is only one dominant Zn\(^{2+}\) complex in solution, and the NMR results give conclusive evidence that this complex involves tetrahedral coordination of the Zn\(^{2+}\) cation.

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Fig. I-12. $^{67}$Zn NMR Spectra of Zn$^{2+}$ Solutions.
Curve a is for 1.5 M Zn$^{2+}$ in ~1 M HClO$_4$, curve b is for 0.6 M ZnO in 16 M KOH, and curve c is for 2.8 M ZnO in 18 M KOH.
II. BATTERY TEST AND EVALUATION

Since the establishment of the National Battery Test Laboratory (NBTL) in 1977, it has played a leading role in battery testing and evaluation. Working with other national laboratories, industry, academic institutions, and professional societies, we have developed and applied test methodologies, procedures, and instruments that yield meaningful characterizations of batteries for electric vehicles, load leveling on electric utility systems, and other applications. The NBTL enjoys an international reputation and is recognized as a center where unprecedented accuracy and reproducibility are provided for testing batteries. It is the only test laboratory that has achieved a good correlation between projections of electric-vehicle range based on laboratory tests and the actual electric-vehicle range attained in road tests. All kinds of batteries, ranging from room-temperature to high-temperature systems and from static to flow systems, can be accommodated. The NBTL operates 365 days a year, 24 hours a day, and contains 91 independently operated test stations.

In addition to battery testing and evaluation, we perform physical and chemical analyses of cycled batteries after termination of testing. These post-test analyses are done for batteries tested at NBTL as well as at other facilities.

A. Performance and Lifetime Characterization

Since 1978, NBTL has tested almost 1700 cells—mostly in the form of three- to six-cell modules, but also full-size electric-vehicle batteries of up to 140 cells. The different battery systems were supplied by 17 developers, domestic and foreign. A summary of the types and quantities of cells tested is given in Table II-1.

During 1985, we initiated testing at the NBTL on the following electric-vehicle battery technologies: Na/S cells from Ford Aerospace & Communications Corp., Li-Al/FeS modules from Gould Inc., a Zn-Br battery (30 kWh) from Exxon, tubular lead-acid modules from Lucas Chloride EV Systems of England, Ni/Fe modules from Société des Accumulateurs Fixe et de Traction (SAFT) of France, and Ni/Cd modules from Energy Research Corp. (ERC).

Of the many tests performed at the NBTL, one of the most useful is the mapping of the specific energy available from a battery as a function of the specific power level at which it is discharged. The resulting relationship is defined as a "Ragone plot." Figure II-1 depicts Ragone plots obtained at NBTL for a number of electric-vehicle modules and cells. These plots illustrate which technologies provide the most energy at a given power demand and which are most sensitive to changes in power demand. Another important NBTL test is the peak power attained for a 30-s pulse as a function of depth of discharge (DOD). These curves are plotted for a number of electric-vehicle technologies in Fig. II-2. We are about to measure the peak power capability of the Ford Na/S cells, the Exxon Zn-Br battery, and the ERC Ni/Cd modules. As reported in Sec. II.C, the Ragone plot, in combination with the peak power plot, can be employed to predict discharge capabilities of batteries for almost any application.

Preliminary indications from testing of the 30-kWh Zn-Br electric-vehicle battery of Exxon are that its specific energy is near that of state-of-the-art...
# Table II-1. Summary of Cells Tested in NBTL (as of December 1985)

<table>
<thead>
<tr>
<th>Battery Type</th>
<th>Number of cells</th>
<th>Capacity, Ah</th>
<th>Application</th>
<th>Number of Developers</th>
</tr>
</thead>
<tbody>
<tr>
<td>SOA Lead-Acid</td>
<td>24</td>
<td>150-184</td>
<td>EV</td>
<td>2</td>
</tr>
<tr>
<td>ISOA Lead-Acid</td>
<td>543</td>
<td>105-260</td>
<td>EV &amp; HV</td>
<td>3</td>
</tr>
<tr>
<td>Advanced Lead-Acid</td>
<td>69</td>
<td>165-285</td>
<td>EV</td>
<td>3</td>
</tr>
<tr>
<td>Advanced Lead-Acid</td>
<td>18</td>
<td>3100</td>
<td>LL</td>
<td>1</td>
</tr>
<tr>
<td>Ni/Cd</td>
<td>20</td>
<td>200</td>
<td>EV</td>
<td>1</td>
</tr>
<tr>
<td>Ni/Fe</td>
<td>625</td>
<td>75-330</td>
<td>EV &amp; HV</td>
<td>4</td>
</tr>
<tr>
<td>Ni/Zn</td>
<td>202</td>
<td>128-400</td>
<td>EV</td>
<td>7</td>
</tr>
<tr>
<td>Na/S</td>
<td>9</td>
<td>55-150</td>
<td>LL &amp; EV</td>
<td>2</td>
</tr>
<tr>
<td>Li-Al/FeS</td>
<td>28</td>
<td>140-390</td>
<td>LL &amp; EV</td>
<td>2</td>
</tr>
<tr>
<td>Zn-Br</td>
<td>132</td>
<td>80-190</td>
<td>EV</td>
<td>1</td>
</tr>
<tr>
<td>Zn-Cl</td>
<td>24</td>
<td>1050</td>
<td>LL</td>
<td>1</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1694</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aSOA = state of the art; ISOA = improved state of the art.

*bMost tests involved three- to six-cell modules; however, up to 140-cell batteries were also tested.

*cLL = load-leveling (stationary) application; EV = electric vehicle; HV = hybrid vehicle.

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**Fig. II-1.**

Specific Energy as Function of Power Level Applied on Discharge for Electric-Vehicle Batteries
Ni/Fe technology (45 Wh/kg at 3-h discharge rate); however, more data are required to determine the relationship of specific energy versus specific power.

Since 1979, CMT has been involved in a DOE program to develop lead-acid batteries for load-leveling applications. The objective is to increase battery life from 2000 to 4000 cycles and yet maintain low initial battery cost. In 1985, NBTL continued accelerated life-cycle tests of three lead-acid modules fabricated by Exide Management and Technology Co. for load-leveling application. These three- and six-cell modules have rated capacities of 3100 Ah and have been cycled to 80% DOD at temperatures up to 60°C. One of these modules has been on life-cycle test at 50°C since April 1982 and has accumulated over 1972 actual cycles (equivalent to over 4907 cycles at 25°C, which exceeds the program goal of 4000 cycles). At present, this module has an estimated capacity of 3390 Ah (109% of rated) at the 5-h discharge rate. The other two modules are under test at 60°C and have accumulated over 1050 and 650 cycles (equivalent to over 3500 and 1500 cycles, respectively, at 25°C); their estimated capacities are 111% of rated. Testing will continue into 1986.

Four Na/S load-leveling cells fabricated by Ford Aerospace have been under test at the NBTL. Two of the cells have achieved over 900 cycles, and the other two have achieved over 600 cycles, as testing continues.

As reported last year, testing is being done on the 50-kWh Zn-Cl load-leveling battery fabricated by Energy Development Associates (EDA). The battery operates under control of the NBTL computer and can be cycled round-the-clock, unattended. At one time, the battery was operated for 96 uninterrupted hours. Figure II-3 is a plot relating the energy available as a function of the discharge time and power level applied on discharge for the battery. This plot indicates that the operation of this battery is optimal near the 6-h discharge rate, which is acceptable for the load-leveling application. The watt-hour efficiency of the battery was generally between 60 and
65% (energy for auxiliary battery equipment not included). A few minor problems were encountered in the testing of this battery; it was necessary to replace the gas pump four times, repair leaks, purify the electrolyte, and adjust the hydrate-forming system; EDA has been most helpful in responding to these problems.

In 1986, we will begin testing Na/S cells and modules fabricated by Chloride Silent Power of England. Also expected for testing are Zn-Br batteries from ERC and, perhaps, Johnson Controls Inc.

**B. Charge/Discharge Studies**

During the past year, we completed a study that correlated the available capacity, overcharge level, and initial DOD level of an improved-state-of-the-art lead-acid module (12 V, 250 Ah) fabricated by Johnson Controls Inc. Figure II-4 shows the state of charge achieved as a function of the "recharge factor" (Ah charge capacity divided by Ah discharge capacity) for the ISOA lead-acid module operated at DOD levels of 25, 50, 75, and 100%. As the DOD level is increased, a greater percent overcharge is needed to attain maximum capacity. About 8% overcharge is needed for 75 and 100% DOD operation, but only ~4% is needed for 25 and 50% DOD operation. In practice, applying an 8% overcharge (4.8 Ah) for 25% DOD operation, instead of the minimal 4% (2.4 Ah), results in an extra 2.4 Ah of electrolysis, which consumes about 0.8 mL of water in each battery cell during each charge. For each charge cycle of a 200-V lead-acid battery, 80 mL of electrolyte water would be needlessly consumed and an extra ~100 L (~3.5 ft³) of hydrogen gas would be generated. Thus, water consumption and gassing can be reduced by proper charge control.

We also completed studies on the internal impedance of three Ni/Fe modules (6V, 270 Ah) fabricated by Eagle-Picher Industries, Inc. Test data
showed that module internal resistance is virtually constant during discharge, regardless of the discharge rate or battery age (number of cycles applied). A constant resistance allows the determination of a voltage that is free of the internal IR drop during discharge from the equation

\[ V_B = V_A + I_AR_B \]

where \( V_B \) is the IR-free voltage, \( V_A \) is the battery terminal voltage, \( I_A \) is the load current, and \( R_B \) is the internal resistance. The values of \( V_A \) for one of the Ni/Fe modules measured at constant-current discharges of 90, 180, and 270 A are plotted in Fig. II-5 as a function of DOD. Also plotted in the figure are the computed curves for \( V_B \) ("IR-free") at the three discharge currents. The plots show that \( V_B \) is essentially independent of the discharge current; only after about 90% DOD (>200 Ah) is there an apparent increase in module internal resistance, which causes the IR-free voltage curves at the different discharge currents to separate slightly. These results indicate that the IR-free voltage may be employed as a DOD measure, and thus could serve as an accurate and reliable "fuel" gauge for electric vehicles equipped with Ni/Fe batteries.

We also conducted tests to measure temperature effects on the available discharge capacity and charge acceptance of an Ni/Fe module (6 V, 200 Ah) fabricated by Eagle-Picher. In these tests, the module was charged at a constant current of 50 A up to 50-250 Ah and discharged at this same current to 100% DOD. Plots of measured discharge capacity versus the applied recharge factor (RF) at temperatures of 0, 25, and 50°C are given in Fig. II-6. The discharge capacities in this figure have been normalized to the battery
discharge capacity determined from a 200-Ah charge at 25°C (RF = 1.39). The plots indicate that the performance of the Ni/Fe module is optimal near 25°C. This optimum is the result of increased self-discharge losses at elevated temperatures (50°C) and a decreased charge acceptance and available energy at reduced temperatures (0°C).

In 1986, we will conduct studies to measure the effect of temperature on Ni/Fe battery charge acceptance from partial DOD levels. Studies will also be conducted to evaluate lead-acid battery resistance and Ni/Fe battery IR-free voltage as DOD indicators.

C. Methodology Development

Battery testing involves discharging a battery under a specific load profile such as the SAE J227a/D—a standard used for testing electric-vehicle batteries under simulated road conditions. According to this profile, the electric vehicle is required to accelerate from rest to 72 km/h in 28 s, cruise at 72 km/h for 50 s, decelerate and brake to a stop in 19 s, and rest for 25 s; this profile is repeated until the battery has reached a specified DOD. The SAE J227a/D has a peak power demand of ~47 W/kg and an average power of ~15 W/kg for the ETV-I vehicle—an electric automobile developed by Chrysler with DOE support.

During the past year, we developed a methodology that combines the use of the Ragone plots and the peak power plots (e.g., Figs. II-1 and -2) to estimate battery discharge times for almost any load profile; from this information, vehicle ranges during a single discharge of the battery can be calculated. If the Ragone and peak power information is known, then the only specifications
required of the load profile are the average and peak power demand on the battery; the detailed structure of the load profile is not essential.

Take, as an example, the Ni/Zn battery of General Motors (Delco-Remy Division) discharged under the SAE J227a/D profile. Figure II-1 shows that the specific energy for an average power demand of 15 W/kg is 53 Wh/kg; hence, the ratio of this specific energy to the average power is 3.5 h. The extent to which the SAE J227a/D peak power limits the discharge time can be obtained by extrapolating the curve for this Ni/Zn battery in Fig. II-2 to 0 at 100% DOD. The point where the extrapolated curve intersects the load-profile peak power of 47 W/kg is at about 98% DOD. At this DOD, the battery would fail to meet the power demand and discharge would be terminated. Accordingly, the discharge time is estimated as 3.5 h x 0.98 = 3.43 h. Since the average vehicle velocity under the SAE J227a/D profile is 47 km/h, the estimated range for the ETV-I vehicle with the GM/Delco-Remy battery is 161 km; the range determined from actual tests of the battery under the driving profile, 147 km, is in reasonable agreement.

Benefits in the use of our new methodology include:

(1) One can estimate battery discharge times for a host of application requirements and need not apply specific load profiles to the battery. Thus testing costs can be reduced. Also, battery discharge times for specific applications can be estimated when the application of such discharges is inconvenient or impossible.
Test results obtained from a battery under a specific discharge profile can be checked. If the results of this test do not agree with the estimate obtained by the methodology, reasons for the variance should be immediately explored.

This methodology was presented in more detail at the first International Workshop on Battery Testing held in Heidelberg, Germany, September 30 through October 2, 1985. The manager of the NBTL served as chairman for this workshop.

D. Post-Test Analyses

The Division has extensive facilities for the examination of aqueous and advanced battery cells after testing. The information gained from the post-test examinations permits assessments of technical progress made by battery developers and provides important feedback to them for future decisions concerning design and material changes.

1. Aqueous Batteries

In FY 1985, we completed post-test examinations on twelve lead-acid and four Ni/Fe batteries upon completion of testing at the NBTL.

For lead-acid batteries, the primary cause of capacity decline with cycling was attributable to deterioration of the positive electrodes. After repeated cycling, the positive active material formed a coralloid microstructure with decreased surface area available for reaction. Moreover, corrosion of the positive electrode grid usually resulted in a loss of contact between the grid and the active materials.

In the Ni/Fe batteries, the migration of iron to the nickel electrode was found to be the primary mode of capacity decline. High iron concentrations were observed on the surfaces of the nickel electrode. X-ray diffraction analysis of this layer revealed that the iron was in the form of a nickel/iron oxide compound (ferroan trevorite). The formation of this compound apparently plays an important role in the capacity loss of the Ni/Fe battery.

Experimental results on the effect of iron contamination on nickel electrode performance are shown in Fig. II-7. In an iron-free environment (curve A), the nickel electrode shows good capacity and satisfactory charge efficiency. However, when cycled against an iron electrode (curves B and C), the capacity of the nickel electrode dropped by up to 25%. Furthermore, a significant amount of iron was found to be incorporated into the nickel active material as a nickel/iron oxide compound. Experimental results also indicated that the presence of LiOH in the electrolyte solution (compare curves B and C) can prevent some of the capacity loss.

Future post-test analyses will focus on two areas: (1) the development of new techniques to measure the distribution and composition of the electrode phases and (2) the identification of mechanisms by which iron is transported to the nickel electrode and forms an inactive nickel/iron oxide compound. The latter information should permit identification of a method for preventing the iron contamination of the nickel electrode.
2. Sodium/Sulfur Cells

This project supports DOE's major contracts for the development of Na/S cells (operation temperature >300°C) for application in electric vehicles and for load leveling in electric utilities. The CMT support entails post-test analyses of Na/S cells built by Ford Aerospace & Communications Corp. The objectives of these analyses include: (1) the identification of life-limiting degradation mechanisms of critical hardware components and (2) the correlation of the sulfur electrode morphology with the observed cell performance.

In 1985, we completed post-test examinations of six load-leveling cells, two electric-vehicle cells, and one cell evaluated for baseload satellite applications. A proprietary agreement with Ford Aerospace limits the disclosure of certain information, but some generalized insights gained from these and past examinations are discussed below.

a. Sulfur Electrode Morphology

The compositional gradients established in the electrode melt before termination of cell operation are retained in the electrode microstructure at ambient temperature. Analysis of these gradients is complicated

by the strong tendency of the polysulfide melt to supercool and form metastable crystal structures. Polarized-light microscopy and X-ray diffraction identified five reoccurring metastable phases in addition to the expected phases of Na$_2$S$_2$, Na$_2$S$_4$, Na$_2$S$_5$, and sulfur. (Sodium monosulfide can also form after an electrolyte failure.) Energy dispersive spectroscopy (SEM-EDS) is being used to determine the composition of the metastable phases. The sodium content is consistently underestimated for a number of reasons, including use of the software program ("ZAP") to derive the initial estimates. During the past year the calibration curve shown in Fig. II-8 was generated by analysis of specially prepared polysulfide standards. This curve enables us to calculate accurate compositional estimates from SEM-EDS-ZAP values for both binary metastable phases and nonstoichiometric compounds. For example, samples of the metastable M-phase taken from cell LL199 have corrected sodium contents within the range of 36 to 38 at. %.

Collectively, these analytical tools enabled us to map out the distribution of sodium throughout the entire electrode. One major finding for a load-leveling Na/S cell was that the positive electrode develops two reaction zones when charged or discharged through the compositional range where two immiscible liquids exist. A semi-continuous ring of sulfur is found near—but not in direct contact with—the $\beta"$-alumina electrolyte. A second semi-continuous ring is located near the cell container. The latter sulfur ring contacts some areas of the container wall.

The information obtained from our analysis provides a valuable starting point toward the development of a predictive model of sulfur
electrode behavior. Such a model will also have to address the influence of corrosion reactions and scale formation on cell performance. For the Na/S system, this factor is complicated by the formation of corrosion products that migrate throughout the electrode. Two such ternary compounds, NaCrS$_2$ and NaAlS$_2$, were identified. The transport mechanism for NaCrS$_2$ migration was studied with particular interest because the highest concentrations are often found as particulate deposits on the electrolyte surface.\textsuperscript{2}

The following conclusions were reached. The NaCrS$_2$ scale that forms on the chromium-plated container of the Na/S cell spalls once the scale reaches a limiting thickness of 10 to 15 $\mu$m. The scale fragments dissolve into the electrode melt during charging cycles, and the chromium diffuses toward the electrolyte under the influence of potential and/or concentration gradients. Ultimately, the electrode melt adjacent to the electrolyte becomes saturated with chromium, and NaCrS$_2$ precipitates onto the electrolyte and nearby graphite fibers. Repeated cycles of NaCrS$_2$ scale formation, spallation, dissolution, and precipitation can lead to extensive deposits adjacent on the electrolyte surface.

The thickness of these deposits is dependent on operating temperature and cycle life. Lower temperatures enhance their growth, apparently because of a decreased solubility of chromium in the electrode melt. The data at 325°C, which are shown in Fig. 11-9, indicate that the deposit thickness is linearly dependent on cycle life. The impact of NaCrS$_2$ deposition on cell performance is not clearly understood at present.

b. Cell Hardware Performance

The post-test examinations also show the recent progress that Ford Aerospace has made in cell development. Its present plating technology used for the cell container provides a chromium layer of sufficient quality and thickness to prevent significant corrosion of the stainless steel substrate. The redesigned glass seal between the $\beta''$-alumina electrolyte and the $\alpha$-alumina insulator showed no deterioration in cells operated for more than three years. Finally, a modified compression seal design eliminated container breaches in the area where the seal is made.

The reliability of the $\beta''$-alumina electrolyte remains an outstanding concern. The chemical stability of this ceramic has been demonstrated by long-term immersion tests in pure electrode melts.\textsuperscript{3} However, the electrolyte is susceptible to fracture during cell operation. Three distinctive fracture patterns have been noted.

One fracture mode is consistent with the initiation and propagation of a crack from a preexisting defect on the inner (sodium) surface of the electrolyte tube. Improved ceramic fabrication procedures have greatly alleviated its occurrence.


Electrolyte failures also result from freeze-thaw cycles. One fracture pattern consists of multiple axial cracks that extend the length of the electrolyte tube. Much of the evidence supports the hypothesis that the primary cracks initiate on the outer electrolyte surface because of shear stresses that develop at the electrolyte surface. During cooldown the tube is placed under compression as the positive electrode solidifies around the electrolyte tube. Void areas in the positive electrode near the electrolyte, such as the gaps between electrode segments, introduce discontinuities in this compressive stress field. Shear fractures can then result if defects in the outer electrolyte surface are aligned with the discontinuities in the stress field.

A different fracture pattern, numerous interacting cracks that radiate outward from a common location of the electrolyte, apparently can also arise from this mode of failure. The formation and buildup of solid sodium polysulfides, $\text{Na}_2\text{S}$ and $\text{Na}_2\text{S}_2$, in a localized region of the sodium annulus (the space between the safety tube and the electrolyte) impart sufficient force to the electrolyte to cause additional fracturing. For this pattern to occur, the direct reaction of sodium and sulfur entails ingress of sulfur into the annulus through the initial crack.

The elimination of these thermally induced failures will entail redesigning the sulfur electrode and its supporting graphite felt structure to prevent void formation at the electrolyte surface.

In FY 1986, we will receive Na/S cells fabricated and tested by Chloride Silent Power for post-test analysis.
III. ADVANCED FUEL CELL DEVELOPMENT

Fuel cell power plants are one of the more attractive energy technologies under development at present. Argonne is predominant among the national laboratories in advanced fuel cell technology, which includes both molten carbonate (MCFC) and solid oxide (SOFC) fuel cells. The ANL fuel cell programs are led and mostly executed by CMT, but there are other important contributions, primarily from the Materials Science and Technology (MST) Division, but also from the Engineering (ENG) and the Energy and Environmental Systems (EES) Divisions. The ANL effort provides the DOE programs in advanced fuel cell technology with research, testing, modeling, systems analysis, and technical management assistance; however, since the primary development effort of the DOE program is by industrial contractors, ANL does not carry out design and development of stacks of fuel cells for DOE. Half of ANL's effort for DOE is research, concentrating mainly on the development of new carbonate cathode materials.

For the Department of Defense, ANL is developing a high-power fuel cell concept—the monolithic oxide fuel cell. The monolith concept originated at CMT and is being developed exclusively by ANL, at least until it has been proved that monoliths can be fabricated and operated successfully. The most difficult of the many challenges in this effort is simply fabrication of the necessary ceramic structure.

A. Molten Carbonate Cell Development

Present-day MCFCs consist of a porous nickel alloy anode, a porous metal oxide cathode, an electrolyte structure separating the anode and cathode, and appropriate metal separator sheets. A schematic of a single cell is shown in Fig. III-1. Separator sheets isolate reactant gases in adjacent cells of a stack, electronically join these cells, and bear upon the electrolyte structure to form a "wet" seal that separates the cell interior from the surroundings. The electrolyte structure is a composite of discrete submicron LiAlO$_2$ particles and a mixture of lithium and potassium carbonates that is liquid at the cell operating temperature of about 650°C. At the anode, electrons are given up to the external circuit when hydrogen and carbon monoxide in the fuel gas react with carbonate ion from the electrolyte to form water and carbon dioxide. At the cathode, carbon dioxide and oxygen react and accept electrons from the external circuit to form carbonate ion, which is conducted through

![Fig. III-1. Schematic of Molten Carbonate Fuel Cell](image-url)
the electrolyte to the anode. In a power plant, many cells (50-1000) with parallel gas flows will be assembled in a series electrical connection to form a stack. Each cell adds about 0.8 V to the stack voltage at the current density of 200 mA/cm²; tens or hundreds of stacks will be used, depending on the plant size. In practical cell stacks, CO₂ for the cathode will probably be obtained from the anode exhaust. An economic advantage exists for large plants to run at pressures of 6-10 atm.

1. Research on Cathode Materials

Nickel oxide, the traditional cathode material for molten carbonate fuel cells, has a long-term stability problem in that it has low solubility under cathode conditions and precipitates as metal under anode conditions. This causes a continuous migration of cathode materials toward the anode and limits cell lifetime. In last year's report,¹ we listed stable compounds in the cathode environment along with their nominal stoichiometry. One of the materials from this list, LiFeO₂, was discussed in some detail. The resistivity of LiFeO₂ (synthesized in Li₂CO₃-K₂CO₃ electrolyte melt and washed free of carbonates) at cell operating temperatures was shown to be a strong function of the cover gas composition, especially CO₂. This effect was found to be due to the lithia activity of the melt.

The previous discussion focused on the lithium-to-iron ratio and its effect on conductivity. In the past year, we also examined the possibility of oxygen nonstoichiometry of the material. It appears that undoped LiFeO₂ in the environments of interest (with respect to temperature, pressure, and gas composition) is nonstoichiometric because of excess oxygen. This produces a p-type conductor, which is enhanced by the previously discussed lithium-to-iron nonstoichiometry. The oxygen excess was inferred from Seebeck coefficient measurements and controlled-environment conductivity tests. Thermal gravimetric analysis is being done to provide a direct quantitative measurement of the lithium and oxygen nonstoichiometries. This analysis is also expected to provide an indirect measurement of the relative defect number in the LiFeO₂ material and may, in combination with conductivity data, provide information on charge carrier mobility. Present indications are that oxygen defects in the LiFeO₂ and its Li/Fe ratio at low CO₂ partial pressures both tend to produce Fe⁴⁺. The resistivity of undoped LiFeO₂ in typical O₂ and CO₂ partial pressures for a fuel cell (Li/Fe=1) is about 300 Ω-cm at 650°C. This value is reduced to ~3 Ω-cm at 650°C in very low CO₂ partial pressures owing to a shift in cation stoichiometry, Li/Fe>1.

We are investigating dopants to the LiFeO₂ that will achieve this resistivity improvement without a shift in Li/Fe ratio and will promote less sensitivity of resistivity to cover-gas composition. The dopants that have been tested to date are magnesium, copper, and manganese. Others have not been precluded from testing, but have not been examined because of time constraints. The doped material was found to be a p-type conductor in all cases.

Absorption spectrophotometry indicated that magnesium could dope LiFeO₂ when the synthesis was done in air, and this doping was found to have a

beneficial effect on the LiFeO$_2$ resistivity. Table III-1 shows the resistivity of an Mg-doped LiFeO$_2$ sample prepared in air and tested under various gas compositions and pressures of 1 and 8.8 atm. The increasing oxygen partial pressure in going from 1- to 8.8-atm pressure caused a decrease in resistivity of this p-type conductor. At 8.8 atm, changing the O$_2$ content of the gas had no significant effect on resistivity. Changing the CO$_2$ content at this pressure had a minor effect, but much less than would be anticipated for undoped LiFeO$_2$. This effect is probably still a manifestation of a shift in the Li/Fe ratio of the material.

Table III-1. Resistivity of Mg-Doped LiFeO$_2$(Mg/Fe-1/10) Prepared in Air

<table>
<thead>
<tr>
<th>Gas Composition</th>
<th>Pressure, atm</th>
<th>Resistivity at 650°C, Ω-cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>1</td>
<td>36-42</td>
</tr>
<tr>
<td>5% CO$_2$-20% O$_2$-N$_2$</td>
<td>1</td>
<td>42</td>
</tr>
<tr>
<td>4.4% CO$_2$-18% O$_2$-N$_2$</td>
<td>8.8</td>
<td>26-29</td>
</tr>
<tr>
<td>5.3% CO$_2$-31% O$_2$-N$_2$</td>
<td>8.8</td>
<td>26-28</td>
</tr>
<tr>
<td>11% CO$_2$-50% O$_2$-N$_2$</td>
<td>8.8</td>
<td>26-28</td>
</tr>
<tr>
<td>23% CO$_2$-37% O$_2$-N$_2$</td>
<td>8.8</td>
<td>36-38</td>
</tr>
<tr>
<td>4.7% CO$_2$-40% O$_2$-N$_2$</td>
<td>8.8</td>
<td>31</td>
</tr>
<tr>
<td>10% CO$_2$-34% O$_2$-N$_2$</td>
<td>8.8</td>
<td>29-32</td>
</tr>
<tr>
<td>19% CO$_2$-37% O$_2$-N$_2$</td>
<td>8.8</td>
<td>34-36</td>
</tr>
<tr>
<td>1-5% CO$_2$-20% O$_2$-N$_2$</td>
<td>8.8</td>
<td>34</td>
</tr>
</tbody>
</table>

At the time of the last report, results indicated little if any beneficial effects from copper doping of LiFeO$_2$. This year, copper was reexamined as a dopant in 1-atm testing. In the reexamination, copper-doped samples were prepared both in air and in CO$_2$/O$_2$ environments of high CO$_2$ partial pressure. Figure III-2 shows data for an air-prepared sample tested under a range of gas compositions at 1-atm pressure. The most significant aspect of the data is the insensitivity of the sample to CO$_2$ in the cover gas. A similar sample, but prepared in 30% CO$_2$/air, had a resistivity of ~10 to 15 Ω-cm at 650°C. The resistivity of this latter sample has not been measured as a function of gas composition. However, it is clear that the copper doping has a positive effect on the LiFeO$_2$ resistivity in gases with high CO$_2$ partial pressure. In addition, the resistivity of this p-type conductor is expected to drop from 10-15 Ω-cm to 7-10 Ω-cm at 10-atm pressure.

Manganese doping of LiFeO$_2$ produced material with little sensitivity to cover-gas composition for a range of anticipated gas compositions. Table III-2 shows the resistivity of a manganese-doped sample prepared in a CO$_2$-containing environment. When the pressure was increased from 1 to 10 atm, a reduction of resistivity occurred owing to the equilibration of the LiFeO$_2$ crystal with the increased oxygen partial pressure. For the 10-atm tests, the
Fig. III-2. Resistivity of Cu-Doped LiFeO_2 Prepared in Air and Tested Under Different Gas Environments at 650°C and 1-atm Pressure

<table>
<thead>
<tr>
<th>Environment</th>
<th>Time, h</th>
<th>Resistivity at 650°C, Ω-cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air (0.1 atm O_2-0.8 atm N_2)</td>
<td>3.6</td>
<td>43</td>
</tr>
<tr>
<td>2.0 atm O_2-8.0 atm N_2</td>
<td>2.0</td>
<td>28</td>
</tr>
<tr>
<td>1.0 atm O_2-9.0 atm N_2</td>
<td>44.0</td>
<td>27</td>
</tr>
<tr>
<td>1.0 atm O_2-0.7 atm CO_2-8.3 atm N_2</td>
<td>20.0</td>
<td>27</td>
</tr>
<tr>
<td>1.0 atm O_2-1.7 atm CO_2-7.3 atm N_2</td>
<td>7.0</td>
<td>27</td>
</tr>
<tr>
<td>1.5 atm O_2-1.7 atm CO_2-6.8 atm N_2</td>
<td>17.6</td>
<td>27</td>
</tr>
</tbody>
</table>

cover-gas composition had no effect on the resistivity of the material, which was ~27 Ω-cm at 650°C. The p-type behavior of the Mn-doped LiFeO_2 cannot be explained by a simple manganese substitution for either iron or lithium; therefore, the explanation must be that a more complex defect structure for the LiFeO_2 material is formed with Mn doping.

In summary, doping has been very effective in improving the conductivity of LiFeO_2 under realistic cathode conditions. The LiFeO_2 remains
p-type conductor for all dopants tested. Apparently, the p-type behavior is primarily due to excess oxygen and cation nonstoichiometries for undoped material and to excess oxygen and dopant effects for the doped materials.

Each dopant has certain advantages. The carbonate melt for Mg-doped LiFeO$_2$ can be saturated with magnesium to prevent dopant loss, and the resistivity for this material is as low as ~7 Ω-cm at 650°C. However, doping has not been proven possible in cover gases with high CO$_2$ partial pressure, and there is concern for the long-term stability of such a cathode in a cell. Copper doping has resulted in LiFeO$_2$ with the best conductivity, but there is concern that dopant loss may occur because copper metal, which is stable at the fuel cell anode, would be precipitated. Manganese appears to be a good prospect for use as an LiFeO$_2$ dopant because it does not precipitate as a metal or lower oxide in the anode environment; thus, the melt can be saturated with manganese to prevent dopant loss. Although the Mn-doped LiFeO$_2$ is not sensitive to cover-gas composition, it has not yet produced as good a conductor as either copper or magnesium.

For a typical cathode structure, the net electronic resistivity from the cathode material should be the same order of magnitude as the net ionic resistivity from the electrolyte when the bulk cathode material resistivity is less than ~20 Ω-cm. The present values of resistivity for the doped LiFeO$_2$ meet this criterion; therefore, this material may be adequate for use in a fuel cell. An existing fuel cell model will be used to examine the effect of cathode microstructure on resistivity.

The emphasis of our research in the future will be on gaining a better understanding with respect to the oxygen dependence of cathode-material properties, which may indirectly provide insight into the doping effects. Also, work will be done to help ensure homogeneity of the cathode material, which may provide further improvement in conductivity.

2. Technical Support

The Advanced Fuel Cell Program Office at CMT provides technical support to the Morgantown Energy Technology Center (METC), which has programmatic responsibility for the MCFC program for DOE. Technical support includes assistance in program planning, systems analysis, technical monitoring of the contracts, and preparation of work statements for new work. During 1985, International Fuel Cells (IFC), formerly the Power Systems Division of United Technologies Corp., continued to be the major DOE contractor for development of molten carbonate fuel cells. Research also was sponsored by DOE at Energy Research Corp. (ERC), the Institute of Gas Technology (IGT), and Physical Sciences, Inc. (PSI). The technical approach of this DOE program is to integrate the development of a fundamental understanding of fuel cell behavior with cell and stack engineering. The DOE goal is to be in a position to construct and operate a full-scale stack with a projected life of 40,000 h in the 1990s. With ANL assistance, DOE/METC is planning the follow-on contract(s) to the present stack development efforts to meet this goal.

In the past year, IFC operated two subscale stacks, each containing 20 cells of 0.1-m$^2$ area. The stacks were operated at about 2 kW for planned testing periods of 1500 and 5000 h. The stacks had excellent initial performance, but then showed several problems affecting endurance. These problems
are principally related to electrolyte management, electrode compaction, electrical contact of end plates with the end cells of the stack following thermal cycles, end-cell short circuiting, and cathode dissolution.

The major problems with electrolyte management result from parasitic fuel cell reactions or electrochemical reactions in the stack. These are being addressed through stack design now that the phenomena involved have been identified. International Fuel Cells has been able to harden the porous anodes so that in-cell compaction is minimized, but cathode compaction still seems excessive. Some compaction is desirable to facilitate good component contact, but excessive compaction of electrodes must be accommodated by the other components to avoid loss of electrical contact or gas seals and to minimize shear stresses. Component compaction also leads to sliding between the stack and the external gas manifolds. As a result of design improvements, IFC has been able to minimize contact problems with the stack end plates and to prevent short circuiting at the end cells of the stack. End-cell short circuiting occurs as a result of corrosion products being transferred from the positive to the negative end cells through electrolyte in the manifold gasket.

As stated in Sec. III.A.1, the ANL program is attempting to identify an alternative cathode; in the meantime, however, IFC is trying to extend the life of NiO cathodes. To this end, IFC has accepted some performance loss from the NiO cathode and lowered the nickel solubility by reducing the CO₂ partial pressure in the cathode gas. The performance loss is a result of both decreased Nernst potential and increased polarization.

In the next months, IFC will be assembling and operating a larger-area stack (0.7 m²) of 20 cells to determine problems with scaleup of area. Potential problems with scaleup of taller stacks will still need to be investigated.

Energy Research Corp. is working on reforming catalysts that can be used in the anode region of a molten carbonate fuel cell. Internal reforming of methane has been demonstrated in cells for periods of over 5000 h, but the cell lifetimes have been limited by accumulation of electrolyte on the reforming catalyst. Energy Research Corp. is attempting to limit wetting of the catalysts and to provide wetting barriers in its cells. In addition, ERC is developing alternative compaction-resistant anodes and intercell separator sheets. Further, ERC is studying whether NiO-cathode lifetime will be extended by lowering the melt acidity (by changing the salt composition) and reducing the partial pressure of CO₂.

The Institute of Gas Technology is completing a study of the sulfur reactions leading to possible poisoning of molten carbonate fuel cells and is working with PSI to model the results of the study. The anode tolerance to sulfur poisoning has been investigated extensively, and the equilibrium and regeneration conditions defined. The major problem is to limit the recirculation of sulfur as a result of anode gas recycling for CO₂ recovery. The IGT results have revealed that corrosion on the cathode side of the cells also may limit the sulfur tolerance of the cells. The IGT has begun a study of the nickel migration mechanism in the electrolyte following cathode dissolution. Observations at several laboratories indicated that this lifetime-limiting mechanism is poorly understood.
Physical Sciences, Inc., is working under a subcontract to ANL to upgrade a performance model for the molten carbonate fuel cell. This model, which is based on fundamental properties of a fuel cell and its components, has been modified to reflect changes in components or new information about reaction mechanisms, electrode structures, electrolyte distributions, etc. The model is verified against the best available experimental data. We use this model in assessing contractor-cell performance, planning research, and performing systems studies.

Our principal current activity in technical support of DOE is program planning and preparation of technical material needed for the procurement packages for (1) follow-on contracts to the stack development effort and for (2) supporting basic research.

B. Solid Oxide Cell Development

The SOFC consists of a lanthanum manganite cathode, a zirconium dioxide (yttria-stabilized) electrolyte, a cermet (Ni or Co with ZrO,) anode, and lanthanum chromite for electronic cell-to-cell interconnections. These components are all ceramic materials. At the anode, hydrogen and carbon monoxide in the fuel gas react with oxide ions from the electrolyte to form carbon dioxide and water, giving up electrons to the external circuit. At the cathode, oxygen in the air accepts electrons from the external circuit to form oxide ions, which are conducted through the electrolyte to the anode. These cells operate at temperatures of 800-1000°C. In a power plant, cells (approximately 100) will be connected in electrical series with parallel gas flows to form a module; depending on desired plant size, hundreds or thousands of modules will be used.

An SOFC power plant would be simpler than an MCFC plant in that recycle of CO₂ from the spent anode stream to the cathode stream and extensive desulfurization of the fuel would not be required. However, efficiency for the oxide cell, because of the less favorable thermodynamics at the higher temperature of operation, is lower than that of the carbonate cell. It is reasonable to assume that SOFC power plants, without a bottoming cycle, would be smaller and less expensive than MCFC plants of the same power, but would have slightly (10 to 20%) lower efficiencies. The addition of a bottoming cycle would increase both the complexity and efficiency of the SOFC plant. In fact, the preferred design for a large SOFC plant (~200 MW) is to use fuel cell modules as the topping cycle and gas and steam turbines as the bottoming cycle. The high temperature of the heat rejected by the cells gives the SOFC the best match of any fuel cell to the bottoming cycle. As a result, SOFC power plants with efficiencies in excess of 60% higher heating value may be achieved in pressurized plants.

We are investigating a new concept for a compact solid oxide cell that promises to deliver very high power density. This concept is based on the premise that the thin solid components of oxide cells can be fabricated into compact shapes having power-to-weight ratios that are a factor of 100 higher than those of conventional fuel cells. Work on this concept began in 1983 with support from DOE. Beginning in mid-1983, support from the Defense Advanced Research Projects Agency (DARPA) made this development effort a major program within the CMT and MST Divisions.
1. **SOFC Technical Support**

The Advanced Fuel Cell Program Office at CMT has provided technical support for the DOE program on solid oxide cells. The principal thrust of this DOE program is the development of a tubular SOFC wherein the thin (25 to 700 mm) ceramic layers of active components are deposited on a thick (1-2 mm), inert zirconia support tube. The tubular SOFC design has a power-to-volume ratio similar to that for conventional fuel cells.

The technical support provided by ANL has included (1) testing contractor cells to assess the state of the technology, (2) investigating fundamental cell phenomena to obtain insight into SOFC behavior, and (3) providing technical insight as required to direct the efforts of the contractor.

The major SOFC contract is with Westinghouse Electric Co. This contract, which is being cost-shared (22%) by Westinghouse, involves demonstration of acceptable cell life and performance, a thermal management system in a submodule (15-25 tubular cells), and a 5-kW generator. In addition, work is in progress on compatibility of cell components, fabrication techniques, sulfur tolerance, and generator design.

In FY 1985, a Westinghouse cell demonstrated over 9000 hours of stable performance. The Westinghouse effort in FY 1985 focused on integrating solid oxide cells into modules; a 400-W unit of 24 solid oxide fuel cells was operated. The test demonstrated that the Westinghouse unit has acceptable gas manifolds and cell-to-cell electrical connections. In FY 1986, the unit will be scaled up to a 5-kW module. Upon completion of this SOFC contract in FY 1986, the program will be directed toward development of a commercial SOFC generator. The ANL support activities were terminated at the end of FY 1985 because conflicts of interest could arise with our development work on a new design for an SOFC.

2. **Monolithic Fuel Cell Development**

A new fuel cell design, called the "monolithic fuel cell," is being developed in a joint program between the CMT and MST Divisions. The monolithic design employs the same thin ceramic components used in other oxide fuel cells in a strong, lightweight honeycomb structure of small cells, and thus can achieve very high power per unit mass or volume. A monolithic fuel cell would convert hydrocarbon fuel to DC power at 50% efficiency, which is higher than any non-fuel-cell technologies that use this fuel.

In the monolithic concept, fuel and air are combined electrochemically in a ceramic cell at an operating temperature of 800-1000°C. Cell components are fabricated as one piece, much like a block of corrugated paperboard. Fuel and oxidant are conducted through alternating passages in the stack, as shown in Fig. III-3. These passages are formed from thin (0.025 to 0.100 mm) layers of the active cell components: the anode, cathode, electrolyte, and the interconnection material that connects cells in electrical series (bipolar plate). The corrugations also form the gas seal at the edges of the structure. Advantage is taken of the ability to fabricate the solid electrolyte and other solid cell components into shapes that cannot be achieved in liquid electrolyte systems. In liquid electrolyte systems, much
of the mass and volume goes into building the inert container for the liquid. Eliminating this unnecessary material gives the monolithic fuel cell a significant advantage in performance.

The potential for the high power density of the monolithic fuel cell results from the small cell size. Cells with gas passages 1 to 2 mm in diameter or smaller are achievable when the inert container for electrolyte and the inert support for the thin active layers are eliminated. The small cell size increases the active surface area per unit volume of the cell. More important, the small cell size in the monolithic design reduces the voltage losses caused by internal electrical resistance. This reduction is a significant consideration, because internal resistance is the principal dissipative loss for the ceramic materials and temperatures of interest. Decreasing the cell size decreases the current path length because current is carried "in-plane" by the electrodes in the monolithic design.

Considerable progress has been made by ANL in developing monolithic fuel cells. In 1985, the first cells of the monolithic design were built and operated. The cells were a three-layer composite of cathode/electrolyte/anode produced through sequential tape casting. The composition and particle size of the composite materials, as well as the processing conditions, were tailored to match the shrinkage of all three layers during one firing step and to give the desired porosity. The cell geometry was flat rather than corrugated in order to simplify gas manifolding. The electrical contacts applied to the cell for test purposes were a platinum paste and platinum screen. The active cell area was 3 cm².

These cells were operated at high current densities (2.2 A/cm²), which is about a factor of two higher than previously achieved with these
The high current density is a consequence of the low internal resistance of the monolithic cells, as shown by the slope of the curve in Fig. III-4, and is nearly four times higher than the design goal. More important, the data indicate that there is no fundamental limitation to achieving high current densities with SOFC materials.

A corrugated three-layer composite of anode/electrolyte/cathode has been fired in one step. As shown in Figure III-5, the desired high-density electrolyte and porous electrodes were achieved. The next step is the fabrication and operation of the first array of cells early in 1986.

C. Analysis of Fuel Cell Systems

Last year, CMT began a new project to assess the future applications of fuel cells. This project was initiated by DOE for two purposes: to obtain independent systems analyses that assess benefit projections made by the developers of fuel cells and to determine R&D priorities among the various types of fuel cells. The project is being conducted as a joint effort of the CMT, EES, and ENG Divisions.

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Fig. III-5. Photograph of Corrugated Three-Layer Structure for Monolithic Fuel Cell

The approach taken in this systems analysis is to derive consistent cost estimates for fuel cells and competing systems for several applications: base-load and dispersed installations for electric utilities, industrial cogeneration plants, and residential and commercial power units. After defining the flowsheets for the competing systems to the same level of detail for comparison purposes, we estimate the overall costs for electricity per kilowatt-hour using the same scaling rules and the same assumptions for capital costs and fuel costs.

The first systems analysis was done for the utility baseload application and is nearly complete. Costs for electricity were projected for two fuel cell systems (phosphoric acid and molten carbonate fuel cells), a combined-cycle (gas and steam turbines) combustion plant, and a pulverized-coal combustion plant. All systems were designed to have a net electrical output of 575 MW and to operate on Illinois #6 coal.

For these four power-producing systems, cost-of-electricity estimates were made based on four factors: (1) all contributions to the capital costs (coal handling and preparation, desulfurization, turbine, cooling tower, etc.), (2) estimates for operation and maintenance cost obtained from the Electric Power Research Institute's Technical Assessment Guide,3 (3) fuel costs, and (4) adjustments to remove inconsistencies. The costs for electricity were estimated to be 53.82 mill/kWh for the carbonate fuel cell system.

60.01 mill/kWh for the phosphoric acid fuel cell system, 49.84 mill/kWh for the combined-cycle system, and 53.03 mill/kWh for the pulverized-coal system. Thus, the costs for electricity of the two fuel cell systems are close to those of the two competing systems, confirming that fuel cells have potential for baseload power applications.

To provide DOE with recommendations on future fuel cell R&D needs, we searched for system design modifications that would decrease the capital-cost contribution of the fuel cells to the cost of electricity. We found that, if the two fuel cell systems could be operated at double the present current densities, then costs could be reduced by an additional 4 to 6 mill/kWh. The technical barrier to achieving these higher current densities is overheating of the fuel cells. An objective of future R&D should be finding methods for achieving higher current densities while preventing this overheating.
IV. ADVANCED RESEARCH PROJECTS IN ELECTROCHEMICAL TECHNOLOGY

Approximately 4% of the U.S. gross national product each year is attributable to costs incurred because of corrosion and its effects. We are searching for new and improved coatings that, besides being corrosion resistant, are durable and easy to apply. In another effort, we are investigating an electrochemical application for a new photochemical complex synthesized in ANL’s Chemistry Division.

A. Cadmium Electrodeposition on High-Strength Steel

Cadmium has been used as a protective coating for steel components exposed to corrosive environments (e.g., marine environment). For decades, cadmium electrodeposits on steel substrates have been obtained by cadmium plating from alkaline cyanide electrolyte. However, codeposition of hydrogen during cadmium electroplating from this aqueous electrolyte is common; this hydrogen migrates to regions of high stress and weakens the metal’s strength. We are investigating two options for producing mechanically adhering, corrosion-resistant cadmium coatings on steel substrate: electroplating from aqueous fluoborate electrolyte and electrodepositing from molten-salt electrolyte containing cadmium species. These options are being investigated for the U.S. Navy.

1. Aqueous Fluoborate Electroplating

A typical composition of the fluoborate electrolyte we used is $\text{Cd(BF}_4\text{)}_2$, 242 g/L; $\text{H}_3\text{BO}_3$, 23 g/L; and $\text{NH}_4\text{BF}_4$, 60 g/L. The initial pH of the electrolyte when the ingredients are mixed is quite low, about 0.9, and must be raised to 2.0-2.5 by the addition of ammonium hydroxide ($\text{NH}_4\text{OH}$). Since this process causes precipitation of a white sediment, the solution must be filtered. After filtration, a small amount of animal glue (2 ppm) is added to the solution; this additive influences the grain size and the coverage of the coating. The animal glue must be replenished from time to time. Electroplating of cadmium in cells having this electrolyte was accomplished by two methods.

In the first method, a steel bar sample (surface area = 6.25 cm$^2$) inserted between two cadmium anodes (separated from the cathode by 2-3 mm) was plated in the fluoborate electrolyte. Good coverage and adhesion, as well as a void-free coating, were obtained when a 500-mA/cm$^2$ nucleating pulse for 0.500 s was followed by a 50-mA/cm$^2$ direct current for <10 min. A typical scanning electron micrograph of the sample coating (surface and cross section) is shown in Fig. IV-1.

In the second method, the fluoborate solution was circulated through a narrow channel in an electrolyte flow cell, shown in Fig. IV-2. The flow cell is constructed from two blocks of polyethylene--one containing a steel disk cathode and the other containing a cadmium disk anode. The electrolyte flow rate can be varied up to 6 m/s. Typically, good deposits were obtained with the flow cell under a pulse current density of 1 A/cm$^2$ (time on, 0.1 ms; time off, 1 ms) and an electrolyte flow rate of 1.4 m/s.

We measured the hydrogen incorporation in the coated samples obtained by both methods. The results indicated that no measurable hydrogen
Fig. IV-1. Scanning Electron Micrographs of Cadmium Electrodeposited from Fluoborate Electrolyte under Nucleating Pulse Followed by Direct Current

Fig. IV-2. Photograph of ANL Electrolyte Flow Cell
was absorbed in the steel substrate during the plating. Thus, the fluoborate electroplating of cadmium coatings is not expected to result in embrittlement of the steel due to hydrogen incorporation.

The next phase of the work will involve optimization of variables (e.g., pulse cycle, nucleating pulse, current density for coating growth, electrolyte additives) so that a final recommendation can be made to the Navy for engineering scaleup.

2. Electrodeposition of Cadmium from Molten Salts

The electrodeposition of cadmium from molten salts has not been investigated extensively, despite the recent discovery of electrolyte systems that may be suitable for the technique. We attempted cadmium electrodeposition in cells having molten salts with low melting points (≤120°C).

Successful cadmium deposition was achieved with a cathode of nickel or Type 434 stainless steel, an anode of cadmium, and an electrolyte of 63.5 mol% AlCl₃ - 34 mol% NaCl - 2.5 mol% BaCl₂ (mp, 50°C) containing purified CdI₂. Results showed that cadmium electrodeposition could be obtained at even ≤1.0 wt% CdI₂ in the melt. Work is being continued to study the cadmium electrodeposition in greater detail, to be followed by studies of nucleation and film formation.

B. Electrochemical Application of Photochemical Complexes

This project deals with a major problem associated with the utilization of solar energy—poor power conversion efficiencies. Recently, ANL’s Chemistry Division synthesized a molecular complex that accurately mimics the "reaction center" of photosynthetic systems; the reaction center is the site where the transduction of the light to chemical energy occurs. This model complex consists of three distinct molecular entities that are covalently bonded together: a porphyrin, a triptycenenaphthoquinone (NO), and a 2-(N,N-dimethylamino)triptycene. Following illumination, the porphyrin is photoxidized concomitantly with the reduction of the quinone. The porphyrin cation and quinone anion are stabilized against recombination by the reduction of the porphyrin cation because of an intramolecular electron transfer in which the aniline donor is oxidized. The structure of the reaction center complex (a) and an analog (b) is given in Fig. 1: 7.

The attractive photochemical properties of the reaction-center complex suggest that it would be adaptable for the development of solar energy converters. We are searching for immobilization techniques that assure appropriate orientation of the cation-anion radical pair so that "short circuiting" caused by intermolecular charge transfer is avoided. Since Brown et al. 1 established that quinones may readily adsorb onto pyrolytic carbon surfaces, we investigated the electrochemical properties of NO on carbon electrodes. Figure IV-4 shows cyclic voltammograms for the solution electrochemistry of the naphthoquinone (curve B), as well as bound NO species on the carbon electrode in contact with an aqueous KCl solution (curve A). In acetonitrile and 0.1 M tetrabutylammonium fluoborate, the sequential two-electron reduction

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of the naphthoquinone derivative was observed at -0.6 and -1.25 V (vs. standard carbon electrode). Following a brief incubation period (20 min), NQ in an acetonitrile solution adsorbed onto a carbon surface. Adsorption of the quinone was verified by cyclic voltammetry of the carbon electrode immersed in a solution devoid of redox components. Integration of the faradaic current determined from the cyclic voltammograms indicated that monolayer coverage of the carbon surface was achieved (about $10^{-10}$ mol/cm$^2$).
Since simple physical adsorption could result in a near random orientation and thus increase intermolecular electron transfer, this immobilization technique is inadequate for application in solar energy converters. Additionally, whereas the NQ molecule readily adsorbed onto carbon surfaces, the efficiency of adsorption was found to decrease significantly for the porphyrin-NQ compound. Further decreases in the efficiency of adsorption would be expected for the more complicated model complex. An alternative method of immobilization is to covalently bind the reaction center to the electrode. This was achieved by utilizing organosilane reagents and the procedure described by Willman et al., in which a metal oxide (M-O) surface is reacted with a silane reagent [e.g., Cl₂Si(CH₃)(CH₂)₂COCl] to form (M-O)-Si bonds. The metal oxide surface could be either a metal oxide electrode (e.g., indium tin oxide, ITO) or electrochemically anodized gold or platinum. X-ray fluorescence verified the silanization of a gold oxide surface. Covalent linkage to the silane surface was achieved by reacting the acid chloride (RCOCl) moiety with a primary amine (R'-NH₂) to form an amide (RCONH-R'). The analog complex in Fig. IV-3 was successfully attached to a variety of electrode surfaces, including bulk Au electrodes and optically transparent Au and ITO electrodes. As shown in Fig. IV-5, the adsorption spectrum of the immobilized reaction center on ITO was nearly identical to that obtained for a solution species (propionitrile). Photoelectrochemical and electrochemical characterization of the modified electrodes is being performed with a cell that was designed to minimize IR drop and to allow illumination of the electrode.

![Absorption spectra](image)

Fig. IV-5.
Absorption Spectra of the Immobilized Reaction Center Analog on ITO (curve A) and in Propionitrile (curve B)

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A. Introduction

Over the past four decades, researchers have worked to develop technologies that would thermally convert high-sulfur coal and solid municipal waste (biomass) either directly into useful heat energy or into synfuels. Although technical progress has been significant, few of these technologies are being commercialized today. The underlying reason for this is low process efficiency, with the result that the energy produced from utilization of high-sulfur coal and municipal waste is not economically competitive with that of conventional fossil fuels. So great is the disparity in efficiency that small incremental refinements in the processes are not likely to alter the situation significantly.

With this in mind, we are seeking new approaches to the thermal conversion of high-sulfur coal and solid municipal waste that would yield dramatic improvements in process efficiencies. To achieve this improvement, we have recently begun investigations into methods that would (1) chemically remove the organic sulfur from coal, (2) enhance the liquefaction reactivity of coal, (3) reduce the need for de-ashing by separating the less-reactive mineral-laden macerals from coal, and (4) capture the sulfur dioxide formed during coal combustion by injecting pressure-hydrated lime into a slagging combustor instead of conventional flue-gas desulfurization. In addition, we are developing design guidelines that would minimize the erosion of heat-transfer surfaces in fluidized-bed coal combustion.

Presented below are highlights of our 1985 research efforts, which cover four areas: (1) energy from municipal waste, (2) fluidized-bed combustion of coal, (3) recovery of heat and seed from the bottoming cycle of a magnetohydrodynamic power plant, and (4) cleaning and preparation of coal.

B. Energy from Municipal Waste

Although conceptually promising, the large-scale pyrolysis of municipal solid waste (MSW) has resulted in low yields of inferior products. The goal of our current research is to gain an understanding of the fundamental mechanisms and kinetics of MSW pyrolysis so that economic processes can be developed for the thermochemical conversion of MSW into clean gaseous and liquid fuels. To this end, we are engaged in efforts (1) to determine the activation energies and to elucidate the pyrolysis mechanisms associated with the gasification, liquefaction, and charring of cellulose and other MSW components, (2) to identify the organic compounds in the primary and secondary products of MSW pyrolysis, and (3) to investigate the upgrading of pyrolysis liquids by catalytic hydrotreating.

1. Pyrolysis Mechanisms and Activation Energies

Municipal solid waste is composed of paper, newsprint, packing materials, wood wastes, grass clippings, and some plastic. We are determining the pyrolytic reactivities of these components with a thermogravimetric analyzer (TGA) and a bench-scale reactor.

Activation energies calculated from the TGA data at heating rates of 4 to 25°C/min up to 500°C are given in Table V-1. The apparent activation
Table V-1. Activation Energies Obtained from Thermogravimetric Analysis of MSW Components

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heating Rate, °C/min</th>
<th>Activation Energy, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whatman No. 1 Paper</td>
<td>4</td>
<td>49.0</td>
</tr>
<tr>
<td>Whatman No. 1 Paper</td>
<td>14</td>
<td>42.8</td>
</tr>
<tr>
<td>Whatman No. 1 Paper</td>
<td>25</td>
<td>39.6</td>
</tr>
<tr>
<td>Newsprint with Ink</td>
<td>5</td>
<td>26.3</td>
</tr>
<tr>
<td>Newsprint without Ink</td>
<td>5</td>
<td>27.1</td>
</tr>
<tr>
<td>Newsprint</td>
<td>20</td>
<td>24.2</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>5</td>
<td>41.7</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>20</td>
<td>34.9</td>
</tr>
<tr>
<td>Kraft Paper</td>
<td>5</td>
<td>40.4</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>5</td>
<td>38.0</td>
</tr>
</tbody>
</table>

energies are in the range of ~25-50 kcal/mol. The results suggest that the activation energy increases as the heating rate is decreased. For example, the apparent activation energy for Whatman No. 1 paper increased from ~40 to 50 kcal/mol as the heating rate was decreased from 25 to 4 °C/min. However, this finding is likely an experimental artifact caused by higher temperature gradients existing in the samples at the higher heating rates. Hence, the results for cellulose could be influenced by heat-transfer limitations. Interestingly, the ink in the newsprint did not significantly influence the apparent activation energy, and newsprint pyrolysis was not very sensitive to heating rate.

The bench-scale unit consists of a fixed bed within a quartz tube (70-mm ID) enclosed in a furnace. The gases generated as the tube is heated are analyzed by gas chromatography, and the liquid samples are analyzed by gas chromatography and mass spectrometry/gas chromatography. The experimental parameters being varied are feedstocks (Whatman No. 1 filter paper, newsprint, Kraft paper, and cardboard), sample size (5-50 g), heatup rate (5-30 °C/min), and final temperature (180-500 °C). Other than the feedstock, we found that the most important parameter in determining the final-product yields (tars, chars, and gases) is the final temperature. Table V-2 gives the Arrhenius parameters that were derived for cellulose decomposition and for the formation of tar, gas, and char from Whatman No. 1 paper. As shown, the activation energies are all the same order of magnitude. This finding suggests that the pyrolysis mechanism involves competing parallel reactions forming the three products of pyrolysis. These data and the other data obtained from the experiments will be used to obtain a kinetic model of the pyrolysis mechanisms associated with gasification, liquefaction, and charring of MSW.

2. Identification of Organic Compounds

The products produced in the pyrolysis of the various feedstocks are also being analyzed. As an example, some analytical results of cellulose and the tar and char pyrolysis products from cellulose are presented in Table V-3.
Table V-2. Arrhenius Parameters for Cellulose (Whatman No. 1)

<table>
<thead>
<tr>
<th></th>
<th>Frequency Factor Constant, min⁻¹</th>
<th>Activation Energy, kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall Cellulose Decomposition</td>
<td>$3.9 \times 10^{14}$</td>
<td>$42.8 \pm 3.4$</td>
</tr>
<tr>
<td>Tar Formation</td>
<td>$1.2 \times 10^{15}$</td>
<td>$45.0 \pm 2.5$</td>
</tr>
<tr>
<td>Gas Formation</td>
<td>$3.8 \times 10^{12}$</td>
<td>$38.4 \pm 2.8$</td>
</tr>
<tr>
<td>Char Formation</td>
<td>$5.5 \times 10^{14}$</td>
<td>$45.6 \pm 5.5$</td>
</tr>
</tbody>
</table>

*Error limits at 95% confidence. Uncertainty due to temperature gradient in the sample would increase the error limits by about 0.7 kcal/mol.

Table V-3. Analytical Results of Cellulose Tars and Chars (heating rate, 5°C/min; final temperature, 475°C)

<table>
<thead>
<tr>
<th></th>
<th>Feedstock*</th>
<th>Tar Product</th>
<th>Char Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating Value, cal/g</td>
<td>4170</td>
<td>4330</td>
<td>7566</td>
</tr>
<tr>
<td>Elemental Analysis, wt %</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>44.7</td>
<td>42.3</td>
<td>81.0</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.9</td>
<td>6.1</td>
<td>3.6</td>
</tr>
<tr>
<td>Oxygen</td>
<td>49.4</td>
<td>51.6</td>
<td>15.4</td>
</tr>
<tr>
<td>Ash Content, wt %</td>
<td>0.074</td>
<td>0.075</td>
<td>0.63</td>
</tr>
<tr>
<td>Yield, wt %</td>
<td>---</td>
<td>~46</td>
<td>~15</td>
</tr>
</tbody>
</table>

*Whatman No. 1 paper.

The elemental composition of cellulose and cellulose tars is very similar, but the tars have a slightly higher heating value than the cellulose. These results strongly suggest that the nature of cellulose tars is similar to that of its parent cellulose. Initial gas chromatographic analyses of silylated tars also support this finding.

When compared with the original cellulose, the cellulose chars have a carbon content that is roughly double, and hydrogen and oxygen contents that are about one-half and one-third, respectively. The richness in carbon content of the chars is indicated by their higher heating value. Unfortunately, the low hydrogen content of the chars makes them an unlikely candidate for the production of transportation fuels (gasoline, diesel fuel, etc.). Roughly 25% of the energy in the feedstock is released in the gaseous products. These pyrolysis gases are considered a low-Btu fuel.
Two subcontractors—the Solar Energy Research Institute (SERI) and the University of Arizona—are also involved in this effort. Using a flame pyrolyzer with a molecular-beam mass spectrometer sampling device, SERI is quantitatively studying the influence of sample properties and reaction conditions on the solid-phase and gas-phase products of low-temperature MSW pyrolysis. In addition, SERI is working on a rapid characterization technique for waste-derived pyrolysis oils so that the oils can be indexed to include all of the products, even those that cannot be chromatographed. The University of Arizona has been performing experimental work with a high-pressure autoclave reactor. This research should help elucidate whether water or carbon dioxide gases are being formed during the pyrolysis of MSW solids under direct liquefaction conditions. Also, the extent of utilizing the water-gas-shift reaction will be clarified.

3. **Catalytic Hydrotreating of Pyrolysis Liquids**

Liquids produced in MSW pyrolysis contain large quantities of oxygen-containing compounds. These liquids require considerable upgrading to increase the heating value and the stability before they can be considered as fuel oil substitutes. The kinetics of catalytic reactions that remove these oxygen-containing compounds is being experimentally determined in a high-pressure fixed-bed microreactor. The data will allow us to identify the relative difficulties in hydrotreating the various oxygen-containing species in the liquids.

For this experiment, model compounds (e.g., eugenol, furans) are added to an n-hexadecane carrier gas and pumped through the microreactor at the appropriate temperature, pressure, and flow rate. In previous experiments, the use of a sulfided CoMo catalyst resulted in hydrodeoxygenation activity, but the catalyst had to be treated with \( \text{H}_2\text{S} \) to maintain it in a sulfided state. Thus, we next tested an unsulfided NiMo catalyst on an alumina matrix. Operating conditions were \( \text{H}_2 \) pressure of 7 MPa (1000 psig), temperatures of 325-375°C, and flow rate through the reactor of 50-200 cm\(^3\)/h. The amount of model compound remaining in the liquid product was determined by gas chromatographic analysis. A large degree of hydrodeoxygenation was indicated in the experiments. We may next study hydrodeoxygenation with a zeolite catalyst.

C. **Fluidized-Bed Combustion of Coal**

Fluidized-bed combustion involves a process in which coal is burned in a fluidized-bed of limestone or dolomite; the limestone bed retains most of the \( \text{SO}_2 \) liberated during combustion. We are doing work on both atmospheric (AFBC) and pressurized (PFBC) fluidized-bed combustion of coal.

1. **Cleanup of Hot PFBC Flue Gas**

In application of PFBC of coal for power generation, a high-temperature, high-pressure flue gas is expanded through a gas turbine to recover energy for improved overall efficiency. Experience in operating gas turbines with hot flue gas from the direct combustion of liquid fuel and pulverized coal indicates a potential problem—hot corrosion of the gas turbines could occur owing to the presence of alkali metal compounds (such as chlorides and sulfates of sodium and potassium) in the flue gas.
A fixed, granular-bed sorber is being developed at CMT to clean up these alkali corrodents from the flue gas. In our earlier laboratory tests under a simulated PFBC flue gas environment, activated bauxite was found to be a very effective sorbent, and we also demonstrated its regenerability by a simple water-leaching process. Because of the promising results obtained from laboratory studies, a laboratory-scale alkali sorber system was designed, fabricated, and installed and is being operated with a pressurized fluidized-bed combustor at CMT (PFBC/alkali sorber system).

For a proper evaluation of the alkali sorber system, a reliable measurement of the alkali vapor concentration in the PFBC flue gas stream is imperative. Temperature is known to be one of the most important factors affecting the fate of alkali vapor in the gas stream. A drop in temperature could cause condensation of alkali vapor. To meet the temperature requirement (850-900°C), the flue gas lines sampling both the sorber inlet gas stream (referred to as "dirty gas stream") and the sorber outlet gas stream (referred to as "clean gas stream") are electrically heated (Fig. V-1). Hot valves, maintained at 850-900°C in an electrical furnace, are connected so that the dirty or clean gas stream can be switched to flow through either of two sample gas lines, one with an ultrafiber filter and another without, for alkali vapor (Na and K) analysis. The filtered line provides particulate-free flue gas for analysis. The alkali analyzer is a computer-controlled flame atomic emission spectrometer from Ames Laboratory. A batch-type alkali and particulate sampling train (APST) is used as a backup for the analysis of both alkali vapor concentration and particulate loading in the gas stream.

Three test series were completed in an attempt to quantify the alkali vapor concentration in the flue gas of the PFBC/alkali sorber system. In these tests, Sewickley coal (Pittsburgh, PA) and Tymochtee dolomite (Huntsville, OH) were combusted at an average combustor bed temperature ranging from 875 to 950°C and a system pressure of 9 atm (absolute). The interior of the alkali sorber vessel and the entire flue gas line for gas sampling were controlled at temperatures between 850 and 900°C.

In the first test series, the Ames alkali analyzer indicated that the sodium and potassium vapor concentrations were only 0.8 parts per billion.
by weight (ppbW) in the dirty gas stream and 0.3-0.4 ppbW in the clean gas stream.

In a later NaCl-vapor calibration of the Ames alkali analyzer, the sample tube of the analyzer burner was found to be sufficiently cool to condense NaCl vapor in the gas stream; therefore, the measured alkali vapor concentration in this test series was thought to be questionable and the burner was redesigned.

The second test series was performed while the Ames analyzer burner was under redesign, and thus the APST was used for the determination of alkali vapor concentration in the dirty gas stream. Results indicated that the sodium and potassium vapor concentrations were 220 and 60 ppbW, respectively, for the first APST measurement and 70 and 40 ppbW, respectively, for the second APST measurement. These results are in agreement with the thermochemical predictions of the alkali vapor concentrations in PFBC flue gas by General Electric.¹

In the third test series, a newly designed burner for the Ames analyzer was used to continuously monitor the alkali concentration in the gas stream. The average alkali concentrations in the filtered gas streams as measured by the Ames analyzer are summarized in Table V-4. For both dirty and clean filtered gas streams, the sodium vapor concentration was measured to be

Table V-4. Alkali Vapor Concentrations Measured by Ames On-Line Alkali Analyzer in Test Series 3

<table>
<thead>
<tr>
<th>Avg. Combustor Bed Temperature, °C</th>
<th>Filtered Gas Stream</th>
<th>Alkali Vapor Concentration, ppbW</th>
<th>Na</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>875</td>
<td>Dirty</td>
<td>5-10</td>
<td>10-30</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Clean</td>
<td>5-10</td>
<td>10-20</td>
<td></td>
</tr>
<tr>
<td>900-925</td>
<td>Dirty</td>
<td>1-2</td>
<td>5-20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Clean</td>
<td>&lt;1</td>
<td>5-15</td>
<td></td>
</tr>
<tr>
<td>925-950</td>
<td>Dirty</td>
<td>&lt;1</td>
<td>5-10</td>
<td></td>
</tr>
</tbody>
</table>

<10 ppbW. The potassium vapor concentration was 5-30 ppbW, which is essentially contributed by dust in the air. The average vapor concentrations in the dirty gas stream were measured by the APST to be 70-140 ppbW for sodium vapor and 20-30 ppbW for potassium vapor. The analytical uncertainty of the two techniques accounts, in part, for the discrepancy in the sodium-vapor results.

The alkali content has also been analyzed for the fly ash collected on (1) the activated-bauxite sorber bed, (2) the ultrafiber filter of the flue gas line, and (3) the front-face ultrafiber filter of the APST. Comparison of the alkali contents in the fly ash with the alkali content in the coal ash suggested negligible evolution of potassium but an appreciable amount of sodium evolution from coal combustion. The latter result is in contrast to the very low measured alkali vapor concentration shown in Table V-4. Therefore, loss of sodium vapor in the PFBC/alkali sorber system is possible. Further testing is needed to investigate this possibility.

Once the reliability of our alkali vapor measurement has been established, we will then be able to test the granular-bed sorber for the control of alkali vapor from PFBC flue gas.

2. Atmospheric Fluidized-Bed Cogeneration Experiment

Argonne is managing the Atmospheric Fluidized-Bed Cogeneration Air Heater Experiment for DOE. The objective of this effort is to assess materials and process performance of in-bed air heaters for cogeneration of electricity and process steam in AFBCs. The effort is expected to be about four years in duration, with the start of air-heater testing at Rockwell International scheduled for the summer of 1987. The experiment is being done in cooperation with Westinghouse Corp. and several boiler vendors under subcontract to Westinghouse. The ANL involvement in this effort includes three tasks.

The first task is to establish a materials data base by collecting and assessing current technical information on the performance of heat exchanger materials, particularly materials that have been exposed at temperatures of 650°C or higher. Thirteen studies were found to contain relevant results for iron-, nickel-, and cobalt-based alloys. Materials degradation (scale formation and penetration) was assessed in order to establish likely limits on material lifetimes. The assessment correlated degradation as a function of time and temperature of exposure. Among the stainless steels, for instance, Type 310 appeared most resistant to corrosion, followed by Type 316 and Type 304.

The second task is to conduct materials tests in the laboratory to complement tests in an actual AFBC unit (described below). Westinghouse has selected materials for laboratory testing at ANL, in addition to those that will be exposed in the AFBC unit. The environmental conditions with the laboratory test apparatus will be maintained as close as possible to those prevailing in the AFBC. Particular attention is being placed on controlling the oxygen and sulfur dioxide partial pressures and the temperature within acceptable limits. The selected materials will be evaluated for resistance to corrosion after 100, 200, and 500 h of testing.

The third task is to initiate and monitor a subcontract with Rockwell International for the required modification, installation, and experimental testing of heat-exchanger tube bundles in the DOE-owned AFBC unit (1.8 x 1.8 m) located at Rockwell International. Argonne will also provide an independent data reduction and assessment of the heat-exchanger performance. Two tests of 1000-h duration each are planned. The first test will emphasize performance of air-cooled heat exchangers in a bubbling fluidized bed, while
the second test will be configured to assess materials and components for air-cooled heat exchangers in circulating or fast fluidized-bed combustors. The materials and other test components will be delivered to ANL by Westinghouse for installation at the Rockwell facility.

D. Recovery of Heat and Seed from Magnetohydrodynamic Power Plants

Open-cycle magnetohydrodynamics (MHD) is a developing technology that promises to improve substantially the electrical efficiency of coal-fired power plants and to reduce their environmental impact. In this technology, a hot combustion gas containing an easily ionized seed material (usually a potassium salt) flows through a channel under a strong magnetic field. An electric potential is developed across electrodes in contact with the gas stream and an electrical current is withdrawn. In this manner, up to 25% of the gas enthalpy can be converted directly into electrical energy.

The fuel-rich combustion gas leaves the MHD topping cycle at 1 atm and about 2300 K and enters a bottoming cycle that is similar to the steam boiler of a conventional electrical power plant. The MHD steam plant must not only extract heat from the combustion gas to produce high-pressure steam, but also must separate ash and seed, recover seed material for reuse, preheat primary combustion air to at least 1000 K, lower NOx concentrations to acceptable levels, and inject secondary air to complete combustion. Moreover, because the combustion gas contains a large amount of seed material, the MHD steam plant must operate under conditions that are more highly fouling and corrosive than those of conventional coal-fired power plants.

Chemical Technology is the lead ANL division in a multidivisional project that is directed toward developing the technology required for the recovery of heat and seed material from an MHD steam plant. Much of the CMT effort involves experiments that are performed at an ANL combustion test facility, the Fossil Energy Users Laboratory (FEUL). One of the two test legs in this facility has an oil combustor capable of burning liquid fuels, including oil-solid slurries. During the past year, a new coal combustor was installed and commissioned in the other test leg. In addition to its potential application to the MHD program, the new coal combustor is being used in programs to develop advanced coal combustors. For example, the new coal combustor is being used to investigate the potential application of slagging combustors with limestone injection to coal-fired gas turbine technology.

The current work in MHD technology includes investigations into the fouling of the boiler tube banks by seed and ash, nitric oxide kinetics, and the interface between the MHD topping cycle and the steam bottoming cycle.

1. Fouling of Steam Heaters by Seed and Ash

The MHD radiant boiler will extract heat from the exhaust gas leaving the MHD channel and produce high-pressure steam for a turbine-driven electrical generator. The convective section of the MHD steam plant will include steam superheaters and reheaters, intermediate- and low-temperature air heaters, and economizers. Because the gas entering the convective section of the steam plant contains K\textsubscript{2}SO\textsubscript{4} and coal ash, the tube banks will be subjected to unusual and severe fouling conditions somewhat similar to those experienced in Kraft recovery boilers.
Over the past few years, we have conducted fouling experiments in the oil-fired test train of FEUL. In this apparatus, the exhaust gas from an MHD channel is simulated by burning a slurry of No. 2 fuel oil, K₂SO₄, and fly ash with preheated air. The gases are then passed through a tube-bank test section representing an MHD steam superheater or air heater. These tests have demonstrated that, at gas temperatures of 1400-1600 K, deposits are formed on the tube bank by the deposition of liquid seed particles and/or condensing vapor, and these deposits can harden and become difficult to remove. Thus, the primary objective of the fouling experiments initiated in FY 1985 and continuing through FY 1986 is to determine the factors that influence the hardness and tenacity of MHD deposits and to evaluate the capability of sootblowers to remove these deposits. This past year we investigated the effects of gas temperature (1300 to 1700 K) and sootblowing frequency (1 to 6 h) on fouling deposits of Montana Rosebud ash and/or seed.

In addition, the data obtained from these experiments (deposition rates and heat transfer characteristics of the deposits) will be used to (1) validate and further improve the ANL deposition and heat transfer model and (2) develop an engineering fouling model for use in the design of MHD plants.

Results obtained to date indicate generally good agreement between experimentally measured fouling deposition rates and heat transfer coefficients and the values predicted by the ANL deposition and heat transfer model. At gas temperatures near 1350 K, tube deposits were powdery and readily removed by sootblowing. At gas temperatures of about 1550 K, however, tube deposits began to sinter and harden. When sootblowing was done on an hourly cycle at this temperature, tube deposits were removed fairly thoroughly by the first two cleaning actions. Subsequent sootblowings, however, could only remove the outer layer of the deposits. The sootblowing pressure needed to remove tube deposits was also found to increase as the sootblower cycle was increased from every hour to every three or six hours.

The measured heat transfer coefficients to the tube bank obtained during the combustion of a slurry of No. 2 fuel oil (75%) and K₂SO₄ (25%) are shown in Fig. V-2. In the test at high gas temperature (>1600 K), a steady-state heat transfer condition was attained because a stable liquid film deposit had formed after about four hours of slurry combustion. In the test at low gas temperature (<1400 K), the tube deposit was solid and gradually increased throughout the test, as evidenced by the steadily declining heat transfer coefficient.

The general trends of the heat transfer data obtained from burning a slurry of No. 2 fuel oil (72.5%), K₂SO₄ (25%), and Montana Rosebud ash (2.5%) were similar to those obtained from burning a slurry of No. 2 fuel oil and K₂SO₄. However, the addition of 2.5% of Montana Rosebud ash to the fuel resulted in a decrease of about 30% in the measured heat transfer coefficients. Results obtained to date indicate that the amount and, possibly, the

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type of fly ash in the slurry (and entrained in the gas stream) could affect the heat transfer rates from the combustion gas to the tube bank.

In FY 1986, the fouling experiments will be continued to provide additional data on deposit characteristics with ash from Illinois No. 6 coal and will include tests to investigate the effects of $K_2SO_4$.

2. Nitric Oxide Kinetics

The MHD combustion temperature of about 2800 K results in the production of possibly as much as 10,000 ppm of nitric oxide (NO). According to the current New Source Performance Standards for coal-fired power plants, the NO concentration must be reduced to below 550 ppm before leaving the stack. The favored technique to reduce NO emissions in MHD plants is to operate the MHD topping cycle with a slightly fuel-rich combustion gas to lower the production of NO, allow sufficient gas residence time at temperatures above 1850 K so that NO will decompose, and perform secondary combustion below about 1850 K to prevent NO re-formation.

Our process calculations have shown that this technique is feasible. A gas residence time of about 2 s at gas temperatures between 1850 and 2350 K is needed to allow the NO to decompose sufficiently. Because the NO decomposition rate is strongly temperature dependent, effective slow cooling for NO decomposition begins only when the gas at about 2260 K enters the radiant boiler.
Our earlier calculations\(^3\) had shown that sufficient decomposition of NO can be obtained with the gas cooling rates typical of moderately large radiant boilers if the gas enters the radiant boiler at a temperature above roughly 2260 K, the gas is fuel-rich, and the gas cooling rate is less than 220 K/s. Experiments to verify the calculations on NO reaction kinetics have been made in the Coal-Pired Flow Facility (CFFF) at the University of Tennessee Space Institute. Argonne was requested by DOE to assist in interpreting the NO data obtained at CFFF and to develop a verifiable chemical kinetics model for NO behavior that could be used for the design of large MHD components.

At CFFF, the NO experiments were conducted both with and without a slag screen in the inlet region of the radiant furnace. The complex gas flow patterns caused by a high-velocity jet (65 m/s) of hot combustion gas (~2400 K) entering the CFFF radiant boiler complicated the analysis of the NO data. As reported last year,\(^4\) ANL incorporated a simplified temperature/flow model simulating the gas flow around the slag screen into the ANL chemical kinetics model and found that the predicted NO concentrations were in good agreement with the measured data for the CFFF tests with the slag screen in place. More recently, the measured and calculated NO values in tests without the slag screen were compared and were also found to be in good agreement, as shown in Fig. V-3. In this case, however, correct modeling of the gas flow profile at the furnace inlet was found to be less important in achieving good agreement between the calculated and measured NO concentrations along the furnace. We found that the accuracy of the gas temperature data in predicting the NO concentration profile in the CFFF tests without a slag screen was more important than the differences in other factors (e.g., gas flow patterns, reaction rates, and kinetics models) considered in the analysis.

Based on these and the earlier CFFF NO\(_x\) results, we have concluded that the ANL chemical kinetics code is reasonably accurate at MHD conditions and can be used to predict NO behavior in prototypic MHD power plants.

3. Diffuser/Boiler Interface Analysis

Although considerable progress has been made in development of both the MHD topping and bottoming cycles, little has been done to address the potential interfacing problem between the two cycles. Work has been initiated at CMT to identify the potential problems in interfacing the MHD diffuser and the radiant boiler and to develop a methodology for analysis of these problems.

One of the major potential problems is burnout and erosion of the boiler back wall, which would be caused by the particle-laden turbulent gas jet (high velocity and temperature) impinging on the boiler back wall. Analytical methodologies have been developed during the past year to investigate the burnout problem. These include methodologies (1) to determine gas velocities and temperatures at the boiler back wall based on turbulent jet theory.
(2) to estimate local wall temperatures, (3) to determine the total heat flux to the boiler back wall, and (4) to estimate the potential for exceeding the critical heat flux.

To date, the analysis has shown that the distance between the diffuser and the boiler back wall in the present MHD design is too short for effective decay of turbulent jet velocity, and there is a significant potential for refractory burnout.

During FY 1986, the interface work will attempt to (1) identify diffuser-boiler configurations that meet the design requirements of this subsystem and are compatible with the overall power plant design, (2) perform a more detailed and comprehensive analysis of major interface issues for the selected configurations, and (3) propose critical experiments to support the analytical activities.

E. Cleaning and Preparation of Coal

1. Chemical Cleaning of Organic Sulfur

The desulfurization of coal before its combustion would greatly simplify the utilization of coal for the production of electric power and process heat and could improve its economics. Physical cleaning (e.g., float-sink washing techniques) can remove most of the inorganically bound sulfur (mostly iron pyrites) as well as the other mineral matter from the coal. However, most high-sulfur coals have a significant fraction of the sulfur bound in the organic structure of the coal, which cannot be removed by physical washing techniques. Processes that have been proposed for the removal of this chemically bound sulfur are very expensive and result in a greatly modified coal that is difficult to use as a fuel.
A process using transition metal cations as mild oxidizing agents is being investigated at ANL for the removal of the organically and inorganically bound sulfur from the coal. The chemistry of the process is being studied in a joint effort between the Chemistry Division and CMT.

In 1985, a sample of Illinois No. 6 coal, which contains about two-thirds of its sulfur bound in the organic matrix, was treated with aqueous cupric chloride at 250°C in an autoclave at autogenic pressure (1.7-2.1 MPa). Approximately 50% of the total sulfur content was removed. Under these conditions, all of the pyritic sulfur is expected to be removed, and a portion of the organically bound sulfur as well. Manganese, ferric, and nickel cations are also being investigated for this desulfurization reaction. Nickel and ferric ions have been found to react with dibenzothiophene in preliminary studies as a part of this project, but experiments with coal have not yet been completed. Dibenzothiophene was used as a model compound because of its similarity to organic sulfur compounds found in coal.

2. Preparation and Characterization of Macerals from High-Sulfur Coal

The objective of this effort is to obtain an improved understanding of the petrographic and chemical properties of pure macerals derived from Illinois Basin high-sulfur coals, especially as they pertain to desulfurization and pyrolysis reactions.

Preliminary work to develop a continuous separation technique in which a magnetic field gradient is used to separate the coal macerals was carried out in 1984 as part of a joint project between the Chemistry Division and CMT. This technique is based on the fact that, when a single, low-density solution with a high paramagnetic susceptibility is placed in a magnetic field, the apparent density of the solution increases with increasing field strength. In a continuous magnetic field gradient, a continuous apparent density gradient is produced. If coal particles with a range of densities are injected into such a system, each particle seeks its own density (just as in an ordinary density gradient), and a good density separation is obtained.

We are now carrying out extensive characterization of coal macerals separated by this technique. Following separation of the coal macerals, we determine their petrographic properties and sulfur distribution. Differential thermal analysis and thermogravimetric analysis are being used to obtain kinetic and thermal data related to the pyrolysis reactions of the macerals. A bench-scale pyrolysis reactor produces sufficient quantities of liquid, gaseous, and solid products for these analyses.

Detailed characterization of the pyrolysis products obtained from the various coal macerals involves the use of gas chromatography/mass spectrometry and microwave plasma emission spectroscopy for structural characterization, as well as for identification of the various sulfur-containing functional groups in the pyrolysis liquids.

Discussions are being carried out with Amoco Oil Company concerning one or more joint research efforts involving the use of purified coal macerals, such as those obtained with our equipment, in improved coal liquefaction processes or in a coal/heavy oil coprocessing scheme.
VI. NUCLEAR TECHNOLOGY

The CMT nuclear technology program is (1) studying the possible interactions between the components of a high-level nuclear waste package and groundwater under realistic repository conditions, (2) developing a process for the extraction, separation, and recovery of transuranic elements in a nuclear waste stream, (3) developing a reprocessing method for the core fuel and blanket material of a sodium-cooled fast reactor, and (4) participating in a project to develop the technology for breeding $^{233}$U from $^{232}$Th in a light water reactor.

A. High-Level Waste/Repository Interactions

1. Waste Form Performance Test Development

   a. Introduction

   Investigation of the volcanic tuff beds of Yucca Mountain, Nevada, as a potential location for a high-level radioactive waste repository is a function of the Nevada Nuclear Waste Storage Investigations (NNWSI) project. One of the topics to be addressed during this investigation is the performance of the waste package components in the repository at the end of the containment period (a 300- to 1000-year period during which the high-level waste must be completely contained). The containment period is followed by the isolation period, during which the potential for canister breach and subsequent contact of the waste form by groundwater exists. Radionuclide release from the waste package would then be possible; however, in accord with Nuclear Regulatory Commission regulations, the total release rate must be less than one part in 100,000 per year of the total inventory of each radionuclide in the repository after the 1000 years.

   To measure this radionuclide release, a test method that incorporates the interactions between the waste package components and the groundwater under realistic repository conditions is required. Results obtained from such a test could be used as source-term data in modeling the long-term behavior of the repository. We are developing such materials interactions tests for NNWSI and using them to produce waste-form release data.

   The NNWSI repository site is located in an unsaturated zone in tuff. There is limited experience to serve as a basis for establishing a reliable experimental method that simulates events in such a location. The guiding principle behind the development of the unsaturated zone test is to provide reliable data using a test procedure that is simple enough to be performed and the results interpreted by different laboratories. The procedure must also produce results within a useful time period. Considerable emphasis is placed on reliability, which implies that the data must be reproducible and site relevant and have adequate quality to be used in further applications.

   b. NNWSI Unsaturated Test Description and Procedure

   We assume that the canister will be breached and that interactions with air, water, waste form, and metal will occur during the isolation period. These interactions may, in part, consist of the waste form being contacted by either standing or flowing water or water adsorbed onto the glass
surface from moist air. The contact could be at a metal/waste-form interface or isolated on the waste form. In addition, the metal could contain weld-affected and nonaffected regions, and the waste form (glass) would likely be stressed. All components will have undergone aging during the containment period and will undergo further changes because of reaction during the isolation period. The test procedures and the design of the test apparatus and associated solid waste-package materials create opportunities for these types of interactions to occur, but they are not designed to be a miniature model of the waste package.

The test apparatus (Fig. VI-1) consists of the test vessel, which provides for collection and containment of liquid and support of the waste package; the waste package, which consists of the waste form and a waste form holder (stainless steel) representing the canister; the tuff cup, which collects a solution that drips directly from the waste package and interacts with vapor; the tuff-cup supporting ring, which separates the tuff cup from the test vessel; and a solution feed system to inject test water.

Specimens representing the NNWSI waste package components (waste form and canister) are contacted intermittently by dripping repository water. The nature and degree of radionuclide release from the waste package are determined by collection and analysis of the water that has contacted the package and by surface analysis of the waste package components. Materials interactions are noted.

Both batch and continuous testing are done. In the batch mode, tests are terminated at selected 13-week intervals. The test apparatus is
disassembled, and analyses of both the solution and components are performed. In the continuous mode, the waste package (including liquid associated with it) is transferred to a new test vessel, and the test is continued while analyses of the solution in the old vessel are conducted. With the continuous mode, investigation of the test components is possible at the termination points, yet the test can continue indefinitely or until information more useful to repository evaluation is obtained.

c. Results and Conclusions

A series of tests using the unsaturated test method has been completed. These tests were done with SRL-165 frit borosilicate glass (a simulated defense waste from the Savannah River Laboratory) that was doped with uranium, cesium, and strontium. The tests were completed through a 52-week period with batch testing and through eight 6.5-week sampling periods with continuous testing.

Several materials interactions were noted. These include the interaction of uranium with test components, the formation of a silicon-rich mat on the stainless-steel waste form holder, and an extensive reaction at the location where the glass contacted "sensitized" stainless steel (a weld-affected region). A close correspondence was found between the laboratory environment of the unsaturated zone test and a realistic repository environment, as simulated by analog tests. A description of the overall glass reaction process was derived based on solution and component analyses. Briefly, the glass is believed to react by waste matrix breakdown and alkali exchange with water. Further details of this process will be presented in a topical report to be published in 1986.

These observations provide confidence that data acquired using the unsaturated test method will establish trends applicable to modeling long-term NNWSI waste package behavior.

2. Gamma Irradiation in a Saturated Tuff Environment

a. Introduction

Low-probability scenarios that relate to conditions in the NNWSI repository site are also of interest. The description of the site is continuously being refined and, although the repository horizon is described as unsaturated, there is the potential that pockets of condensed water may appear for brief interludes. If a premature canister failure occurs during the waste containment period (within 300 to 1000 years after emplacement), standing water and air might contact the waste form in the presence of a radiation field.

The probability of this situation occurring is extremely low, especially because the heat generated during this period would likely drive any liquid water away from the waste package. However, the present experiments were undertaken because our earlier studies had indicated that increased release from glass waste forms can occur when the air/water/glass system is exposed to a gamma-radiation field. The previous studies were conducted with air present during the reaction and used deionized water, simulated waste glass, and a limited test matrix that restricted the assessment of any dynamic interactions such as glass dissolution and nitric acid generation.
In the current experiments, the behavior of waste package components was studied under unanticipated but possible conditions of the NNWSI repository site. Components included in the tests are defense and commercial glass formulations that contain both uranium and transuranic elements, Type 304 L stainless steel, equilibrated J-13 well water, and tuff rock. The experiments provide information concerning the degradation of the waste form and the behavior of important waste elements in the presence of tuff, stainless steel, and a gamma-radiation field produced by a $^{60}$Co source.

b. Results and Discussion

The test matrices concluded to date have included 200 tests using 400 glass samples and test periods of up to 182 days. Dose rates of $2 \times 10^5$ and $1 \times 10^4$ rad/h were used.

The test results indicated that the reaction of glass with water is dependent on the interactive processes of glass dissolution and nitric acid generation. Anything that artificially upsets these processes will unnaturally affect the glass reaction. Thus, if a gamma field that is larger than expected in the repository is used to accelerate the reaction, the actual effect may be to alter the mechanisms by which the glass reacts. Nitric acid generation would be accelerated by the larger dose rate, and this may overcome the buffering action of the glass and cause dissolution of certain glass constituents that might not occur at lower dose rates. Alternatively, gamma-radiation tests conducted with deionized water as the starting solution begin with an initial pH of 5.8 and quickly become more acidic. This may introduce pH conditions that would not be attained in tests using actual repository dose rates and repository waters, thereby artificially influencing glass leaching.

The current experiments indicate that a generic prediction of the effect of gamma irradiation on repository behavior would be difficult. Perhaps, under expected NNWSI conditions, the effect of gamma irradiation would be to moderate the reaction between glass and water by exerting an influence toward keeping the system at a neutral pH. The effect of dose rate on the buffering action of the system will be investigated in future experiments, done at $1 \times 10^3$ rad/h, which will provide an indication of the limits on accelerated testing conditions that preserve relevant reaction mechanisms.

B. Separations Science and Technology

In 1985, the Division's work in separations science and technology consisted of three projects. The first project, supported by Rockwell Hanford Operations, entails development of the TRUEX (TRansUranic EXtraction) process for removing americium and plutonium from waste generated by the Hanford Plutonium Finishing Plant while recovering a purified plutonium stream. The second project, supported by Los Alamos National Laboratory (LANL), involves the design and fabrication of a centrifugal contactor to be used at LANL for solvent-extraction processing of concentrated HCl/brine waste streams. The third project is a study to determine the feasibility and cost of demonstrating a TRUEX-based process for reprocessing nuclear fuel.
1. **TRUEX Processing of PFP Waste**

The TRUEX solvent extraction process can extract, separate, and recover transuranic (TRU) elements from nitrate media containing a wide range of acid, fission-product, and salt concentrations; thus it could become an important tool for processing a variety of TRU-containing waste streams. The application of TRUEX processing of nuclear waste streams in the United States would have two important results: (1) a much lower quantity of waste that must be buried as TRU waste at the Waste Isolation Pilot Plant or as glass in a high-level nuclear waste repository and (2) the recovery of substantial amounts of TRU elements (e.g., plutonium) that otherwise would be lost.

The TRUEX solvent extraction process was invented by members of the Chemical Separations Group in ANL’s Chemistry Division; process application and flowsheet development and testing have since become a cooperative effort between this group and CMT’s Separations Science and Technology Group. The extractant found most satisfactory for the TRUEX process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is abbreviated CMPO. Its chemical structure is

```
\[
\begin{align*}
\text{C}_8&\text{H}_{17} \quad \text{P} \quad \text{O} \\
\text{CH}_2 & \text{C} \quad \text{O} \\
\text{CH}_2\text{CH(CH}_3\text{)}_2 & \text{N} \\
\text{CH}_2\text{CH(CH}_3\text{)}_2
\end{align*}
\]
```

This extractant is combined with tributyl phosphate (TBP) and a diluent to form the TRUEX process solvent. The diluent is typically a normal paraffinic hydrocarbon or a nonflammable chlorocarbon such as carbon tetrachloride or tetrachloroethylene.

In 1985, we directed our process development work toward a raffinate typical of that produced by a TBP-based solvent extraction process used to remove uranium and plutonium from dissolved waste generated during the processing and production of plutonium. This waste stream is designated "PFP waste" because it is typical of that exiting the Hanford Plutonium Finishing Plant. The TRUEX process solvent chosen for this waste stream is 0.25 M CMPO and 0.75 M TBP dissolved in carbon tetrachloride and is designated TRUEX-CCl$_4$. Our primary objective was to develop a TRUEX-CCl$_4$ flowsheet and to demonstrate it on a simulated PFP waste stream.

Our TRUEX-CCl$_4$ flowsheet$^1$ includes an extraction/scrub section that recovers most of the TRU elements from a PFP waste solution, so that the raffinate is a nonTRU waste. The organic product from the extraction/scrub section is then sent to a stripping section, which separates the americium and plutonium from each other and from the TRUEX-CCl$_4$ solvent.

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This flowsheet was demonstrated in a countercurrent experiment using a 14-stage centrifugal contactor bank (five extraction stages, two scrub stages, four americium-strip stages, and three plutonium-strip stages). The organic solvent was recycled in the contactor without any cleanup. The conclusions of the demonstration are as follows:

1. A raffinate that has an activity level <10 nCi per gram of solid is easily attainable with five extraction stages. At this activity, the raffinate would be classified as nonTRU waste.

2. An americium product stream containing >99.9% americium and very little plutonium contamination is attainable under properly selected conditions.

3. A plutonium product stream containing >99.9% plutonium and very little americium contamination is attainable under properly selected conditions.

4. Batch distribution ratios measured for trace concentrations of radionuclides can be used to predict the extraction behavior of Pu(IV) and Am(III) in this process.

5. The centrifugal contactor worked as expected during the demonstration. Stage efficiencies were calculated to be >97%, and physical entrainment of one liquid in the other (aqueous in organic phase and vice versa) was <0.1 vol %.

An experimental study was also done on the stability of the TRUEX-CCl$_4$ solvent to hydrolytic and alpha- and gamma-radiolytic degradation. The conclusions of this study are as follows:

1. Hydrolytic and radiolytic damage to the TRUEX-CCl$_4$ solvent will be of no consequence for periods equivalent to several years of processing of typical PFP wastes.

2. Observed reductions in the extraction capability of the solvent can be largely explained by degradation of tributyl phosphate to dibutyl phosphoric acid. Scrubbing the degraded solvent with aqueous sodium carbonate solution restored, and in most cases increased, the solvent's original capability for extraction of americium and ease of disengagement for the aqueous and organic phases.

The overall conclusion of this effort is that there are no foreseeable problems in implementing a TRUEX solvent extraction process on solutions having the general composition of a typical PFP waste. Modifications were made in the flowsheet to improve TRUEX performance. Future work will be directed to testing these improvements and to assisting Rockwell Hanford in implementing the process in the PFP facility.

2. Solvent Extraction Processing of HCl/Brine Waste Solutions

A 16-stage annular centrifugal contactor with a 4-cm-dia rotor was designed and fabricated for use in processing HCl/brine waste solution.
Figure VI-2 is a photograph of the 16-stage unit. Materials of construction (Hastelloy C-276, tantalum, and various fluorocarbons) were chosen because of their chemical stability to both acidic chloride solutions and organic solvents and their radiation stability. Other parts, not in direct contact with corrosive liquids, were fabricated of Type 304 stainless steel. These parts and the motor shaft were protected from HCl fumes by a newly designed air purge system. Other design changes that were made in this contactor to make it more amenable to production applications were (1) face-mounted motors for easy maintenance and (2) a high-liquid-level alarm system to warn that a rotor is failing to turn (likely due to motor failure).

A process to separate actinides from chloride salt wastes (Fig. VI-3) was designed and will be tested in FY 1986; this process has been designated the CLEANEX process by LANL.

3. PUREX/TRUEX Processing of Nuclear Fuel

A preliminary scoping effort was made in 1985 to study the feasibility of using equipment and facilities from the Proof-of-Breeding (POB) Project (see Sec. VI.D) to demonstrate a close-coupled PUREX/TRUEX process for reprocessing a variety of nuclear fuels. In the PUREX/TRUEX process, most of the uranium and plutonium would be recovered from nuclear fuel by the PUREX process, and the TRU elements in the high-level waste leaving the PUREX process would be removed by the TRUEX process.

The conclusion of the scoping study was that there are no technical, economic, or institutional barriers to performing this demonstration at ANL. The demonstration would be performed in a shielded-cell facility using the fuel rod shear, the tantalum-lined dissolvers, and the waste disposal equipment of the POB project. In addition, two banks of ANL-designed centrifugal contactors would be used.
If the PUREX/TRUEX process is implemented, considerable cost savings should be realized by DOE defense waste programs as a result of TRU removal from the raffinate; 99% of the waste would be classified as nonTRU and, therefore, would be a candidate for near-surface burial.

C. The Integral Fast Reactor Concept

A major new initiative at ANL is the Integral Fast Reactor (IFR), a sodium-cooled, pool-type fast reactor. The IFR core (driver fuel), which is an alloy of plutonium (15 wt%), zirconium (10 wt%), and uranium (75 wt%), is surrounded by a blanket of metallic uranium. During operation of the reactor, most of the power is provided by fissioning of the plutonium in the core; at the same time, plutonium is bred in the blanket material by the absorption of neutrons. The concept is similar in principle to that of EBR-II, in which the fuel was processed and recycled in a close-coupled facility adjacent to the reactor. However, subsequent advances in reactor design, fuel performance, and safety of metal fuels have been incorporated into the IFR. As now conceived, the IFR would be a self-contained system that would not require shipments of fuel to or from the site, and the radioactive wastes would be stored on the site until the activity decays to a level that is acceptable for ultimate storage in a waste repository.

The CMT Division has the responsibility of developing the onsite process for removing fission products from the core fuel and blanket material and for concentrating plutonium in the blanket for reenrichment of the core fuel.

The two basic steps of the process are electrorefining, which removes fission products from the core and blanket materials, and halide slagging, which concentrates the plutonium from the blanket material. The electrorefining and halide-slagging steps both use liquid metals and molten salts as process media.
In the electrorefining process, the metallic fuel is dissolved away from the cladding material by liquid cadmium; the resulting cadmium solution then becomes the anode for electrolytic transport of the uranium and plutonium through a molten chloride electrolyte to a solid metal cathode, where they are codeposited. The resulting deposit is recovered mechanically and consolidated by melting to form an ingot for the preparation of new fuel or blanket material by injection casting. The fission products remain in the liquid metal and salt, which become wastes. In the halide-slagging step, the metallic product from the electrorefining step is melted under a molten chloride salt containing a small amount of oxidant such as \( \text{UC}_3 \), which extracts the plutonium preferentially into the salt phase. This salt is added to the core electrorefining step for plutonium enrichment. The operating temperatures for electrorefining and halide slagging are about 500 and 1250°C, respectively.

During Phase I of the IFR program (FY 1985-1986), the objective of the CHT process development effort is to demonstrate the "chemical feasibility" of the process steps. Chemical feasibility means providing assurance that product yields and fission-product removals are adequate, that container materials and process reagents will perform as expected, and that the process steps are amenable to fully remote operation. Although engineering development of remotely operable equipment will not be undertaken until Phase II of the program, the design of the experimental equipment reflects, to the extent possible, preliminary plant concepts. The development program also includes characterization of the radioactive wastes produced by the process and methods of converting these wastes to forms suitable for ultimate disposal.

In 1985, we devoted a major effort to installing and outfitting two inert-atmosphere glove boxes with instrumentation and argon purification systems that permit investigations of electrorefining and halide slagging with plutonium-bearing materials. At the same time, we conducted preliminary small-scale (300 g of uranium) experimental studies of the electrorefining step, which showed that high uranium recoveries (>99%) can be obtained at satisfactory rates and that fission-product removals are in general agreement with theoretical predictions. We also demonstrated, on about the same scale, that over 90% of the plutonium can be extracted from metallic uranium by the halide-slagging procedure. Smaller-scale tests (20-30 g of plutonium) indicated that plutonium can be electrorefined both individually and as a uranium-plutonium mixture. Cyclic voltammetric studies showed that the electrochemical reactions are reversible and that the uranium and plutonium species involved are \( \text{UC}_3 \) and \( \text{PuCl}_3 \). The radioactive waste streams that would be produced by the process were characterized, and preliminary evaluations of various methods of disposal were made. In addition to this work, we provided the chemical flowsheets and process equipment concepts for a cost and design study of the IFR and its associated fuel-cycle facility.

We will concentrate the major experimental effort in 1986 on small-scale engineering studies of the electrorefining and halide-slagging steps, using uranium, plutonium, and inactive or tracer-level fission-product elements. The effects of process variables will be investigated, and a coupling of the two steps will be demonstrated. Experimental work will also be directed toward the handling of waste streams and their treatment for ultimate disposal. Among the supporting chemical studies, we expect to investigate the behavior of zirconium, which is present in the fuel both as an alloying element and as a fission product, and to evaluate possible in situ electrochemical analytical methods.
for process monitoring and control. Later in the year, work will begin on the
design of prototype plant-scale equipment for electrorefining and halide
slagging.

D. LWBR Proof-of-Breeding Analytical Support Project

This project is part of a national effort to develop the technology for
breeding $^{233}$U from $^{232}$Th in a light water reactor. In this program, the
Bettis Atomic Power Laboratory (BAPL) is carrying out a nondestructive assay
of a statistical sample (500 fuel rods from a total of 17,192 rods) from the
end-of-life (EOL) core of the Light Water Breeder Reactor (LWBR), which was
operated at Shippingport, PA, from September 1977 to October 1982. The BAPL
assay uses a delayed-neutron device, the production irradiated-fuel assay
gauge (PIFAG), to measure the fissionable content of each rod in the sample
and hence to estimate the fissile inventory of the entire LWBR core. A com-
parison of the beginning-of-life core with the EOL core will establish the
extent of breeding.

In August 1984, we began the EOL campaign, which involved destructive
analyses of 17 full-length LWBR fuel rods that had been assayed by BAPL with
the PIFAG. The purpose of this campaign was to provide BAPL with analytical
data to "fine-tune" the PIFAG and to corroborate its nondestructive fissile
material measurements. The processing of the rods, which were about 3 m
(10 ft) long and ranged in diameter from 0.76 to 2.1 cm (0.30 to 0.83 in.),
included this sequence of steps: (1) initial characterization of the rod, (2)
gas sampling of the rod plenum, (3) segmenting of the rod with a high-
precision shear, (4) dissolution of the individual segments, (5) analysis of
the individual batches of dissolver solution, and (6) off-gas sampling and
analysis. The bulk analytical residues (dissolver solution) are being con-
verted to a monolithic cement waste form and packaged for shipment to an
interim storage site, pending final transfer to the Federal Waste Isolation
Pilot Plant (WIPP).

The rod analyses were completed in November 1985 and will be followed by
equipment dismantling, waste disposal, and cleanout by the end of FY 1987.
The major operations and results for FY 1985 are discussed briefly below.

1. Full-Scale Shear Facility (FSSF)

The FSSF provides for the contiguous segmenting of full-length fuel
rods from the LWBR according to cutting plans provided by BAPL. Segments
range from 17.5 to 53.3 cm (6.9 to 21.0 in.) in length, but are actually
produced by cutting pieces having a length-to-diameter ratio of 1/2. The FSSF
has capabilities for accurate measurement of length and weight of entire fuel
rods, precise location of shear cuts (to within 0.00254 cm), weight measure-
ments of segments sheared from the rod, sampling for fission product gas, and
monitoring of $^{85}$Kr releases during shearing.

The shear operation is almost fully automated through use of a com-
puterized operating procedure, which provides (1) computer control of shear
operations, including the repetitive feed/cut cycle used in shearing a fuel
rod, and (2) automatic data collection, storage, and retrieval. Tabulation
and graphical presentations of results were also computerized.
The sheared rod segments were collected directly in preweighed, aluminum cans that were nominally 3.8-cm dia by 15.2-cm length (1.5-in. dia by 6.0-in. length). The capped cans were weighed in a hot cell to the nearest 0.001 g (or 0.01 g if the segment weight exceeded 286 g).

The performance of the shearing operations was assessed by two measurements: (1) recovery of the sheared rod materials and (2) location of individual segment boundaries relative to the boundary locations specified by BAPL. A summary of the results related to these measures of performance is presented in Table VI-1.

High rod recovery is important because it reduces the potential error associated with corrections applied to the destructive assay results for fuel losses during shearing. A minimum fuel recovery of 99.75% was set as an

<table>
<thead>
<tr>
<th>Rod Letter</th>
<th>Rod Type</th>
<th>No. of Cuts</th>
<th>Rod Recovery, wt %</th>
<th>Deviation Between Specified and Actual Segment Boundary Locations, in.</th>
<th>Average</th>
<th>Std. Dev.</th>
<th>Total</th>
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<td>99.920</td>
<td>+0.0001 ± 0.0012</td>
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*PFB = power-flattening blanket; SB = standard blanket.

<sup>b</sup>Segments collected in Al cans that were 7.6 cm (3.0 in.) high; segments for other rods were collected in cans twice as high. Performance was judged acceptable on a best-effort basis, although the recovery value was below the requirement of 99.75%.
acceptance criterion during the developmental shearing work with unirradiated materials (high-density ThO₂ pellets). However, because we had no rigid way of establishing whether irradiated fuel (and cladding) would behave differently in terms of recovery during shearing, recovery was on a "best-effort basis."

As Table VI-1 shows, recovery during shearing of the fuel rods exceeded the 99.75% recovery criterion in every case except Rod M, the first of five of the smallest diameter (seed) rods. The low recovery (39.55%) obtained with this rod was linked to the use of shorter aluminum cans [7.6-cm (3.0-in.) length] to collect the sheared segments, as compared with the 15.2-cm (6.0-in.) cans used for collecting segments from the other (larger diameter) rods. The shorter cans had been designated for seed-type rods to provide a consistent concentration ratio of aluminum-to-acid in the dissolver, since the lower mass of ceramic oxide fuel in the seed-rod segments permitted a lower-volume dissolution. The small cans had adequate volume to collect the longest seed-rod segments, but their use apparently caused greater pressure pulses within the shears' cutting chamber (which includes the can volume) as each cut was made and contributed to a greater loss (blowout) of fine fuel fragments. Owing to the relatively poor results with Rod M, the taller cans were used for collecting the segments from the next seed rod. Recovery for Rod N showed a marked improvement (up to 99.819%), and this size can was used thereafter, with continued satisfactory results.

With regard to the second acceptance criterion, the BAPL limit specified that the total of the bias in, and the standard deviation of, the segment boundary locations should not exceed 0.025 cm (0.010 in.). Under normal conditions, the ANL shear system is capable of easily meeting this requirement. However, problems related to properties of the irradiated rods were encountered during shearing of all but the seed rods. For example, shearing of the power-flattening and standard blanket rods was characterized by slippage of the rod in the carriage clamp jaws and occasional movement (kickback) of the spring-loaded clamp jaws during the shear stroke. These movements are measured by built-in transducers and, in most instances, are compensated for and do not affect the results of the shearing operations. If, however, kickback of the rod occurs during a segment boundary cut, an error in the segment boundary location can occur. Such was the case for one segment boundary in Rod K, and for many of the boundaries in the more highly irradiated sections of the largest diameter rods (H and R). For these rods, the kickback was so frequent and severe that the requirement on location of the segment boundaries was not met. However, BAPL indicated that, because this failure resulted from the unpredictable behavior of the rod and because the actual locations of these segment boundaries are reliably known, the performance of the shear in segmenting Rods H and R was satisfactory.

Preliminary cleanup and some waste disposal work in the FSSF are scheduled for FY 1986, while the shear remains idle. Dismantling and cell cleanout have been deferred to FY 1987.

2. Dual Dissolver System (DDS)

The DDS consists of two independently operated dissolver systems in which fuel-rod segments are dissolved in Thorex solution (13.5 M HNO₃ and 0.06 M HF) at high temperature (195°C) and pressure (860 kPa), the solution is
sampled for analysis, and then the bulk solution is discarded to a waste tank. The requirement for the dissolution procedure was quantitative dissolution on a segment basis. Qualification testing of the procedure was carried out using high-density, unirradiated ThO$_2$-UO$_2$ pellets of known composition.

In the course of the EOL campaign, we successfully processed 156 separate segments produced during fuel-rod shearing. Upon completion of dissolving each rod’s segments, we performed a blank dissolution (cleanup) run in each dissolver to verify the absence of residual uranium; the amount of uranium in each blank run was less than 0.01% of that in the previously dissolved fuel segment, considered an acceptable level. These post-processing cleanups gave confidence that there was no buildup of uranium in either of the dissolvers. The two-stage dissolution procedure consistently achieved 99.99% dissolution of, and recovery from, each dissolved segment.

A few operational mishaps that resulted in some loss of fuel solution for a given segment occurred as a result of either equipment failure or operator error. These mishaps sometimes required analysis of special samples (e.g., tissue wipeups) and application of special calculational techniques in evaluating the results. However, through use of conservative models (for fuel losses), assay results for all segments were shown to have met or exceeded error requirements.

From a mechanical standpoint, the DDS operated extremely well, especially if one considers the round-the-clock operation and demanding service (e.g., highly corrosive mixture of HNO$_3$-HF as reagent, elevated pressure and temperature dissolutions, and remote operations). The several-hundred-step computerized dissolution procedure provided reliable replication of the segment dissolution operation; dissolution of a given segment required 30 to 40 h of continuous operation.

As with the FSSF, the DDC will remain idle until FY 1987. Archive dissolver samples will be stored until approval to discard is received from BAPL.

3. Scrap and Waste Disposal

Emphasis of work in this area has been on disposal of the ~700 L of dissolver solution produced during the EOL campaign. To date, about 400 L of dissolver solution has been processed to a cement TRU waste form, producing over 130 cans of waste. The primary-can volume is 5.7 L, which provides for disposal of approximately 3 L of dissolver solution. Use of excess lime with the cement-water-lime slurry ensures acid neutralization. Drying of the cement waste before packaging reduces the chance for overpressurization from radiolytic decomposition of residual water.

Two of the primary cans are placed in a secondary can, which is, in turn, loaded into an approved 55-gal drum containing a specially designed lead-shielded cask. The cask reduces the activity readings on the drum surface to <200 mR/h, qualifying it as a contact-handled waste for permanent disposal at WIPP. Each drum is loaded into a separate, reusable steel bin, and the bin, in turn, is loaded into a commercial (Polypanther®) overpack. Seven shipments, each containing six loaded Polypanthers®, have been made to the interim (up to 25 y) storage site operated by Rockwell International at
Richland, WA. Shipments have been curtailed for the winter months but will be resumed in the spring. Meanwhile, production of the cement waste form and packaging of the waste material will continue at ANL through FY 1986. Clean-out of the cell is scheduled for late FY 1987.

4. Analytical Operations

Chemical and radiometric analyses of samples are performed by the Analytical Chemistry Laboratory (ACL, see Sec. IX) using facilities, instrumentation, and methodology that were established to meet the stringent error requirements and rapid pace of the EOL campaign. The analytical measurements included (1) determination, by gas mass spectrometry, of the fission gases Kr and Xe in the gas released during puncture of the rod plenums and in the dissolver off-gas; (2) measurement, by two virtually independent mass spectrometric isotope dilution (MSID) assay procedures, of the uranium in each dissolved segment from the rods; (3) measurement of the uranium isotopic composition of each segment; (4) determination of fission-product monitors (\(^{137}\text{Cs}, {^{144}\text{Ce}}, \text{and} {^{95}\text{Zr}}\)) in each dissolved segment by gamma spectrometry; and (5) other measurements on samples taken to verify the adequate cleaning of reusable dissolver components, such as blend tanks, prior to their use.

Performance of the analytical operations and systems during the EOL campaign proved quite satisfactory. The results from the two separate MSID uranium assays showed an average difference for 135 fuel-bearing segments from the LWBR rods of only 0.01%. Total uncertainty, including contributions from random and systematic errors, in the more reliable MSID assay for an individual segment was estimated to be less than 0.05% at the one-sigma level; this easily met project requirements (bias and standard deviation each lower than 0.15%). Measurement precision and accuracy of \(^{137}\text{Cs}\) and \(^{144}\text{Ce}\) in each segment also exceeded requirements. The \(^{95}\text{Zr}\) isotope was measured on a best-effort basis for most of the campaign because requirements on measuring it were waived as of October 1984; ongoing radioactive decay of this short-lived (half-life, 64 days) nuclide reduced it to levels that were barely measurable by the end of the campaign.

Besides providing analytical support to the project, the ACL also provided statistical support by analyzing data and generating reports using a set of computer programs created especially for this purpose. Results from the destructive analysis of each fuel rod were reported to BAPL, along with complete estimates of uncertainty in each result, usually within one week of completion of the analyses. The ANL data are currently under review by BAPL.
VII. APPLIED PHYSICAL CHEMISTRY

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

A. LWR Fission Product Chemistry

The objective of this effort is to understand the processes that control the release and transport of fission products from light water reactor (LWR) fuel so that accurate predictions can be made of the "source term." We are investigating (1) the release of fission products from a breached irradiated fuel pin, (2) their transport, condensation, and deposition within the reactor primary system, and (3) their release during the interaction of molten fuel with the concrete basemat following a breach of the bottom of the primary vessel.

1. Release of Fission Products from Breached Fuel

The objective of these experimental studies is to determine the chemical form and the rate of release of fission products from a defected LWR fuel pin. In these experiments, a sample of irradiated fuel is inductively heated, and the gaseous species that are released from the sample are identified and measured with a quadrupole mass spectrometer. In the past year, we determined fission product release from a nickel Knudsen effusion cell containing pieces of irradiated fuel without cladding. The nickel Knudsen cell was connected to a gas manifold located outside the vacuum chamber to facilitate the introduction of an oxidizing gas (oxygen) and a calibration gas (xenon) to the Knudsen cell.

The cell was heated stepwise to about 1270 K so that the easily released noble gases would escape from the fuel samples. Continued stepwise heating gave xenon release rates that were an exponential function of temperature. The sample was then held at a selected temperature (1190, 1300, or 1410 K) until a constant rate of xenon release was established. Oxygen was allowed to leak into the cell and the rate of release of xenon was monitored. Mass spectrometric observation of the oxygen leaving the cell allowed us to determine the rate of reaction of oxygen within the fuel sample.

During the first six oxidation cycles, no significant change in the xenon release rate was observed, even though nearly all of the oxygen being leaked into the cell was retained within it. About 40 min into the seventh oxidation cycle, conducted at about 1410 K, the mass spectrometric signal for the xenon ion current increased rapidly from $1.5 \times 10^{-10}$ to $1.9 \times 10^{-8}$ A, at which value it remained constant. When the oxygen flow was stopped, the xenon ion current returned to about the same value observed before the oxygen flow was started. Additional oxidation cycles yielded results similar to those observed in the seventh cycle, except that the increase in the xenon ion current occurred as the oxygen flow was started. Weak peaks on the mass spectra, which had been ascribed to cesium, completely disappeared as the number of oxidation cycles was increased.

If the observed enhanced release of xenon is due to the reaction of oxygen with the fuel, then the lack of an effect during the first six oxidation cycles suggests that most of the oxygen that was retained in the cell...
reacted with its nickel surface. Only after the formation of a layer of nickel oxide did the rate of oxidation of the nickel decrease and oxidation of the fuel sample begin. After this initial period of nickel oxidation, the release of xenon was found to be directly proportional to the amount of oxygen retained in the Knudsen cell. If it is assumed that all of the oxygen retained in the cell (after the xenon release increased) reacted with the fuel, then about 10% of the fuel would have been converted to $\text{U}_4\text{O}_9$, or an increase of the overall O/U ratio to 2.05. About 0.15% of the total xenon in the sample was released during these oxidation cycles. The dependence of the rate of release of xenon on oxygen absorption was the same at the higher temperatures (1300 and 1410 K). However, the amount of xenon released was lower at the lower temperature (1190 K) for the same amount of oxygen uptake. A new Knudsen cell with a platinum liner and gas delivery tube has been constructed and will be used for testing to ensure that all of the oxygen retained in the cell is held there because of reaction with the fuel.

2. **Downstream Behavior of Volatile Fission Products**

During a nuclear accident in which cooling water flow is interrupted, the temperature of the fuel will rise above its normal operating level. Consequently, the cladding of some fuel pins may rupture, releasing fission products. We are studying the interaction of these fission products with a steam/hydrogen mixture, which could flow up from the lower regions of the reactor core during an accident. The goal of this study is to characterize the chemical and physical transformation of a synthetic mixture of volatile fission products (VFPs) after being released into a steam/hydrogen environment.

We constructed an experimental apparatus for the injection of VFP solutions into flowing superheated steam at a temperature of ~1270 K (1000°C). The apparatus consists of a stainless steel transport duct that is 3.6 m (12 ft) long and lined with a collection surface that can be removed for inspection and analysis of VFP deposits. The experiment allows for a preset temperature gradient along the duct during operation through independently controlled zone heaters. Of the possible VFPs present in a reactor accident, Cs, I, and Te were chosen for study because of their harmful health consequences if released to the atmosphere.

In 1985, we performed five experimental runs: two with CsI, one with CsOH, one with CsI/CsOH, and one with Te/CsI/CsOH. A relatively large amount of material (more than 20 g) was injected into the duct to obtain accurate mass-balance information. The temperature of the duct walls was varied from ~1270 K (1000°C) at the inlet to ~440 K (170°C) at the end of the duct, and the superheated-steam flow rate ranged from 89 to 142 g/min.

The experiments with CsI and CsOH alone showed that VFP deposition on the duct walls occurs when the wall temperature is reduced to the vapor saturation temperature of the VFP species in the steam [943 K (670°C) for CsOH and 953 K (680°C) for CsI]. As the gas temperature in the duct drops below these temperatures, a point is reached where nucleation of the species takes place, with the subsequent formation of aerosol particles. The maximum vapor saturation ratio (observed vapor pressure/saturation vapor pressure) was calculated to be ~2.7 for CsI and ~1.7 for CsOH. Typically, more than 50% of the injected species escaped the duct in the form of submicrometer-size aerosols.
To evaluate the effect of introducing two components, we injected a mixture of CsOH and CsI into the superheated steam at a CsOH/CsI molar ratio of 8.4. Analysis of the deposited species showed that CsOH started to deposit at the duct location predicted from the test of CsOH alone. However, contrary to predictions based on the single-component behavior, the CsI in the CsOH-CsI deposited farther downstream. The percent deposited for the two species along the duct is shown in Fig. VII-1.

![Graph showing temperature and deposit distribution](image)

**Fig. VII-1. Temperature and Deposit Distribution in the Transport Duct for CsI-CsOH Mixture**

This behavior was explained by postulating the following vapor-phase equilibrium:

\[
\text{CsOH} + \text{CsI} \rightleftharpoons \text{CsOH-CsI}
\]

The formation of the CsOH-CsI complex favored by the large excess of CsOH molecules prevents CsI deposition until the CsOH concentration drops and condensation of CsOH frees the CsI molecules to deposit on the duct wall.

The next experimental run was performed with a mixture of the three VFP species (CsOH, CsI, and Te). Metallic tellurium was suspended as a fine powder in a CsOH/CsI solution and injected into the superheated steam at a CsOH/CsI/Te molar ratio of 5.6/1/2. All three elements (Cs, I, and Te) were detected at the downstream end of the duct. The VFP species flowing out of the duct were intercepted on a collector. A scanning electron microscope image of the deposit is shown in Fig. VII-2, together with energy dispersive
Fig. VII-2. Scanning Electron and Elemental X-Ray Analysis of a Deposit at a Center Location on a Vertical Collector 3.6-m (12-ft) Downstream (300X magnification)
X-rays of the three elements. One interpretation from the detailed elemental analysis is that the deposit may be $\text{Cs}_2\text{TeO}_3$.

In another set of experiments, we injected a small amount of the VFPs (<1 g) into the duct. This resulted in the formation of a relatively small number of aerosol particles, allowing particle-size analysis to be performed. Two experimental runs were completed—one with CsI and the other with CsOH. The objective of these experimental runs was to determine the particle-size distribution of VFP aerosols formed under operating conditions characteristic of low-pressure LWR accidents. The aerosol particles formed in the gas stream were collected on fine wires and on stainless steel strips. We analyzed scanning electron micrographs of the deposits with an image analyzer, constructed the particle size distribution, and calculated the collection efficiencies for different size particles.

For the CsI experiments, 0.25-μm dia particles constituted the largest fraction of particles collected from the gas stream at the cold end of the duct. Moreover, their collection efficiency was the lowest at $10^{-4}$; this gave a particle number density in the gas of $3 \times 10^4$/cm$^3$ for the 0.17 to 0.33 μm range. In the CsOH experiment, 0.17-μm dia particles were the largest fraction of aerosols collected at the cold end of the duct. Particles of this small size will carry a long distance before depositing.

Future work will focus on the phenomenon of revaporization of deposited VFPs in a flowing steam environment. This is a potentially important mechanism for the transport of fission products out of the primary system of an LWR several hours after an accident.

3. Fission Product Release from Core-Concrete Melts

The objective of this task is to obtain thermodynamic and vaporization data for key fission products that are likely to be present in a molten core during a nuclear accident. Emphasis is placed on investigating the vaporization behavior of three fission products (La, Ba, and Sr) as functions of temperature and oxygen potential. These fission products tend to form solid solutions with urania during irradiation and are considered to be released only at high temperatures.

In 1985, we ran an experiment to investigate the release of La, Ba, and Sr gaseous species from a core-concrete melt by means of a previously developed transpiration technique.\textsuperscript{1,2} The core-concrete configuration consisted of a 5-g layer of limestone chips; a 5-g layer of urania fuel granules containing $\text{La}_2\text{O}_3$, $\text{BaO}$, and $\text{SrO}$ (mol fraction of 0.01, 0.002, and 0.004, respectively); and a metal between the fuel and concrete consisting of 5-g stainless steel and 1-g zirconium chips. The core-concrete charge, about 5-cm thick, rested on a perforated tungsten plate at the bottom of a Mo-30W charge support tube. The carrier gas was ultra-high-purity helium saturated with water vapor at room temperature and had an input flow rate of 160 mL/min. The core-concrete temperature was maintained at $2385 \pm 10$ K for 132 min.

Upon completion of the run, the apparatus was cooled to room temperature in flowing helium and dismantled, and the tungsten condenser tube was

removed. The sublimates inside the condenser tube were dissolved by repeated washings with hot concentrated nitric acid. The combined washings were analyzed for the three fission products, the fuel, and other species of the core-concrete configuration (Fe, Cr, Ni, Mn, Ca, and Mg).

The core-concrete charge was found to have dropped into the bottom of the Mo-30W support tube. The perforated tungsten disc, which was supporting the core-concrete charge, had disappeared. Severe corrosion of the Mo-30W support tube was observed in the region where the core-concrete charge had been located.

The results of chemical analyses of the dissolved sublimate dissolution are given under "amount vaporized" in Table VII-1. From a knowledge of the composition of the core-concrete charge ("inventory in charge"), one can estimate the fractional release of the species in the core-concrete charge. These results are also given in Table VII-1, which shows that the trend in the measured fractional release values for the fission products follows the sequence Ba>La>Sr.

<table>
<thead>
<tr>
<th>Species</th>
<th>Amount Vaporized, (\mu g)</th>
<th>Inventory in Charge, g</th>
<th>Fraction Released</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>494</td>
<td>0.0585</td>
<td>0.008</td>
</tr>
<tr>
<td>Sr</td>
<td>16</td>
<td>0.0058</td>
<td>0.003</td>
</tr>
<tr>
<td>Ba</td>
<td>95</td>
<td>0.0060</td>
<td>0.016</td>
</tr>
<tr>
<td>U</td>
<td>4840</td>
<td>4.35</td>
<td>0.010</td>
</tr>
<tr>
<td>Fe</td>
<td>1020</td>
<td>3.6</td>
<td>0.0003</td>
</tr>
<tr>
<td>Cr</td>
<td>257</td>
<td>0.9</td>
<td>0.0003</td>
</tr>
<tr>
<td>Ni</td>
<td>1025</td>
<td>0.4</td>
<td>0.003</td>
</tr>
<tr>
<td>Mn</td>
<td>33110</td>
<td>0.1</td>
<td>0.33</td>
</tr>
<tr>
<td>Ca</td>
<td>201</td>
<td>1.62</td>
<td>0.0001</td>
</tr>
<tr>
<td>Mg</td>
<td>251</td>
<td>0.17</td>
<td>0.015</td>
</tr>
</tbody>
</table>

The high release value obtained for manganese (0.33) can be attributed to the fact that elemental manganese has a relatively low boiling point, 2314 K, compared with the values for Fe, Cr, and Ni in stainless steel.

Using the free energy of formation of the condensed phase and gaseous species (from JANAF tables) and assuming an ideal solution of \(La_2O_3\), \(BaO\), and \(SrO\) in the urania, we were able to estimate the fractional release of the three fission products and the uranium. As shown in Table VII-1, the experimental and calculated release values for La, Sr, and U are in fair agreement. The discrepancy between the measured and calculated values for barium indicates the possibility of compound formation (such as \(BaZrO_3\), \(BaSiO_3\), \(BaUO_3\), or...
BaMoO$_4$) among the components of the core-concrete melt. The stability of such compounds will be investigated by thermodynamic calculations.

The O/U ratio of the fuel was estimated from the oxygen potential model of Blackburn$^3$ and measured release values. We determined that O/U is 2.003 from the lanthanum release value, 2.005 from the uranium release value, and 2.006 from the iron release value.

X-ray diffraction analysis of the residue from the core-concrete charge revealed two major face-centered cubic (fcc) phases of lattice parameter $a = 5.42$ and 5.31, along with minor phases of Ca$_2$Al$_2$SiO$_7$ and FeSiO$_4$. X-ray fluorescence analysis showed U, Ca, Cr, and Al in the residue, as well as small amounts of Fe, Zr, and Si. The fcc phases indicate the possible formation of solid solutions: (CaO)$_2$(UO)$_2$ for $a = 5.42$ and U$_{1-x}$Zr$_x$O$_2$ ($x = 0.52$) for $a = 5.31$. Dissolution of iron in Mo–30W was indicated by a decrease in the lattice parameter of a scraping from the surface of the refractory alloy, and CaWO$_4$ was identified on the outer and inner surfaces at the bottom of the charge support tube. Firm conclusions concerning the phase relationships existing in this complex residue are difficult to make at this time.

Additional experiments are planned to investigate the temperature dependence of the release of the three fission products from the core-concrete melt.

B. Metal Fuels Properties

An assessment of the information available on the thermophysical properties of metal fuel and blanket materials for the Integral Fast Reactor (IFR) program (see Sec. VI.C) has revealed some important gaps. The data currently available have been evaluated and compiled in a handbook giving the thermodynamic, transport, and mechanical properties for metal fuels. This handbook will be used as a source of data for the IFR program and will be updated regularly as new results become available.

Because some essential data are not available, we are undertaking an experimental effort to supply them. The properties for which data are most urgently needed are thermal conductivity, thermal expansion, and solidus and liquidus temperatures. Our work in 1985 was concentrated on thermal conductivity measurements.

In another experimental effort, we tested a technique for preparing UCl$_3$ by oxidation of uranium metal with CdCl$_3$.

1. Thermal Conductivity of Metal Fuel

We obtained equipment to measure the thermal conductivity of metal fuel by a comparative (axial rod) method, which has a precision (1σ) of about 5%. (In the near future, this equipment will be installed in a glove box so that measurements can be made on plutonium alloys.) In this comparative method, a sample stack is prepared with the alloy of unknown thermal conductivity (the test material) placed between two samples of a reference material of known thermal conductivity. Two thermocouples are placed a known distance

apart in each of the reference materials in the stack. Heaters are used to establish a thermal gradient in the stack. The heat flux through the reference materials is calculated from their thermal conductivity and the temperature difference and distance between the thermocouples. Guard heaters are used to minimize radial heat losses. The heat flux through the test material is taken to be the average of the heat fluxes through the two reference samples. From this heat flux and the temperature measured by the thermocouples located in the test sample, the thermal conductivity of the test material is found. Computer software to control and monitor this experiment is also being developed.

To test the operation of this equipment, we determined the thermal conductivity of a National Bureau of Standards (NBS) stainless steel standard, using Inconel reference material. Our measured values for the thermal conductivity of the standard agreed well with NBS values in the temperature range of 598 to 1098 K. With the exception of one point (which differed by about 4%), our experimental thermal conductivities were within 2% of the NBS values. These deviations are well within the spread of data used by NBS to arrive at its recommendations. Because IFR alloys are expected to interact with stainless steel and Inconel, tantalum was evaluated as the reference material for measurements of IFR alloys. Since the existing data on thermal conductivity of tantalum are scattered, we measured the thermal conductivity of tantalum using Inconel as the reference material. A comparison of our data with available literature data for the thermal conductivity of tantalum⁴ indicated that our values are reliable.

Measurements were next undertaken on a uranium-zirconium alloy with 11.36 wt % Zr. We measured the thermal conductivity of this alloy at temperatures from 535 to 800 K, using tantalum as the reference material. The results of our measurements are in good agreement with estimated values based on the thermal conductivity values of U-5% Zr and U-20% Zr obtained by Westphal.⁵

Before proceeding to higher temperatures, we performed tests to determine the compatibility of the U-Zr sample with stainless steel coated with yttria. This coating was applied to stainless steel-clad thermocouples by use of a commercial colloidal suspension. Samples were heated to about 1250 K for three hours. The yttria-coated thermocouples performed very well and appeared to be compatible with the U-Zr. Thus, Inconel or standard stainless steel cylinders could be coated with this yttria suspension and used as references. In comparison with tantalum, the thermal conductivity of stainless steel is much closer to that of U-Zr, thus simplifying the experiments and allowing the use of a well-characterized reference material.

Future work will include measurements of thermal conductivity, thermal expansion, and solidus and liquidus temperatures for IFR alloys of interest.

2. Oxidation of Uranium Metal with CdCl₂

Our previous work on the distribution of Zr between liquid U-Zr alloy and MgCl₂-CaCl₂-BaCl₂ salt demonstrated that MgCl₂ is not an efficient oxidizer for zirconium to produce ZrCl₃. More importantly, the oxidation of uranium itself was also found to be significantly suppressed. However, it appears that, in the halide slagging steps for the IFR, the MgCl₂ in the salt might be replaced with the chloride of a less electronegative element, e.g., CdCl₂. The feasibility of this replacement was tested by performing the experiment reported below.

The principal oxidation reaction expected in the experiment can be written as

\[ 2U(\text{metal}) + 3\text{CdCl}_2(\text{salt}) \rightarrow 2\text{UCl}_3(\text{salt}) + 3\text{Cd}(\text{metal}) \]

where the salt-phase substrate is made up of the CaCl₂-BaCl₂ eutectic mixture (2:1 mol ratio). The experimental procedure was as follows. In a helium-atmosphere glove box, uranium rods (~40 g) were placed in an alumina crucible and covered with powdered CaCl₂-BaCl₂ eutectic that contained CdCl₂. The crucible was loosely covered with tantalum foil and placed in an alumina tube, which was heated to 500°C for further sample degassing. After exposure to high-purity argon, the charge was heated for 4 h at 700°C and then cooled overnight to room temperature. The product was removed from the alumina crucible by gentle tapping. The reddish-brown salt phase separated easily from the metal phase. The latter phase consisted of a frozen pool of cadmium containing partially embedded remnants of the uranium rods.

The results showed a 90% yield of UCl₃, when judged by the quantity of CdCl₂ consumed. Since the weight of the recovered metal (U and Cd) phase was somewhat less than expected from stoichiometric considerations, one can assume that small material losses occurred during the reaction. Such losses could be explained, for example, by the vaporization of CdCl₂ and Cd or by the reaction 3U + 2Al₂O₃ → 4Al + 3UO₂. With somewhat improved operating conditions, the method of UCl₃ synthesis described here could be successfully applied to a larger scale required by the IFR.

C. Fusion-Related Research

1. Studies of Tritium Breeder Materials

A critical element in the development of the fusion reactor is the blanket for breeding tritium fuel. Within the blanket, neutrons from the fusion plasma will react with lithium to breed tritium. We are conducting several studies with the objective of determining the feasibility of using lithium-containing ceramics as breeder material.

a. Effects of Protium Purging and Surface Adsorption

In a computational study, we are assessing the tritium release achieved by applying a protium-purge gas stream (in the form of gaseous H₂ and H₂O) to three candidates for the ceramic tritium breeder (LiAlO₂, Li₂O, and Li₄SiO₄). Control of oxygen activity requires control of both the H₂ and the
H₂O content of the purge gas because the H₂O:H₂ ratio defines the oxygen activity. The protium-purge effect has been examined for the three breeders at two temperatures (900 and 1300 K) and two extreme ratios of H₂O:H₂ (100:1 and 1:100). Each breeder system was treated as containing 10⁻⁴ g-atoms tritium, with a volume of breeder material equal to that of 1 mol Li₂O and with 15 vol % gas phase.

Figures VII-3 and -4 summarize the findings for the tritium content of the gas phase for the three breeders at temperatures of 900 and 1300 K, respectively. In these figures, OX and RED refer to the oxidized (HTO and T₂O) and reduced (HT and T₂) forms, respectively, of the gaseous species; LA, LO, and LS refer to LiAlO₂, Li₂O, and Li₄SiO₄, respectively. The H₂O:H₂ value of 100:1 corresponds to an oxygen activity of 1.0 × 10⁻¹⁹ at 900 K and to 7.4 × 10⁻¹¹ at 1300 K. For the 1:100 ratio, the oxygen activities are 1.0 × 10⁻²⁷ at 900 K and 7.4 × 10⁻¹⁹ at 1300 K. For each ratio, at least three orders of magnitude of hydrogen activity are covered.

The calculations presented in Figs. VII-3 and -4 suggest that both Li₂O and LiAlO₂ release more tritium at 900 K than at 1300 K, in either the oxidized or reduced form and at either H₂O:H₂ ratio. However, for Li₄SiO₄, the calculations suggest slightly greater tritium release at 1300 K than at 900 K for both H₂O:H₂ ratios. At a given temperature and for a given breeder material, the total amount of tritium released is greater at the lower oxygen activity.
activity, and the reduced form is preferred. For both temperatures, the most tritium is released from LiAlO₂, and the least from Li₄SiO₄. Thus, the predicted performance of the candidate breeder materials under protium purge conditions can be ranked as LiAlO₂ > Li₂O > Li₄SiO₄. This is also the ranking found earlier for the systems in the absence of a protium purge.⁶

The slopes of the curves are indicative of the enhancement of tritium release with protium purging. The release of tritium, at a fixed oxygen activity, is affected only slightly in some cases and moderately in others as the amount of protium increases. In all cases but one, the H:T ratio across a given curve increases by a factor of at least 30 (values not shown in figures), yet the gain in released tritium in most cases is less than a factor of ten, and barely a factor of two in some. Examination of the H:T ratios also leads to the conclusion that a smaller quantity of protium in the form of H₂ at low oxygen activity is more effective in releasing tritium than is a larger quantity of protium in the form of H₂O at a higher oxygen activity.

The inventory of tritium that is related to the solid breeder consists of a contribution not only from solubility in the bulk material, but also from adsorption on the surface. We made a preliminary estimate of the amount of water adsorbed on LiAlO₂ surfaces, assuming an enthalpy of adsorption of -25 kcal/mol, an entropy of adsorption of -30 cal/mol-K, and a sample surface area of 1 m²/g. We calculated values of the fractional monolayer coverage on the LiAlO₂ at temperatures of 700-1300 K and oxygen activities of 10⁻²⁵ to 10⁻⁵.

At 700 K, there is a buildup of 0.24 monolayer, a coverage that is independent of oxygen activity over the 10⁻²⁵ to 10⁻⁵ range. At 1000 K, the coverage is 0.012 monolayer at 10⁻²⁵ oxygen activity and is constant at 0.042 monolayer for oxygen activity ≥10⁻²⁰. At 1300 K, the coverage is 0.0001 to 0.0057 monolayer, becoming constant at the latter value for oxygen activities ≥10⁻¹⁵. The 0.24 coverage constitutes 89% of the entire system's inventory of tritium, whereas the 0.0001 value represents only 0.034%. Higher temperature favors less adsorption, but the actual magnitude is sensitive to oxygen activity, becoming less at lower oxygen activity. At the lowest temperature, there is substantial adsorption, which shows little variation with oxygen activity.

The results from our calculations of protium purging and surface-adsorption effects have been useful in understanding several observations from the TRIO experiment—a test of in situ tritium recovery.⁷ These include the observed dominance of HT as the released species, the promotion of tritium release by addition of protium to the purge gas, and the pronounced diminution of release when oxygen was added to the purge gas.

Experiments are currently in progress to provide measured values for the thermodynamic variables related to adsorption of H₂O or H₂ on LiAlO₂ and to provide information on the kinetics of the adsorption-desorption process.

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The frontal analysis version of gas chromatography (also known as the "breakthrough technique") is being used to gather data for the adsorption/desorption isotherms. Since the experimental temperatures of interest are higher than the ones available in commercial gas chromatography instruments, we designed and constructed a high-temperature gas chromatograph. A special feature of the instrument is the provision for making periodic measurements of the sample surface area by the BET method. Isotope effects related to adsorption/desorption can also be studied because of the provisions for $D_2O$ and $D_2$ streams to be mixed with the carrier gas.

b. Tritium Transport and Inventory Issues in Ceramic Breeders

An important observation from the TRIO experiment was that the presence of a small amount (~1000 ppm) of $H_2$ gas in the helium carrier gas significantly improved tritium release from the $\gamma$-LiAlO$_2$ breeder material. The chemical form of the released species was found to be predominantly HT. These results suggest that more than one process may be responsible for tritium transport and release from $\gamma$-LiAlO$_2$. Many possibilities have been conjectured, among which are bulk diffusion and surface processes. We have constructed a model for tritium release from $\gamma$-LiAlO$_2$ that includes an accounting of $H_2$ adsorption, surface reaction between $H_2$ and $T$ arriving onto the breeder surface from the interior of the solid, and the final desorption step in which HT (the observed dominant species) leaves the breeder material.

Using this model and data from the TRIO experimental runs with hydrogen in the carrier gas, we were able to deduce an effective desorption rate constant, $k_{\text{eff}}$ (units of centimeters per second), for HT. This $k_{\text{eff}}$ is dependent on the $H_2$ partial pressure over the $\gamma$-LiAlO$_2$ breeder material, the temperature, and other details of the dominant surface processes leading to the desorption of HT from the surface. Using this rate constant together with the bulk diffusion coefficient determined by Clemmer et al., we analyzed the relative importance of surface processes versus bulk diffusion in determining the tritium inventory at temperatures of 733-1430 K and two hydrogen concentrations in the carrier gas (3 ppm and 1000 ppm).

The model calculations are presented in Fig. VII-5 in terms of a convenient dimensionless parameter, $\alpha$, which measures the relative importance of the two contributions:

$$\alpha = \frac{5D}{a k_{\text{eff}}}$$

where $a$ is the effective diffusion distance, and $D$ is the effective bulk diffusion coefficient for tritium. For a hydrogen concentration of 3 ppm and temperatures of 973 and 873 K, the values of $\alpha$ are much larger than unity ($\alpha = 285$ and 56, respectively). This result is consistent with surface processes being the rate-limiting step in tritium release. The results for a hydrogen concentration of 1000 ppm (the amount used in most of the TRIO experimental runs) are interesting. At 1273 K ($\alpha = 24$), surface processes are

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still rate limiting. At 973 K (α = 0.85), both surface and diffusion processes are comparable. At 873 K (α = 0.17), diffusion processes are becoming important, but surface phenomena are certainly not negligible. At 773 K (α = 0.02), diffusion processes are definitely dominant.

In evaluating the TRIO data, we have selected the reasonable criterion that, when one process is slow enough to contribute 10% or more of the total inventory, then that process is the dominant one. In terms of this criterion, when α is between 0.1 and 10, both surface and bulk processes need to be considered as making important contributions to the tritium inventory. If α is less than 0.1, then bulk diffusion is the dominant process; if α is greater than 10, then surface processes are much more important. In the rectangle ABCD of Fig. VII-5, the lines AB and DC represent α = 10 and α = 0.1, respectively. The two vertical lines AD and BC represent the temperature limits of the TRIO experiment (973 and 773 K). A value of α inside ABCD indicates that neither surface nor bulk processes can be neglected. Thus, within the temperature regime of TRIO, one is passing through a transition where, at lower temperatures, diffusion is the rate-limiting step, whereas neither process is dominant at higher temperatures.

c. Improved Thermal Conductivity

Concerns have been expressed about the possible fracturing of a lithium-containing ceramic breeder under relatively low stress levels and its consequent degradation in thermal response. The "sphere-pac" configuration (i.e., packed spheres of the breeder material) provides a possible solution to
these problems. However, for the present sphere-pac breeder design, the effective thermal conductivity is significantly lower than that of the corresponding solid-component configuration. We are investigating a concept that should lead to an enhancement of thermal conductivity for materials of a sphere-pac configuration.

Because breeder blanket systems must be tritium self-sufficient (i.e., tritium breeding ratios >1.0), consideration must be given to the fact that, for most solid breeder materials, the addition of neutron multipliers (e.g., Be, BeO) is necessary. In the current sphere-pac configuration, the neutron multiplier is randomly introduced into the blanket in the form of spheres similar to those of the breeder material. We are investigating another configuration in which the conductive component (BeO) is introduced into the sphere-pac bed of breeder material (γ-LiAlO₂), giving rise to improved thermal conductivity. With this new configuration, the solid spheres are coated by a layer of the BeO with appropriate thickness.

Using various effective medium theories, we calculated the thermal conductivity of the two types of sphere-pac beds (coated spheres and randomly mixed spheres). The relative volume fraction of BeO for the two beds was assumed to be the same (0.1-0.2), and both beds were assumed to be under a helium atmosphere. The spheres were given a diameter of 1200 μm, a value that is typical for a coarse sphere-pac bed from fission reactor experience.

Plotted in Fig. VII-6 is the calculated thermal conductivity for the two sphere-pac bed configurations. Throughout the temperature range of 700-1300 K, the enhancement in effective thermal conductivity (K_bed) is between 22% and 30% for the coated-sphere bed; the thermal conductivity for both sphere-pac beds increases with temperature, the coated-sphere bed somewhat less rapidly at T > 1000 K. In general, the bulk thermal conductivity of a gas increases with increasing temperature, whereas, for a solid, it usually decreases with increasing temperature. Thus, the temperature dependence of the thermal conductivity for a sphere-pac bed immersed in an inert gas reflects a competition between these two opposing trends. The thermal behavior of the coated-sphere configuration indicates that the contribution from the solid component becomes increasingly important at a relatively low temperature. This behavior has been observed in sphere-pac beds of UO₂ and ThO₂.

We concluded from our analysis that a significant enhancement in the thermal conductivity of the sphere-pac bed is possible with this new configuration.

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11J. P. Moore, R. J. Dippenaar, R. O. A. Hall, and D. L. McElroy, Thermal Conductivity of Powders with LiO₂ or ThO₂ Microspheres in Various Gases from 300-1300 K, Oak Ridge National Laboratory, ORNL/TM-8196 (June 1982).
2. Reactor Design Studies

Fusion reactors have been proposed as commercial energy sources for baseload electrical power. At present, the tokamak reactor, which uses toroidal magnetic fields to confine a thermonuclear plasma, is the most advanced fusion design. In a tokamak, the vacuum boundary of the plasma is called the first wall; behind it are two layers, a shield and a breeder blanket, wherein fusion neutrons react with lithium to generate tritium and heat. The tritium is used as fuel for the reactor, and the heat is used to generate power. Most commercial reactor designs use the tokamak concept.

For fusion to be attractive as a commercial energy source, an order of magnitude improvement in the total reactor cost per kilowatt-hour is needed. The goal of our present fusion design studies is to determine which design concepts have the potential to achieve a significant performance improvement without an increase in the total capital and operating costs of the reactor.

We made two design assessments this year: (1) the technical and economic benefits associated with the use of polarized fuels in a deuterium-tritium reactor and (2) the technical benefits of employing high-temperature, high-pressure helium as a heat transfer medium. The advantages expected in using polarized fuels are a 50% increase in plasma reactivity, improved control of the spatial distribution of the neutrons, and a reduction in the size of the confining magnets. With high-pressure helium as a coolant, a higher reactor power efficiency is expected.

In the assessment for polarized fuels, two types of reactors were considered: (1) a reactor with a moderate radius, a conventional plasma
design, and a magnetic field of 11.1 Tesla and (2) a reactor with a small radius, an advanced plasma design, and a magnetic field of 6 Tesla. We made a comparison of these two reactor concepts both with and without polarized fuel. Because the radius of a reactor significantly affects the cost of the toroidal field magnets, these two reactor concepts provided a means of separating the size effect from effects attributable to the use of polarized fuels.

A conclusion from the assessment was that capital costs for the magnets were projected to decrease by $40M for reactor concept 1 and $4M for reactor concept 2 when polarized fuel was used. In addition, capital costs for the system that drives the current in the plasma were reduced by $15M and $5M, respectively. These savings were the same order of magnitude as the projected capital costs of producing polarized fuel ($30M and $15M, respectively). Therefore, to improve the economic attractiveness of polarized fuels, inexpensive methods of producing and storing them would have to be developed. The neutronic benefits of polarized fuel were a smoothing of the spatial distribution at different nuclear responses and a reduction in the total nuclear heating for the first wall by 8%.

The main conclusion from this assessment was that the primary value of polarized fuels is as a design option that can be used if a required plasma condition cannot be attained with other operating modes.

In the high-pressure helium assessment, we determined the effect of higher operating pressures (~150 atm vs. ~50 atm) on a helium-cooled first wall and solid breeder blanket.

In the first wall, high-pressure helium coolant was assumed to improve the heat transfer characteristics of the steel structure so that heat fluxes up to 1 MW/m² can be withstood. We analyzed a range of flow-induced frequencies (0.1, 0.2, and 0.4 Hz) for the coolant path of a helium-cooled first-wall design. The results showed that, at 0.1 Hz (the worst case considered), the temperature oscillation in the helium coolant is of the order of 60°C, which corresponds to a material strain of 0.12%. Thus, when the characteristic frequency is ≥0.1 Hz, fatigue will not be a problem for a helium-cooled first wall.

The major benefits from high-pressure operation in the blanket are reduced pumping power losses (88% reduction) and a reduced coolant velocity (40-60% reduction). However, high-pressure operation requires thicker coolant channels and vessel walls, which would lower the breeder material fraction and thereby reduce the breeding ratio.

The maximum thermal efficiency achieved at 150 atm and 650°C in the first-wall/blanket system is 31.4%. This is only moderately better than the 25.4% achieved at 50 atm and 650°C. To obtain higher thermal efficiencies requires a higher operating temperature, 973-1273 K (700-1000°C). However, current material technology limits the acceptable operation temperature below this range. If there are no improvements in material technology, then only marginal gains would be achieved by using helium-coolant pressures above 80 atm.

The two concepts assessed this year did not provide a significant reactor performance improvement. We will continue to investigate promising design concepts.
3. **Dosimetry and Damage Analysis**

Materials are being tested in a variety of facilities to simulate the damage expected from the high fluxes of energetic neutrons in a fusion reactor. Our objective is to characterize these irradiation facilities in terms of measured neutron fluence and energy spectra as well as calculated damage parameters (such as atomic displacements, gas production, and other transmutations) and to routinely provide experimenters with exposure data for materials irradiations. The ultimate goal of this work is to correlate materials property changes between different facilities and to predict materials performance in fusion reactors.

Neutron measurements and damage calculations are performed for irradiations in the High Flux Isotopes Reactor (HFIR) and the Oak Ridge Research Reactor (ORR), both located at Oak Ridge National Laboratory; the Omega West Reactor at Los Alamos National Laboratory; the Rotating Target Neutron Source (RTNS) II at Lawrence Livermore National Laboratory; and the Intense Pulsed Neutron Source at ANL. In each case, dosimeter packages consisting of small wires and foils are irradiated with materials specimens. Neutron activation products are then analyzed by gamma spectroscopy, and the results are used to adjust calculated neutron energy spectra. These spectra are employed to calculate damage induced in various materials using SPECTER—a comprehensive computer code that we have developed for the routine calculation of atomic displacements and their recoil energy distributions, gas production, and total energy deposition. These data are then provided to experimenters at various laboratories in the U.S. and Japan by means of DOE quarterly reports and access to our DOSFILE computer program on the Magnetic Fusion Energy (MFE) computer network.

The reliability of our neutron measurements depends on our knowledge of neutron activation cross sections. Consequently, a key part of our program is the determination of these cross sections. Integral and differential neutron measurements are performed at Argonne and other facilities, and the results are used to establish new reactions and to adjust poorly known or discrepant nuclear data. We are especially interested in the production of very long-lived radioisotopes in fusion reactors for dosimetry as well as waste-material assessments. After being irradiated near 14 MeV, the activated materials are analyzed by a variety of techniques, including gamma spectroscopy, radiochemistry, and the relatively new technique of accelerator mass spectrometry. We have determined production cross sections for the \((n,2n)\) reactions on \(^{27}\text{Al}\) and \(^{54}\text{Fe}\) to form \(^{26}\text{Al}\) (7.3 x 10^5 y) and \(^{53}\text{Mn}\) (3.7 x 10^6 y) and the \(^{94}\text{Mo}(n,p)\) reaction to form \(^{94}\text{Nb}\) (2.0 x 10^4 y). Measurements are in progress with other isotopes such as \(^{92}\text{Nb}, \(^{59}\text{Ni}, \) and \(^{55}\text{Fe}.\)

Helium production is considered to be important in fusion irradiations because the 14-MeV neutrons will produce high levels of helium via \((n,\alpha)\) reactions in an operating fusion reactor. This is not the case in conventional fission reactors and, hence, several changes are required to enhance the helium production in these reactors. In mixed-spectrum reactors such as HFIR and ORR, the thermal neutrons react with \(^{58}\text{Ni}\) to form \(^{59}\text{Ni},\) which has a high helium-production cross section. As the \(^{59}\text{Ni}\) builds up with time, we can thus irradiate nickel-bearing materials (such as stainless steel) to the desired ratio of helium production to atomic displacements. In collaboration with Rockwell International, we discovered a similar effect in copper. Radiometric and helium analyses of irradiated copper specimens established that \(^{63}\text{Cu}\) captures a
thermal neutron to form $^{64}$Cu, which rapidly decays to $^{64}$Zn, which is then converted to $^{65}$Zn. The $^{65}$Zn has a large thermal cross section (4.7 ± 1.5 barns) for the formation of helium. Our measurements on numerous samples have established the cross sections for each step in this chain, permitting the routine prediction of helium generation in materials experiments.

Figure VII-7 shows helium production in copper as a function of thermal neutron fluence in HFIR. The measured data show an exponential growth typical of multistep reactions, which clearly exceeds the usual fast-neutron prediction. There is excellent agreement between the measured data and predictions from our new model based on neutron cross-section measurements.

![Figure VII-7](image)

Although the helium production with irradiated copper is less pronounced than that with nickel (since three reactions are involved rather than only two), copper irradiation enhances the helium level by an order of magnitude in less than a year in high-flux reactors such as HFIR. This enhanced helium production will be useful for simulating fusion-like gas production in copper- or zinc-bearing materials. We have also compared measurements and calculations of helium production in many other materials irradiated in reactors and accelerator-based neutron sources and have shown that significant discrepancies exist in fast-neutron helium cross sections for Cu and Ti.

We will continue to provide dosimetry measurements and damage calculations to the fusion materials community. At present, we have about a dozen different experiments in progress, mainly in HFIR, and several more are now being planned. Our neutron cross-section work will provide new data for improved assessments of radiation damage in materials, and we will continue to develop our computer codes for neutron spectral adjustment and radiation damage calculations.
VIII. BASIC CHEMISTRY RESEARCH

Basic chemistry research is being pursued in several different areas—new catalysis mechanisms in the areas of catalytic hydrogenation and catalytic oxidation; materials chemistry for liquids and vapors at high temperature; interfacial processes of importance to corrosion science, surface science, and catalysis; the thermochemistry of zeolites and related silicates; and the geochemical processes responsible for trace-element migration within the earth's crust.

A. Fluid Catalysis

This research is designed to explore new catalysis mechanisms in the areas of catalytic hydrogenation and catalytic oxidation. Currently under investigation is the mechanism by which oxides promote carbon monoxide and carbon dioxide hydrogenation. We are now able to describe the first soluble oxide catalyst system for carbon monoxide hydrogenation and all of the reactions by which a key formate intermediate is converted to methanol. Also investigated is the concept of utilizing organic bases as oxygen carriers in air separation and in controlled oxidation processes. Tested in this period was the catalytic air oxidation of an olefin mediated by a tertiary amine.

1. Catalytic Hydrogenation

Earlier experiments conducted in this laboratory demonstrated that well-defined transition metal mononuclear complexes, $\text{HCo(CO)}_4$ and $\text{HMn(CO)}_5$, are capable of catalyzing the hydrogenation of carbon monoxide in solution. Studies of the kinetics of these metal carbonyl systems have suggested that catalysis occurs by a mechanism involving homolytic splitting of hydrogen followed by successive hydride migrations to coordinated carbon monoxide, forming formyl and formaldehyde complexes. (Dombek\textsuperscript{1} reviewed our work and that of others on the mechanism of the homogeneous metal-carbonyl-catalyzed reaction.) An important question concerning this mechanism is: does it have relevance to the carbon monoxide hydrogenation chemistry occurring on the metal oxide surfaces of the commercial methanol synthesis catalysts (supported CuO/ZnO)? The answer to this question is far from clear, since the catalytic chemistry of the metal oxides (CuO and ZnO) would be expected to be fundamentally different from that of the neutral metal carbonyls. Oxide is virtually the antithesis of the soft polarizable ligands of choice for stabilization of the coordinated carbon monoxide, formyl, and formaldehyde complexes evident in catalysis by the metal carbonyls.

We have found a possible answer to the above question through our research on catalysis of the reaction converting carbon monoxide and water to alcohols. In this work, we demonstrated for the first time that a variety of metal oxides (MO) catalyze the conversion of formate to methanol, i.e.,

$$\text{MO}\quad 4\text{CO}_2\text{CH}^- \rightarrow \text{CH}_3\text{OH} + \text{CO} + 2\text{CO}_2^- \quad (\rightleftharpoons 2\text{CO}_2 + 2\text{O}^{2-})$$  (1)

In contrast to the low stabilities expected for carbonyl, formyl, and II-formaldehyde on metal oxide surfaces, formate ion is stable enough to have been observed spectroscopically on ZnO surfaces when exposed to hydrogen and carbon monoxide at high pressures. From the standpoint of reactivity, formate ion, at least under some conditions, is reactive enough to be involved in the highly active commercial catalyst system. For example, in the presence of PbO (suspended in a slurry of molten alkali metal formate salt), the reaction in Eq. 1 produces methanol from formate at a rate comparable to that for production of methanol from CO and H₂ using the CuO/ZnO catalyst.

Our earlier work with formate chemistry in molten formate salt slurries encouraged us to seek soluble organometallic formates and oxides so that solution kinetic and spectroscopic techniques could be focused on the chemistry involved. As a result of these efforts, the mechanism by which a soluble oxide, hexamethyldisiloxane (Me₃SiOSiMe₃), promotes carbon monoxide hydrogenation can now be described.

Methanol synthesis occurs as a result of formate-formation and disproportionation reactions:

\[ \text{Me}_3\text{SiOSiMe}_3 + \text{H}_2 + \text{CO} + \text{CO}_2 \rightarrow 2\text{Me}_3\text{SiO}_2\text{CH} \]  \hspace{1cm} (2)

\[ 4\text{Me}_3\text{SiO}_2\text{C} \rightarrow 2\text{Me}_3\text{SiOSiMe}_3 + \text{CH}_3\text{OH} + 2\text{CO}_2 + \text{CO} \]  \hspace{1cm} (3)

which occur in dioxane solution at temperatures near 250-300°C and pressures near 270 atm. Most of our efforts in the past year were focused on the mechanism of the formate disproportionation reaction (Eq. 3), which was investigated by heating Me₃SiO₂CH in organic solvents. Our initial attention was focused on the determination of reactive intermediates, whose identities and modes of growth and decay during the course of the reaction would ultimately allow us to describe the reaction mechanism. We found that the intermediates present at high enough concentrations to be observed with gas chromatography or gas chromatography/mass spectrometry are Me₃SiH, Me₃SiOCH₂OSiMe₃, CH₃O, and CH₃O₂CH. Once the intermediates were identified, possible reactions of the intermediates with other species present could be tested. Our results are consistent with the following pathway:

\[ \text{Me}_3\text{Si}-\text{O}_2\text{CH} \rightarrow \text{Me}_3\text{SiH} + \text{CO}_2 \]  \hspace{1cm} (4)

\[ \text{Me}_3\text{SiH} + \text{Me}_3\text{Si}-\text{O}_2\text{CH} \rightarrow \text{Me}_3\text{Si}-\text{OCH}_2\text{O-SiMe}_3 \]  \hspace{1cm} (5)

\[ \text{Me}_3\text{Si}-\text{OCH}_2\text{O-SiMe}_3 \rightarrow \text{CH}_2\text{O} + \text{Me}_3\text{Si-0-SiMe}_3 \]  \hspace{1cm} (6)

\[ 2\text{CH}_2\text{O} \rightarrow \text{Me}_3\text{Si-0-SiMe}_3 \rightarrow \text{CH}_3\text{O}_2\text{CH} \]  \hspace{1cm} (7)

\[^2\text{J. W. Rathke and R. J. Klingler, Logos 1(2), 2-7 (1984).}\]
Each of the proposed steps was independently verified to occur. Indeed, some of the reactions were shown to be reversible, at least under forcing conditions (i.e., elevated temperature and pressure); these include the decarboxylation reaction in Eq. 4, the formaldehyde disproportionation reaction in Eq. 7, and the net result of Eqs. 4-7:

$$4\text{Me}_3\text{SiO}_2\text{CH} \rightleftharpoons \text{CH}_3\text{O}_2\text{CH} + 2\text{CO}_2 + 2\text{Me}_3\text{SiOSiMe}_3$$

Equilibration was confirmed in each case by establishing that the same equilibrium constant is achieved when equilibrium is approached from the forward and reverse directions. The test results for equilibration of the reaction in Eq. 9 are shown in Fig. VIII-1. We are in the process of determining the energetics of the reversible steps by measurement of the temperature variation of the equilibrium constants for trimethylsilyl and other silyl and stannyl analogs.

The slowest step in the disproportionation of trimethylsilyl formate is the decarbonylation of methyl formate (Eq. 8). This step is slow enough that the reaction in Eq. 9 (and, thus, all the reactions in Eqs. 4-7) reaches equilibrium before the methyl formate is completely decarbonylated.

![Fig. VIII-1. Reversible Formate Disproportionation in Dioxane Solution at 250°C](image)
The rate of trimethylsilyl formate consumption (which determines the rate of methyl formate formation by Eq. 9) is first order, as is evident from the linearity of the plots shown in Fig. VIII-2. The equilibrium constant for the reaction in Eq. 9 is large enough that the effect of its back-reaction on the rates is negligible, except at very high conversions (more than three half-lives of reaction). We now have substantial evidence that the rate-limiting step in trimethylsilyl formate consumption is the decarboxylation step (Eq. 4). Besides the first-order dependence on $\text{[Me}_3\text{SiO}_2\text{CH]}$, key facts supporting rate-limiting decarboxylation are (1) the equivalence of the rate of $\text{Me}_3\text{SiO}_2\text{CH}$ consumption with an estimated value for the rate of decarboxylation, (2) the presence of a significant deuterium kinetic isotope, indicating that C-H bond breakage occurs in the rate-determining step, (3) the observation that the reaction in Eq. 4 does not reach equilibrium (at least until the reaction in Eq. 9 is equilibrated), indicating that decarboxylation is slower than the step following it, and (4) the observation that a catalyst (zinc phthalocyanine) which promotes the reaction in Eq. 4 also accelerates methyl formate formation in the system.

![Fig. VIII-2.](image)

First-Order Rate Plots for the Disproportionation of Trimethylsilyl Formate in Dioxane Solution

Further efforts in the area of carbon monoxide hydrogenation using soluble oxides will focus on the formate generation step (Eq. 2), for which we hope to determine how $\text{H}_2$, $\text{CO}$, and $\text{CO}_2$ are activated by the oxide.

2. **Catalytic Oxidation**

We are undertaking fundamental chemistry studies that test the concept of employing an organic base (e.g., an amine or sulfide), in the presence of a dioxygen activation catalyst, as an oxygen carrier system. This new type of oxygen carrier may have potential applications in air separation or controlled aerobic oxidation processes. In this concept, the role of the base $\text{B}$ is to reversibly bind oxygen to form an organic oxide adduct ($\text{B-O}$, which may be an amine oxide or a sulfoxide). The function of the catalyst is to improve the kinetics of the oxygen binding process:
Consequently, equilibration can occur rapidly at moderate temperatures and pressures. Oxygen carriers based on this approach are expected to achieve higher oxygen capacities than attainable with conventional metal complex carriers because of the comparatively low equivalent weight of organic bases. In addition, since the oxygen activation and storage functions are located separately in these new oxygen carriers, participation of unstable metallo-dioxygen adducts (which often lead to irreversible oxidation processes in oxygen carriers based on metal complexes) can be minimized or avoided entirely. This characteristic may result in improvements in long-term stability.

a. Air Separation

Pure oxygen is used for a variety of large-scale (steel refining, coal gasification) and small-scale (aircraft and medical oxygen systems) technologies. The main consumer of pure oxygen (15 million tons in 1984) is the steel industry. Although the current physical separation method (which involves the liquefaction and distillation of air) has been refined to a high degree, separation methods involving oxygen carriers can be advantageous in cases where compactness or mobility is required. Adaptation of oxygen carriers to large-scale air separation may also be possible, although present oxygen carriers have high cost and lack long-term stability.

Separation of oxygen from air can be accomplished by alternate charge (driving Eq. 10 to the right) and discharge (driving Eq. 10 to the left) of the oxygen carrier; in turn, the cycling process can be induced by alternating pressure and/or temperature changes. The equilibrium in Eq. 10 should not lie too far in either the forward or reverse directions in order that substantial conversion can occur from either direction in response to relatively small changes in oxygen partial pressure. The equilibrium constant ($K_p$) is related to the oxygen partial pressure ($P$) by the equation:

$$K_p = \frac{[B-0]^2}{[B]^2 P_{O_2}}$$

Thus, with an equilibrium constant of 5.0 atm$^{-1}$, the concentrations of $B$ and $B-0$ will be equal at an ambient oxygen partial pressure of 0.2 atm. Although maximum oxygen capacity is achieved with slightly larger $K_p$ values, a value near 5.0 atm$^{-1}$ at 25°C is a satisfactory target at this stage of the research. To achieve this equilibrium constant, our estimates indicate that the bond enthalpy in $B-0$ should be close to 68 kcal/mol.

A collaboration between us and the National Institute for Petroleum Energy Research has resulted in the first calorimetric determination of the N-0 bond enthalpies in amine-N-oxides. The value for pyridine-N-oxide was found to be 70 kcal/mol. Preliminary measurements on trimethylamine-N-oxide indicated that its bond enthalpy is also close to this value. Since the experimental values are close to the 68-kcal/mol target, these compounds are good candidates for testing reversible oxygen binding. However, autoclave
experiments on trimethylamine indicated that, under conditions where oxidation is rapid and selective for trimethylamine-N-oxide production, the equilibrium constant for the reaction with molecular oxygen is too large to demonstrate reversibility. Future efforts in this area will focus on trimethylamine and pyridine analogs containing functional groups designed to slightly decrease the N-O bond enthalpies.

b. Controlled Oxidation

The purpose of this research is to test the feasibility of using organic base oxygen carriers in the presence of catalysts to control the aerobic oxidation of desired substrates. The concept is based upon the expectation that transfers of single oxygen atoms to organic moieties (S) as illustrated in Eq. 12

\[
\text{Catalyst} \quad \text{B-O + S} \xrightarrow{} \text{B + S-O}
\]

may avoid some of the difficulties encountered when attempts are made to transfer oxygen from metallo-dioxygen intermediates. Note that the overall process (combining Eq. 10 with Eq. 12) is catalytic in organic base (R consumed in Eq. 10 is regenerated in Eq. 12). Since both oxygen atoms in molecular oxygen are transferred to the substrate, the system corresponds formally to a dioxygenase in biological systems. It is also noteworthy that bases whose corresponding oxides have oxide bond enthalpies close to 68 kcal/mol are ideal candidates for the air oxidation of substrates. Oxides with weaker bonds would be more powerful oxidants but cannot be formed in appreciable concentrations from molecular oxygen. Conversely, oxides with stronger bonds can be produced in high concentrations but will be weaker oxidants.

To verify the concept of using organic base oxygen carriers for controlled oxidation, we are studying a test case which involves both trimethylamine oxidation and osmium tetroxide-catalyzed transfer of oxygen from trimethylamine-N-oxide to cyclohexene:

\[
2\text{Me}_3\text{N} + \text{O}_2 \rightleftharpoons 2\text{Me}_3\text{N-O}
\]

\[
\text{Me}_3\text{N-O} + \text{H}_2\text{O} + \text{OsO}_4, \text{Me}_3\text{N} \xrightarrow{} \text{Me}_3\text{N-OH}
\]

Note that trimethylamine and cyclohexene correspond to B and S in Eqs. 11 and 12. The overall reaction attempted in the catalytic hydroxylation of cyclohexenes employing molecular oxygen as oxidant is illustrated by

\[
2\text{H} + 2\text{H}_2\text{O} + \text{O}_2 \xrightarrow{\text{OsO}_4, \text{Me}_3\text{N}} 2\text{OH}
\]
Figure VIII-3 shows the results of carrying out the reactions in Eqs. 13 and 14 simultaneously under temperature and pressure conditions selected to allow both reactions to proceed at moderate rates. As can be deduced from the figure, added trimethylamine-N-oxide is rapidly converted to trimethylamine whose concentration remains at a relatively high steady-state level as further reaction proceeds. A possible explanation for this behavior is that the amine oxidation step in Eq. 13 is rate limiting for the overall oxidation process. In confirmation of this explanation, we found that the rate for the reaction in Eq. 13, determined in a separate experiment in the absence of OsO₄ and cyclohexene, is 0.04 M-h⁻¹. This value compares well with the average rate of cyclohexanediol formation in Fig. VIII-3 (time = 0-8 h) of about 0.03 M-h⁻¹. The catalytic effect of trimethylamine (and trimethylamine-N-oxide which is converted to it) on the overall reaction in Eq. 15 is also confirmed in the experiment illustrated in Fig. VIII-3. During the reaction, 4.3 moles of cyclohexanediol were produced for each mole of added trimethylamine-N-oxide, and 130 moles of diol were produced for each mole of added OsO₄.

We are encouraged by the preliminary results thus far and expect that the method (with improvements) may be applicable to the broader areas of olefin hydroxylation, epoxidation, and Wacker synthesis of aldehydes. We also have reason to believe that the method may be applicable to alkane oxidations. Future efforts in this area will focus on investigating the catalytic chemistry associated with the amine oxidation step and on improving the stability of amines toward undesired oxidation processes at high temperatures and pressures.
B. High-Temperature Materials Chemistry

Our goal for this effort is to perform experimental and theoretical studies that lead to a fundamental understanding of materials chemistry at high temperatures. Our focus has been largely on associated and ordered solutions such as chloroaluminates, silicates, and "ionic" alloys.

1. Ab Initio Quantum Mechanical Calculations of Molten-Salt Complexes

We are investigating the possibility of using ab initio molecular orbital theory for predicting the vibrational frequencies of species in molten salts. Ab initio molecular orbital calculations at the Hartree-Fock level allow one to predict harmonic vibrational frequencies of molecules; in general, these calculated frequencies are approximately 10-15% higher than the observed anharmonic vibrational frequencies. This degree of accuracy is often very useful in assigning vibrational frequencies in the observed infrared and Raman spectra of gas-phase molecules and in calculating thermodynamic properties.

Since the vibrational frequencies of AlCl$_4^-$ in a melt of aluminum chloride and alkali halide do not appear to be greatly perturbed by the alkali cation, one would expect the frequencies of AlCl$_4^-$ to be similar to those of the gas-phase anion. To test whether ab initio molecular orbital methods predict the vibrational frequencies of anions in melts, we employed a large basis set with d-orbitals$^3$ to calculate the harmonic frequencies of AlCl$_4^-$ and compared the results to the observed frequencies for AlCl$_4^-$ in aluminum chloride/alkali chloride melts.

Hvistendahl et al.$^4$ determined that the Raman spectra of molten AlkAlCl$_4$ (Alk = Li, Na, K, Rb, Cs) have bands at approximately 349, 120, 485, and 180 cm$^{-1}$. Our calculated vibrational frequencies for AlCl$_4^-$ are $\omega(A_1) = 353$ cm$^{-1}$, $\omega(E) = 121$ cm$^{-1}$, $\omega(F_2) = 510$ cm$^{-1}$, and $\omega(F_3) = 192$ cm$^{-1}$, in good agreement with the observed bands. We also calculated the frequencies of four other anions (AlF$_4^-$, BF$_3^-$, BeF$_2^-$, MgCl$_2^-$) and seven related neutral species (AlF$_3$, AlCl$_3$, BeF$_3$, BeF$_2$, BeCl$_2$, MgF$_2$, MgCl$_2$), which already had most of their vibrational frequencies assigned. For the complete set of anions and neutral species, the average absolute deviation was about 9%, which is somewhat better than expected for ab initio calculations. The good agreement between the predicted and observed frequencies suggests that predictions for related anions such as AlCl$_3$O$_2^-$, AlF$_5^-$, AlCl$_7^-$, and S$_3^-$ could be useful in assigning the bands of these species in melts and in making a reasonable estimate of their thermodynamic properties. Further work will involve application of this technique to anions for which frequencies are not known, as well as continued testing of the technique on anions and neutral species for which frequencies have been previously assigned.

In continuation of previous work on reaction energies in molten-salt systems, we have studied the energy of Mg$_2$O$_2^+$ and MgO in a lithium fluoride melt. The formation of complex species involving Mg$_2$O$_2^+$ and MgO in molten salts is of fundamental scientific interest, as well as of technological


importance for applications such as magnesium production. We made reaction energy calculations based on ab initio molecular orbital theory at the Hartree-Fock level. In comparing the energetics of Mg$_2$O$_2^+$ with MgO in lithium fluoride melts, we considered reactions involving Li$_2$Mg$_2$OF$_4$ and Li$_2$MgOF$_2$. Determination of the structures and bond energies of these species indicated that the coordination of the oxygen anion by either one or two magnesium atoms in the lithium fluoride melt is of nearly equal stability energetically. Further work on reaction energies will involve calculation of the stability of the Mg$_2$O$_2^+$ and MgO species in other melts such as sodium chloride, inclusion of entropic effects in the calculations, and the consideration of other oxide or sulfide reactions. In addition, a proton activation technique will be used to measure solubilities, from which experimental reaction energies will be obtained for the Mg$_2$O$_2^+$ and MgO species.

In addition to these studies, several collaborative investigations are under way with scientists outside of CMT. Ab initio molecular orbital theory in combination with photoionization mass spectrometric experiments is being used to study ionization and bonding in a series of F-H compounds (collaboration with J. Berkowitz of ANL's Physics Division), and the ionization energies of a series of hydrides and heats of formation of the resulting cations are being calculated (in collaboration with J. Pople of Carnegie-Mellon University).

2. Studies of Associated and Ordered Liquids

a. Neutron Diffraction Studies of Molten LiAlCl$_4$

We investigated the structure of LiAlCl$_4$ by neutron diffraction of isotopically enriched samples. The lithium contribution to the scattering was removed by using a "null" scattering mixture of $^6$Li and $^7$Li so that the diffraction measurements were sensitive only to the Al and Cl ions. Measurements were made using samples with three different chloride isotope compositions: natural chloride (largely $^{35}$Cl), the mass 37 isotope ($^{37}$Cl), and a mixture of natural chloride with $^{37}$Cl. The measurements were performed at the Institut Laue-Langevin in Grenoble, France. Three independent structure factors [designated $S_{AlAl}(k)$, $S_{AlCl}(k)$, and $S_{ClCl}(k)$, where $\hbar k$ is the momentum transfer in the scattering process] were derived from the measurements for the three samples. The Fourier transform of these factors yielded three pair radial distribution functions: $g_{AlAl}(r)$, $g_{AlCl}(r)$, and $g_{ClCl}(r)$, where $r$ is the interionic distance.

We found that the uncertainties in $g_{AlAl}(r)$ are larger than the magnitudes of the values for this quantity. Results for the other two radial distribution functions are plotted in Fig. VII-4. The first peak in $g_{AlCl}(r)$ is at 2.13 Å and that in $g_{ClCl}(r)$ is at 3.51 Å. The ratio of these two quantities (3.51/2.13 = 1.65 ± 0.03) is close to the expected ratio of 1.63 for a tetrahedral distribution of Cl$^-$ ions about Al$^{3+}$. The height of the first peak in $g_{AlCl}(r)$ is 9 for the neutron diffraction experiment, which is the highest such peak ever measured in a molten salt. Furthermore, $g_{AlCl}(r)$ drops down to very low values at about 3 Å. These results indicate that the

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*S. Biggin, J. E. Enderby, and M. Blander, Proc. of Fifth Int. Symp. on Molten Salts, in press.*
melt contains tightly bound AlCl₄ moieties. For comparison with the measurements, we also plotted molecular dynamics calculations for simple ionic melts analogous to a chloroaluminate for two different ionic pair potentials, designated c and d. There are distinct similarities between the molecular dynamics and neutron diffraction results. Comparisons of these curves should enhance the information we deduce from the neutron diffraction measurements. Further studies are planned on NdCl₃ and on other compositions of the LiCl-AlCl₃ binary system so that we can determine their structures and the possible presence of the intermediate-to-long range order predicted earlier from our molecular dynamics calculations.⁶

b. **Electromotive Force Measurements in Lead-Based Alkali Alloys**

Despite the recent strong interest in the properties of liquid alloys undergoing a metal-to-nonmetal transition (MNM), our basic understanding of these solutions remains rather primitive. A comprehensive theoretical treatment in which the various electronic, magnetic, electrical, and thermodynamic properties of these alloys are included has been lacking, perhaps

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because of the paucity of information on the nature and degree of the local atomic ordering characteristic of this class of alloys.\(^7\)

We have focused our effort on the investigation of the composition and temperature dependence of the activity coefficients of some alkali metals (Li, Na, and K) alloyed with metals having very different electronegativities (Pb, Sb, and Bi). Such alloys are considered to be "liquid semiconductors" since their electrical conductivities (and their temperature dependence) exhibit minima (and change sign) as the solution composition, \(X_A\) (expressed as atomic fraction of alkali metal in the alloy), approaches the composition corresponding roughly to the ratio of their chemical valences.\(^8\) Our work is intended to answer the following questions: (1) Do the thermodynamic properties of the alloy reflect this continuous change from metallic to semiconductor-like behavior? (2) Is it possible to derive information on the alloy ordering and structure and their relation to the MNM transition from thermodynamic measurements, especially in the dilute regime? (3) Are thermodynamic properties helpful in defining possible differences between alloys in which the MNM transition leads to an ionic-like solution and those in which it leads to a covalent-like solution?

The binary systems that we have examined so far include molten Li-Pb, Na-Pb, K-Pb, Na-Sb, K-Sb, and K-Bi; previously published electrical and nuclear magnetic resonance measurements had shown that these alloys undergo an MNM transition. The thermodynamic properties were investigated by using electro motive force (emf) measurements and a coulometric titration technique. We used a solid electrolyte, \(\beta\)-Al\(_2\)O\(_3\) or \(\beta''\)-Al\(_2\)O\(_3\),\(^9,10\) for all the alloys except Li-Pb, which had a molten LiCl-KCl electrolyte. This year is the first time we were able to use a potassium \(\beta\)-Al\(_2\)O\(_3\) solid electrolyte. In addition, a unique seal between the \(\alpha\)-Al\(_2\)O\(_3\) insulator and \(\beta\)-Al\(_2\)O\(_3\) electrolyte allowed us to reach higher temperatures than previously possible and to hermetically contain sodium or potassium at fairly high pressures. These recent additions have considerably broadened the range of alloys we can study.

The K-Pb alloy showed unexpected behavior, since the MNM transition occurred at the equiatomic composition \((X_K = 0.50)\) and not at the composition corresponding to the ratio of the chemical valences \((X_K = 0.80)\). The behavior of the alkali metals alloyed with lead is rather complex, as illustrated in Fig. VIII-5, where the excess stability (as defined by Darken\(^11\)) of A-Pb (where A is Li, Na, or K) is plotted along with the variations of the electrical resistivity with composition as measured by Meijer et al.\(^12\)

The degree of ordering as derived from the thermodynamic measurements (i.e., magnitude and width of the ES peaks) differs from that deduced

\(^11\)L. S. Darken, Trans. AIME 239, 60 (1967).
\(^12\)J. A. Meijer, W. Geertsma, and W. vander Lugt, J. Phys. F, in press.
from the electrical resistivity. However, the curves confirm the presence of an unexpected peak at the equiatomic composition in K-Pb, two peaks in Na-Pb at $X_{Na} = 0.2$ and 0.5, and one peak in Li-Pb at $X_{Li} = 0.2$. (For Na-Pb, Meijer et al.\textsuperscript{12} report the presence of a "hump" in the resistivity curve at the equiatomic composition.) More-sophisticated approaches to deal with the detailed information recently derived from the thermodynamic measurements are clearly needed.

Our measurements with alkali-based alloys undergoing the MNM have shown, for the first time, the complex features of the phenomenon of ordering in liquid alloys. The presence of double peaks in the excess stability functions and of one peak but at an unexpected composition is unexplainable by present theories. It is hoped that improvement of the present theoretical framework will be made possible by the kind of experimental observations that we have reported.

c. Predictions of Activity Coefficients of Oxygen in the Ag-Cu-Sn Solvent System

The Coordination Cluster Theory (CCT) is a statistical mechanical theory for the activity coefficients of a dilute solute in a solvent.\textsuperscript{13} We have recently generalized the theory for multicomponent solvents so that one

can predict solute properties in multicomponent solvents based upon the solute properties in the subsidiary binary solvent. The resultant equation is:

\[
\frac{1}{\gamma_S} = \sum \left\{ \frac{Z!}{\Pi_{i_J} i_J!} \prod J \left( \frac{X_J \gamma_J}{\gamma_{S(J)}} \right)^{i_J} \exp \left( \frac{-g_m}{RT} \right) \right\}
\]

where \( \gamma_S \) is the activity coefficient of the solute, \( S \); \( Z \) is a coordination number (taken as 6); \( i_J \) is the number of atoms of the \( J \)th component of the solvent that are nearest neighbors to the solute atom for a particular cluster; the product \( \Pi \) is taken over all possible combinations of values of \( i_J \) such that \( \Sigma i_J = 6 \); \( X_J \) and \( \gamma_J \) are the mole fraction and activity coefficient, respectively, of the \( J \)th component; \( t \) is a geometric factor taken as \( 1/3 \); and \( \gamma_{S(J)} \) is the activity coefficient of the solvent in the pure component \( J \). The \( g_m \) term is the "excess free energy of mixing" of solvent atoms in the first coordination shell of the solute given by the expression

\[
g_m = \sum_{J< J'} i_J i_{J'} \frac{h_{JJ'}}{2} + \ldots
\]

where \( h_{JJ'} \) is a binary interaction parameter, which can be deduced from the subsidiary binary solvent. Therefore, to predict the solvent properties of solutes in the multicomponent systems, we require parameters deduced from the binary subsystems (\( \gamma_{S(J)} \) and \( h_{JJ'} \)) as well as the activity coefficients of the solvent atoms (\( \gamma_J \)).

Activity coefficients for oxygen in the Ag-Cu-Sn system have been measured by Block and Stüwe.\textsuperscript{14} The three subsidiary binaries were analyzed previously using the CCT.\textsuperscript{13} Activity coefficients for the ternary solvent components have not been measured. Thus, we calculated these from data for the subsidiary binary systems by using a well-known approximation.\textsuperscript{15} The results of the calculation are given in Fig. VIII-6 and are compared with the measurements of Block and Stüwe.\textsuperscript{14} The agreement between the measurements and calculations is very good, considering that the solvent properties were approximated, and is considerably better than that calculated in the pioneering work of Jacob and Alcock.\textsuperscript{16} Our results support the use of the CCT for making predictions of solute properties \textit{a priori} in metallurgical systems. The theory should be particularly useful for complex alloys and slags of industrial importance.

3. Electrochemical Reactions in Submerged Arc Welding

High currents (e.g., 500 A) and DC voltages (e.g., 30 V) are used in submerged arc welding of steel plate. As a consequence, one expects electrochemical reactions to take place at the surfaces of the weld pool and the weld wire that is fed in. Because heat release at the anode is greater than at the cathode, the weld wire is usually anodic, and the base plate being welded and the weld pool are cathodic. We are engaged in efforts to determine the mechanisms for alteration of weld metal chemistry; this knowledge is expected to lead to methods for controlling the composition of the weld metal and for improving the quality of the welds.

We propose that the following chemical changes take place in weld metal after submerged arc welding with SiO$_2$-MnO-FeO fluxes containing 40 wt % SiO$_2$.$^{17}$ The anode will have relatively high oxygen partial pressure at the weld wire, and the half-cell reaction can be written as

$$nO^2- + M(\text{metal}) \rightarrow MO_n + 2ne^- \quad (18)$$

---

where \( M \) is a metal at the weld wire-slag (or weld wire-arc) interface, and \( n \) is related to the valence of \( M \) in the oxide. For steel, \( M \) would be largely iron. This reaction produces an oxide at the interface, which partly dissolves in the metal and slag. After the molten weld wire forms a droplet that separates from the wire, the electrochemical reaction ceases but the oxide continues to dissolve in the metal and slag. The rate of dissolution into the flux depends on kinetic factors and on the driving force, which is related to the differences between the chemical potential of the oxide at the interface and in the slag. Experimental results for the increase of oxygen in weld metal for \( \text{SiO}_2-\text{MnO}-\text{FeO} \) fluxes as a function of the FeO and MnO content of the flux are given in Fig. VIII-7, where "nominal" is the oxygen content expected if no oxygen is transferred to the metal, "analytical" is the actual oxygen content after welding, and "delta" is the oxygen transferred into the weld metal. These results are consistent with the above mechanism.

The cathodic reactions lead to the electrodeposition of metals as follows:

\[
M^{2+}(\text{slag}) + 2e^- \rightarrow M(\text{metal})
\]

\[
\text{Si}^{4+}(\text{slag}) + 4e^- \rightarrow \text{Si}(\text{metal})
\]
where \( M \) can be \( \text{Fe}^{2+} \), \( \text{Mn}^{2+} \), or other metals that are electrodeposited at the interface. The relative amounts of all these deposits will be readjusted by chemical reactions such as

\[
\text{Si(metal)} + 2\text{M} \rightarrow \text{SiO}_2 \text{(slag)} + 2\text{M(metal)} \\
\text{Mn(metal)} + \text{FeO} \rightarrow \text{MnO} \text{(slag)} + \text{Fe(metal)}
\] (20)

The resultant changes in the compositions of the weld metal and the slag depend on the rates of the electrochemical reactions (Eq. 19) relative to the rates of the back reactions (Eq. 20). An analysis of experimental results on Mn and Si contents of the weld metal indicated that both the electrochemical and back reactions are important. We are planning experiments to study the electrochemical effects on weld metal in much more detail.

4. Pyrochemical Solvolysis of Ore-Bound Transition Metals

This research effort involves studies of the pyrochemical dissolution and electrochemical recovery of strategic and critical metals (e.g., Co, Mn, Cr) contained in low-grade domestic minerals, deep sea nodules, and industrial wastes. Experimentation has centered on the application of low-melting alkali and alkaline earth halide eutectics as the extraction media. The objectives are to (1) elucidate the solution-chemical and electrochemical mechanisms that control the transfer of transition metals from the ore-bound state to the solution state and (2) identify new compact pyrochemical and pyroelectrochemical methods for the recovery of strategic/critical metals from minerals and industrial by-products. The findings of this research have led to a novel approach for the production of two strategic and critical metals (Co and Mn); and there is good reason to expect that this approach could be adapted to the recovery of other essential metals such as chromium and copper.

During the past year we investigated the lixiviation mechanism involved in the extraction of transition metals from Pacific Ocean deep sea nodules. We performed sparged equilibriations of nodule material and MgCl\(_2\)-KCl-NaCl eutectic at 450°C in an apparatus equipped to permit trapping and analysis of the off-gases. Chlorine gas (Cl\(_2\)) and HCl were found to be major products of the lixiviation reaction. These results coupled with absorption spectrophotometric scans of the molten extract salt, subsequent X-ray and chemical analyses of the insoluble residues, and reported information on the phases present in the nodules produced a complete picture of the solvolysis process. Manganese is extracted as Mn\(^{2+}\) through a reduction of higher oxidation state phases (MnOOH and MnO\(_2\)). This reduction produces both Cl\(_2\) and HCl. Cobalt and nickel are extracted as Co\(^{2+}\) and Ni\(^{2+}\) (from reduction of CoOOH and NiOOH phases in the nodules). Iron is recovered as Fe\(^{3+}\) through direct solvolysis of FeOOH phases. Copper is extracted as Cu\(^{2+}\) from a phase(s) of unknown character.

We did several large-scale extractions (50 g of nodule, 250 g of salt) and then subjected the filtered extract salt to a transition metal separation scheme. Iron and copper were recovered as FeCl\(_3\) and CuCl\(_2\) by volatilization at 450-500°C. The vapor complex species FeCuCl\(_5\), identified by
Papatheodorou several years ago,\textsuperscript{18} appears to be integrally involved in the volatilization. Next, we performed low-voltage electrolysis in the region of the Ni\textsuperscript{2+}/Ni\textsuperscript{0} reduction potential, using cyclic voltammetry to monitor the progress of the deposition. At the end of the low-voltage electrolysis, the Ni\textsuperscript{2+}/Ni\textsuperscript{0} reduction wave in the cyclic voltammogram was greatly reduced, and a >96\% grade of dendritic nickel metal was recovered from the deposition electrode.

After the low-voltage electrolysis had been completed, the deposition potential was set to a more negative value in the region of the Co\textsuperscript{2+}/Co\textsuperscript{0} reduction potential. The cobalt present in the original nodule specimen (~0.25 wt \% cobalt) was almost entirely recovered in this step, together with some residual nickel (remaining after low-voltage deposition). The remaining extract salt at this point contained only the manganese from the original extraction. Although we conducted no detailed studies to demonstrate manganese recovery, preliminary tests indicated that controlled oxidation (with O\textsubscript{2}) results in precipitation of Mn\textsubscript{2}O\textsubscript{3} and other related phases from the extract salt. The processing scheme that evolved from this work was awarded one of the Industrial Research Magazine IR-100 awards for 1985.

C. Interfacial Materials Chemistry

The research into interfacial materials chemistry embodies a family of experimental and theoretical studies that focus on interfacial processes of importance to corrosion science, surface science, and catalysis. The experimental work has three thrusts: (1) investigations of aqueous corrosion over a wide range of temperatures and pressures, using novel procedures based largely on the integration of spectroscopic and electrochemical techniques; (2) coupled infrared and mass spectroscopic studies of the chemistry of species adsorbed on materials with high surface area, e.g., zeolites; and (3) spectroelectrochemical investigations of the catalytic activity of macrocyclic molecular ligands. Paralleling \textit{ab initio} theoretical research (e.g., on adsorbate/substrate interactions) and vibrational dynamics analyses are employed to support and extend the experimental findings.

1. Electrode Kinetics Studies of Aqueous Corrosion

This project is focused on the kinetic and mechanistic aspects of metallic corrosion in aqueous media at temperatures and pressures ranging from ambient to about 300\degree C and 10 MPa. Aqueous corrosion processes are almost exclusively electrochemical and involve reduction of a component of the solution medium together with the anodic dissolution of the metal. Our research has two purposes: to determine the key factors that influence the active anodic dissolution of metals, with special emphasis on the charge transfer step and the effect of the structure of the interfacial region on charge transfer, and to elucidate the kinetics and mechanism of incipient passivation of the metallic surface. Since the interfacial reactions should be rapid, we are using relaxation techniques that we previously adapted for kinetic measurement in

molten salts. Because of the short time (high-frequency equivalent) nature of the measurements, the measuring cell must have special characteristics, such as low impedance and a well-defined working electrode surface with uniform current distribution.

During the past year, a high-temperature/high-pressure test loop with a built-in, fast-pulse electrochemical cell was constructed and is operating satisfactorily. In addition, several working-electrode/counter-electrode combinations and reference electrodes were designed, built, and tested. Using the test loop, we completed experiments to characterize a palladium/hydrogen reference electrode, which serves as a pH-sensitive (pseudo-reference) electrode, with hydrogen supplied by diffusion through a closed-end palladium tube. The tests were done in the temperature range from 100 to 300°C, at a pressure of 10 MPa, pH range of 4 to 10, and internal hydrogen pressure range of 0.3 to 7 MPa. The behavior of this novel electrode was close to theoretical in basic solutions, although some deviations were found at low pH. The electrode was shown to be a stable reference electrode (in a constant pH solution) suitable for electrochemical relaxation measurements at high temperature and pressure.

In related work, a cooperative project was initiated with J. W. Halley of the University of Minnesota to determine the effect of temperature on the kinetic parameters for heterogeneous charge transfer at electrochemical interfaces. Halley will carry out molecular dynamics calculations while we make the corresponding experimental measurements. Because determination of the ion transfer involved in the anodic dissolution of metals is beyond existing computational capability, our initial efforts are directed toward the determination of temperature effects for some simple electron transfer reactions. Selected for initial study are the Fe$^{2+}$/Fe$^{3+}$ and Cr$^{2+}$/Cr$^{3+}$ redox reactions on an inert (e.g., gold) electrode.

In support of the above-described experimental projects, we are developing a computer model that will estimate the effect of the structure of the interfacial solution layer on the transient electrode kinetics measurements. The essential purpose of the transient measurements is to separate the diffusional effects from the surface reaction kinetics. In past efforts of this kind, the double-layer structure at the electrode/electrolyte interface has been neglected. The justification for this has been the assumption that the thickness of the double layer is much smaller than the diffusion layer that develops during the measurement. For fast reactions (short-time measurements), this assumption may not be justifiable, in which case the structure of the double layer must be known not only for a correction of the calculated kinetic parameters but also for the separation of diffusion effects from those of the surface reaction. It will be important to determine whether our kinetic measurements at high temperature are complicated by this effect. We have also developed a computer model that will numerically solve the set of differential equations describing the processes that occur during the relaxation measurements. The model is being tested.

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In a related project, we developed a computer model that will determine the effect of mass transport on the calculation of corrosion rates from electrochemical polarization measurements. The model includes a polarization equation that can be used as a basis for curve-fitting data evaluation under any conditions. This equation was used to determine the error caused by the neglect of mass transport effects in conventional data analysis. The error of the calculated corrosion rate was found to be a function of two dimensionless terms: \( \frac{i_{\text{corr}}}{i_1} \) and \( \frac{\beta_a}{\beta_c} \), where \( i_{\text{corr}} \) is the corrosion current density, \( i_1 \) is the diffusion-limiting current density, and \( \beta_a \) and \( \beta_c \) are the anodic and cathodic Tafel slopes, respectively. Results from this study clearly show that the error associated with conventional corrosion rate calculations can be considerable, even for small \( \frac{i_{\text{corr}}}{i_1} \), i.e., for cases where the corrosion process is far from completely diffusion controlled. This error can be avoided by using our new equations for data evaluation.

In the future, we expect to make charge transfer rate measurements at high temperatures and pressures on well-characterized single crystal surfaces. These measurements will be accomplished by coupling electrochemical relaxation measurements to an X-ray photoelectron spectroscopy/Auger electron spectroscopy/low-energy electron diffraction system. We also expect to extend the theoretical (molecular dynamics) and experimental work on electrode kinetics to more-complex electrode processes occurring in aqueous corrosion, e.g., anodic metal dissolution and incipient anodic oxide film formation (passivation/repassivation kinetics).

2. Spectroelectrochemical Studies of Aqueous Corrosion

The objective of this effort is the elucidation of corrosion and passivation phenomena in metals exposed to aqueous solution environments. Detailed studies of the structure of the metal/solution interface are undertaken using spectroscopic, electrochemical, and theoretical methods. The results are correlated with measured properties of the double layer and the rates of charge and mass transport processes occurring at the metal/solution interface. Investigations are currently focused on the behavior of base metals whose alloys are of interest in light water nuclear power reactors, i.e., iron and nickel.

In collaboration with the Materials Science and Technology Division, we constructed a cell and electrolyte-recirculation system that allows simultaneous spectroscopic and electrochemical studies of aqueous corrosion at high temperature and pressure (-300°C and ~10 MPa). The system has been successfully tested and is now routinely operated. Using this system, we completed cyclic voltammetry studies of nickel in 100 ppm Na_2SO_4 solution at temperatures between 25 and 290°C. The results indicate the disappearance of passivity in nickel above 100°C and the occurrence of pitting corrosion above 250°C. This finding suggests potentially severe corrosion problems in the use of nickel-containing alloys in high-temperature aqueous media containing sulfate.

Our earlier laser Raman spectroscopic investigations of the composition of anodic corrosion films on nickel were extended to near-neutral

borate buffer and sulfate solutions (pH ~ 8.4). The surface film in the region of secondary passivity was identified as a form of hydrated Ni$_2$O$_3$. This film was found to persist up to about 100°C in borate solution. Furthermore, the rate of the film formation at 100°C appeared to be four times faster than is observed at room temperature. The verification of the presence of Ni$_2$O$_3$ is the first unequivocal confirmation of the existence of a higher oxidation state of nickel at potentials close to the region of O$_2$ evolution, in accord with predictions of the corresponding Pourbaix diagram.

An AC impedance instrument for more-detailed electrochemical characterization of the metal/solution interface has been acquired and is currently in use. This instrument is providing information on such properties as double-layer capacitance, adsorption pseudo-capacitance, solution resistance, polarization or charge-transfer resistance, and diffusional resistance. Initial measurements show that the AC technique can be successfully applied to the study of metal corrosion in reactor coolant-type water with sulfate impurities (e.g., 10-100 ppm Na$_2$SO$_4$).

In the future, we will undertake further spectroscopic investigations, as well as DC and AC electrochemical measurements, on nickel in dilute sulfate solutions of various pH at temperatures from 25 to 290°C. We will also attempt to explore the use of infrared spectroscopy to further characterize the structure of anodic corrosion films. Extension of our investigations to Ni-Cr alloys and stainless steel samples is planned.

3. Studies of the Chemistry of Zeolite Catalysts

This research effort involves detailed studies of the relationship between the structure and catalytic activity of synthetic zeolites, with emphasis on those classes of zeolites that have potential for utilization as shape-selective adsorbents and catalysts. Advanced infrared spectroscopic techniques, including diffuse reflectance and attenuated total internal reflectance (ATR), are employed in situ to probe the structure of zeolites and of chemical species adsorbed in and attached to zeolite frameworks. There are also collaborative interactions with other ANL scientists involving such tasks as the synthesis of new zeolites and the use of ANL's Intense Pulsed Neutron Source to study the vibrations of chemical species lodged in zeolite channels and cages. Group theory and vibrational dynamics analyses are employed to support the experimental effort.

The diffuse reflectance studies are focused on the reactivity of iron-modified versions of the materials ZSM-5 and offretite--two synthetic zeolites that have potential utility as molecular shape-selective adsorbents and catalysts. Investigations of the effects of the temperature and chemical environment on protonated-site behavior in these zeolites were carried out using a diffuse reflectance cell. The intensities of the infrared active O-H stretching vibrations at various sites within the framework of the zeolite provide a means of measuring their relative stability and reactivity. By employing deuterated probe molecules (e.g., D$_2$O and CH$_3$OD) and controlling their addition to the zeolite at preset temperatures, we have been able to independently titrate protonated sites of differing stability. We have also carried out chemical reactions catalyzed by these isotopically "tagged" zeolites. Analysis of the infrared band positions of reactants and products in the zeolite structure has produced new insights concerning the role of the various protonated sites in dehydration and hydrogenation reactions.
In earlier work,\textsuperscript{21} e developed ATR-based procedures for the study of zeolite structure through examination of framework vibrations. These procedures have been refined to the point where definitive determinations of the degree of structural continuity of synthetic aluminosilicates and alumino-ferrisilicates can be made rapidly and nonintrusively. In parallel with this effort, we have initiated group theoretical analyses of zeolite structures; to date, calculations have been completed for over a dozen common zeolite structures. The predicted number of Raman and infrared active vibrations for the zeolites studied was found to be always considerably greater than the number observed experimentally. This suggests that there are many instances of pseudo-degeneracy in the normal vibrational modes of zeolites.

In the coming year, the emphasis of this research effort will continue to be on transition-metal-modified synthetic zeolites (e.g., alumino-ferrisilicates). Determination will be made of the extent to which "clustering" of the transition metal atoms in the zeolite cages controls the performance of the zeolite as an adsorbent and as a catalyst in chemical synthesis applications.

4. Investigations in Electrocatalysis

The objective of this effort is to gain an understanding of the factors that influence the mechanisms and rates of electrochemical reactions occurring at surfaces covered with thin films of catalytically active substances. Information regarding the molecular electronic structure of the electrode surface, the double-layer region, and species in solution is correlated with kinetic parameters and mechanisms characteristic of the electrochemical reaction. Raman spectrometry, cyclic voltammetry, rotating disc with ring, potentiostatic pulse, and AC impedance together with quantum theoretical approaches are being employed. Emphasis is placed on the development of the capability to perform experiments in situ using coupled spectroscopic and electrochemical techniques.

In the past year, we conducted laser Raman spectroscopic and cyclic voltammetry studies of the structures and properties of iron protoporphyrin IX (FePP) as they relate to its catalytic activity for the electrochemical reduction of oxygen. This work is being done in collaboration with J. J. McMahon, Williams College. In contrast to iron phthalocyanine (FePc), which we had previously studied,\textsuperscript{22} relatively weak catalytic properties were exhibited by FePP. However, FePP appears to be fairly stable in borate buffered solutions. A reduction of the iron center from Fe\textsuperscript{3+} to Fe\textsuperscript{2+} was found to occur at potentials more cathodic than O\textsubscript{2} reduction. Shifts in the frequencies of certain vibrational bands were found to correlate with the change in oxidation state of the adsorbed macrocycle. Our initial observations are that catalytic activity and stability are a very sensitive function of two factors: (1) the molecular electronic structure of these compounds and (2) perturbations caused by interactions with surrounding atoms, molecules, and surfaces.

Future plans involve a continuing study of the structure of the adsorbed state of macrocyclic compounds and its correlation with catalytic activity and stability. We shall attempt to determine the molecular orientation of FePc and FePP on the electrode surface as a function of potential. We also hope to synthesize other macrocycles with modified structures so that the effect of changes in electronic density around the central metal atom on electrocatalytic properties can be systematically studied.

5. Adsorbate-Substrate Interactions

Theoretical studies of molecules adsorbed on surfaces are being carried out with the use of ab initio quantum mechanical methods. The properties of the molecule-surface interactions are studied as a function of the number of atoms in the cluster used to model the surface. This provides an understanding of how clusters approach the properties of a bulk surface and what properties of the interaction are localized, i.e., involve only a few of the atoms within bonding distance. This work focuses on such properties as the chemisorption energy, binding sites, distance of the adsorbate above (or below) the surface, the nature of the bonding, and vibrational frequencies of the adsorbate-substrate complex. Information on all these properties will be useful in analyzing spectroscopic, electrochemical, and other types of measurements on surface-adsorbed molecules. Knowledge concerning these adsorbate-substrate interactions will be useful to research being conducted in such areas as heterogeneous catalysis, aqueous corrosion, and other surface-related processes.

In collaboration with John Pople of Carnegie-Mellon University, we are investigating the interaction of a water molecule with clusters of beryllium atoms \( \text{Be}_n-\text{OH}_2 \), \( n = 1-5 \). The dependence of interaction energy, vibrational frequencies of the adsorbed \( \text{H}_2\text{O} \), and structure on the size of the cluster was determined with a large basis set,\textsuperscript{23} including polarization functions. A dramatic increase in the interaction energy was found to occur when the cluster size reached three atoms. The dissociation energy showed no further large changes when the cluster size was increased to four and five atoms. The shifts in \( \text{H}_2\text{O} \) vibrational frequencies and the distance of \( \text{H}_2\text{O} \) from the cluster also approximately leveled off at \( n = 3 \). Other significant findings from this study include: (1) no correlation exists between the interaction energy and the shifts in the vibrational frequencies of the adsorbed \( \text{H}_2\text{O} \) molecule, and (2) \( \text{H}_2\text{O} \) molecules prefer corner binding sites over edge or face binding sites on the clusters. We are now calculating the interactions of water with larger clusters of beryllium atoms to determine the relevance of these small clusters to the surface chemistry of metals.

The interaction of \( \text{H}_2\text{O} \) with Mg and Na atoms was also investigated. As in the case of Be and Li interactions with \( \text{H}_2\text{O} \), Mg and Na form complexes with \( \text{H}_2\text{O} \) that have metal-oxygen bonds with charge transfer to the metal atoms. The calculated shifts in the bending frequencies of \( \text{H}_2\text{O} \) are in agreement with the shifts observed by Hauge et al.\textsuperscript{24} for these complexes in a low-temperature


matrix. The calculated shifts in stretching frequencies of \( \text{H}_2\text{O} \) should prove useful in assigning these bands in future experiments. These calculations will be extended to the interactions of other molecules such as \( \text{CO} \), \( \text{NH}_3 \), \( \text{O}_2 \), etc., with metal atoms and their clusters.

In collaboration with Frank Weinhold, University of Wisconsin, we have applied a new theoretical method for analysis of intermolecular interactions based on "natural bond orbitals" to a series of hydrogen-bonded molecular complexes, e.g., \( \text{(H}_2\text{O})_2 \), \( \text{CO-HF} \), \( \text{H}_2\text{O-N}_2 \). Natural bond orbitals are localized bond orbitals, determined in an optimal fashion by an occupancy criterion, which can provide a novel means of viewing the forces responsible for binding. This method of analysis is a more reliable method of assessing the importance of charge transfer than the commonly used Mulliken- and Morokuma-type of analyses, which have well-documented deficiencies. Charge transfer was found to have a strong influence on the equilibrium intermolecular distances and binding energies in the series of complexes studied. These methods are now being extended to \( \text{CO} \), \( \text{NH}_3 \), and \( \text{H}_2\text{O} \) interactions with \( \text{Al} \) clusters in order to gain a better insight into the nature of adsorbate-substrate interactions. For \( \text{Al}_4 \) interacting with \( \text{CO} \), the traditional \( \sigma \)-donor picture of \( \text{CO} \) and metal \( \pi \) donation was well confirmed by this method. There has been some question recently concerning the importance of the \( \sigma \)-donor contribution.\(^{25}\)

D. Thermochemistry

Rock-water interactions play a crucial role in many geochemical processes of both practical and theoretical interest. These interactions cannot be understood without a knowledge of the thermodynamic properties of the reacting and product minerals as well as the brine solutions. Zeolites are produced by the low-temperature (\(-500 \text{ K}\)) reaction of lava and water in geothermal areas. As a contribution to the understanding of such interactions, we are determining thermodynamic properties of zeolites and related silicates. Before this program was initiated, there were virtually no reliable thermodynamic data for zeolites.

The following calorimetric measurements are usually performed: low-temperature (5 to 350 K) heat capacity, from which the standard entropy is obtained; energy of combustion (in \( \text{F}_2 \) or \( \text{O}_2 \)) or enthalpy of reaction or solution in aqueous media, from which the standard enthalpy of formation at 298.15 K is derived; and enthalpy increments relative to 298.15 K, determined by drop calorimetry (to 1500 K). In addition, enthalpies of transition may be determined by differential scanning calorimetry.

During the past year, we determined the thermodynamic properties of a natural sample of the zeolite mordenite having the composition \( \text{Ca}_{5.06}\text{Na}_{0.36}\text{Al}_{2.84}\text{Si}_{5.06}\text{O}_{12} \cdot 3.46\text{H}_2\text{O} \). Since this is one of the few natural zeolites that can be dehydrated without altering the framework structure, we have also determined the thermodynamic properties of dehydrated mordenite. To date, we have completed measurements of the enthalpy of formation on dehydrated mordenite and have low-temperature calorimetric measurements in progress. Based on the enthalpies of formation of mordenite, \((-6750.3 \pm 5.6) \text{ kJ/mol}\), and dehydrated mordenite, \((-5655.9 \pm 5.7) \text{ kJ/mol}\), we concluded that the

water in mordenite has an average binding enthalpy of 29.7 kJ/mol. In analcime, the binding enthalpy of the water is somewhat higher, 40.9 kJ/mol. These values illustrate that the water in zeolites is more strongly bound than in inorganic hydrates. Thus, the average binding energy is 16.2 kJ/mol in CaCl₂·6H₂O, 8.2 kJ/mol in Na₂SO₄·10H₂O, 8.6 kJ/mol in NaClO₄·H₂O, and 9.2 kJ/mol in Na₂CO₃·10H₂O.

Silicalite has been recently synthesized at Union Carbide. It is essentially pure SiO₂ and can be considered an aluminum-free end-member of a series of silica-rich ZSM-5 zeolites. Because it is organophilic and hydrophobic, silicalite has potential use for purifying water contaminated with organic materials. We had previously determined its enthalpy of formation by combustion in fluorine and its enthalpy of reaction with HF(aq) and had proposed that this material might make a better reference material for silicate thermochemistry than α-quartz. We recently finished measurements of the low-temperature heat capacity and the high-temperature enthalpy for this material. As a result of this work, the thermodynamic properties of silicalite are known from 5 to 1500 K. Two interesting observations were made in these studies. First, the reported monoclinic-to-orthorhombic transition in the range 297 to 353 K was not observed. Secondly, silicalite is reported to be stable in air to over 1373 K and only slowly to convert to glass at 1573 K. However, our enthalpy measurements at temperatures greater than 1300 K showed increasing positive deviation from the expected smooth relationship between enthalpy and temperature. X-ray diffraction measurements following the experiment in which the sample attained a maximum temperature of 1500 K showed both amorphous silica and cristobalite. Clearly, then, this material is not as stable as had been previously believed.

E. Trace-Element Migration

We are pursuing basic research concerning the redistribution of elements in active geothermal systems, and the time-scale thereof, through detailed analytical studies of drill cores and thermal water from Yellowstone National Park, Wyoming. To obtain a comprehensive picture of the hydrothermal processes in geothermal systems, we are employing a wide range of analytical methods, including instrumental neutron activation analysis, inductively coupled plasma atomic emission spectrometry, atomic absorption spectrometry, electron microprobe analysis, mass spectrometry, and alpha spectrometry. Data collected in this program have diverse applications in the fields of geothermal energy, nuclear waste disposal, and ore mining.

During FY 1985, we completed a fundamental study of element redistribution during hydrothermal alteration of rhyolite. We determined the content of a large group of elements (Ti, Al, Fe, Mg, Ca, Na, K, Li, Sc, Mn, Co, Rb, Sr, Y, Zr, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, Th, and U) in 30 samples from two drill cores (Y-7 and Y-8) in the Biscuit Basin Rhyolite Flow, Yellowstone National Park. Figure VIII-8 shows activity ratios for uranium

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and thorium isotopes in the Y-7 samples, indicating that those having excess uranium are deficient in $^{230}$Th [compare center plot with one at right for a depth of 60-67 m (196-220 ft)]. For most Y-7 samples, the data are consistent with a model of single-stage uranium addition involving water/rock mass ratios as high as $10^5$ or more. Data for Y-8 samples indicate much less uranium mobility and no consistent trend in the data for isotopic activity ratios. The time of apparent uranium addition in Y-7 corresponds approximately to the Late Pinedale deglaciation event (which occurred ten- to fifteen-thousand years ago), suggesting a possible hydrogeologic relation between glacial unloading and the initiation of thermal activity in the area of Y-7 and Y-8 drill holes. In collaboration with C. H. Lewis III of Mobil Exploration and Production Services, Inc., we derived mathematical expressions for $^{238}$U-series evolution in open geological systems.

In collaboration with K. Muehlenbachs of the University of Alberta, we also completed oxygen isotope analysis of the rhyolite. Three conclusions were reached: oxygen isotope disequilibrium exists between thermal water and all primary and secondary phases analyzed except calcite; modest depletions of $^{18}$O (1-2 ‰) apparently occurred in the plagioclase and obsidian in the Y-8 core; and celadonite and β-cristobalite might have precipitated from water locally enriched in $^{18}$O (up to ~8 ‰ heavier than present thermal water).
In another project, we are determining the age of $^{238}\text{U}$ hydrothermal precipitates from drill cores and sinter throughout Yellowstone. Much of the initial analytical work on these samples was performed by C. M. Binz, Loras College (Dubuque, IA). The goal of this study is to refine our current speculations regarding the longevity of thermal areas. Our preliminary results indicate that none of the samples analyzed is older than 200,000 years. Also, we are performing a study of the gold and associated "epithermal" elements (As, Sb, Hg, and Tl) in a subset of the 30 samples from Y-7 and Y-8 drill cores. Gold anomalies were found in two silicified samples that exhibited evidence for alteration at $>170^\circ\text{C}$. The data from this study will be of use in models for the genesis of epithermal precious-metal deposits.
IX. ANALYTICAL CHEMISTRY LABORATORY

The Analytical Chemistry Laboratory (ACL) is a full-cost-recovery service center, with the primary mission of providing a broad range of technical support services to the scientific and engineering programs at ANL. In addition, the ACL conducts a research program in analytical chemistry, works on instrumental and methods development, and provides analytical services for governmental, educational, and industrial organizations.

The ACL functions administratively within CMT, the principal user (about 57% in FY 1985), but provides analytical support for all of the technical divisions and programs at ANL. The ACL has three groups—Chemical Analysis, Instrumental Analysis, and Organic Analysis—which together include about 30 to 35 technical staff members.

The Chemical Analysis Group performs wet-chemical, instrumental, spectrochemical, and coal analyses and does sample preparation. The Instrumental Analysis Group uses nuclear decay counting techniques, analyzes gases with mass spectrometry (MS) and gas chromatography (GC), analyzes solids with X-ray techniques, performs remote analysis of radioactive samples, and does work in dosimetry, neutron activation, inert gas fusion, and isotope analysis. The Organic Analysis Group uses a number of complementary techniques to separate and analyze complex organic mixtures and compounds, including synthetic fuels, toxic substances, fossil fuel residues and emissions, pollutants, biologically active compounds, pesticides, and drugs.

The majority of the technical accomplishments of the ACL staff are contained in technical summaries given in the previous sections of this report and in similar reports of other ANL divisions. Selected accomplishments are also summarized here.

The single project that required the largest effort by ACL staff was the Proof-of-Breeding (POB) Project in CMT (about one-quarter of the total ACL budget in FY 1985). Seventeen end-of-life fuel rods were destructively assayed for the POB Project in FY 1985. The ACL role was to analyze dissolver solutions and gas samples for fission gases, including Kr and Xe isotopes, obtained during the processing of 152 segments sheared from the fuel rods. More than 1000 aliquots of dissolver solution were prepared and analyzed for uranium content and isotopic composition by thermal ionization mass spectrometry, and an additional 550 aliquots were analyzed for $^{137}$Cs, $^{144}$Ce, and $^{95}$Zr by gamma spectrometry. Two audits—one by Bettis Atomic Power Laboratory and the other by ANL's Quality Assurance Division—demonstrated the ability of the ACL to generate reliable data during normal processing, as well as to respond to off-normal situations such as process equipment malfunctions. Project requirements for precision on the individual analyses were met or exceeded in every case. Further analytical results are included in Section VI.D.

For the Integral Fast Reactor (IFR) Project (Sec. VI.C), the ACL determined the oxygen and nitrogen content of U-Pu-Zr alloy in an inert-gas-fusion glovebox. For this measurement, the sample is first fused in a platinum bath within a graphite crucible being maintained at a temperature of about 2000°C. A helium carrier gas flows over the crucible and carries reaction gases (CO and N$_2$) to a gas analysis train through which the CO is oxidized to CO$_2$ (using hot CuO). Both the CO$_2$ and N$_2$ are collected and measured manometrically.
Typically, the uncertainties for oxygen and nitrogen measurements using this technique are \( \pm 3\% \) and \( \pm 5\% \), respectively, at the 95\% confidence level.

A solvent extraction process (the TRUEX process, described in Sec. VI.B) is being developed in CMT to separate and concentrate transuranic (TRU) elements from acidic nuclear waste streams. A mixture of octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide and tributyl phosphate (TBP) dissolved in carbon tetrachloride is currently being tested for the separation of TRU elements from an aqueous stream generated during the recovery of plutonium from metallurgical scrap. A method was needed to monitor the concentrations of the extractants so that optimum extraction efficiency would be obtained. A gas chromatographic method was developed that minimized potential decomposition of the two extractants and resulted in a fast, accurate, and precise means of simultaneously determining the concentrations of the two extractants. The relative standard deviations were less than 5\% for all runs with both extractants and less than 1\% for most runs with TBP alone.

The ACL carried out X-ray diffraction (XRD) analysis of crystalline materials for phase identification. Results of this work for the CMT electrochemical programs (Secs. I, II, and III) led to the following findings: a change in LiFeO\(_2\) lattice constant was associated with the extent of manganese doping in the LiFeO\(_2\), which is being considered for the cathode material in molten carbonate fuel cells; several XRD patterns of the sulfur electrode in the Na/S cell, which had not been previously recorded, were discovered and tentatively identified as metastable phases; and electrode products formed by the charging and discharging of Li-Si/FeS\(_2\) cells to different states were identified and found to depend on the physical location of the sample on the electrode.

The Energy from Municipal Waste Program (Sec. V.B) requires characterization of the mixture produced from the thermal degradation of cellulose in several forms (filter paper, newsprint, wood chips, etc.). Thus, the ACL is performing GC and GC/MS analyses of gaseous and liquid products from pyrolysis of municipal solid waste components. The latest work involved preparing a GC/MS library with information obtained from Battelle Pacific Northwest Laboratory and from authentic standards. The objective was to aid identification of the components in liquids produced from the pyrolysis of cellulose. Tentative identification was made of 65 of 86 compounds and their relative concentrations in the sample. In general, the classes of compounds included furfurals (9.4\%), phenols (2.5\%), methoxyphenols (16.9\%), cyclic compounds such as methyl cyclopentanones (10.8\%), methoxy benzenes (3.8\%), and substituted propane (36.8\%).

In collaboration with CMT staff, the ACL also analyzed samples for sodium and potassium content in order to evaluate the performance of alkali vapors in the flue gas produced by pressurized fluidized-bed combustion of coal. The results of these analyses, at the parts per billion level, are reported in Sec. V.C.

Three projects were completed to enhance the ACL capabilities for coal analysis. In the first project, a methodology involving energy dispersive X-ray fluorescence spectrometry was developed to determine major and minor elements in coal ash and other siliceous materials (Si, Al, Fe, Ca, Mg, Ti, and K, reported as oxides). Agreement was good between the precisions obtained
with this new method and those obtained by other laboratories using the atomic absorption method (D 3682) of the American Society for Testing and Materials (ASTM). The advantage of this new method is that results of comparable precision are obtainable in less time. The second project involved development of a methodology for the determination of total halogens (especially fluorine and chlorine), phosphorus, and sulfur in coal by ion chromatography; the oxygen bomb combustion method is used to prepare the coal samples. Quantitative analysis indicated precisions of 5 to 10% for each of the elements (measured as anions). An advantage of this method is that elements are simultaneously determined on the same sample. To date, this simultaneous analysis has been achieved for all elements except phosphorus. The third project involved determination of major and minor elements in coal ash by inductively coupled plasma/atomic emission spectrometry (ICP/AES). The objective was to derive a more rapid alternative to the ASTM method D 3682. For some elements (e.g., Si and Ti), this method has better precision than the ASTM method, but for other elements (e.g., Na) the ASTM method shows better precision. Nevertheless, the ability to do analyses more rapidly by the ICP/AES method was demonstrated.

A study has been completed on the relative merits of gas chromatography/matrix-isolation/infrared (GC/MI/IR) versus GC/light-pipe/IR. A GC/MI/IR instrument is now commercially available; the conceptual design for the GC/MI/IR and a prototype instrument were developed in the ACL. The advantages of this system relative to GC/MS have been explored previously. For many determinations such as isomers of PCBs or dioxins, the IR measurement gives information about chemical structure that is not as readily obtainable with mass spectrometry. The GC/MI/IR instrument has a limit of detection for organic samples of 1 ng or less, which is from one to three orders of magnitude better than that obtainable with the light pipe. However, the disadvantages of the GC/MI/IR method are the higher cost of the instrumentation, the greater time for analytical measurement, and the absence of suitable libraries. Thus, although the GC/MI/IR system has advantages over both GC/MS and the light pipe system, this technique should be viewed as a complement and not as a replacement of either alternative.

The ACL is also involved in a program to evaluate the performance of high-burnup fuel from a pressurized water reactor (PWR). Uranium and plutonium compositions were determined for PWR fuel that had spanned five power cycles, culminating in 55,000 to 57,000 MWd/ton burnup. Analyses have been performed on ten samples excised from selected sections of the fuel rods. Hot cell operations required the separation of fuel from cladding and the comminution of the fuel. These tasks were successfully accomplished using a SpectroMil: a ball-pestle-impact grinding and blending instrument manufactured by Chemplex Industries, Inc. (Eastchester, New York). The fuel was dissolved using strong mineral acids and bomb dissolution techniques. Separation of the fuel from fission products was done by solvent (hexone) extraction. Fuel isotopic compositions were determined by the mass spectrometric isotope dilution method using NBS standards SRM-993 and SRM-996. Alpha spectrometry was used to determine the $^{238}$Pu content. Relative correlations of composition with burnup were

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obtained by gamma-ray spectrometry of selected fission products in the dissolved fuel. These experimental results are being used to test computational methods (developed in the Applied Physics Division) for determining the fuel isotopic dynamics in reactor operation.

The Gas Research Institute (GRI) sponsors a multidisciplinary program at ANL to characterize, on a chemical and molecular basis, polyethylene pipe, resins, and other materials used in the manufacture of the pipe and to relate this characterization with mechanical properties such as long-term stability, crack resistance, degradation, and strength. Complementary work on mechanical properties of the pipe is done in the Materials Science and Technology Division.

Over 20 pipe samples were analyzed with the $^{13}$C nuclear magnetic resonance technique. Four types of branching were found: ethyl, n-butyl, n-pentyl, and long (> n-hexyl). The number of branches per thousand backbone carbons ranged from 1.5 to 7.2. Generally, pipes with n-butyl branching fared best in constant tensile load testing. X-ray diffraction measurements on 11 pipe samples indicated that, with one exception, the polyethylene crystallites are larger on the inner surfaces than the outer surfaces. This phenomenon is the result of more-rapid cooling of the pipe on the outer surface during extrusion. In analyses of eight pipe samples, no specific trends relating to mechanical strength could be found; thus, limited amounts of metals in the resin probably have little effect on the mechanical strength of the pipe.

Gel permeation chromatography was used to make molecular weight determinations of commercial polyethylene pipe. The number-average molecular weight ($M_n$) and the weight-average molecular weight ($M_w$) were found to have a slight correlation with the mechanical strength of the pipe; as $M_w$ increased and $M_n$ decreased, the mechanical strength increased. The ratio $M_w/M_n$, a measure of the dispersion of molecular weight, favored a broader molecular weight range.

With GC/MS, a direct relationship was found between the concentration of low-molecular-weight polyethylenes (n-alkanes and n-alkenes) and the strength of the pipe. As the concentration of the low-molecular-weight polyethylenes increased, the mechanical strength of the pipe increased. In experiments with pipe having poor mechanical properties, an extremely low concentration of low-molecular-weight polyethylenes was found. The GC/MS technique has been found to be useful as a fingerprinting tool to identify sources of the pipe and the manufacturer, resin, and additives.

The National Park Service is coordinating a study under the National Acid Precipitation Assessment Program to find ways of maintaining historical monuments and buildings. There is much concern about protection of marble and limestone exposed to the acidic outdoor environment because these materials are widely used as the exterior structures of buildings and monuments. Calcium carbonate stones are especially sensitive to acid. Field tests of these building materials under carefully monitored environmental conditions are being conducted to measure damage rates. The AC.$^+$ is providing analytical support for this project. Three to four hundred samples of limestone and marble exposed to a variety of atmospheric conditions have been analyzed by ACL to date. Adsorbed anions (especially fluoride, chloride, nitrate, and sulfate) have been determined by ion chromatography, and metals present in the
samples have been determined by ICP/AES. These results will be used in an effort to quantify the individual effects of the important damage parameters, which should lead to improved strategies for environmental protection of stone.

The ACL completed several projects under an interagency agreement with Region V of the Environmental Protection Agency. These projects included application of GC and GC/MS techniques to analyses of samples posing unusual or difficult analytical problems, the evaluation of the accuracy and reproducibility of published analytical methods, and quality control tests on work done by other laboratories. Completed and ongoing projects include analyses for a drinking water survey, methods development for atmospheric loading tests, analyses for particulate organic carbon, analysis for PCBs, analysis of glass fiber filters, volatile organic analysis, and development of analytical methods for dioxins.

In the past year, a containment room (see Fig. IX-1) was set up to process potentially hazardous samples. It allows laboratory chemists to safely
handle hazardous waste samples while being isolated from them. These wastes must be characterized before they can be properly handled, transported, stored, or disposed of. The containment facility is a 41-m$^2$ (440-ft$^2$) room that contains a large glovebox assembly, lab bench space, cabinets, a stainless steel hood, a vented solvent cabinet, and a sink. The air pressure in the facility is held negative with respect to the building. After samples have been obtained in the field by the sampling crew, they can be brought into the containment room from the building hallway using a pass-through lock. They can then be placed in the first module of the glovebox assembly, which is isolated from the remainder of the assembly by another pass-through lock. Testing of the samples for ignitability, corrosivity, and reactivity can then be carried out in the larger section of the assembly. Following these tests, the waste can be safely sampled for identification and quantitation of the toxic metal and organic contaminants (priority pollutants).

Other improvements in ACL facilities and capabilities include the following:

- Facilities are available to handle samples generated by work on the IFR project; on order is an ICP/AES unit for analyzing radioactive samples from the IFR and other projects.

- New equipment installed in FY 1985 includes an atomic absorption spectrometer (with graphite furnace, Zeeman background correction, and automatic sampling), a trace gas analyzer, a multichannel gamma analyzer system, a backscatter detector for the scanning electron microscope, an X-ray generator, and a new data system for a set of gas chromatographs.

- Our multidimensional GC capabilities have been expanded to include dual detectors (application includes the analysis of Freon degradation products).

New projects initiated in FY 1985 in which ACL staff are involved include the following:

- The homogeneity of samples obtained from the fluidized-bed mixer in the Premium Coal Sample Facility is being determined by neutron activation analysis.

- Hypochlorite-treated hydrazine fuels are being characterized by GC/IR and GC/MS techniques.

- The distribution of lead in soils collected from playgrounds is being determined by atomic absorption spectrophotometry as part of a program to relate potential lead exposure to traffic patterns.

- Techniques are under development for the simultaneous removal of NO$_x$/SO$_x$ from the stack gases in wet scrubbers used in coal-fired power plants and industrial boilers.
The Computer Applications Group provides assistance to CMT members in many aspects of computer-related activities, including (1) laboratory data acquisition and control, (2) computer modeling and simulation studies, (3) post-analysis of experimental results, (4) graphics applications, (5) information management systems and data-base development, (6) operating system maintenance, (7) computer networking, (8) procurement of equipment for automatic data processing, and (9) advisory, educational, and consulting services.

The Computer Applications Group has responsibility for (1) software maintenance and development for nearly 20 minicomputer data acquisition systems and the Division's VAX 11/780 central computing facility [manufactured by Digital Equipment Corp. (DEC)] and (2) hardware maintenance of various small systems and peripherals, including the Division's terminal communications system.

This year's major technical achievement was in the area of laboratory data acquisition and control for the proof-of-breeding (POB) project (see Sec. VI.D). To meet the stringent limits placed on errors in measurements and analytical determinations, this project required automatic, error-free collection and processing of data and rigorous control over the execution of the multistep operating procedures for the shear and dissolvers. Thus, it was decided to use a DEC PDP-11/23 minicomputer for control of the shear and dissolvers, another DEC PDP-11/23 minicomputer for data collection and processing for a gamma analyzer, and a Hewlett-Packard desktop computer for data collection and processing for a high-resolution mass spectrometer. Our work for the POB project demonstrated the substantial benefits that can be derived from a distributed network approach to data acquisition and reduction and process control. For example, results from the data processing and analysis were transmitted to the VAX for further analysis and collation, and then the analytical results were made part of detailed reports generated by text processing systems on the VAX. Incorporating new and existing computer systems into the Division's local area network has routinely provided users of these systems with convenient access to the many software aids available on the VAX.

At present, the VAX 11/780 is being used by over 220 members of the Division and other ANL personnel. Major improvements to the VAX during 1985 include expansion of its disk storage capacity to approximately 2000 megabytes (Mb). Memory has been increased to 16 Mb and supports up to 50 simultaneous users. In 1986, CMT plans to upgrade the VAX to a model 11/785, which will increase capacity by 50-70% to better accommodate its increased usage. Installation of a Divisional local area network, based upon Ethernet, has provided increased reliability and communications bandwidth for interprocessor communications within the Division. We are also assisting in the formulation of plans to develop a Laboratory-wide network for interconnecting the many DEC computers on site. The expected procurement of a Private Branch Exchange (PBX) at ANL (to be installed in 1987) will further improve data communications at the Laboratory by providing the capability for high-speed terminal-to-host and host-to-host data links.

The VAX 11/780 continues to be used for a wide variety of applications including analysis of experimental data, theoretical calculations in basic energy science, graphics, electronic mail, and other office automation and
management functions. The interconnection of CMT's VAX to the National Magnetic Fusion Energy Computing Center (NMFECC) at Livermore National Laboratory has been heavily utilized for file transfer and interactive terminal sessions. This link is also being used to access a Cray supercomputer at Livermore.

The High-Temperature Thermodynamics Group in CMT has recently acquired a DEC MicroVAX-II. This computer, which has approximately 90% the computational power of a VAX 11/780 and is connected to CMT's Ethernet to provide access to various peripherals, will be used for theoretical research by group members.

A block diagram of the CMT computing facilities is presented in Fig. X-1. A DEC PDP-11/44 computer serves as a front-end communications processor to which many of the other laboratory computer systems in CMT are connected. The RSX-11M-Plus Development System is employed by the Computer Applications Group for software development.

Fig. X-1. Block Diagram of CMT Computing Facilities
XI. ADDENDUM.

CHEMICAL TECHNOLOGY DIVISION
PUBLICATIONS--1985

The Division's publications and oral presentations for 1985 were entered into a bibliographic data base on the VAX-11/780 computer. The pages that follow are a printout of this information sorted into six categories: (1) journal articles and book chapters, (2) patents, (3) ANL progress and topical reports, as well as contributions to reports published by organizations other than ANL, (4) abstracts and papers published in proceedings of conferences, symposiums, workshops, etc., (5) oral presentations at scientific meetings and seminars not referenced in the fourth category, and (6) papers accepted for publication but not yet published.
A. Journal Articles & Book Chapters

Compensation Effect in the Pyrolysis of Cellulosic Materials
R. K. Agrawal

On the Use of Arrhenius Equation to Describe Cellulose and Wood Pyrolysis
R. K. Agrawal

The Effect of Pressure on the Pyrolysis of Newsprint
R. K. Agrawal and R. J. McCluskey
Fuel 64, 1502-1504 (1985)

The Hydration Alteration of a Commercial Nuclear Waste Glass
J. K. Bates, M. J. Steindler, B. S. Tani, and F. Purcell
Chem. Geol. 51, 79-87 (1985)

Modeling of Tritium Transport in Lithium Aluminate Fusion Solid Breeders
M. C. Billone and R. G. Clemmer
Fusion Technol. 8(1), 875-880 (1985)

Rotational Analysis of the Red Electronic Emission Spectrum of Molybdenum Nitride (MON)
R. C. Carlson, J. K. Bates, and T. M. Dunn

The TRIO Experiment
R. G. Clemmer, P. A. Finn, B. Misra, M. C. Billone, A. K. Fischer, S. W. Tam,
C. E. Johnson, and A. E. Scandora
J. Nucl. Mater. 133-134, 171-175 (1985)

Steam Rapidly Reduces the Swelling Capacity of Bentonite
Rex A. Couture
Nature 318(6041), 50-52 (November 1985)

Theoretical Investigation into the Nature of the Second Vertical Ionic State of the Water Dimer
L. A. Curtiss
Chem. Phys. Lett. 113(5), 409-411 (December 1984)

Vibrational Analysis and Ab Initio Molecular Orbital Calculations of the Molecular Force Constants of Gaseous CF$_4$ and SiF$_4$
L. A. Curtiss and V. A. Maroni

Investigation of the Differences in Stability of the OC-···HF and CO-···HF Complexes
L. A. Curtiss, D. J. Pochatko, A. E. Reed, and F. A. Weinhold
J. Chem. Phys. 82(6), 2679-2687 (March 1985)
Theoretical Investigation of Li and Be Atom Complexes with $H_2O$
L. A. Curtiss and J. A. Pople
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Theoretical Investigation of $H_2O$ Complexes with the Metal Atoms, Li, Be, Na, and Mg
L. A. Curtiss and J. A. Pople
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Theoretical Studies of the Interaction of $H_2O$ with Small Clusters of Beryllium Atoms
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D. G. Ettinger, L. A. Raphaelian, and D. T. Raske

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Experimental Comparison of $^{18}$O/$^{16}$O Ratios in $\text{H}_2\text{O}_2$, $\text{H}_3\text{O}$, and $\text{SO}_4^{2-}$ in Rainwater
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Volatilization and Reaction of Fission Product Deposits in Flowing Steam
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Proposed Methods for Treating High-Level Pyrochemical Process Wastes
T. R. Johnson, W. E. Miller, and R. K. Steunenberg

Helium Production in Copper by a Thermal Three-Stage Reaction
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M. Krumpeit
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G. H. Kucera, N. Q. Minh, J. L. Smith, and F. C. Mrazek
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J. E. Kulaga

Measurement of Alkali Vapors in PFBC Flue Gas and Their Control by a Granular-Bed Sorber
Presented at Fifth Annual Contractors' Meeting on Contaminant Control in Coal-Derived Gas Streams, Morgantown, WV, May 7-9, 1985
Use of Electronic Worksheets for Calculation of Stagewise Solvent Extraction Processes

R. A. Leonard

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Demonstration of a Modified TRUEX Process for Actinide Removal from Liquid Wastes Where the Organic Phase Is More Dense Than the Aqueous Phase

R. A. Leonard and G. F. Vandegrift

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The TRUEX Process for Actinide Removal from Nuclear Waste

R. A. Leonard, G. F. Vandegrift, and E. P. Horwitz


Variation of Maximum Throughput with Time in Staged Solvent Extraction Equipment

R. A. Leonard and A. A. Ziegler


Modified-PUREX/TRUEX Demonstration Program

N. M. Levitz

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Analyzing the Rock That Burns—Atomic Spectroscopy in Coal Analysis

P. C. Lindahl

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Solid Tritium Breeders for D-T Fusion Reactors


Presented at Sixth Topical Meeting on the Technology of Fusion Energy, San Francisco, CA, March 3-7, 1985

Infrared Spectroscopic Studies of Zeolite Catalysts

V. A. Maroni

Presented to Department of Chemistry and Physics, State University of New York, Old Westbury, NY, October 2, 1985

Preparation of High-Density Yttria-Stabilized Zirconia by Tape Casting

C. C. McPheeters, G. C. Mejicano, R. K. Steunenberg, and F. C. Mrasek


Advanced Lead-Acid Battery Technology—Status of Flow-Through Cell Development

J. F. Miller

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Laboratory Test Experience on Nickel/Iron Batteries
J. F. Miller
Presented at Joint Europe-USA Workshop on Status of Electric Vehicle Battery Systems, Essen, West Germany, June 19-21, 1985

Laboratory Test Results on EV-2300 Lead-Acid Batteries
J. F. Miller
Presented at Joint Europe-USA Workshop on Status of Electric Vehicle Battery Systems, Essen, West Germany, June 19-21, 1985

Facilities for Development of IFR Pyrochemical Processing
W. E. Miller
Presented at the Fifth Annual Plutonium Pyrochemical Workshop, Rocky Flats Plant, CO, October 7, 1985

Laboratory Scale Demonstration of Electrorefining Process
W. E. Miller
Presented at the 22nd NEEC Student/Faculty Conf. (on the Integral Reactor), Argonne, IL, September 19-20, 1985

Choice of Pyroprocess for Integral Fast Reactor Fuel
W. E. Miller, T. R. Johnson, and Z. Tomczuk

Emissivity of Lithium Ceramics
B. Misra and C. M. Jones

Electrode Kinetic Measurements of Very Fast Reactions: Metal Deposition—Dissolution in Molten Halides
Z. Nagy and J. L. Settle
Presented at Int. Workshop of High-Temperature Molten Salt Batteries, Argonne National Laboratory, November 5-7, 1985

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M. J. Pellin, C. E. Young, W. F. Calaway, and D. M. Gruen
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Fluidized-Bed Combustion Technology
W. F. Podolski
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Pressurized Fluidized-Bed Combustion Technology Status
W. F. Podolski
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A Data Processing Technique for Deconvoluting Capillary Column GC/MS Data; Its Use in the Analysis of Priority Pollutants
L. A. Raphaelian

A Technique for Deconvoluting Capillary Column GC/MS Peaks and Correcting Skewed MS Data
L. A. Raphaelian
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Characterization of Some Low-Molecular-Weight Components of Commercial Plastic Fuel Gas Pipe by Gas Chromatography/Mass Spectrometry
L. A. Raphaelian and D. G. Ettinger

Cryogenic Matrices Applied to Analytic and Spectroscopic Studies
G. T. Reedy, D. G. Ettinger, and J. F. Schneider

Applications of GC/Matrix-Isolation FTIR
J. F. Schneider
Presented at Amoco Research Center, Naperville, IL, October 23, 1985

A Comparison of GC/IR Interfaces: The Light Pipe Versus Matrix Isolation
J. F. Schneider and J. C. Demirgian
Presented at 190th Am. Chem. Soc. Meeting, Chicago, IL, September 8-13, 1985

Matrix Isolation Versus the Light Pipe as an Interface for GC/FTIR
J. F. Schneider, J. C. Demirgian, and J. Stickler
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Environmental Analysis by GC/Matrix Isolation/IR
J. F. Schneider, G. T. Reedy, and D. G. Ettinger

Characterization of Colloids from Gorleben and Basalt Groundwaters and Their Influence on the Condition of Dissolved Americium
M. G. Seitz and G. Buckau
Presented at the Institute for Radiochemistry, Technical University of Munich, Garching, West Germany, May 30, 1985

Post-Test Analysis of FACC Sodium/Sulfur Cells
J. A. Smaga and J. E. Battles
Presented at Cerametec, Salt Lake City, UT, September 17, 1985
Molten Carbonate Cathode Material Development
J. L. Smith, N. Q. Minh, G. H. Kucera, and F. C. Mrazek

The Interaction of High Energy Protons with Metals
R. K. Smither
Presented at LTH-4 Particle Beam Quarterly Review Meeting, Kirtland Air Force Base, NM, November 20-21, 1985

Expected Behavior of Plutonium in the IFR Fuel Cycle
R. K. Steunenberg and I. Johnson

Element Redistribution during Hydrothermal Alteration of Rhyolite: Yellowstone Drill Cores Y-7 and Y-8
Neil Sturchio

Non-neutron Test Stands for Blankets (Liquid Metal)
D.-K. Sze
Presented at FINESSE Int. Workshop, UCLA, Los Angeles, CA, March 11-13, 1985

Modified Flibe as the Coolant for Fusion Reactor
D.-K. Sze, J. Jung, and E. T. Cheng
Presented at Nuclear Engineering Department, University of Wisconsin, Madison, WI, May 22, 1985

Quantum Percolation Thresholds and Random Walk Fractal Dimensions
S. W. Tam and C. E. Johnson
Presented at the Symp. on Fractal Aspects of Materials, Materials Research Society, Boston, MA, December 2-6, 1985

The Thermal Conductivity of Ceramic Materials at High Temperatures
S. W. Tam and C. E. Johnson

Electrorefining of Uranium and Plutonium from Liquid Cadmium
Z. Tomczuk, D. S. Poa, W. E. Miller, and R. K. Steunenberg

Greater-Confinement Disposal of Radioactive Wastes
L. E. Trevorrow
Presented at the Third Annual Midwest Workshop on Low-Level Radioactive Waste Management, Post '86: Expectations and Looming Decisions, Columbus, OH, October 23-24, 1985

Studies of the Hydrolytic and Gamma-Radiolytic Degradation of the TRUEX-CC14 Process Solvent
G. F. Vandegrift
Presented at the Actinide Workshop, Rockwell Hanford Operations, Richland, WA, May 22-24, 1985
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G. F. Vandegrift, R. A. Leonard, and M. J. Steindler
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Presented at the 64th Annual Meeting Transportation Research Board, Washington, DC, January 14-17, 1985

Thermal Radiation from Potassium Atoms in MHD Systems
C. S. Wang, L. S. H. Chow, and E. B. Smyk
Presented at 23rd Symp. on Engineering Aspects of MHD, Pittsburgh Energy Technology Center, Somerset, PA, June 25-28, 1985

An Overview of Atmospheric Organic Compound Sampling and Analysis
R. J. Wingender
Presented at the Annual Meeting of the National Atmospheric Deposition Program, Fort Collins, CO, October 7-11, 1985

Angular, Velocity, and Excited State Distributions of Sputtered Atoms
C. E. Young, M. J. Pellin, W. F. Calaway, and D. M. Gruen
Presented at the 1985 Conf. on the Dynamics of Molecular Collisions, Snowbird, UT, July 14-19, 1985
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Aqueous Corrosion of Natural and Nuclear Waste Glasses I: Comparative Rates of Hydration in Liquid and Vapor Experiments of Elevated Temperatures
T. A. Abrajano, C. D. Byers, and J. K. Bates
To be published in J. Cryst. Solids

On the Compensation Effect
R. K. Agrawal
To be published in J. Therm. Anal.

Photoionization Mass Spectrometric Study and *Ab Initio* Calculations of the Ionization and Bonding in P-H Compounds; Heats of Formation, Bond Energies and the $^4\text{B}_1-^2\text{A}_1$ Separation in PH$_2^+$
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High-Conductivity Glass Electrolytes for Sodium-Sulfur Batteries
I. Bloom, P. A. Nelson, and M. F. Roche
To be published in Proc. of the 32nd Int. Power Sources Symp.

Products of the Neutralization of Hydrazine Fuels with Hypochlorite
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Rekindled Interest in Pyrometallurgical Processing (The 1984 Robert E. Wilson Memorial Lecture)
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