Chemical Technology Division

Annual Technical Report 1987

Argonne National Laboratory

Operated by The University of Chicago for the U. S. Department of Energy under Contract W-31-109-Eng-38

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Cover Description

1. Geometric relationship between M^+ and AX_4^- tetrahedron derived from molecular dynamics calculations of a complexing ionic liquid similar to tetrachloroaluminate.
2. Gas chromatograph/matrix isolation infrared spectrometer, which is being used for analysis of organics in solid waste.
3. Eight-cell stack of monolithic solid oxide fuel cells.
4. Geyser at Yellowstone National Park under investigation to gain better understanding of the water/rock interactions in active hydrothermal systems.
5. Facilities for large-scale electrorefining of simulated fuel for the Integral Fast Reactor.

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Available from
National Technical Information Center
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

NTIS price codes
Printed copy: A10
Microfiche copy: A01

Distribution Category:
General, Miscellaneous, and Progress
Reports (Nuclear) (UC-2)
General, Miscellaneous, and Progress
Reports (Nonnuclear) (UC-13)

ANL-88-19

ANL--88-19

DE88 011588

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CHEMICAL TECHNOLOGY DIVISION
ANNUAL TECHNICAL REPORT
1987

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May 1988

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ANL-87-19	January-December 1986
ANL-86-14	January-December 1985
ANL-85-9	January-December 1984
ANL-84-26	January-December 1983

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**CHEMICAL TECHNOLOGY DIVISION
ANNUAL TECHNICAL REPORT
1987**

ABSTRACT

Highlights of the Chemical Technology (CMT) Division's activities during 1987 are presented. In this period, CMT conducted research and development in the following areas: (1) high-performance batteries--mainly lithium-alloy/metal sulfide and sodium/sulfur; (2) aqueous batteries (lead-acid, nickel/iron, etc.); (3) advanced fuel cells with molten carbonate or solid oxide electrolytes; (4) coal utilization, including the heat and seed recovery technology for coal-fired magnetohydrodynamics plants and the technology for fluidized-bed combustion; (5) methods for the electromagnetic continuous casting of steel sheet and for the purification of ferrous scrap; (6) methods for recovery of energy from municipal waste and techniques for treatment of hazardous organic waste; (7) nuclear technology related to a process for separating and recovering transuranic elements from nuclear waste, the recovery processes for discharged fuel and the uranium blanket in a sodium-cooled fast reactor, and waste management; and (8) 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 fluid catalysis for converting small molecules to desired products; materials chemistry for liquids and vapors at high temperatures; interfacial processes of importance to corrosion science, high-temperature superconductivity, and catalysis; the thermochemistry of various minerals; 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 and Development*

The Division is engaged in a variety of activities related to the development of high-performance secondary batteries (lithium/metal sulfide with molten-salt electrolyte and sodium/sulfur with glass electrolyte) and aqueous-electrolyte batteries (lead-acid, nickel/iron, etc.). These activities include research, performance and lifetime testing, post-test examination, modeling, and test data analysis of battery systems. In addition, the Division provides technical management of industrial contracts from the Department of Energy (DOE) for battery R&D. The batteries being developed by CMT are primarily intended for electric-vehicle propulsion, with secondary consideration given to utility energy storage and military uses.

The research effort on the Li-alloy/FeS₂ cell has resulted in several advances in this technology. A small-scale prismatic cell with the discharge limited

to the upper voltage plateau has been operated for almost 500 cycles with only a 5% decline in capacity. Capacity stability had been a major problem in earlier designs of the FeS_2 cell. In addition, techniques have been developed for over-discharge and overcharge protection of the FeS_2 cell. A new cylindrical design for the FeS_2 cell shows promise of achieving similar performance to the improved prismatic FeS_2 cell. This design has the added advantage of using positive-electrode current collectors in the shape of a wire rather than sheet, which is expensive and difficult to fabricate. Several bipolar FeS_2 cells have shown excellent pulse-power capability in tests under repetitive 1- to 10-ms pulses.

An effort is underway to develop glass electrolytes for Na/S cells as an alternative to the present ceramic electrolytes. In 1987, a high-soda glass electrolyte (composition in mol%: 42 Na_2O , 8 Al_2O_3 , 5 ZrO_2 , and 45 SiO_2) was fabricated and successfully tested in a small-scale Na/S cell. This glass can also be used as the membrane in a miniature reference electrode. Such reference electrodes in sodium polysulfide melts demonstrated emf reproducibility to ± 1 mV and emf stability for 18 h. A reference electrode containing a glass membrane with slightly modified composition showed promising emf stability (23 ± 3 mV for 5 h) in NaCl-AlCl_3 melts.

The CMT Division is also participating in a program to develop the Li-alloy/FeS battery for electric van propulsion. During 1987, two van batteries (36 V each) fabricated by Gould Inc. underwent stationary testing at CMT. The performance of the first battery was satisfactory but its lifetime was inadequate (113 cycles). Testing of the second battery is still in progress.

In 1987, the Division continued to provide DOE with technical management of industrial contracts for development of lead-acid batteries (Johnson Controls, Inc.) and Ni/Fe batteries (Eagle-Picher Industries, Inc.). In addition, CMT was assigned technical management responsibility for a program involving the research, development, and demonstration of an urban passenger bus powered by a methanol-fueled fuel cell/battery. This program is being funded by the Departments of Energy and Transportation.

The Analysis and Diagnostics (A&D) Laboratory in CMT continues to play a leading role in the testing and evaluation of various battery technologies (Na/S, Zn/Br, lead-acid, and Ni/Fe) fabricated by both domestic and foreign battery developers for electric-vehicle and load-leveling applications. In the past year, technology evaluation was completed on 200 cells and was continued on 295 others.

Physical and chemical analyses of battery cells are performed at CMT after termination of testing at the A&D Laboratory or at other facilities. In 1987, post-test analyses were conducted on Na/S cells from Chloride Silent Power Ltd., lead-acid modules from Lucas Chloride EV Systems and Exide Management and Technology, and Li-alloy/FeS cells from Gould Inc. These examinations served to identify failure mechanisms, to assess the reliability of hardware components, and to characterize changes in electrode morphology. For example, the Li-alloy/FeS cells examined were part of the van battery built by Gould and tested at CMT for 113 cycles. Analysis of three Li-alloy/FeS cells from the battery indicated that iron deposition in the electrode separator had caused the short circuit.

Finally, electrochemical models were developed to predict the energy and power capability of cylindrical Li-alloy/FeS₂ cells and Na/S cells with beta-alumina electrolyte and large diameter-to-length ratios. The information obtained from model calculations is being used in making design improvements for these two cell systems.

2. *Advanced Fuel Cell Development*

Two advanced fuel cells are being studied at ANL: the molten carbonate fuel cell and the solid oxide fuel cell. The work on the molten carbonate fuel cell emphasizes development of an alternative cathode material to the present nickel oxide, which has been found to have a long-term stability problem. The work on the solid oxide fuel cell is concentrated on development of a novel cell design that promises to yield very high power per unit mass or volume.

In 1987, fabrication techniques were developed to obtain the desired complex microstructure for the cathode in the molten carbonate fuel cell. The techniques involve the fabrication of very small ceramic tubes or ceramic fibers. Several cathode structures were fabricated from NiO fibers and tubes and were then characterized by scanning electron microscopy and mercury porosimetry. The results indicated that both the fibers and tube materials can be tailored to yield the structure needed for a working cathode. This finding was confirmed in cell tests with NiO cathodes fabricated by the new techniques. Testing of cells with an alternative cathode material (LiFeO₂) fabricated by the new techniques is in progress.

During 1987, ANL continued to provide technical support to the molten carbonate fuel cell program of the DOE Morgantown Energy Technology Center. This support includes assistance in program planning, systems analysis, technical monitoring of contractor efforts, and preparation of work statements for new work. The major contractors for this program are International Fuel Cells and Energy Research Corp. Other contractors include Ceramtec, Inc., the Institute of Gas Technology, the Illinois Institute of Technology, the University of Minnesota, and the Illinois Institute of Technology Research Institute.

Also under development at ANL is the monolithic solid oxide fuel cell. The monolithic design employs the same thin ceramic components used in other oxide fuel cells in a strong, lightweight honeycomb structure of small cells. At present, the major challenge for development of this design is fabrication of multilayer components containing the anode, cathode, electrolyte, and cell-to-cell interconnection. Fabrication involves tape casting thin-layer ceramic components, assembling the desired configuration, and firing the configuration in one high-temperature operation. Progress during 1987 includes improvement of the monolith's structural integrity by better matching of sintering shrinkages and thermal expansion coefficients of the four components. This improvement is reflected by the fabrication of three- and four-cell arrays with few gas-transmitting defects.

The Division also performs systems analysis in support of the DOE fuel cell program. The purpose is to assess the economic viability of fuel cell systems for utility power plant applications and to define R&D priorities. In 1987, a systems analysis was completed for various fuel processing alternatives with the

solid oxide fuel cell. The results indicated that emphasis should be placed on the development of *in situ* sulfur-capturing gasifiers and on pressurized cell operation.

3. Fossil Fuel Research

The fossil fuel program at CMT consists of activities associated with (1) fluidized-bed combustion technology, (2) heat and seed recovery technology for coal-fired magnetohydrodynamics (MHD), (3) slagging combustion for control of SO_x/NO_x emissions, (4) methods for separation and characterization of coal macerals, and (5) modeling of the deposits arising from coal-fired combustion and conversion systems.

For several years, CMT has been investigating the use of sorbents for the removal of alkali metal vapor compounds from pressurized fluidized-bed combustion. Previous laboratory tests had indicated that activated bauxite would be an effective sorbent, and a granular-bed sorber has been tested on the pressurized fluidized-bed combustor in CMT. Results of these tests and subsequent investigations indicated that the sampling and analysis of the alkali vapor compounds were complicated by the interaction of these compounds with ash particulates and also with the stainless steel sampling lines. The interference caused by ash particles has been reduced by filtering the gas stream with ceramic filters, and further work is being directed toward overcoming the capture of alkali vapor by the stainless steel sampling lines.

Argonne is involved in an experimental effort to assess materials and process performance of in-bed air heaters for cogeneration of electricity and process steam in an atmospheric fluidized-bed combustor (AFBC). A series of six laboratory tests completed in 1987 has provided corrosion information on a variety of structural materials, coatings, claddings, and weldments under conditions that simulate the atmosphere of fluidized-bed combustion. A test of heat-exchanger tube bundles for 1000 h in a large AFBC unit at Rockwell International is planned for next year.

In another effort, a fluidized-bed combustor (0.15-m dia) at ANL was used to investigate the combustion characteristics of a high-volatile coal and three samples of the coal at different levels of devolatilization. Improvements in combustion efficiencies occurred with increases in bed temperature, percent of fuel volatile matter, and air/fuel stoichiometric ratio.

The CMT Division is the lead ANL division in a multidivisional effort that is directed toward developing the technology required for the design of components in the MHD bottoming cycle. During this past year, three combustion tests in the 2-MW(t) Fossil Energy Users Laboratory (FEUL) at ANL were completed to obtain data on the enhancement of radiant heat transfer caused by the presence of potassium atoms in the combustion gas. The test results provided further validation of a model used in generating scale-up data on the effective emissivity of MHD combustion gases. The gas flow in MHD diffusers and radiant boilers was numerically analyzed with a three-dimensional model; this model is being used to predict the potential for erosion and burnout of the boiler back wall by the high-velocity, high-temperature gas jet exiting the diffuser in an MHD plant. Laboratory autoclave corrosion tests of candidate alloys for use in the bottoming cycle were initiated this year. The test results will be compared with materials performance in other MHD pilot plant facilities. A particle evolution code developed by ANL was used in the analysis of particle size distribution

measurements in a small-scale combustion test facility. Comparison of actual versus predicted values of number density and average particle size showed excellent agreement. Other tests carried out in FEUL have provided further validations of a model that evaluates the fouling efficiency of a convective heat exchanger.

Tests were conducted to investigate injection of pressure-hydrated limestone into the first stage of a 2-MW(t) two-stage slagging combustor. These tests demonstrated that the staged slagging combustor has potential for controlling SO_x/NO_x emissions.

A continuous process is being developed for the separation of coal into its maceral fractions. This process is based on the fact that, when a paramagnetic fluid is placed in a magnetic field gradient, the apparent density of the fluid increases. A new coal-maceral separation system has been designed and constructed. This system includes a colloidal suspension of magnetite, a centrifugal cell, and an electromagnet. Tests are underway with polymer and coal suspensions to determine the efficiency of separation with this system.

An investigation has begun into the physical and chemical nature of deposits that may form on cooled surfaces of fossil fuel combustion and conversion systems. The objective of the effort is to develop a model of the deposit's chemical composition, physical and morphological characteristics, and interactions with the substrate. Under certain conditions, these deposits penetrate the protective oxides on the metal, and accelerated corrosion may occur. During the last year, an invasion percolation model was constructed to describe the capillary infiltration process of molten deposits through the oxide scale.

4. *Steel Industry/Federal Laboratories Research Initiative*

The Division participated in efforts to develop (1) an electromagnetic casting process for large-aspect-ratio shapes such as steel sheet and (2) processing schemes that will produce high-quality steels from low-grade ferrous scrap.

The work on an electromagnetic casting process was principally concerned with development of magnet technology, a liquid metal feed system, a coolant system, and sensors and process controllers. In 1987 a test magnet was designed and built for performing horizontal levitation experiments with liquid tin. Experiments were conducted by energizing the magnet from a power supply with frequency of 10 kHz and power of 30 kW. Results indicated that a higher power and frequency source may be needed to achieve stable levitation of the liquid metal. Also, extensive computer simulations of many magnet designs for both horizontal and vertical casters were made in two and three dimensions.

The casting process requires a system that will provide a suitable feed stream from the liquid metal source to the caster. The requirements of the liquid metal feed system (tundish, pump, nozzles, and flow controls) for various scales of electromagnetic continuous casters were identified, and conceptual designs were developed. Both analytical computer models and physical models were used to obtain information and data needed for conceptual and engineering system designs. Experiments established the important geometrical and hydrodynamic parameters that control and influence fluid flow patterns in the tundish, nozzle, and stream entering the electromagnetic casters.

A key element in the development of the electromagnetic casting process is a coolant system able to remove a large amount of heat in a short time. Extensive theoretical and numerical analyses were conducted to define the coolant requirement and identify possible solutions to the design problems. Reference operating conditions have been selected. These conditions include a casting speed of 30 cm/s, magnet length of 4-10 m, coolant pressure of 140-210 kPa, steel emissivity of 0.4-0.6, and coolant velocity of 30-40 m/s. Consistent with these operating conditions, work was directed toward (1) parametric investigations for establishing the cooling requirements in terms of casting speed, magnet length, coolant mass flow rate, and degree of heat transfer augmentation, (2) experiments to obtain supporting data for heat transfer augmentation, and (3) development of nomograms for studying the interaction of various operating parameters in the casting process.

Sensors and control systems are required for on-line monitoring and automatic control of the electromagnetic casting process. A capacitance-type wave detector was developed for quantifying the surface-wave formation in experiments on liquid metal stability. An assessment of feed system sensors and controls was initiated.

In another research effort, preliminary work was carried out on a process to remove copper and other tramp elements from scrap steel. Copper, present at about 0.6 wt% in common scrap steel, must be reduced by a factor of six or higher to produce high-grade steel. It was determined from thermodynamic considerations that using FeS-Al₂S₃ slag could remove the copper as Cu₂S. Copper distribution factors between slag and metal phases were measured in laboratory experiments using carbon-saturated iron at 1365-1455°C. Distribution factors as high as 30 were obtained. Such a slag refining step can be incorporated into the electric arc steel-making process. After melting the scrap in the arc furnace, the steel would be treated with a sulfidic slag to remove the copper; any added sulfur would be removed in a follow-on step to yield the desired clean steel. Tin and other electronegative elements could be removed using an electropositive element such as calcium.

Cost analysis showed that the copper removal process could produce liquid steel at potential savings of 20 to 30% compared with the costs of producing liquid steel from iron ore using blast furnaces, coke ovens, and basic oxygen furnaces. However, the costs of disposal of the spent sulfidic slags were not included in these evaluations.

5. *Municipal and Hazardous Waste*

The Division is engaged in (1) research on the thermochemical conversion of municipal solid waste (MSW) into gaseous and liquid fuel and (2) the development of methods for treating reactive metal and hazardous organic waste.

Past attempts at producing an economical fuel from MSW have not been successful. Before commercial processes can be developed, more information is needed about the basic mechanisms, kinetics, and chemistry of MSW pyrolysis. Thus, CMT is conducting experiments to determine the basic mechanisms of the thermokinetic degradation of cellulosic MSW feedstock (newsprint, kraft paper, cardboard, and maple wood chips) under pyrolysis conditions. Infrared spectra

were obtained for tars produced at 450 and 700°C with kraft paper as the only feedstock. The results indicated that, at the higher temperature, either the kraft paper radicals undergo aromatization, or that the lignin component of the kraft paper decomposes. Work was also done on the development of a kinetics model for cellulose decomposition. This model assumes that, as cellulose is heated in a nonreactive environment, it decomposes homogeneously by a first-order process to three products: tars, chars, and gases. Although this model does not accurately reflect the actual pyrolysis mechanism, it is capable of predicting various product yields. Further model development is underway.

The research on hazardous waste treatment includes an investigation of a process for the conversion of reactive metal (primarily sodium) to a glass for disposal. A high-soda silicate glass was selected as the most desirable glass form for sodium disposal. A conceptual process for sodium conversion to a soda-silica-lime glass form was designed.

In another effort, the technical feasibility of using a microwave-assisted chemical process for the detoxification of trichloroethane was demonstrated. Test results showed that, at >500°C, this process will almost completely detoxify trichloroethane, whereas thermal heating will only partially detoxify it (~27-36%).

6. *Nuclear Technology*

Separation Science and Technology. The Division's work in separation science and technology consists of four projects. Three of these projects are concerned with removing and concentrating actinides from waste streams contaminated by transuranic (TRU) elements.

The major project in this area involves development of a generic data base and modeling capability for the TRUEX (TRAnsUranic EXtraction) solvent extraction process. This capability will allow us to design flowsheets for specific waste streams and to predict the cost and space requirements for implementing a site- and feed-specific TRUEX process. Work in this report period was chiefly concerned with collection of batch distribution-ratio data to be used in modeling the partitioning behavior of actinides and important components of nuclear waste. The effects of TRUEX solvent composition, aqueous phase composition, and temperature on its distribution ratio were measured for many different species. The modeling of the extraction behavior of nitric acid and americium is nearly completed. Also as part of this program, a centrifugal contactor was designed for remote operation using standard manipulators.

The second project entails development of the TRUEX process for removing americium and plutonium from waste generated by the Hanford Plutonium Finishing Plant (PFP) while recovering a purified plutonium stream. Major tasks related to this effort included designing and fabricating a prototype centrifugal contactor to be used in the full-scale operation, assisting Hanford in planning and demonstrating the TRUEX process on actual PFP waste, and developing means to monitor the solvent composition through density measurements.

In the third project, a PUREX/TRUEX flowsheet is being developed for removing plutonium from concentrated HCl/brine waste streams. Results of laboratory measurements have permitted refinements to the flowsheets that were defined by earlier studies.

The fourth project, which is unrelated to the first three, is concerned with examining the feasibility of substituting low-enriched uranium (LEU) for the high-enriched uranium (HEU) currently used in the production of fission product ^{99}Mo . Technetium-99m, the daughter of ^{99}Mo , is widely used in medical diagnosis. The three major suppliers of fission-product ^{99}Mo use different target designs and, therefore, different chemical processing to separate the molybdenum from the irradiated uranium. To substitute LEU for HEU, both targets and target processing must be modified for all suppliers. The work in 1987 dealt with demonstrating (1) the fabrication of electrodeposited uranium metal targets to substitute for the currently used electrodeposited UO_2 targets and (2) the processing of uranium silicide targets, which are likely to replace the current uranium aluminide targets in the conversion from HEU to LEU. These demonstrations have shown that conversion to LEU is likely to be technically feasible.

Uranium Metal Electrodeposition. An effort is underway to develop an electrochemical process that will form uniform, dendrite-free deposits of uranium metal from molten salt systems. Application of this technology includes the fabrication of LEU targets for the production of ^{99}Mo and the formation of hollow, free-standing, hemispherical shells of uranium for nuclear application. With both applications, the uranium must be uniform, dense, and dendrite free.

In this report period, experiments were carried out on the plating of uranium onto various substrates from molten LiCl-KCl salt containing 30 wt% uranium trichloride. With pulse plating, the best deposits were formed on nickel and tantalum substrates under a plating regime that included a preanodization step and nucleation pulse. Further studies are needed to improve the uniformity of the uranium deposit.

The Integral Fast Reactor Pyrochemical Process. The Integral Fast Reactor (IFR) is an advanced reactor concept proposed by, and under development at, Argonne. One of its distinguishing features is an "integral" fuel cycle in which the discharged reactor core and blanket materials are processed and fabricated into new fuel elements in an on-site facility. The CMT Division has the responsibility for developing the on-site process for recovering plutonium and uranium from the core and blanket, removing fission products, reenriching the core alloy with plutonium bred in the blanket, and immobilizing fission product wastes in suitable media for disposal.

Pyrochemical-type processes are under development for processing core and blanket fuel materials because metal products can be produced directly. Electrorefining is the key step in the process under development. In this operation, plutonium and uranium are electrolytically transported from solution in a liquid metal anode (cadmium) through a molten chloride salt electrolyte to a suitable cathode. The nonvolatile fission products are removed in electrolyte salt and cadmium anode fractions. Gaseous fission products, xenon and krypton, are released to the inert argon cell gas, from which they are subsequently removed and packaged for disposal.

Currently, the favored process is selective deposition of uranium on a solid steel mandrel for recovery of blanket uranium, and then deposition of uranium and plutonium together into a liquid cadmium cathode. This dual

cathode process has been shown to be feasible, both by experiment and thermodynamic modeling. Interestingly, other actinide elements such as americium and curium accompany plutonium through the process. An engineering-scale facility (capacity, 20 kg uranium) has been constructed to demonstrate large-scale electrolytic transport of uranium and other engineering operations associated with an electrorefiner.

Two methods for dissolving fuel out of segmented (1/4-in.-long pieces) fuel pins are under study--direct dissolution in cadmium at 500°C and anodic dissolution. The latter method involves electrolytic transport of uranium and plutonium from a basket of fuel pins located in the electrolyte, the reverse of product deposition. Anodic dissolution appears to be the fastest of the two methods.

Methods of converting wastes generated by processing IFR fuel to disposable forms are being developed. In the present flowsheet, the rare earth fission products are removed by extraction into cadmium containing 0.1 wt% lithium. The waste salt (now containing cesium, strontium, and iodine) is dispersed in portland cement mortar, which is cast into corrosion-resistant metal containers for disposal. Leaching tests are being performed on mortars of various compositions. The metal waste stream contains the cladding hull, noble metal fission products, and rare earths extracted from the electrolyte salt waste. Cadmium will be first removed by vaporization, and the resulting mixture will be mixed with copper and compacted into a dense copper matrix by hot isostatic pressing for disposal in a geologic repository.

High-Level Waste/Repository Interactions. The Division is investigating the performance of materials under projected repository conditions to provide input to the licensing of the nation's first high-level waste repository. Work over the past year has included (1) the testing of a waste package assemblage in contact with water to measure radionuclide release rates and to establish the mechanism of reaction and (2) the development of laser-based techniques to study the speciation of actinides in groundwater.

As part of the first effort, laboratory tests are in progress to obtain data on the release of waste components from the waste package in a potential site for a high-level waste repository. Variability in materials interactions was found to have been caused by different degrees of sensitization in the weld-affected regions of the metallic waste-form holder. The sensitized metal interacted strongly with the waste glass in the presence of small volumes of repository water. This interaction increased elemental release up to ten times the amount observed without the interaction.

As part of the second effort, the ultra-sensitive detection method known as laser photoacoustic spectroscopy (LPAS) has been applied to the speciation of actinides in simplified groundwater solution at temperatures up to 90°C. The LPAS apparatus demonstrated unprecedented sensitivity in the analysis of americium and plutonium in this solution.

7. *Applied Physical Chemistry*

Fission Product Chemistry. Work is in progress to determine fission product release and transport under accident-like conditions in a light water reactor.

During a loss-of-coolant accident, the fuel temperature will rise above its normal operating temperature and will lead to a rupture of the cladding and release of fission products. Experimental results have been obtained on the interactions between iodine, cesium, and tellurium in a flowing steam/hydrogen mixture. Analysis of the experimental data has shown that the downstream behavior of iodine is dependent upon its reaction with cesium and steam, and the behavior of tellurium is dependent on its reaction with cesium. These complex interactions must be taken into account if accurate predictions of the downstream behavior of volatile fission products are to be made.

Another effort involves investigation into the release of refractory fission products--strontium, barium, and the rare earths--from the molten core-concrete mixtures that would form if a molten core penetrated the bottom of a reactor vessel in a severe accident. The vaporization of the core-concrete mixtures is being experimentally measured using a transpiration method. For these measurements, mixtures of stainless steel, concrete (limestone or basalt), and urania (doped with La_2O_3 , SrO , BaO , and ZrO_2) are vaporized at 2150-2400 K from a zirconia crucible into flowing He-6% H_2 gas. Up to 600 ppm H_2O is added to the gas to fix the partial molar free energy of oxygen in the range -420 kJ to -550 kJ. The fraction of the sample that is vaporized is determined by weight change and by chemical analyses on the condensates that are collected in a condenser tube. The results are being used to test the thermodynamic data base and the underlying assumptions of computer codes employed for prediction of release during a severe accident.

In another effort, the iodide-hydroxide vapor species that form over a solution of CsI and CsOH have been studied. These two molecules are expected to condense on reactor system surfaces after release from the fuel pins and form a solution that will be heated by radioactive decay. Our experimental and calculational work indicated that revolatilization from a solution consisting of 0.1 CsI -0.9 CsOH would produce nearly equal partial pressures of CsI(g) and CsI-CsOH(g) . The existence of the complex molecule CsI-CsOH could lead to a doubling of the iodine released from the reactor containment.

Metal Fuels Properties. An earlier literature survey revealed serious shortcomings in the data available on the thermophysical properties of fuel and blanket materials for the Integral Fast Reactor. An effort was therefore initiated to correct the most important of these deficiencies by performing selected experiments on fuel alloys and cladding materials. In addition, study of other physicochemical areas of importance to the project has been undertaken. To date, thermal expansion measurements have been completed on four fuel alloys and two cladding alloys (D9 and HT9). In addition, thermal conductivity measurements have been made on a U-Zr fuel alloy and the two cladding alloys. Increased attention is now being devoted to clarification of the solid-state transitions in the U-Pu-Zr system.

Fusion-Related Research. A critical element in the development of the fusion reactor is the blanket for breeding tritium fuel. Several studies are underway with the objective of determining the feasibility of using lithium-containing ceramics as breeder material.

One study is focused on determining the adsorption, dissolution, and desorption characteristics of the $\text{LiAlO}_2\text{-H}_2\text{O}$ system--a candidate breeder blanket.

Isotherms at 673 and 773 K were derived for surface adsorption of $\text{H}_2\text{O}(\text{g})$ and for solubility of OH^- in LiAlO_2 as a function of $\text{H}_2\text{O}(\text{g})$ partial pressure. The surface adsorption curves were of the Freundlich type, indicating surface heterogeneity such as the presence of more than one kind of surface site for adsorption. The solubility curves suggested that LiAl_5O_8 is soluble in LiAlO_2 at 673 K, but not at 773 K. The rate of $\text{H}_2\text{O}(\text{g})$ evolution from LiAlO_2 showed the kinetics of the process to be second order in hydroxide.

A computer model has been developed to predict tritium release from a ceramic breeder. In this model, it is assumed that diffusion and desorption are the rate-controlling mechanisms. Calculated results showed excellent agreement with observed values of tritium release from Li_2SiO_3 samples under a pure helium purge gas (from the LISA experiment). Work is in progress to develop a more sophisticated model that takes into account transport in the gas phase.

Since permeation losses from thermally hot blanket systems can be severe, methods are needed to reduce the molecular tritium partial pressure in these systems. A method that has been proposed is the oxidation of tritium to tritiated water. Experiments are in progress to study tritium oxidation in a stainless steel apparatus. Results to date indicate that the yield of tritiated water increases with oxygen level. The maximum yield was 97.2% at 823 K and 912 ppm oxygen.

In neutron dosimetry and damage analysis, neutron facilities (fission reactors and accelerator-based neutron sources) are being characterized in terms of neutron flux and energy spectrum. The goal is to obtain data relevant to materials properties in fusion reactors. In a collaborative effort with Rockwell International, helium-production cross sections were measured for a wide range of elements and alloys in irradiation facilities. Helium production is considered important because 14-MeV fusion neutrons produce considerably more helium than fission neutrons. The results indicated that helium production in ferritic materials during irradiations can be increased in mixed-spectrum reactors by isotopically enriching the samples. In another effort, production rates are being measured for long-lived isotopes in order to assess potential waste-handling problems.

8. Basic Chemistry Research

Fluid Catalysis. Basic research on the nucleophilic activation of hydrogen has shown that alkali metal formates, hydroxides, and carbonates catalyze the water-gas shift reaction in triethylene glycol solution. These are the first examples of main group homogeneous catalysts for this reaction and could be forerunners of improved catalysts that tolerate high concentrations of sulfur since they contain no transition metals. Work was also done on homogeneous phthalocyanine chemistry and resulted in the discovery of a facile method to incorporate solubilizing organic groups into phthalocyanines. It is expected that this method can be used to construct shape- and size-selective catalysts for catalytic studies at high temperature and pressure.

Multinuclear NMR spectroscopy has been the single most useful spectroscopic tool in our studies. To obtain full advantage of the NMR method, a new design has been developed for an NMR probe that allows *in situ* measurements to be made on reacting catalytic systems.

High-Temperature Materials Chemistry. Under investigation in this effort are superconducting oxides and associated and ordered solutions.

Emf measurements of oxygen fugacities as a function of stoichiometry of superconducting phases ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) were made at 750°C by an oxygen titration technique with a ZrO_2 electrolyte doped with Y_2O_3 . The measurements covered an oxygen pressure range of 0.21 to 10^{-4} atm. An irreversible orthorhombic tetragonal phase transformation was observed at oxygen pressures of 10^{-3} - 10^{-4} atm for a stoichiometry of $\text{YBa}_2\text{Cu}_3\text{O}_{6.1-6.2}$.

Quantum mechanical calculations of Al_2Cl_7^- and Al_2F_7^- anions revealed differences in structure which are important for understanding ordering in aluminum halide solutions. Molecular dynamics calculations were made of ionic MAX_4 melts in which the X^- anions are polarizable. These melts are analogous to chloroaluminates. With the polarization of the anions, A_2X_6 molecules as well as AX_4^- ions are present in the melt. This result is to be contrasted with the observation of AX_4^- , A_2X_7^- , and $\text{A}_3\text{X}_{10}^-$ anions in an ionic melt with nonpolarizable anions. Thus, we have observed all of the species postulated to exist in chloroaluminate melts in our calculations; however, the relative stabilities of these species differ from those of real melts. In another effort, neutron diffraction studies of the molten equimolar K-Pb alloy revealed the presence of a tetrahedral K_4Pb_4 molecule analogous to structures found in the solid.

Calculations (based on geometric programming) of the combustion of Illinois No. 6 coal under oxidizing and reducing conditions showed that silicates are the major constituents of the liquid condensates at high temperatures (above 1327°C), and that the concentrations of sulfates (under oxidizing conditions) or sulfides (under reducing conditions) in these solutions increase with a decrease in temperature. These results differ significantly from the assumptions generally made concerning the compositions of corrosive deposits from coal combustion or conversion.

Interfacial Materials Chemistry. The investigations into interfacial materials chemistry have led to several discoveries on corrosion of metals and alloys in aqueous media, the properties of species adsorbed on molecular sieve materials, and the characteristics of high-critical temperature (T_c) superconducting oxides. The aqueous corrosion research yielded important data that highlight the changing nature of nickel corrosion processes in various types of aqueous media as a function of temperature up to 210°C . Also, the incorporation of oxyanions into corrosion films formed on nickel has been detected by *in situ* Raman spectroscopy. In related work, the temperature dependence of the anodic Tafel slope for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox reaction was found to be independent of temperature from 25 to 125°C . The empirical potential function that was used to model this electron transfer reaction was verified by *ab initio* molecular orbital calculations. Theoretical studies of molecular sieve materials resulted in insights concerning the templating mechanisms that control the crystallization of molecular sieve frameworks. *In situ* infrared spectroscopic/gas chromatographic measurements were employed in determining the relationship between catalytic activity and acid site structure for both aluminosilicate and aluminophosphate molecular sieve materials. Research on the recently discovered high- T_c superconducting ceramic materials has led to the characterization of their lattice dynamical properties, an improved understanding of charge fluctuations and oxygen stoichiometry effects, and a potentially useful route to the preparation of high- T_c ceramic structures from metallic precursors.

Thermochemistry. The thermochemical properties of several minerals (schoepite, dehydrated schoepite, clinoptilolite, dehydrated clinoptilolite, tobermorite, and four synthetic faujasites) were determined by calorimetry measurements and

thermodynamic calculations. This information should be useful in research into nuclear waste burial.

Thermodynamic properties are also being determined for "high-tech" materials. The measurement technique is, in general, fluorine combustion calorimetry. Materials studied in this report period included VS_{1.043} (which is used as a catalyst and plays an important role in the mechanical and other properties of stainless steel) and allotropes of phosphorus. Several superconducting and related phases will be investigated in the next year.

Geochemistry of Natural Hydrothermal Systems. An effort is underway to study the geochemical processes involved in water/rock interactions that occur in active hydrothermal studies in the Earth's crust. In the past year, large-volume thermal water samples were collected from 13 hot springs and geysers in Yellowstone National Park. These samples are being analyzed for Ra, Th, and U isotopes to determine the geochemical behavior of these isotopes, as well as their potential applications as tracers and as indicators of groundwater flow rates in active hydrothermal systems.

A new technique was developed for microanalysis of fluid inclusions trapped in minerals. Simultaneous analysis of noble gases and halogens in fluid inclusions could greatly increase our ability to resolve questions about past fluid reservoirs and their interactions in ancient hydrothermal systems.

In another effort, the hydrothermal system of the Nevado del Ruiz volcano, which erupted in 1985, is under investigation. Analysis of dissolved SO₄²⁻ from acidic hot springs on the slopes of the volcano indicated that the acidity of the hot springs is related to the emission of magmatic SO₂.

9. Analytical Chemistry Laboratory

The Analytical Chemistry Laboratory (ACL) is administratively within CMT, the principal user, but collaborates with 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 groups--Chemical Analysis, Instrumental Analysis, and Organic Analysis.

During 1987, the ACL was involved in a diverse array of activities, including the following: U, Pu, and metals analyses for the Integral Fast Reactor Program; analyses of environmental samples for the DOE Environmental Survey, which is designed to identify current and/or potential environmental problems and areas of risk at DOE facilities; analysis of dioxins from municipal waste incineration; studies of organics in solid and sludge wastes from emerging energy technologies such as coal gasification and liquefaction; analytical support for the establishment of the Premium Coal Sample Facility at ANL; development of an improved method for dioxin analyses; development of a methodology that uses Fourier transform infrared spectroscopy for analysis of stack gases; application of an array of analytical methods to determine correlations between the chemical and physical properties of polyethylene pipes and their mechanical properties; analysis of spent fuel for isotope correlation studies; and study of fluid degradation for Rankine-cycle engines.

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 Division's central computing facility is a VAX 11/785. In 1987, two Vaxstation 2000 workstations were added to this facility as part of a local area VAX cluster. In providing technical support to CMT staff, the Computer Application's Group has assisted in the effort to develop a model that can be used to design and optimize flowsheets for processing waste streams by the TRUEX process. This work was concentrated on improving the spreadsheet section of this model, called the Spreadsheet Algorithm for Stagewise Solvent Extraction.

I. BATTERY RESEARCH AND DEVELOPMENT

The battery program at ANL encompasses a variety of activities with high-performance batteries (lithium/metal sulfide and sodium/sulfur) and aqueous batteries (lead-acid, nickel/iron, etc.). These activities involve battery research, technical management of DOE contracts to industry, performance and lifetime tests, post-test analysis, battery modeling, and analysis of test data. The batteries being developed by ANL are primarily intended for electric-vehicle application, with secondary consideration given to utility energy storage and military uses.

A. Molten-Electrolyte Cell Research

Research is being conducted to attain major improvements in the performance of advanced batteries having molten-salt electrolyte, lithium alloy negative electrodes, and metal disulfide positive electrodes. This research program includes the following tasks: (1) the development and testing of new cell designs, (2) development of overcharge and overdischarge protection for future cell operation in a battery configuration, and (3) optimization of electrode materials through electrochemical and mechanical characterization studies.

In 1987, work continued on development of the lithium-alloy/ FeS_2 cell. The principal goal of this effort 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 300 W/kg, and a cycle life of 1000 cycles. As reported earlier, an improved lithium-alloy/ FeS_2 cell has shown promise of achieving these performance and cycle-life goals.¹ Our improved FeS_2 cell has a novel electrolyte, 25 mol% LiCl-37 mol% LiBr-38 mol% KBr (mp, 310°C), rather than the 58 mol% LiCl-42 mol% KCl (mp, 352°C) used in earlier FeS_2 cells. It also has a higher loading density (2.4 vs. 1.5 Ah/cm³) for the FeS_2 -15 mol% CoS_2 positive electrode, which is operated only on the upper of its two voltage plateaus (1.75 V vs. Li-Al). Earlier tests with small-scale cells (12-24 Ah) at 400°C showed that this new design yields high performance and stable capacity during extended cycling.

Tests underway in this report period have confirmed the capacity stability of the improved FeS_2 cell. A small-scale cell replicated the initial high performance demonstrated earlier, with 89% FeS_2 utilization at a current density of 50 mA/cm² and 4-h discharge rate. Test facility problems, however, caused this cell to short circuit after 70 cycles; the cell was repaired and operated over 250 cycles at 96% of the initial capacity. A second cell (operated at a 2-h discharge rate) remains on test after over 600 deep discharge cycles with a coulombic efficiency of 98-99%. As shown in Fig. I-1, the initial upper-plateau FeS_2 capacity had declined by only 5% after almost 500 cycles (our goal was to achieve 500 cycles with <10% capacity decline).

Also tested in this period were small-scale cells with FeS_2 - NiS_2 - Li_2S electrodes. The FeS_2 / NiS_2 ratio for these electrodes was 50:50 with 5 mol% Li_2S added. These cells were also operated on the upper voltage plateau and showed stable capacity for over 200 cycles at temperatures of 400-450°C and current

¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1985*, Argonne National Laboratory Report ANL-86-14, pp. 18-20 (1986).

Fig. I-1.

Utilization of Upper-Plateau
FeS₂ Capacity as Function
of Deep Discharge Cycles

densities of 50-150 mA/cm². This electrode composition trades off a 5% increase in capacity for about 25% decreased power at 80% depth-of-discharge. The decreased power is caused by a slightly lower cell voltage and 50% higher resistivity at 80% depth-of-discharge. Adjustments in this mixed-disulfide electrode composition may improve the cell power.

Increased understanding of the reasons for the improved stability and high performance of the upper-plateau FeS₂ cell has been obtained through an investigation of its molten-salt electrochemistry.² The LiCl-LiBr-KBr molten salt allows one to operate the cell at a lower temperature (400 vs. 450°C) and a higher lithium ion activity (62 vs. 58 mol% Li⁺) than are possible with LiCl-KCl salt. Additionally, its broad liquidus range supports cell operation at high current density (100-150 mA/cm²) with high utilization (above 80% of the upper-plateau FeS₂ capacity). The high-voltage reaction peaks (FeS₂ ⇌ Li₃Fe₂S₄) in the cyclic voltammograms for the upper-plateau electrode in LiCl-LiBr-KBr electrolyte exhibited improved reversibility. The difference in lead-edge potentials between anodic and cathodic peaks at 400°C was only 0.085 V (this value is 0.120 V for FeS₂ electrodes in LiCl-KCl³). The capacity stability of the upper-plateau FeS₂ electrode is aided by the kinetics at 400°C being similar to the kinetics of FeS₂ in LiCl-KCl at 450°C. In addition, thermal decomposition and solubility of the FeS₂ electrode are held in check at this temperature. Generation of soluble polysulfides at potentials of 1.95-2.1 V was not indicated in cyclic voltammograms for this electrode/electrolyte system.

Overdischarge protection for the upper-plateau FeS₂ electrode has been demonstrated in a cell whose capacity was limited by the negative electrode (i.e., a lithium-limited design). Because of the high loading density of the FeS₂ electrode, the discharge must be restricted to the upper voltage plateau to avoid excessive electrode expansion. This has been achieved in cell testing by limiting the discharge cutoff voltage to ≥1.25 V. However, for battery operation, this requirement is unacceptable. A lithium-limited cell with upper-plateau FeS₂

²T. D. Kaun, "Evaluation of LiCl-LiBr-KBr Electrolyte for Li-Alloy/Metal Disulfide Cells," Proc. of Joint Int. Symp. on Molten Salts, 172nd Electrochem. Soc. Meeting, Honolulu, HI, October 18-23, 1987, Vol. 87-7, p. 621 (1987).

³S. K. Preto, Z. Tomczuk, S. von Winbush, and M. F. Roche, J. Electrochem. Soc. 130, 231-233 (1983).

electrode has been operated with discharge cutoff voltages ranging from 1.0 to 1.3 V and has maintained 99% coulombic efficiency for over 200 cycles.

Overcharge protection methods for FeS_2 cells were also investigated. Among several options, a simple lithium shuttle method was found to offer the best protection for the positive electrode against overcharge. With this method, negative electrodes of proper composition release metallic lithium into the electrolyte under the overcharge condition, and then the dissolved lithium, having been oxidized on the positive electrode, maintains cell potential below the detrimental level. Preliminary test results have indicated the general feasibility of this overcharge protection method. Calculations of lithium solubility from polarized lithium-alloy electrodes and experiments with a Li-Al electrode poised at -200 to -250 mV vs. a Li-Al reference electrode indicated a self-discharge rate of 1-3 mA/cm². Thus, battery cell capacity equalization could be accomplished at trickle-charge current densities of about 3 mA/cm².

The goal of cell hardware development for the disulfide cell has been to improve specific energy and power by reducing nonactive material weight without compromising cycle life. Cost reduction is also being investigated by design changes that reduce the expensive molybdenum current collectors. In FeS_2 cells having rod-shaped electrodes,⁴ molybdenum wire produced by powder metallurgy can be substituted for present sheet current collectors, which are expensive and difficult to fabricate. A multi-rod cell design (Fig. I-2) affords relatively high amounts of electrode area for a given cell capacity and thereby reduces working current density. A computer model is being developed to determine the performance characteristics of a rod-electrode cell with the upper-plateau FeS_2 electrode and LiCl-LiBr-KBr electrolyte (see Sec. I.G). The effect of reduced current-collector weight can be modeled with a good degree of confidence, but the change to a radial current distribution requires further model development. A few small-scale test cells, which simulate a section of a rod-electrode cell and also duplicate details of flat-plate test cells, have been operated. High capacity utilization (85-90%) was obtained at a current density of 25-50 mA/cm². This indicates good prospects for attaining comparable (if not higher) specific energy to that of a flat-plate cell. At this point, the rod-electrode cell resistivity is about 50% higher than that of the flat-cell cell. Its reduced capacity utilization at discharge current densities >50 mA/cm² (Fig. I-3) may be improved by further increases in the FeS_2 electrode-bed conductivity. A multi-rod cell has been projected to achieve a specific energy of 194 Wh/kg at the 3-h discharge rate and a peak power of 303 W/kg.

In addition to the upper-plateau FeS_2 cell, we are investigating a new class of lithium-alloy/metal disulfide cell with a thin, bipolar cell construction (termed "galvanic capacitor"). Such cells hold promise of achieving very high specific power and power-to-energy ratio and are being assessed for their pulse-power capability. Several versions of these cells (varied in their chemistry and geometry) were tested under high-intensity (3 to 50 A/cm²) current density pulses of 0.1- to 1000-ms duration. High peak power (25 W/cm²), power density (200 kW/dm³), and energy density (350 Wh/dm³) were demonstrated in repetitive 1- to 10-ms pulses over several cycles for these cells. In investigating the operational principles of this system, we found that (1) the power of well-designed

⁴P. A. Nelson and H. Shimotake, "Electrochemical Cell Having Cylindrical Electrode Elements," U.S. Patent No. 4,357,398 (1982).

Fig. I-2.
Schematic of Li/FeS₂
Rod-Electrode Cell

Fig. I-3.

Capacity Utilization as Function of Discharge Current Density for Upper-Plateau FeS₂ Cells with Rod and Plate Electrodes

battery cells is controlled by the ohmic resistances of the cell components when the current pulses are less than 10 ms, and (2) for a given pulse length, the voltage loss vs. current density relationship for these cells at any specified state of discharge is nearly linear. The latter relationship offers a precise and simple way to measure, characterize, and compare various power-performance indicators of bipolar battery cells. Further details can be found in Ref. 5.

⁵L. Redey, "Power Performance of High-Temperature Li-Alloy/FeS₂ Bipolar Cells in Short Pulses," 22nd Intersoc. Energy Conversion Eng. Conf., August 10-14, 1987, Philadelphia, PA, pp. 1091-1096 (1987).

The above work concerns secondary battery cells. We are also engaged in electrochemical investigations of primary Li-Si/FeS₂ cells in collaboration with the Sandia National Laboratories. The work done in this report period quantified the effect of compression force on cell performance. Figure I-4 shows the area-specific impedance for small-scale primary cells with a 15-s current interrupt (ASI_{15s}) as a function of discharge depth and applied compression from 6.5 to 180.3 kPa. The results indicate that increasing the compression force increases specific energy by better utilization of the active materials (as shown by the higher Q_m values at discharge termination) and dramatically increases the power capability of the cell (as shown by lower area-specific impedances). These experiments also revealed that increasing the volume ratio of electrolyte to active material improves electrode kinetics until an optimum value is reached, after which the ohmic resistance of the electrode bed increases and performance deteriorates. Consequently, these important design parameters must be considered in the development of thin-cell systems such as the primary batteries presently under development at Sandia.

Fig. I-4.

Effect of Compressive Force on Area-Specific Impedance of Discharged Li-Si/FeS₂ Primary Cell. (Q_m is the progression of discharge in faradays per mole of FeS₂.)

Future work on molten-electrolyte cells will include optimization of electrode materials for overcharge and overdischarge protection of new cell designs, investigation of electrolyte-starved cell operation with MgO powder separators (instead of electrolyte-flooded operation with BN felt separators), and development of fabrication and assembly techniques for the thin-layer components of bipolar cells.

B. Glass-Electrolyte Research

Glass electrolytes for Na/S cells are alternatives to ceramic electrolytes, such as sodium β'' -alumina, that are currently being used. The objective of our research is the development of a glass that will be highly conductive for sodium

ions, will be chemically stable in the hostile Na/S cell environment, and can be easily fabricated 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 literature review.

On the basis of our conductivity experiments and chemical stability tests, we selected the following glass composition for further development (in mol%): 42 Na₂O, 8 Al₂O₃, 5 ZrO₂, and 45 SiO₂. This composition, hereafter called ANL Glass, met our initial acceptance criteria: high sodium-ion conductivity (221 $\Omega \cdot \text{cm}$ at 300°C) and acceptable chemical stability⁶ (comparable to those of sodium β'' -alumina and the Dow borate glass⁷⁻⁹).

Close attention to the physical and chemical properties is needed in making electrolyte structures from ANL Glass, such as tubes. Because of the hygroscopic nature of ANL Glass, all fabrication is performed in the absence of moisture. Under a dry O₂/N₂ atmosphere (synthetic air), straight tubes of ANL Glass have been drawn using a stainless-steel blowpipe tipped with Swagelok connector. The resulting tubes have been of sufficient quality to allow construction and testing of small-scale cells.

In the fabrication of sealed Na/S cells, the above glass tubing was filled with a sulfur-graphite mixture (22 mAh) and sealed using the Swagelok connector left from the blowpipe. The cathode material was sodium in iron Retimet. After overnight conditioning at 310°C, cycling was started with low currents (400 μA discharge for 0.5 h and 200 μA charge for 1 h). Cycling was continued until 100 cycles had been achieved at 2-3% depth-of-discharge. The temperature and current were increased to 326°C and 1 mA/cm², respectively. Under these conditions, the cell achieved greater than 50% utilization of the sulfur electrode. Operation was terminated after 30 cycles because of cell breakage.

Sulfur is not the only cathode material that can be used in glass-electrolyte cells. We also built a cell with FeCl₂ cathode (76 mAh) using some of the sulfur-based cell techniques. The design changes were in the current collector (now iron) and in the use of NaAlCl₄ as secondary electrolyte. At about 300°C, this cell achieved more than 70 cycles to about 30% depth-of-discharge. Cell failure was caused by areas of high current density, which, in turn, were due to poor sodium electrode contact. Sodium electrode construction is an area for future effort.

In one Na/S cell design, the glass electrolytes are connected to a central sealing member for mechanical support and for cell seal. Because of the high soda content of ANL Glass, the thermal coefficient of expansion is very high (about $16 \times 10^{-6}/^\circ\text{C}$). Sealing tubes of ANL Glass to a header will require careful matching of thermal expansion coefficients of the materials involved. Besides this, the header must be an insulator (ionic and electronic), be chemically

⁶I. Bloom, J. Bradley, and M. F. Roche, *J. Electrochem. Soc.* **134**, 2102 (1987).

⁷A. Herczog, *J. Electrochem. Soc.* **132**, 1539 (1985).

⁸C. A. Levine, in *The Sulfur Electrode*, R. P. Tischer, ed., Academic Press, New York (1983).

⁹W. E. Brown, R. G. Hietz, and C. A. Levine, "Battery Cell," U.S. Patent No. 3,476,602 (1969) and F. Y. Tsang, "Sodium Borate Glass Compositions and Batteries Containing Same," U.S. Patent No. 3,829,331 (1974).

stable with respect to the Na/S cell system, be as pore free as possible, and be chemically compatible with ANL Glass (so they will chemically bond).

Magnesium oxide materials would be stable with respect to chemical reaction with sodium and sulfur and may have the necessary high thermal expansion coefficient. Ceramics in the $\text{MgO-Al}_2\text{O}_3\text{-BaO-B}_2\text{O}_3$ system were chosen for further study based on thermodynamic calculations of model compounds. Barium oxide was included to help preserve the high thermal expansion of MgO , and B_2O_3 was included to help strengthen the material by "cross-linking" the MgO particles. High-magnesia ceramics in the $\text{MgO-Al}_2\text{O}_3\text{-BaO-B}_2\text{O}_3$ system (Table I-1) were prepared and characterized by metallography, dilatometry, and differential thermal analysis. A plot of percent expansion versus temperature for these materials, along with that of ANL Glass, is given in Fig. I-5. This figure shows that the thermal expansion behavior of the materials designated G and J is close to that of ANL Glass. Further experimentation is in progress to lessen the thermal expansion differences between these materials and ANL Glass.

Future work on the glass-electrolyte Na/S cell will continue to focus on the fabrication and testing of glass-electrolyte structures and sealed electrolyte-to-ceramic header units.

As reported last year,¹⁰ we have developed a miniature reference electrode that will measure either sodium or sodium polysulfide activity. The reference electrode uses small ($\sim 2\text{-mm}^2$ active area), thin membranes of ANL Glass. The small, electrochemically active area allows precise positioning in an electrochemical system of interest. The new reference electrode system completely isolates the reference material from the rest of the system.

Table I-1. Composition of Candidate Materials for Na/S Cell Header

Code	Nominal Composition, mol%			
	MgO	Al_2O_3	BaO	B_2O_3
A	89	1	1	9
E	89	1	5	5
G	89	1	1 ^a	8
I	91	--	--	9
J	90	1	--	9
K	75	--	--	25
L	66.7	--	--	33.3
M	33.3	--	--	66.7
N	90	5	--	5
O	89	5	--	6
P	85	5	5	5

^aAlso contains 1 mol% CaO .

¹⁰M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory ANL-87-19, p. 19 (1987).

Fig. I-5. Relative Expansion vs. Temperature for $\text{MgO-Al}_2\text{O}_3\text{-BaO-B}_2\text{O}_3$ Ceramics Prepared at 1200°C . (Glass compositions given in Table I-1.)

Reference electrodes containing sodium polysulfides were tested in sodium polysulfide melts to determine their emf stability and reproducibility. In these experiments, several reference electrodes of identical construction and content were placed in a common sodium polysulfide melt. These experiments showed that, in systems such as $(\text{Mo})\text{Na}_2\text{S}_x|\text{ANL Glass}|\text{Na}_2\text{S}_y$ ($x, y = 3, 4, 5$) at 309°C , after thermal equilibration, the emf measurements were reproducible to ± 1 mV and were stable for at least 18 h.

Coulometric titrations of polysulfide and transition-metal-chloride electrodes (~ 2 mAh capacity in $16.7 \mu\text{Ah}$ steps) were performed using the reference electrode. A coulometric titration curve for the polysulfide electrode at 327°C is given in Fig. I-6. The curve shows a broad plateau down to 71 mol% sulfur, as expected. Immediately following the plateau is a linear region from 71 to 60 mol% sulfur (2.06 to 1.77 V). This titration very precisely shows the transformation from two-phase to single-phase material.

In polysulfide melts, the reference electrode with ANL Glass membrane was constructionally stable for periods of greater than 100 h of operation at $300\text{--}400^\circ\text{C}$. When it occurred, reference electrode failure was largely due to thermal expansion mismatch of the glass and the alumina-tube/electrode body, causing the glass membrane to crack or fall off.

In 40 mol% NaCl -60 mol% AlCl_3 melts at 125°C , the measured resistivity of the ANL Glass membrane in the reference electrode was on the order of

Fig. I-6.

Coulometric Titration of
Polysulfide Electrode at
327°C

$10^4 \Omega \cdot \text{cm}$. However, stable potentials in $\text{Al}|\text{Na}_2\text{S}_4, \text{NaCl}, \text{AlCl}_3|\text{ANL Glass}|\text{NaCl}, \text{AlCl}_3|\text{Al}$ could not be obtained. Post-test examination of the glass membrane indicated that the melt had reacted with the glass. Improved emf stability ($23 \pm 3 \text{ mV}$) was observed for 5 h when the glass composition was changed to (in mol%) 40.7 Na_2O , 10.8 Al_2O_3 , 8.3 ZrO_2 , and 40.2 SiO_2 . The much higher $\text{ZrO}_2 + \text{Al}_2\text{O}_3$ concentration (19.1 mol% vs. 13 mol% in ANL Glass) gives this glass much higher chemical stability toward the melt. Over the next year, we will continue to explore the operating temperature range and stability of the glass-membrane reference electrode.

C. Engineering Development of Li-Alloy/FeS Batteries

We are currently in the last phase of a program involving the transfer of Li-alloy/FeS battery technology to industry. The program involves a joint effort between ANL and Gould Inc. to develop the Li-alloy/FeS battery for electric van propulsion. The program is funded by the Department of Energy (DOE), Electric Power Research Institute (EPRI), and the Tennessee Valley Authority (TVA) and has as a goal the testing of a full-scale battery in a van by 1990.

During 1987, two 36 V batteries employing full-scale cells were tested. The first, Mark I, was fabricated by Gould to be tested in the laboratory for power, energy, and lifetime. Battery design was based on the 12-V Li-alloy/FeS module that was fabricated by Gould and tested earlier.¹¹ The second, Mark II (Fig. I-7), was designed to meet the compactness and weight restrictions imposed by in-vehicle test requirements.

¹¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1985*, Argonne National Laboratory Report ANL-86-14, pp. 20-21 (1986).

Fig. I-7. Photograph of the Mark II Li-Alloy/FeS Battery

The laboratory tests on the Mark I battery demonstrated satisfactory power and energy outputs (e.g., 49-110 Wh per kilogram of cell at 40-A constant current discharge and 77-112 Wh per kilogram of cell under simulated driving profiles) but showed that its lifetime was inadequate (113 cycles). Post-test analysis of the failed cells at CMT identified iron deposition in the separator as the failure mode (Sec. I.F.3). We are investigating changes in the electrode composition and charge regime as a means of minimizing the rate of iron deposition.

The energy output of the Mark II battery was limited by the thermal control auxiliaries. The vacuum insulated case was a new design that failed to provide the required insulation. Problems were also experienced in cooling the cells uniformly during tests involving high current pulses. Our plans are to reassemble and test the Mark II battery with a new case (a redesign of the previous one) and a modified cooling system.

D. *Electric and Hybrid Vehicle Battery Support*

1. Aqueous Electric-Vehicle Batteries

The Division provides technical support to DOE for the development of aqueous battery technology for electric vehicles. The technical support includes assistance in program planning, preparation of work statements, technical assessments, and system analyses. In this capacity, CMT continued to provide technical management of two major industrial contracts: one with Johnson Controls, Inc., for the development of advanced lead-acid batteries, and the other with Eagle-Picher Industries, Inc., for the development of Ni/Fe batteries.

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--an innovative design approach that yields better utilization of the active materials. In typical commercially available lead-acid batteries, only about 30% of the active materials can be utilized; in the flow-through lead-acid cells, up to 55% of the active materials is utilized in the

electrochemical storage of energy. During 1987, the useful life obtained with flow-through lead-acid cells was increased to over 125 deep discharge cycles in tests at Johnson Controls, compared with only 20-30 cycles attained previously. This development effort will be continued in 1988, with emphasis on further extending cycle lifetimes and on scaleup from single cells to 12-V modules.

The effort at Eagle-Picher is directed toward reducing the cost of advanced Ni/Fe batteries. The work is focused on the development of thick (3 mm) nickel electrodes that have the desired porosity and strength required for good performance and long life. In 1987, improvements in sintered-powder nickel electrodes were achieved, and a major effort directed at the development of a fiber-type nickel electrode was initiated. An advanced Ni/Fe module (NIF225) with sintered-powder electrodes that are 50% thicker than those previously available yielded 30% greater energy in the same weight and volume as the previous state-of-the-art design. Experimental Ni/Fe cells were also successfully fabricated using fiber-type nickel electrodes. Because nickel metal is the major cost factor in the manufacture of Ni/Fe batteries, the lower nickel requirements of the fiber-type approach provides significant cost-reduction potential for future Ni/Fe batteries. Meanwhile, laboratory and in-vehicle tests continued to confirm the ruggedness and long life of Ni/Fe batteries developed under this project. A complete Ni/Fe battery system has powered an electric vehicle for over 67,000 km of operation to date at the TVA Electric Vehicle Test Facility. Nickel/iron batteries also continue to perform well after six years in commercial fleet operations at industrial sites. Efforts to further reduce the cost of this technology will be continued in 1988.

2. Fuel Cell/Battery Powered Bus System

The U.S. Departments of Energy (DOE) and Transportation (DOT) initiated a cooperative multiyear program in FY 1987 for the research, development, and demonstration of a methanol-fueled fuel cell/battery powered bus for urban passenger transport. Argonne National Laboratory provided key technical support to DOE in the development of the program plan for these activities, and CMT has been assigned technical management responsibility for the program.

With the fuel cell/battery propulsion system, the fuel cell would provide the average power requirement, and the battery would provide the additional power required during acceleration. For maximum energy efficiency, the energy released during braking would be used to charge the battery (regenerative braking). Evaluation of various fuel cell types now under development led to selection of phosphoric acid fuel cells as the most viable candidate for the bus application in the next few years.

The first phase of the planned four-phase program is directed at demonstrating the feasibility of using a phosphoric acid fuel cell/battery system as the prime source of power for an urban bus. It was determined that an evaluation of both air-cooled and liquid-cooled phosphoric acid fuel cells would provide the greatest probability of success in applying fuel cell technology to transportation needs. In 1987, DOE awarded a two-year cost-shared contract to Energy Research Corp., Bus Manufacturing USA, Inc., and Los Alamos National Laboratory for development of an air-cooled phosphoric acid fuel cell/battery system. A similar contract was awarded to three industrial firms (Booz-Allen & Hamilton, Inc., Chrysler Corp., and Engelhard Corp.) for development of a liquid-cooled phosphoric acid fuel cell/battery system.

After completion of Phase I, a decision will be made to select one technology for the Phase II effort. Phase II will involve the development of the proof-of-concept fuel cell/battery power source and the power train components and the integration of these into a small test bus. Track testing and field evaluation of this bus with the proof-of-concept fuel cell/battery power source will be accomplished in Phase III. Phases I through III will provide the technology development and demonstration needed to proceed to Phase IV, which will entail field testing of small fleets of prototype buses in various urban applications.

E. Performance and Life Evaluations

Cells, multicell modules, and full-scale batteries fabricated by industrial firms are being evaluated in the Analysis and Diagnostics (A&D) Laboratory in CMT to determine their performance and life characteristics. These evaluations provide an interim measure of the progress being made in battery R&D programs, a comparison of battery technologies, and basic data for modeling and continuing R&D. The experimental results and analysis of data, in combination with post-test examination (Sec. I.F) and modeling (Sec. I.G) of advanced battery technologies, provide insight into their deficiencies and help identify the most-promising R&D approaches for overcoming these deficiencies. The battery technologies being evaluated are primarily applicable to utility load-leveling and electric-vehicle applications.

During 1987, technology evaluation was completed on 200 cells and was continued on 295 others. These cells are mostly in the form of three- to six-cell modules, but also in the form of full-sized 30- to 50-kWh batteries with up to 140 cells, and are primarily Na/S, Zn/Br, lead-acid, and Ni/Fe technologies from a variety of battery manufacturers. Highlights of these evaluations are given below.

1. Sodium/Sulfur Technology

Testing is underway on eight Na/S cells (rated at 10 Ah and 20 Wh) fabricated by Chloride Silent Power Ltd. Performance characterization testing was completed on four of the cells. The averaged test results for the four cells (assumed cell weight of 240 g) under a simulated driving profile (SAE J227aD/IETV-1) yielded a vehicle range of 218 km and a peak power of 108 W/kg at 50% depth-of-discharge. All but one of the cells are still undergoing life-cycle testing and have accrued from 524 to 807 cycles. The failed cell breached its top seal on the 388th test cycle. All of the other cells continue to operate with no sudden changes in their capacities.

2. Zinc/Bromine Technology

Performance characterization testing of a full-size (30-kWh) Zn/Br battery from Exxon was completed in 1987. Tests were conducted over the temperature range of 10 to 40°C and over the discharge power conditions of 10 to 40 W/kg. The specific energy was 40-51 Wh/kg for discharge power up to 25 W/kg but decreased to 25-37 Wh/kg at 40 W/kg. Projected vehicle ranges up to 150 km were obtained under two driving profiles (J227aD/IETV-1 and SFUDS79/IDSEP), and the peak power of the battery at 50% depth-of-discharge, as derived from the J227aD/IETV-1 driving profile, was 80 W/kg. The last series of tests measured the loss in energy capacity during open circuit after charge (stand-time test). In one hour on open circuit, the battery lost 13% of

its energy capacity at 40°C, 6.6% at 20°C, and 5% at 10°C when compared to its energy capacity without stand time at those temperatures. The energy capacity of the battery was 27.7 kWh at 10°C, 27.5 kWh at 20°C, and 22.4 kWh at 40°C. The results of the testing also indicated that component failures and electrolyte leakage are significant problems.

3. Advanced Lead-Acid Technology

The second of a series of advanced lead-acid cells with the flow-through design from Johnson Controls (see Sec. I.D.1) was evaluated. With an assumed cell weight of 3.72 kg, the specific energy of the cell was 47.0 Wh/kg at a 3-h discharge rate. Life-cycle testing was halted at the 70th cycle when cell capacity fell below 60 Ah, which is 80% of the rated capacity. This cell maintained relatively stable capacity throughout much of its cycling life. Adjustments and repairs were made to the electrolyte pumping system and the electrolyte specific gravity during its life. The lifetime of 70 cycles is considerably better than the 27 cycles attained by the first flow-through cell tested in the A&D Laboratory but still less than the program goal of 200 cycles.

4. Advanced Nickel/Iron Technology

Advanced Ni/Fe modules from Eagle-Picher Industries and the Dual Shaft Electric Propulsion (DSEP) program of Eaton Corp./Eagle-Picher were evaluated to obtain the performance and life characteristics of this technology.

Six Ni/Fe modules from Eagle-Picher underwent performance characterization tests. Three modules had fiber-type nickel electrodes, and three had sintered-powder plates. The modules with fiber-type electrodes achieved specific energies to 54 Wh/kg and peak powers to 96 W/kg (derived under the J227aD/IETV-1 driving profile), as compared with 53 Wh/kg and 102 W/kg for the modules with sintered-powder plates. These modules were operated for only ~220 cycles before testing was voluntarily suspended. During cycling, module peak power and capacity declined by about 10%. The reduction in capacity occurred in the first 100 cycles, while the decline in peak power occurred after that point.

Testing on a full-size (140 cell) nickel/iron battery fabricated by Eaton/Eagle-Picher/DSEP was suspended in October 1987 after completion of 502 cycles. At that time, the battery still maintained 90% of rated capacity with a 220-Ah charge and 1-h open circuit after charge. Pending a review by DOE, the battery has been placed on a constant-current trickle charge of about 3 A. Testing is expected to be resumed in January 1988.

F. *Post-Test Analyses of Battery Cells*

The Division maintains specialized facilities for the examination of aqueous and high-temperature battery cells. These examinations serve to identify existing and potential failure mechanisms, to assess the reliability of hardware components, and to characterize changes in electrode morphology as a function of a cell's operational history. Analysis of the cell data provides a measure of the technical progress made by battery developers and an indication of needed design and/or material changes.

1. Sodium/Sulfur Cells

Nine Na/S cells (10 Ah) that were built and tested by Chloride Silent Power were examined. Operation of seven cells in this group was terminated after less than 65 cycles; the other two cells were operated for 242 cycles and 520 cycles. The nine cells represented three different states of charge. The examinations provided information on the sulfur electrode used in this new Na/S cell design.

In cells whose operation was terminated at full charge, variations were found in the active material distribution and were attributed to the eccentricity of the electrolyte with the cell case. In one cell, the electrolyte was centered, and the sulfur content averaged 40 vol% in the cylindrical section and 75 vol% in the base section. In a second cell, the electrolyte was off-center by 0.5 mm, and more sulfur was found in the cylindrical section, particularly the thinner cross section where greater compression of the graphite felt matrix had occurred. These findings suggest that slumping of active materials had occurred in the charged cells. This condition can be counteracted by using higher density felt for the cylindrical section of the cell.

Radial compositional gradients were detectable for cells whose operation was terminated when discharged into the single-phase polysulfide melt region. One cell, for example, was discharged to 1.76 V and rapidly cooled by transference to an unheated furnace. Figure I-8 shows the electrode microstructure (as determined by optical microscopy) and the sodium profile across this area (as measured by energy dispersive spectroscopy). The slope of the regression line is one measure of the severity of electrode polarization. Another indication was the difference between the average sodium content (35 at.%) and the equilibrium value (40 at.%) for a cell whose operation was terminated at 1.76 V (IR-free). This difference represents a polarization loss equivalent to 12.5% of the theoretical capacity.

Quantitative determinations were made of the ambient-temperature gases present in the sulfur electrodes of two cells. One of these cells was heated and held at the operating temperature (350°C) for 94 days but was not cycled. Upon examination at ambient temperature, it contained Ar and N₂ as the primary constituents. Trace amounts (<0.5%) of He, H₂, O₂, CH₄, and CO₂ were also detected. The other cell completed 242 cycles before operation was voluntarily terminated. The electrode gas content was five times greater and radically different in composition. The major constituents were H₂S and CO₂. Low levels (0.5 to 2.5%) of COS and SO₂ were also generated. The H₂ content in this cell was greater, but O₂ and CH₄ were undetectable. Argon, N₂, and He were present in reduced amounts.

The change in electrode gas composition was attributed to the presence of water. The atomic ratio of hydrogen to oxygen for the gases found in the cycled cell was 1.9, and a value of 2 fell within the limits of experimental error. For the uncycled cell, an absorbed film of H₂O on a high-surface-area component, such as the graphite felt, would be difficult to detect with the static vacuum used to extract the gases from the electrode for mass spectrometry analysis. However, in a cycled cell, the adsorbed H₂O would readily react with sodium polysulfides to form H₂S. At the cell operating temperature, subsequent reaction with the graphite would consume the oxygen liberated by the polysulfide reaction to form gases like CO₂ and COS.

Fig. I-8. Composite Micrograph and Sodium Profile for a Discharged Sulfur Electrode from a Rapidly Cooled Na/S Cell Fabricated by Chloride Silent Power

The cell hardware was also examined for evidence of existing or potential degradation mechanisms. In general, the glass and thermocompression bonded seals in the cells were in very good condition. A number of defects, however, were noted for the electron-beam welds. These defects included incomplete fusion, intergranular cracking, and weld porosity.

In the Chloride Silent Power cells, a chromized coating is used to minimize corrosion of the cell case. In all of the examined cells, this protective layer was crack free. Within 60 cycles, a 2- to 3- μm scale of NaCrS_2 was the only evidence of corrosion. Preferential attack of the bottom of the cell case, however, was apparent in the two cells operated for longer than 65 days. In the cell operated for 520 cycles, the thickness of the chromized layer was reduced by a factor of two.

2. Lead-Acid Modules

We analyzed four lead-acid modules from Lucas Chloride EV Systems and two long-lived 3100-Ah cells from Exide Management and Technology. The Lucas Chloride modules were part of a 24-module battery pack tested by the TVA in an electric van. The Exide cells are prototypes of the cells being built for a Southern California Edison load-leveling plant.

Analyses conducted on the Lucas Chloride modules revealed that deterioration of their microporous rubber separators resulted in increased self-discharge and was the primary cause of capacity loss. A pattern of grooves

was formed on the separators due to the abrasive action of active material particulate from the tubular positive electrodes. Some abrasion would be expected owing to the tendency of PbO_2 electrodes to expand during cycling. However, the vibrations incurred by this battery pack during road tests probably increased separator abrasion. One consequence of abrasion was the formation of penetrating holes through the separators of modules with low remaining capacity. Another result was the embedding of this particulate within the interior of the separators. The particulate levels within the separators were sufficient to form conductive paths through the separators. As shown in Fig. I-9, an excellent correlation existed between the final remaining cell capacity and the increase in separator weight caused by the buildup of active material.

Fig. I-9.

Relationship Between Final Cell Capacity and Increase in Average Separator Weight for Lead-Acid Modules of Lucas Chloride

Both Exide cells had completed extended testing programs and retained capacities in excess of their rated value at termination of operation. One cell was tested at 40°C and had accumulated over 2300 cycles at 80% depth-of-discharge, while the other cell achieved over 1050 cycles at 60°C . The different test temperatures were used to accelerate positive grid corrosion, a potential life-limiting mechanism in cells of this design. The positive grids of the 60°C cell definitely showed more deterioration. Corrosion of the grid wires was twice as severe and resulted in sulfate formation. Grid corrosion was sufficient to cause one or more fractures at the perimeters of the grids. These conditions were not observed for the 40°C cell. The sulfate formation and grid cracking impede electron transfer and could ultimately make the positive electrodes limit cell capacity. At the time of termination, however, capacity for both cells was limited by their negative electrodes. Degradation of the lead plates was noted in the form of surface blisters that served as the sites for sulfate buildup.

The physical and chemical analyses conducted on the active materials indicated that the positive and negative electrodes were capable of extended cycling at 80% depth-of-discharge. However, test results did reveal one limitation of these cells at elevated temperatures. Oxidation of the polycarbonate jar that

houses the electrodes and electrolyte is accelerated at 60°C. The reduction in the strength of the polymer chains led to edge cracks midway up the jar wall, leaving the cell susceptible to electrolyte loss. Exide has identified an alternative material for the cell jar.

3. Lithium-Alloy/Iron Sulfide Cells

Examinations were also completed on three Li-Si-Al/FeS cells from the Mark I battery built by Gould (Sec. I.C). Testing of this battery at ANL was halted after 113 cycles when a short circuit prevented a cell from recharging. The short circuit in this cell was located between the central positive electrode and an adjacent negative electrode and caused extensive damage to the stainless steel electrode retainers in the vicinity of the short circuit. The shorted condition originated because of the formation of metallic deposits in the separator. Similar deposits caused declining coulombic efficiency in the two other cells. These deposits were predominantly iron from the iron monosulfide electrode but also contained some nickel, which was generated by corrosion of the nickel current collectors. On average, the deposits penetrated the separator thickness to a depth of 60%. High charge cut-off voltages and high operating temperatures are known to accelerate metallic deposition.

A second factor contributed to the loss in coulombic efficiency in one of the above cells. The room-temperature resistance of the feedthrough was ~200 Ω . Examination revealed a crack in the lower insulator between the positive terminal rod and the feedthrough housing. A film, rich in nickel from the terminal rod, was developing inside this crack. The cracking of insulators normally occurs during cell assembly.

In general, corrosion of the negative-electrode collectors and retainers was more severe than found for the positive-electrode components. The galvanic reaction between the Li-Al-Si alloy and the hardware produced multi-phase, intermetallic layers. For the nickel current collectors, the approximate compositions were as follows: Ni_3Si_2 for the innermost layer, Ni_2Al_3 for the intermediate layer, and NiAl_2 for the outermost layer. Scanning electron microscopy/energy dispersive X-ray spectroscopy detected traces of nickel in the active material of the negative electrode as well. The galvanic reaction rate is accelerated by increasing operating temperatures and is also more vigorous for cells designed to be negative-electrode limited.

G. *Modeling and Analyses*

In 1987, the effort on electrochemical modeling and analysis was focused on two advanced battery systems: lithium/iron disulfide and sodium/sulfur.

For the lithium/iron disulfide system, a cell model was developed to study the effects of various design parameters on the energy and power capabilities for a rod-electrode cell design (Fig. I-2). In this design, the current is collected through molybdenum wires, thus lowering cost and minimizing fabrication difficulties compared with the conventional molybdenum sheet collectors. In analyzing the energy and power performance of such a cell, we used the model to calculate the variation of open-circuit voltage and potential drops associated with various electrode and cell components. Used as input were the physical and chemical properties of the rod-electrode system and some experimental data obtained previously.

The model calculations indicated that a seven-rod cell (150 Ah) with a molybdenum collector diameter of 2 mm and positive-electrode bed thickness of 4.5 mm is capable of delivering a specific energy of 194 Wh/kg at the 3-h discharge rate and a peak power of 303 W/kg. Figure I-10 shows the calculated effects of molybdenum-wire diameter on the specific energy and peak power of the cell. This figure indicates that the collector diameter has a large effect on peak power but a slight effect on specific energy.

Fig. I-10.

Effect of Molybdenum Wire Diameter and Positive-Electrode (P.E.) Bed Thickness on Specific Energy and Peak Power for Rod-Electrode Cell Design

For the Na/S system, a model was developed to account for the design features of the Chloride Silent Power cells (Sec. I.E.1), which have beta-alumina electrolyte and a large diameter-to-length ratio. The model calculates current, potential, composition, and temperature distributions based on the cell geometry, sulfur polarization, and the resistances of current collector, electrolyte, graphite fiber matrix, and polysulfide melt.

Preliminary calculations showed that the large diameter-to-length ratio of the Chloride Silent Power cells does not significantly affect the performance of the cells at moderate discharge rates. Because of the small resistance of sodium phase relative to beta-alumina, the current distribution near the bottom of the cell is quite uniform. Therefore, the active material near the bottom of the cell can be properly utilized. However, as the discharge rate increases, the utilization of active material near the corner of the cell becomes less complete. For good performance, the diameter-to-length ratio should be matched with the size of the negative-electrode collector and the intended rate of discharge of the cells. Model calculations are also being made for comparison with the test results of two selected Chloride Silent Power cells.

II. ADVANCED FUEL CELL DEVELOPMENT

Two advanced fuel cells are being studied at ANL: the molten carbonate fuel cell and the solid oxide fuel cell. The work on the molten carbonate fuel cell emphasizes development of an alternative cathode material to the present nickel oxide. Argonne also is providing technical support for the molten carbonate fuel cell program of the DOE Morgantown Energy Technology Center. The work on the solid oxide fuel cells is concentrated on development of the monolithic fuel cell—a new design of fuel cell developed at ANL that promises to deliver very high power density. Also underway are systems analyses and cost assessments in support of the DOE fuel cell program.

A. Molten Carbonate Fuel Cell Development

Present-day molten carbonate fuel cells consist of a porous nickel anode, a porous metal oxide cathode, an electrolyte structure separating the anode and cathode, and appropriate metal separator sheets. 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 (650°C). An economic advantage exists for large plants of such cells to run at pressures of 6-10 atm.

Several years ago the NiO cathode was found to undergo continuous migration toward the anode, which limited cell lifetime. An effort to develop an alternative cathode was thus initiated. This effort has been focused on finding stable materials that meet the known requirements for the complex microstructure needed for in-cell use, developing methods for fabricating the complex cathode microstructure required for in-cell use, and testing cells to evaluate cathode performance and improve our understanding of cathode-materials behavior. The progress made in these three areas is summarized below.

1. Materials Studies

In earlier work, we found that both LiFeO_2 and Li_2MnO_3 were thermodynamically stable in the cathode environment.¹ The undoped materials, however, have very high resistivities, ranging from a few hundred to about one thousand ohm-centimeters. Doping was necessary to reduce the resistivity to levels that meet the requirements projected by a cathode model developed by Physical Sciences, Inc. (PSI) ($<20 \Omega\cdot\text{cm}$ at 650°C). Extensive studies were conducted on the effectiveness of Mn, Co, and Cu as dopants for LiFeO_2 ; however, little work was done on Li_2MnO_3 .

In this report period, we doped Li_2MnO_3 with magnesium and then evaluated the resultant material in laboratory tests. Under realistic cell operating conditions at 10-atm pressure, the optimum dopant concentration resulted in a bulk resistivity of approximately $20 \Omega\cdot\text{cm}$ at 650°C . There was excellent correlation between dopant level and resistivity (Fig. II-1). These data suggest that the dopant is completely incorporated and is homogeneously distributed in the parent material. The data for Mg/Mn mole ratios >0.05 suggest that this amount of magnesium is in excess of that which can be accommodated by the Li_2MnO_3 lattice.

¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 37 (1987).

Fig. II-1.

Resistivity of Magnesium-Doped Li_2MnO_3 for Different Dopant Levels at 650°C

We also studied the resistivity of a sintered Li_2MnO_3 specimen containing the optimum dopant level as a function of oxygen partial pressure at 650°C . When the partial pressure of oxygen was increased from 0.2 to 1.4 atm, the resistivity increased from approximately 18 to $25 \Omega \cdot \text{cm}$; this is indicative of an n-type conductor. A simple substitution of Mg^{2+} for Li^+ would result in an n-type conductor (i.e., $\text{Li}_{2-x}\text{Mg}_x\text{Mn}_x^{3+}\text{Mn}_{1-x}^{4+}\text{O}_3$) and in the observed behavior. Initial Seebeck measurements also indicated n-type behavior in cathode conditions. Further studies are required to obtain a more complete understanding of the conduction mechanism and defect structure of the Li_2MnO_3 material.

2. Development of Fabrication Techniques

a. Materials Requirements

The state-of-the-art cathode is a sintered body with a mixture of large and small pores. Conventional understanding of cathode mechanisms dictates that the working structure should have small agglomerates consisting of small particles to provide adequate reaction sites and short diffusional paths for reactants; large, open gas passages to permit reactants to reach the internals of the structure; and sintered, electronically conductive material to conduct electrons.

The particles from which the cathode is to be fabricated must be of submicron size to obtain adequate catalytic surface area and to form agglomerates flooded with molten electrolyte. The agglomerate size is of importance because the reactants must diffuse to the reaction site through the liquid phase in the agglomerate. The path length can be minimized by keeping the agglomerate size small; $3\text{--}8 \mu\text{m}$ is a typical diameter. The diameter of the large gas passages is determined by the pore characteristics of the anode and electrolyte structure.

Typically, the pore diameter of the gas passages is approximately $10\text{ }\mu\text{m}$. Finally, a sintered-cathode porosity of approximately 50-60% is being sought.

Spherical agglomerates alone cannot be used to achieve the desired structure because it is impossible to obtain the desired combination of small agglomerates and large pores. Consequently, pores are being made using a variety of pore formers, and agglomerates are being made in nonspherical geometries.

b. Fabrication Techniques

To achieve the above requirements, we fabricated the agglomerates first, then the cathode from the agglomerates. For this method to work, rod-like or elongated agglomerates are required. Two methods were developed for fabricating elongated agglomerates. The first was the fabrication of very small ceramic "tubes." This is done by a process that coats organic fibers (rayon) with a slurry of submicron ceramic particles, binder, and solvent. The binder and fibers are burned off, and the tubes are crushed to form tube-wall fragments, which are then fabricated into the final cathode.

The second process involved the fabrication of very small ceramic fibers. These are made by a spray technique. A slurry of submicron ceramic particles with binder and solvent is sprayed to form small fibers. Fibers with diameters between approximately 1 and $10\text{ }\mu\text{m}$ can be fabricated in this manner. With appropriate burn-off and sintering procedures, these fibers retain their geometry as sintered ceramic fibers. They are then crushed, cast, and sintered into a cathode in a manner identical to that for the tube fragments.

The final casting and sintering procedures differ from the usual tape casting procedures, since the slurry being cast consists of pre-sintered agglomerates rather than the usual fine particulate ceramics. This precludes many of the conventional processing steps and also inherently results in a tape with a rough surface. This surface texture is eliminated by rolling. The presintered agglomerates also tend to sinter into a very weak body; thus, a sintering aid is used, which also increases surface area. After sintering, the cathode structures are reinforced for breakage resistance and improved ease of handling during cell assembly.

c. Structural Analysis

Analysis of the cathode structure is done with a combination of scanning electron microscopy (SEM) and mercury porosimetry. Mercury porosimetry gives the pore size distribution; large ($\geq 7\text{ }\mu\text{m}$) gas passages and small ($\leq 2\text{ }\mu\text{m}$) electrolyte-filled pores are desired. The mean pore size will be around 5-10 μm for a cathode with an appropriate structure. These data alone do not assure a good structure. The fine pores must be contained in agglomerates with diameters of approximately 1-10 μm . Indication of this parameter is obtained by electron microscopy of the precursor agglomerates and the finished structure.

Several cathode structures, fabricated from NiO fibers and tubes, were characterized by SEM and mercury porosimetry, and the results compared with those from a state-of-the-art cathode. Figure II-2 shows the porosimetry results from two cathodes made from NiO fibers and a conventional cathode.

Fig. II-2.

Cathode Pore Characteristics for Fiber and Conventional Cathodes

The mean pore diameter of the conventional cathode is $\sim 4 \mu\text{m}$. The NiO fiber cathodes have mean pore diameters of ~ 2.5 and $10 \mu\text{m}$. Both fiber cathodes were made from the same starting material; however, we were able to reduce the mean pore size to $\sim 2.5 \mu\text{m}$ by rolling and using submicron fines. The SEM analysis indicated that the agglomerates were approximately 3.5 to $5 \mu\text{m}$ in diameter for the state-of-the-art cathode and approximately 6 to $10 \mu\text{m}$ in diameter for the fiber cathodes. The agglomerate diameter could also be tailored to smaller sizes with the technique used for making fibers; this is illustrated in Fig. II-3, where the average agglomerate diameter is approximately $2 \mu\text{m}$. Figure II-4 shows the porosimetry results for a cathode made from NiO tubes and for a conventional cathode. The mean pore diameter is $\sim 2 \mu\text{m}$ for the tube cathode. The SEM

Fig. II-3. Micrograph of Tailored Agglomerates in Fiber Cathode

Fig. II-4.

Cathode Pore Characteristics for
Tube and Conventional Cathodes

analysis showed the agglomerates to be hollow and thin walled. From these characterizations, it appears that both the fibers and tubes are materials capable of being tailored to yield a structure needed in a working cathode.

3. Cell Testing

a. Tests with NiO Cathodes

The strategy for development of alternative-material cathodes was to first fabricate and test NiO cathodes to verify the efficacy of the new fabrication techniques (Sec. II.A.2.b). The initial cells with in-house fabricated NiO cathodes exhibited significantly lower performance than cells with conventional cathodes. This occurred in spite of the fact that better performance should have been achieved due to the improved microstructure.

Analysis of the constituents used in all phases of the fabrication revealed that chlorides were present in the two commercial binders that we had been using, and that sodium was present in the rayon fibers and one of the binders. We found that only the sodium-containing materials with NiO had an adverse effect on performance.

Without sodium present, the chlorides are apparently driven off during heat-up and do not have an adverse effect on cathode performance. When combined with sodium, the chlorides remain through sintering and apparently affect performance in a combination of ways. There is a liquid-phase sintering effect. This is manifest by grain growth, observed with electron microscopy; similar conditions with and without contamination resulted in about a factor of two difference in NiO grain size. The sintering effect is also manifest as reduced cell performance. Additionally, the voltage-equilibration time at a new current setting increased greatly. Although voltage-equilibration time was quite long (on the order of hours), there was a unique voltage for each current setting. This suggests that equilibrium is being established at each current density. This effect is apparently caused by cathode-related poisoning because it occurs very early in cell life; hence, it is not probable that contaminants diffuse across and poison the anode.

While this appears to be a clear case of cathode poisoning, the mechanisms have not been investigated. It may be that poisoning by chlorides cannot occur in an operating cell and that the poisoning we observed can occur only during the extreme conditions of cathode fabrication. For many practical applications, this will be an important point to clarify. The possibility that the NiO was providing the contamination was examined by tests with different sources of NiO. The results confirmed that the source of the problem was the chlorides from binders and fibers.

Figure II-5 shows performance curves for several NiO cells. State-of-the-art performance was obtained from conventional (*in situ* oxidized) NiO cells, and the performance curve for one such cell is plotted as curve 1.

Fig. II-5.

Cell Potential as Function of Current Density. Curves represent (1) conventional NiO cathodes, (2) NiO cathode fabricated with low-contaminant materials, and (3) (4) NiO cathodes fabricated with sodium- and chloride-containing binders.

The performance with an in-house-fabricated NiO cathode of low contamination is plotted in Fig. II-5 as curve 2. The performance is somewhat better than the conventional cathode. This is as predicted by the PSI model; this cathode was fabricated with agglomerates that were smaller than those of a conventional cathode. The liquid-phase diffusion overpotential was reduced by the smaller agglomerate size. The mean pore size was determined by mercury porosimetry to be 10 μm , which is somewhat larger than necessary. A cathode with a slightly smaller mean pore size would be expected to perform even better.

Performance curves for several poisoned cathodes are plotted in Fig. II-5 as curves 3 and 4, which indicate poor performance. In addition, the equilibration times were quite long for these two cells.

The performance of the cell represented by curve 2 verifies the viability of our new fabrication techniques. Other organizations have tried to develop techniques for fabricating cathode structures from ceramic materials; however, our techniques are the only ones that have been successful.

b. Alternative Materials

With the confirmation of our new fabrication techniques, cell testing with alternative materials began. Two cells with LiFeO₂ cathodes were run. In one case, the cathode was contaminated with chlorides. Performance

was poor, just as the contaminated NiO cathodes performed poorly. The second had a much lower contaminant level. This cell improved continuously, particularly when running under load, and was shut down due to anode-side corrosion of the wet seal area. At termination of operation, the cathode performance was still improving. The damage to the anode housing has been repaired so that testing of the cathode can continue. The impact of contaminant level and microstructure on performance will continue to be evaluated.

B. *Technical Support*

The Advanced Fuel Cell Technical Support Group at CMT provides technical support to the Morgantown Energy Technology Center (METC), which has programmatic responsibility for the molten carbonate fuel cell program of DOE. Technical support includes assistance in program planning, systems analysis, technical monitoring of the contracts, and preparation of work statements for new work. In 1987, International Fuel Cells (IFC), formerly the Power Systems Division of United Technologies Corp., and Energy Research Corp. (ERC) continued to be the major contractors for development of the molten carbonate fuel cell. There were also fuel-cell contracts with Ceramtec, Inc., the Institute of Gas Technology, the Illinois Institute of Technology, the University of Minnesota, and the Illinois Institute of Technology Research Institute.

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 capable of operation on gases from a coal-based system, with a projected life of 40,000 h, by the 1990s.

In the past year, IFC continued operation of a 20-cell full-area (approximately 0.7 m²) stack. This stack was intended to evaluate the effects on performance of scaleup of area to the size proposed for large plants. The stack, which was tested for 1700 h, operated at about 25 kW and had good initial performance, but several problems affecting performance were observed later in the test. Fuel distribution seems to have been one source of difficulty, and test-stand problems also resulted in subsequently lower performance. The cause of individual cell performance problems has not yet been identified by the post-test examination. The stack had slightly higher compaction of cell components and more electrolyte transport than its subscale precursor. International Fuel Cells has begun work on a new cell design to address these problems.

Energy Research Corp. is developing cell and stack components and a reference MCFC plant design. They are also testing cells and stacks with reforming catalysts in the anode region that convert methane to carbon monoxide and hydrogen. Based on a 2-MW plant design, a subscale stack of four cells was successfully tested using simulated fuel gas and the desired oxidant gas for ~3000 h. The performance of the cells in the stack (~0.4 kW total) matched the performance from single-cell tests. Scaled-up components for a full-area (0.38 m²) stack (about 2 kW) were designed and are being fabricated. Development work is continuing on bipolar plates, cathode current collectors, and the catalyst support section of the anode region.

As stated in Sec. II.A, ANL is searching for an alternative cathode; in the meantime, however, both IFC and ERC are attempting to extend the life of NiO cathodes. To address this acid/base dissolution problem, both contractors have

accepted some performance loss from the NiO cathode and lowered the nickel solubility by reducing the CO_2 partial pressure in the cathode gas. The performance loss is a result of both decreased Nerst potential and increased polarization. Another approach being examined by ERC is to make the electrolyte more basic and decrease nickel solubility by the addition of selected cations (e.g., barium) to the melt.

Throughout the extended lifetime of a fuel cell (up to 40,000 h), the porous nickel anode is subject to creep, changing the pore size distribution and morphology and resulting in reduced surface area. Ceramtec is carrying out research to alleviate this problem by using ceramics coated by nickel or copper/nickel alloy as anode material, since ceramics show significantly greater creep resistance than metals. Electroless plating, sputtering, and chemical vapor deposition have been investigated as techniques to plate the metal onto LiAlO_2 powder. However, insurmountable problems were encountered with the metal dewetting from the ceramic, followed by extensive sintering of the metal. Success has been achieved in obtaining a high-quality anode of metal-coated LiFeO_2 powders. This material is currently being characterized extensively, and cell tests have been started.

The Institute of Gas Technology is investigating a new concept for the fuel cell anode that is expected to be tolerant of hydrogen sulfide (H_2S). The current anode utilizes porous nickel or nickel/chromium alloys, whose electrochemical catalytic properties are severely poisoned by H_2S . The IGT concept is based on the fact that hydrogen has a significant solubility in elemental nickel; hence, H_2S contaminants in the fuel stream can be isolated from the anode region of the cell by means of a thin nickel membrane through which the dissolved hydrogen passes from the fuel inlet region to the anode. During 1987, IGT's research found that the adsorption of hydrogen onto the nickel foil, a necessary step prior to dissolution, is also partially poisoned by H_2S and becomes rate limiting in the presence of H_2S . Thus, IGT is investigating means of enhancing the adsorption of hydrogen on nickel through the use of alloying agents and/or coatings on the nickel foil.

As a part of the DOE base technology program on the molten carbonate fuel cell, IGT is carrying out a search for alternative anodes that would be tolerant to H_2S . Numerous ceramic materials as well as other transition metals are being investigated. None of the candidate ceramics tested to date has been stable in the presence of the molten Li/K carbonate eutectic.

Other areas being investigated as a part of the DOE base technology program include electrolyte optimization (Energy Research Corp.), cathode reaction mechanisms (Illinois Institute of Technology), cathode dissolution mechanisms (University of Minnesota), and corrosion mechanisms of fuel cell hardware (Illinois Institute of Technology Research Institute).

For this base technology effort, Energy Research Corp. is investigating numerous electrolyte compositions and additives with respect to corrosivity, cathode kinetics, LiAlO_2 matrix stability, cathode solubility, and electrolyte migration. The Illinois Institute of Technology is attempting to determine reaction intermediates and rate-limiting reaction steps for the cathode reaction involving oxygen, carbon dioxide, and the electrolyte. Because of the continuing problem of NiO cathode losses in operating molten carbonate fuel cells, the University of Minnesota is determining the mechanisms by which the NiO cathode

material is dissolved into the electrolyte and then redeposited as elemental nickel in the electrolyte matrix near the cell, eventually short-circuiting the cell. Equilibrium solubilities and solution kinetics are being determined as a function of cathode gas composition, temperature, and electrolyte composition. A model is being developed and cell tests are being carried out to verify the model.

Fuel cell hardware components are exposed to both reducing (anode) and oxidizing (cathode) environments. Thus, the Illinois Institute of Technology Research Institute is measuring and modeling the corrosion of various candidate alloys as a function of gas composition, electrolyte composition, and temperature. At this time, it appears that type 310 stainless steel is most resistant to corrosion in the various fuel cell reaction conditions.

The ANL technical support in 1987 included assisting DOE/METC in the evaluation of proposals resulting from five Program Research Development Announcements (PRDAs), which had solicited proposals for base technology studies addressing areas of concern and follow-on contract(s) to promote stack development efforts to meet the DOE goal. We also assisted DOE/METC in preparation of statements of work resulting from the PRDAs. We also assisted in the review of the responses to a PRDA for stack development. Although DOE elected not to award any contracts, follow-on work (supporting systems design and improvement in areas of weakness) was proposed by the bidders. We have assisted DOE/METC in evaluating these proposals and the resulting statements of work. We have also participated in contractor design reviews and assisted DOE/METC with review of the final reports by IFC and ERC on completed contract efforts.

We will continue our technical monitoring of contractor efforts in 1988 and provide technical support for DOE/METC as appropriate. This effort will cover the present contracts on base technology and cell/stack development, as well as any new contracts on system design and stack development.

C. Solid Oxide Fuel Cell Development

The solid oxide fuel cell consists of a lanthanum manganite cathode, a yttria-stabilized zirconia electrolyte, a nickel and zirconia cermet anode, and lanthanum chromite for electronic cell-to-cell interconnections. These components are all oxide-ceramic materials. At the anode-electrolyte interface, 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-electrolyte interface, oxygen in the air accepts electrons from the external circuit to form oxide ions, which are conducted through the electrolyte to the anode interface. These cells operate at temperatures of 800 to 1000°C.

We are investigating a new concept for the solid oxide fuel 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 made this development effort a major program.

The "monolithic" solid oxide fuel cell is being developed in a joint program between CMT and the Materials and Components Technology Division. The monolithic design employs the same thin ceramic components used in other oxide fuel cells in a strong, lightweight honeycomb structure of small cells. This structure 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.

In the monolithic concept, fuel and air are combined electrochemically in a ceramic cell at an operating temperature of 800 to 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. II-6. 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 the 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, for which 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.

Fig. II-6. Monolithic Solid Oxide Fuel Cell Co-Flow Design

At present, the major challenge for development of the monolithic fuel cell is fabrication of the intricate structures. Well-developed ceramic fabrication techniques are being employed. Tape casting is used in the ceramic capacitor industry, and this method is being optimized to fabricate thin, high-density layers of electrolyte and interconnection materials. Tape casting is also being used to form the thin, porous layers of anode and cathode. Alternative thin-layer fabrication techniques, such as spraying, curtain coating, and hot roll milling, are also being considered.

The principal building blocks of the monolithic structure are the two multilayer composites: the anode/electrolyte/cathode (A/E/C) and the cathode/interconnection/anode (C/I/A). Good performance of the monolithic fuel cell requires that the layers in these composites be well bonded and free from cracks or other gas-transmitting defects. Considerable attention is given to achieving defect-free structures and good bonding between the layers.

In the "co-flow design" shown in Fig. II-6, the fuel and oxidant gases flow in adjacent channels in the same direction. While this design provides the highest power density, the manifold design to supply fuel and oxidant gases to the fuel cell is somewhat complex. Therefore, a simpler design, shown in Fig. II-7, is being developed for the monolithic fuel cell. In this "cross-flow" design, corrugated layers of anode and cathode materials are placed between flat A/E/C and C/I/A layers. The electrode corrugations are oriented at right angles from each other so that fuel gas is introduced on one face of the fuel cell, while the oxidant is introduced on an adjacent face at right angles. The gas manifolds are simpler in this design, and the power density is not greatly reduced from that of the co-flow design.

Fig. II-7. Monolithic Solid Oxide Fuel Cell Cross-Flow Design

In 1986 the first monolithic fuel cell arrays (stacks) were built and operated to demonstrate the feasibility of the concept. During 1987, the principal effort has been on improving the performance of the cross-flow design and on reducing the number of defects in the ceramic structures. Many factors influence the performance of the monolithic fuel cell, including the density, purity, and integrity of the electrolyte; the porosity, nickel content, particle size, and distribution of the nickel in the anode; the density and purity of the interconnection material; and the porosity and particle size distribution in the cathode. Improvement in the performance of the monolithic fuel cells has involved optimization of these parameters, along with improvements in the structural integrity of the ceramic layers.

Integrity of the monolithic fuel cell structure requires that the shrinkages of the different materials during sintering and their coefficients of thermal expansion be carefully matched. The shrinkage that occurs in each component during firing must be matched among components for each detail of the shrinkage curves. This matching must include the binder-burnout shrinkage that occurs at low temperatures as the organic portion of the tapes is burned off, and the sintering shrinkage that occurs at high temperatures as the powder particles sinter together to form solid ceramic structures. The binder-burnout shrinkages are easily controlled by proper selection of the ceramic/binder ratio in the tape-casting slips. The sintering shrinkages are controlled by tailoring the ceramic powder particle size distributions, compositions, and specific surface areas. Figure II-8 shows the matching in sintering shrinkages that we achieved for yttria-stabilized zirconia electrolyte, nickel-zirconia cermet anode, strontium-doped lanthanum manganite cathode, and magnesium-doped lanthanum chromite interconnection.

Fig. II-8. Dilatometer Traces of Electrolyte, Anode, Cathode, and Interconnection during Sintering

The thermal expansions of the four materials are fairly well matched in their pure states, except for the nickel-zirconia cermet anode. The coefficient of thermal expansion of nickel is high (about $16 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$) compared with the other components of the fuel cell (in the range of 10.5 to $12 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$). The thermal expansion coefficient of the anode was reduced by minimizing the nickel content while maintaining good conductivity. A series of experiments showed that the optimum nickel content was about 30 to 31 vol% nickel. This nickel content yielded an anode with a thermal expansion coefficient of $12 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$, which is within the acceptable range of the other fuel cell components. At lower nickel contents, the conductivity dropped precipitously about three orders of magnitude, and the anode became nonconductive.

Progress during 1987 includes improvement of the monolithic fuel cell structural integrity by improvement of the matching of sintering shrinkages and thermal expansion coefficients of the four materials. This progress is quantitatively expressed by the number of defects observed in fabricated arrays as a function of time. At the beginning of the year, the defect frequency was about 10 to 20 defects in two-cell arrays that were tested. By the end of 1987, the defect frequency had been reduced to zero to two defects in each tested array, and the array size had been increased from two cells to three and four cells. The number of defects is also reflected in the open-circuit potentials that have been achieved. Early arrays showed an average open-circuit potential of about 0.8 V/cell, and recent arrays average about 0.95 V/cell (1.05 V/cell theoretical). The higher open-circuit potentials result from very low leakage of fuel into the oxidant stream and vice versa. Theoretical open-circuit potentials are routinely achieved in single-cell tests.

The emphasis of future research will be on improving performance, reducing the defect frequency still further, and scaling up the size of the arrays. Improvement in the internal resistance of the arrays is also needed. The height of the arrays will be increased by linking more cells in electrical series to produce greater voltage, and the active area will be increased so that more current can be produced. During the scaleup effort, industrial participation will be sought so that commercially viable fabrication methods are incorporated.

D. *Analysis of Fuel Cell Systems*

Fuel cells have the potential of replacing present technology in many applications where combustion machinery is used, e.g., utility and industrial power plants generating electricity with turbines, smaller portable power plants, and even internal combustion engines in vehicles. Most of the fuel cell R&D supported by DOE is directed at the utility power plant application. To help guide the major fuel cell development efforts of the industrial contractors to DOE (Sec. II.B), we are comparing the economics of fuel cell power plants with existing technology. In earlier years, two types of fuel cell power plants (molten carbonate and phosphoric acid fuel cells) were compared with a gasification/combined-cycle plant and a pulverized coal combustion plant for utility base-load applications. The conclusion was reached that the power density of the fuel cells would have to be almost doubled from the earlier design goals if fuel cell systems are to be competitive.²

One of the assumptions in the earlier analysis was that the fuel processing technology was identical in the two fuel cell systems and the combined-cycle system. It was further assumed that the coal was gasified in an entrained bed gasifier (Texaco), the synthesis gas was cleaned by solvent extraction (Selexol), and the sulfur was recovered by the Claus process. The Texaco/Selexol/combined-cycle technology is in the demonstration stage at Barstow (California) and, therefore, relatively well established. It was felt that having this proven technology would keep uncertainties in the economic estimates to a minimum.

²M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 48 (1987).

However, a Texaco/Selexol fuel processing sequence is not ideal for fuel cell systems because the Texaco gasifier operates at a very high temperature, but the Selexol is an ambient-temperature process. Cooling the synthesis gas and then reheating it to the operating temperature of the fuel cells are expensive operations. As a result, we are analyzing fuel processing alternatives that might give fuel cell systems further advantages.

Three approaches were used. First, other relatively well-established options to Texaco/Selexol were analyzed. Oxygen- and air-blown fluidized-bed gasification was considered, as was hot-gas cleanup. Second, more-speculative concepts (such as capturing sulfur in the gasifier to obviate gas cleanup and separating the hydrogen from the impurities by membranes) were examined. Third, the ANL systems simulation code was expanded to allow simultaneous optimization of many of the design specifications.

The results of our analysis are illustrated in Fig. II-9 for solid oxide cells. Relative to the Texaco/Selexol system and a tubular solid oxide fuel cell operating under pressure (option 3), an air-blown fluidized bed gasifier with lime injection to capture sulfur *in situ* (option 5) has a 10-15% lower cost of electricity. The cost of electricity for the same system but with a monolithic solid oxide fuel cell (option 6) is decreased by another 7%. Present solid oxide fuel cell technology cannot be operated under pressure. The ambient-pressure systems (options 1, 2, and 4) are more expensive, but the system with sulfur-capturing capability (option 4) has a clear advantage over conventional gas cleanup. Based on these results, we recommended to DOE that increased emphasis be placed on the development of *in situ* sulfur-capturing gasifiers and on pressurization of solid oxide fuel cells.

Membrane separation technology may be another alternative to conventional gas cleanup, but the economic incentive was found to be insignificant. We suspect that this new technology may, nevertheless, have potential for applications where fuel cells would be added to already constructed combined-cycle plants to increase the power.

Fig. II-9. Results from Economic Analyses of Various Fuel Processing Alternatives for the Solid Oxide Fuel Cell (SOFC). Bars in graph represent:

1. Oxygen-blown fluidized-bed gasification, Selexol cleanup, ambient-pressure SOFC.
2. Same as 1 but air-blown gasification.
3. Texaco gasifier, Selexol cleanup, pressurized SOFC.
4. Air-blown sulfur-capturing fluidized-bed gasifier, ambient-pressure SOFC.
5. Same as 4 but pressurized SOFC.
6. Same as 5 but monolithic SOFC.

III. FOSSIL FUEL RESEARCH

The fossil-fuel research at CMT includes investigations into the fluidized-bed combustion of coal, the recovery of heat and seed from the bottoming cycle of a magnetohydrodynamics power plant, slagging combustion for the control of SO_x - NO_x emissions, the continuous separation of coal macerals with a magnetic field gradient, and the deposits resulting from coal combustion and conversion processes.

A. *Fluidized-Bed Combustion Studies*

Fluidized-bed combustion involves a process in which coal is burned in a fluidized bed of limestone or dolomite under atmospheric or pressurized conditions. We are developing the hot-gas cleanup technology for pressurized fluidized-bed combustors (PFBCs), assessing materials for air heat exchangers in atmospheric fluidized-bed combustors (AFBCs) for cogeneration applications, developing design guidelines that will minimize metal wastage in FBCs, and determining the combustion characteristics of various partially devolatilized coals.

1. Removal of Alkali from Hot Off-Gas

This effort is focused on developing the hot-gas cleanup technology for PFBCs. The high-temperature, high-pressure off-gas generated from the PFBC is expanded through a gas turbine to recover energy. Alkali-metal compounds present in the hot off-gas, such as chlorides and sulfates of sodium and potassium, could cause corrosion of the gas turbine. A fixed, granular-bed sorber is being developed at CMT to remove these alkali corrodents from the off-gas. Because of promising laboratory results, an alkali sorber of activated bauxite was designed, fabricated, and installed. This device will be operated with a PFBC at CMT to (1) measure the alkali-vapor concentration in the off-gas on a real-time, on-line basis and (2) demonstrate the fixed, granular-bed sorber for the control of alkali vapors from actual PFBC off-gas.

In earlier tests, the alkali vapor concentrations in the PFBC off-gas measured by a batch-type alkali and particulate sampling train (APST) were found to be at least an order of magnitude greater than values measured by an Ames on-line alkali analyzer.¹ The test results also suggested that the fate of the NaCl vapor being injected into the PFBC off-gas was affected by the presence of high ash loading in the off-gas and the use of a stainless steel sampling line (about 6.5-m long).

To investigate the latter problem, we constructed a pressurized stainless steel unit for generation of alkali vapor and integrated it with both the Ames alkali analyzer and the APST. In high-pressure tests (9.2 atm absolute), we measured both NaCl and KCl vapors transported in either a N_2 gas stream or a simulated PFBC flue gas stream. The test results showed that the alkali vapor concentration measured by both analyzers were in reasonably good agreement. These calibration results indicated that the earlier discrepancy observed for these two analyzers is partially attributable to the stainless steel sampling line.

¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, pp. 53-57 (1987).

We thus sought to determine the extent of alkali-vapor capture in a stainless steel line at simulated PFBC off-gas conditions. In our experimental setup, the Ames alkali analyzer continuously monitored (1) the sodium and potassium concentrations when a nitrogen gas stream or a simulated PFBC gas stream (both bearing NaCl-KCl vapor) was flowing through a heated (850-950°C) 304 stainless steel line and (2) the subsequent release of both sodium and potassium from the stainless steel line.

The 304 stainless steel was found to capture appreciable amounts of both NaCl and KCl vapors. As shown in Fig. III-1, this alkali capture was increased when the gas stream was switched from nitrogen to simulated PFBC gas (indicated by the drop in alkali concentration at 1817 h). The increased capture was attributed to water vapor in the gas stream, because the alkali capture with a nitrogen stream bearing water vapor was about the same as that with the simulated PFBC gas. The captured alkalis were found to be reversibly released to the alkali-vapor-free gas stream. This release is indicated in Fig. III-2 by the alkali concentration being much higher than the baseline value after NaCl-KCl vapor injection into the nitrogen gas was stopped at 2343 h. The simulated PFBC gas stream showed much greater scouring power (5 to 10 times) than the N₂ gas for the release of the captured alkalis. The water vapor in the gas stream accounted for this greater scouring power. Also, a nitrogen gas stream that contained water vapor had the same scouring power as the simulated gas stream.

Fig. III-1. Measured Alkali Vapors in N₂ and Simulated PFBC Gas Stream Passed through Stainless Steel Heated to 850-950°C

These results show that the stainless steel sampling line in our earlier experiments with the Ames analyzer had captured appreciable amounts of alkali vapor and thus distorted the measurements of alkali concentration in the flue gas. The mechanism of the alkali-vapor capture by, and its release from, the stainless steel line is not clear at this time. Studies will be continued to gain this understanding. A thermogravimetric analyzer will be used to measure the rate of alkali-vapor capture by stainless steel materials and also to screen suitable materials (with little or no alkali-vapor capture) for use as a sampling line.

Fig. III-2. Measured Alkali Release from Stainless Steel Heated to 850-950°C and Exposed to N₂ Gas Stream Bearing NaCl-KCl

To reduce the fly ash loading in the off-gas, we modified the alkali sorber vessel by replacing the existing secondary and tertiary cyclones with three high-temperature SiC candle filters. In a hot commissioning test of these candle filters under the same operating conditions as previously examined, the particulate removal efficiency of the filters from the PFBC off-gas was greater than 98%. In future work, the complication caused by the presence of fly ash in the off-gas should be eliminated. It is expected that the sampling of this PFBC off-gas for alkali will become more reliable. Further testing of the alkali sorber of activated bauxite is planned for next year.

2. Atmospheric Fluidized-Bed Cogeneration Air Heater 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 an AFBC. The ANL divisions involved in this effort are CMT and Materials and Components Technology.

a. Laboratory Materials Tests

One of the tasks in this effort is to conduct materials tests in the laboratory that will complement tests in an actual AFBC unit and to fill in data gaps noted in an earlier literature review.² Westinghouse Corp. and three boiler vendors (Babcock & Wilcox, Foster Wheeler Development Corp., and Combustion Engineering, Inc.) designated materials for laboratory testing at ANL, in addition to those that will be exposed in the actual AFBC unit. These firms are also involved in the selection and design of air heater tube-bundle materials. A series of six laboratory materials tests was completed at ANL in 1987.

²K. Natesan, S. A. Miller, and W. F. Podolski, *An Assessment of the Performance of Heat Exchanger Materials in Fluidized-Bed Combustors*, Argonne National Laboratory Report ANL-86-42 (1986).

The results from the first 1000-h test (Test A) were discussed in last year's report and published in a topical report.³ Results are now available from a 3000-h test (Test A2), a 1000-h test (Test G), and a 3000-h test (Test E) under different operating conditions. In these tests, ring specimens were used to simulate heat exchanger tubes exposed to the environment of an FBC. In addition, experimental alloys were exposed in flat-form coupons to evaluate their corrosion resistance. Photographs of the fully assembled corrosion probes for Tests A2, G, and E are shown in Fig. III-3. The entire probe for all tests was inserted in a reaction chamber constructed of aluminized Type 310 stainless steel. The heating of the specimens (to ~870°C) and the gases (to ~900°C) was accomplished by resistance-wound heating elements surrounding the reaction chamber. The alloy coupons were placed in the annular region between the probe and furnace wall.

In Test A2, the outer surfaces of the ring specimens and one surface of the flat coupons were coated with reagent grade CaSO_4 , whereas in Tests G and E the same surfaces were coated with spent fluidized-bed material supplied by Combustion Engineering.

Upon completion of the tests, we performed macroscopic and microscopic examinations of various specimens. Cross sections of the ring specimens were examined using a scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (EDAX) and an electron microprobe to identify the morphological features of corrosion-product phases in the scale layers. In addition, SEM and optical metallography were used to determine the thickness of scale layers and depth of intergranular penetration in the substrate material. Surface recession was calculated from measurements on the exposed specimens and the initial wall thickness.

The main conclusions from Tests A2, G, and E are as follows:

1. Austenitic stainless steels such as Types 304 and 316 showed acceptable corrosion behavior, even after 3000-h exposure in the presence of simulated sulfur sorbent. However, the sub-surface sulfidation noted in Type 316 should caution against extrapolation of the data to longer exposure times. Type 310 stainless steel exhibited significant sulfidation attack (in contrast with the earlier results from the 1000-h test A).
2. Alloys such as Incoloy 800, Haynes 188, and RA 330 were susceptible to substantial or catastrophic attack.
3. The chromized alloys and CoCrAlY-coated 800 specimen exhibited a low rate of attack in the presence of CaSO_4 deposit. The attack zone thicknesses, in general, were smaller than the initial coating thicknesses, indicating resistance of the coated layers to catastrophic attack.

³K. Natesan and W. F. Podolski, *Atmospheric Fluidized-Bed Cogeneration Air Heater Experiment: 1000-h Laboratory Test A*, Argonne National Laboratory Report ANL-87-11 (1987).

Fig. III-3. Photographs of Specimens before and after Exposure in Tests A2, G, and E

4. All of the materials (except nickel aluminide IC-50) exposed in tests G and E exhibited an oxidation-type attack in the presence of an ash deposit from a circulating fluidized-bed combustor (CFB).
5. The scale thickness and internal penetration in the presence of CFB ash were much less than those reported with reagent grade CaSO_4 (Tests A and A2).

Analysis of the results from the remaining materials tests will be completed in the next year.

b. Heat Exchanger Test in AFBC

Rockwell International has been subcontracted for the required modification, installation, and experimental testing of heat-exchanger tube bundles in the DOE-owned AFBC unit (1.8 by 1.8 m) located at Rockwell. Argonne will provide an independent data analysis and assessment of the heat-exchanger performance. A test of at least 1000-h duration is planned. This test will emphasize performance of air-cooled heat exchangers in a bubbling fluidized bed. The hot commissioning activities required to ensure satisfactory operation prior to committing to the long-term test are underway.

3. Metal Wastage in Fluidized-Bed Combustors

Metal loss from in-bed heat transfer tubes in FBCs is a recurring problem that is impeding the commercialization of this technology for coal combustion. To address this problem, a cooperative research and development venture has been initiated with the following organizations: DOE, Electric Power Research Institute (EPRI), State of Illinois, Tennessee Valley Authority, ASEA Babcock, Foster Wheeler, and Combustion Engineering. The ANL divisions involved in this effort are CMT, Energy and Environmental Systems, and Materials and Components Technology.

The objective of this effort is to develop guidelines for the design and operation of FBCs to minimize metal loss. As part of this effort, ANL is developing (1) improved *in situ* erosion monitors for application in FBCs and (2) models of the fluidized-bed hydrodynamic and erosion processes. The Illinois Institute of Technology, the University of Illinois, Combustion Engineering, and Foster Wheeler have initiated (or will soon) experiments to provide hydrodynamic and erosion data and test the validity of the models.

4. Char Reactivity Studies

The pyrolysis (or mild gasification) of coal will produce a partially devolatilized char. The volatiles could be recovered for their chemical value, and the clean char product combusted in industrial or utility boilers. Information is needed on the combustion characteristics of low-volatile chars in order to assess their suitability as solid fuels. As part of this assessment, we are determining the combustion characteristics of a high-volatile Illinois coal and three samples of the coal devolatilized to different levels in an AFBC of 0.15-m (6-in.) dia at ANL. In this effort over the past year, a coal containing 35.7% volatiles was partially devolatilized in a mild gasification unit to produce separate batches of partially devolatilized coals containing 23.0, 15.4, and 11.4% volatiles.

Over the range of experimental test conditions (750-900°C bed temperature, 10 or 30% excess combustion air), combustion efficiencies for the four coals ranged from 66 to 92%. (It should be noted that these combustion efficiencies are considerably lower than those achievable in larger-diameter FBC units at optimized conditions of bed temperature, gas residence time, and excess air.) Figure III-4 illustrates the improvement in combustion efficiency with increasing volatile content of the char at three bed temperatures. The experimental results also indicated improvement in combustion efficiency for each of the four coals with increasing bed temperature and flue gas O₂ level.

Fig. III-4.

Combustion Efficiency of Coals
as Function of Temperature
and Volatile Content

The observed effect of fuel volatile matter on combustion efficiency in the AFBC tests was consistent with thermogravimetric (TGA) measurements performed by the Illinois State Geological Survey. The TGA results clearly indicate that the high-volatile coal was the most readily combustible, followed by the partially devolatilized coals in order of decreasing volatile content. Current plans are to further test the combustion characteristics of a low-volatile fuel ($\leq 15\%$) in a larger-scale [~ 2 MW(t)] pulverized coal burner.

B. Magnetohydrodynamic Heat and Seed Recovery and Slagging Combustion

Open-cycle magnetohydrodynamics (MHD) is a developing technology with the potential to improve substantially the electrical efficiency of coal-fired power plants and to reduce their environmental impact. In the coal-fired concept of MHD, an easily ionized seed material (usually a potassium salt) is injected into a high-temperature, slag-rejecting coal combustor. The resulting electrically conductive fuel-rich combustion gas then flows through a high-velocity channel in the presence of a strong magnetic field. An electrical potential is developed across electrodes in contact with the gas stream in the channel walls and an electrical current is produced. The fuel-rich combustion gas leaves the MHD topping cycle at 1 atm and approximately 2300 K and enters a bottoming cycle that is somewhat similar to the steam bottoming cycle of a conventional power plant. However, the MHD steam plant must not only extract heat from the combustion gas to produce high-pressure steam, but also separate the seed from the ash, recover the seed material for reuse, preheat the primary combustion air to at

least 1000 K, lower NO_x emissions to acceptable levels, and inject secondary air to complete combustion of the fuel.

Chemical Technology is the lead ANL division in a multidivisional project that is directed toward developing the technology required for the heat and seed recovery in an MHD plant. The program involves experiments that are performed in the Fossil Energy Users Laboratory (FEUL), an ANL combustion test facility that includes a 2-MW slagging coal combustor and a 3-MW combustor for burning liquid fuels, including slurries.

Our effort in 1987 was focused on investigations into the enhancement of radiant heat transfer by potassium atoms in the combustion gases, the interface between the MHD topping and bottoming cycles, the corrosion of materials for superheater and air-heater service, particle evolution by homogeneous and heterogeneous nucleation, and fouling of the boiler tube banks.

1. Thermal Radiation in MHD Systems

Potassium atoms and coal slag particles absorb and emit thermal radiation similar to carbon dioxide and water vapor. Thus, in the MHD system, radiation heat transfer should include the contributions from potassium atoms and slag particles, as well as from carbon dioxide and water vapor.

This past year, three combustion tests were completed in FEUL to obtain data on the enhancement of radiant heat transfer caused by the presence of potassium atoms in the combustion gas. The results will be compared with a theoretical model of radiation heat transfer in MHD systems that has been developed at ANL and was partially validated in previous combustion tests.⁴ The recent tests were run at lower potassium concentrations in the combustion gas (0.7 to 0.8 wt%) and higher gas temperatures (1950 to 2200 K) than in the previous studies.

A preliminary analysis of the data from one of the combustion tests indicated that the agreement between experiment and theory is within 30%. Although this agreement is not as good as that obtained in previous tests ($\leq 16\%$), the results are adequate to validate the model for use in generating scale-up data on the effective emissivity of MHD combustion gases containing CO_2 , H_2O , and potassium atoms.

2. Interface Analysis

As the coal-fired MHD plant is generally configured, gases flow through the MHD diffuser in the horizontal direction, whereas the flow is essentially vertical in the radiant boiler. In this conceptual design, the potential exists for erosion and burnout of the boiler back wall by the gas jet exiting the diffuser at high velocity and temperature.

The gas flow in MHD diffusers and radiant boilers was determined numerically with three-dimensional fluid flow models. Asymmetric axial flow and

⁴M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 65 (1987).

transverse flow conditions at the diffuser inlet were both found to significantly affect the centerline velocity of the gas jet exiting the diffuser. The results also indicated that the flow within the diffuser was influenced by the flow field in the radiant boiler.

The calculated centerline gas velocities (on the order of 350 to 375 m/s) at the diffuser exit were used to estimate particle impact velocities at the back wall of the radiant boiler. Results indicated that, for small ash particles ($<10\ \mu\text{m}$) leaving the combustor, impact velocities are negligible. For larger slag particles that shed from the molten slag layers on the MHD channel and diffuser walls, the impact velocity may be unacceptably high. This latter result is valid even if the design of the diffuser can reduce the gas velocity at the diffuser exit to less than 100 m/s. Slag particle size distributions and number densities need to be determined before attempting to assess potential erosion damage to the back wall of the radiant boiler.

3. Materials Studies

Laboratory autoclave tests have been initiated to study corrosion of candidate superheater and air-heater alloys exposed to simulated MHD conditions of gas temperature and chemistry, deposit chemistry, and metal temperatures. Test duration will range from approximately 500 to 8000 h. This past year, candidate air-heater alloys (low Cr-Mo steels, Incoloy 800, 300-Series austenitic stainless steels, and selected weldments) were exposed at different gas and metal temperatures for up to 2000 h. The specimens are being analyzed to determine which alloys, if any, should be eliminated from a 8000-h test. Testing of superheater alloys is scheduled to begin toward the end of FY 1988. In addition, the results of the tests will be compared with the results of materials performance in shorter-duration tests at the Coal Fired Flow Facility, a bottoming-cycle pilot plant located at the University of Tennessee Space Institute.

4. Particle Evolution

The objective of this effort is to provide support to Mississippi State University (MSU) in the analysis of the particle evolution resulting from homogeneous and heterogeneous nucleation in MHD gas streams. Measurements of particle size distribution are being made by MSU at large-scale MHD test facilities, such as the Coal Fired Flow Facility and the Component and Development Integration Facility. As part of this effort, we used a particle evolution code developed at ANL to analyze particle size and number density data generated in a small-scale test facility at MSU. The researchers at MSU used a laser transmissometer to determine average particle size and number density along the test train. Considering the complexities of the measurements and the model calculations, we found good agreement between our calculations and the MSU measured values. The difference in these values was $1\ \mu\text{m}$ for the average particle size and one order of magnitude for the particle number density. An observed bias in the model calculations is under investigation. Also planned is a comparison between ANL predictions and MSU measurements for the larger MHD test facilities.

5. Fouling of Steam Heaters by Seed and Ash

The objective of this ongoing task is to identify potential fouling problems associated with the seed/ash deposits in the superheater sections of an

MHD steam plant. Because the combustion gas contains large amounts of seed and ash, the steam plant must operate under conditions that are more highly fouling and corrosive than conventional plants.

This past year, the data from four tests in FEUL were used to validate an ANL model that calculates the fouling efficiency of a convective heat exchanger operating at a gas temperature below about 1600 K. In the fouling tests, tube banks were exposed to simulated MHD combustion gases at various temperatures and test durations. During the tests, MSU completed *in situ* measurements of the gas temperature, as well as the temperature and emissivity of the fouling deposit. At the end of each test, we measured tube-deposit thickness. The ANL model assumes that thermophoresis is the predominant fouling mechanism, the deposit thickness is uniform, the deposit does not become molten, and the density and thermal conductivity of the deposit remain constant as it accumulates on the tube surface.

Data obtained from the tests were gas-side heat transfer coefficients to clean and fouled tubes, tube surface temperatures, deposition rate of seed and ash to the fouled tubes, and deposit density and thermal conductivity. These data were used to determine an experimental fouling efficiency (gas-side heat transfer coefficient for clean tube divided by that for fouled tube) and a fouling efficiency calculated from the fouling model. A comparison of the results is given in Table III-1. The results indicate very good agreement between the calculated and measured fouling efficiencies for all tests.

Table III-1. Measured and Calculated Fouling Efficiencies

Test	Fouling Efficiency		Error, %
	Measured	Calculated	
1	0.80	0.82	2.5
2	0.85	0.75	12
3	0.73	0.77	5.5
4	0.69	0.69	0

Two long-duration (30 to 35 h) fouling tests were also conducted in FEUL to assess the tenacity of the fouling deposits formed at gas temperatures of 1400-1600 K. The characteristics of the resulting fouling deposits were very dependent on tube location. Deposits exposed to high radiant heat flux from the combustion flame were tenacious and could not be removed by a sootblower operating at 2- or 4-h intervals. However, deposits on tubes shielded from the intense radiant heat flux were considerably less tenacious and were easily removed by the sootblower operating at 2-h intervals. No further fouling tests are planned.

6. Slagging Combustion Studies

Slagging combustors are being developed for their potential application to coal-fired gas turbine systems and for retrofitting of existing gas- and oil-fired

boilers. In 1987, tests at FEUL were conducted to investigate pressure-hydrated limestone injection into the first stage of a 2 MW(t) two-stage slagging combustor for the control of SO_x - NO_x emissions. The coals tested were a medium-sulfur coal (1.5% S) and a high-sulfur coal (3% S). Previous tests at ANL had investigated the use of a conventional limestone sorbent.⁵

Sulfur retention (as determined by the reduction in SO_2 levels during limestone injection) varied from as low as 17% at a Ca/S ratio of 1.2 to a high of 80% at a Ca/S ratio of 3.5 (see Fig. III-5). First-stage combustion with excess air (110 to 120% of stoichiometric) or low overall excess air (120% of stoichiometric) resulted in lower sulfur retention than tests in which the first stage of the combustor was operated fuel rich (60 to 70% of stoichiometric air) and the second stage was operated at high excess air (160 to 170% of stoichiometric). The latter conditions avoided excessively high gas temperatures (>1920 K) in either the first or second stage of the combustor. The results are qualitatively similar to those obtained with the limestone sorbent in the previous tests.

Fig. III-5.

Reduction in SO_2 Emissions as
Function of First-Stage Ca/S
Molar Ratio and First- and Second-
Stage Air/Fuel Ratios

Emissions of NO_x during the pressure-hydrated limestone injection tests averaged 390 ng NO_x /J with the medium-sulfur coal and 200 ng NO_x /J with the high-sulfur coal. This difference might be due to the slightly higher nitrogen content of the medium-sulfur coal (1.4% vs. 1.2% N_2). These results indicate that emissions below the standard of 260 ng NO_x /J can be achieved with the slagging combustor.

⁵M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 68 (1987).

Although the potential of the staged slagging combustor for controlling SO_x - NO_x emissions has been demonstrated, additional testing is required to determine the following: the effects of first- and second-stage gas temperature and stoichiometry on SO_x and NO_x emissions, the effect (if any) of coal nitrogen on NO_x emissions, the potential of second-stage sorbent injection for SO_x control, and the addition of promoters to improve sorbent performance.

C. *Magnetohydrostatic Separation of Coal Macerals*

Coal is a heterogeneous material that is difficult to characterize. To date, petrographic methods, in which individual coal macerals are not separated but examined under a microscope, have been primarily used to characterize coal macerals. Coal macerals differ widely in reactivity, hydrogen-to-carbon ratio, heteroatom content, and density.

For several years, the ANL Chemistry Division has been using density gradient centrifugation to separate macerals. However, with this technique, only small amounts (milligram to gram quantities) of material can be separated and isolated in a single run. The CMT Division, in cooperation with the Chemistry Division, is developing a continuous process for the separation of coal macerals. This process is based on the fact that, when a paramagnetic fluid is placed in a magnetic field gradient, the apparent density of the fluid increases. When coal particles are suspended in this fluid, they will float or sink, depending on the strength of the magnetic field and its gradient. Hence, the density at which coal macerals are separated can be "tuned" merely by adjusting the magnetic field.

In earlier work, the feasibility of this concept was demonstrated in tests with a simple flow cell arrangement.⁶ The separation cell used a magnetic solution of manganese chloride, which required very high magnetic fields to produce the desired density, and a superconducting quadrupole magnet loaned by Fermilab. Polymers of known density as well as coal macerals were separated in these tests. However, the necessary residence times in the separation cell were unacceptably long, and design of a new cell was initiated.

In 1987, a new separation system designed to operate at 7000 rpm was constructed. The manganese chloride solution was replaced by a colloidal suspension of magnetite, which has a magnetic susceptibility approximately 1000 fold that of manganese chloride. This permits the use of a simple electromagnet rather than the superconducting magnet. Special pole caps designed by the High Energy Physics Division were machined to produce the desired region of constant force. A schematic of the separation system is shown in Fig. III-6. The centrifuge and pole cap design are shown in Fig. III-7. Tests are underway with polymers and coal suspensions to determine the efficiency of separation with this system.

D. *Physical and Chemical Nature of Deposits*

The objective of this effort is to model the physical and chemical nature of the deposits that form in coal-combustion environments. When materials of

⁶M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1985*, Argonne National Laboratory Report ANL-86-14, p. 74 (1986).

Fig. III-6.

Schematic of New Separation System

Fig. III-7.

Schematic of Centrifuge and Pole Caps for New Separation System

construction in fossil-combustion system components (such as boiler tubes and high-temperature gas turbines) are exposed to combustion environments, mixed alkali salts frequently deposit onto their surfaces. These mixed deposits (e.g., sodium and potassium sulfates) often form low-melting eutectics that become molten in the typical temperature regimes encountered ($\sim 600\text{--}1000^\circ\text{C}$). These molten deposits could penetrate the protective oxide scales usually found on top of the alloys through various processes, including direct frontal chemical attack via acidic or basic fluxing of the oxides, grain boundary diffusion, and infiltration via capillary action.⁷ Penetration of the protective scales would lead to accelerated attacks on the underlying alloys, increased internal oxidation/sulfidation, and

⁷C. S. Giggins and F. S. Pettit, *Hot Corrosion Degradation of Metals and Alloys--A Unified Theory*, Pratt & Whitney Aircraft Report FR-11545 (June 1979).

degradation of scale integrity and adherence. If the underlying networks of channels through which capillary infiltration occurs are of sufficient long-range connectivity, then oxide scale penetration could be rapid and extensive.

We have developed an invasion percolation model that describes this capillary infiltration process of the molten deposits. This model employs a Monte Carlo simulation method to reflect the stochastic and irregular nature of this process. The physical basis of our model lies in the fact that the molten deposits tend to penetrate the protective scale via a convoluted network made up of microcracks and fissures linking up various pores in the oxide scale. The principal driving force for penetration (besides possible chemical interactions) is capillary action. In the invasion front made up of the molten deposits, interfacial tension tends to drive the front through the smallest available opening.⁸ As a result, the advancement of the front is intermittent and "jittery" on a short time scale. The structure of the front can be extremely rough and highly irregular. Similar models have been constructed in the recent geophysics literature to simulate the relative displacement of two immiscible fluids (e.g., oil and water) in a geomedium.⁸⁻¹⁰ However, for the phenomena we are modeling, there are some important differences in the physical processes. The "fluid" being displaced is actually a vapor mixture assumed to be in equilibrium with the oxide, the molten deposits, and the alloy. This "fluid" is compressible, unlike the two fluids in the geomedium. Consequently, when our displaced fluid (the vapor mixture) is completely surrounded by the displacing fluid (the molten deposit), further shrinkage of these isolated pockets can take place.

Calculated results with our model have indicated that it can be used to better understand the long-range transport of molten deposits through a medium of complex morphologies, such as interconnected porosity or microchannels along grain boundaries/edges within the oxide scales. We plan to utilize this tool to analyze the scale thickness dependence of critical parameters characterizing the penetration processes. The model will also be further refined to include consideration of more general grain boundary morphology. The more general model will be used to analyze the extensive available data on hot corrosion in fossil combustion systems.

⁸D. Wilkinson and J. F. Willemsen, *J. Phys. A*, **16**, 3365 (1983).

⁹P. G. DeGennes, *Rev. Mod. Phys.* **57**, 827 (1985).

¹⁰R. Lenormand, in *Physics and Chemistry of Porous Media II*, eds., J. R. Banavar, J. Kopolik, and K. W. Winkler, AIP Conf. Proc. No. 154, American Institute of Physics, New York (1987).

IV. STEEL INDUSTRY/FEDERAL LABORATORIES RESEARCH INITIATIVE

This R&D program resulted from a Steel Industry/Federal Laboratories Research Initiative to identify innovative technologies that would significantly benefit the U.S. steel industry through substantial reductions in equipment, operating, and energy cost. The Argonne effort is twofold: (1) the development of an electromagnetic (EM) process for the continuous casting of various grades of steel in large-aspect-ratio shapes such as steel strip and (2) the development of an economical process for the purification of ferrous scrap. The ANL divisions involved in the effort are Chemical Technology, Energy and Environmental Systems, Electromagnetic Technology, and Materials and Components Technology.

A. *Electromagnetic Casting of Steel*

During FY 1987, the research activities on the electromagnetic continuous casting of steel sheet were focused on (1) levitation experiments with a test magnet to investigate magnetohydrodynamic (MHD) instabilities, (2) development of an electromagnetic caster design, (3) fluid flow analysis and experimentation, (4) heat transfer analysis, and (5) identification of sensors for on-line monitoring and process control.

1. Levitation Experiments

The development of an electromagnetic process for continuous casting of steel in large-aspect-ratio shapes is being pursued with two basic concepts. The first levitates a sheet of molten metal horizontally by the interaction of a horizontal, high-frequency magnetic field and longitudinal eddy currents induced in the sheet by the high-frequency magnetic field. In the second concept, a vertical molten sheet passes through a vertical high-frequency magnetic field produced by a large-aspect-ratio solenoid. The sheet is shaped by the interaction of peripheral horizontal eddy currents and the vertical solenoid field.

In support of efforts to develop a bench-scale caster for horizontal levitation, a test magnet was designed and fabricated for low-temperature ($\sim 250^{\circ}\text{C}$) experiments. The test magnet was designed to have a very uniform horizontal field and simulate the conceptual design of the horizontal caster magnet (described in Sec. IV.A.2). The primary purpose of the test magnet is to investigate liquid-metal MHD stability. Other functions include verification of calculated current and flux distribution, verification of eddy current losses, and optimization of magnetic circuit components (edge guards, heat shields, eddy current shields, etc.).

Figure IV-1 shows a view of the test magnet. The ferrite core is 30-cm long, and the aperture for experiments is 20-cm wide and 13-cm high. Experiments with the test magnet were initially conducted with liquid tin (mp, $\sim 230^{\circ}\text{C}$) in a stationary mode and required the use of a special test fixture (a closed copper loop or shorted turn), which is inserted into the bore of the magnet. Most of the magnetic field is excluded from the interior portion of this shorted-turn insert. Capacitance is added to the power supply circuit to tune the system to the largest magnetic field. An opening or window is in the bottom portion of the insert in a location such that it is exposed to the good-field region of the magnet, i.e., where the magnetic field is uniform. A sheet of tin is fitted

Fig. IV-1. View of Test Magnet for Horizontal Levitation of Molten Metal

into this window. After the magnetic field is turned on to a low level, eddy current heating is used to melt the tin in the window.

In the experiments, the liquid tin sheet was disrupted before achieving levitation by the growth of an instability that was always associated with the interface between the solid window and the molten metal. In the early experiments, a stainless steel window frame was used, and the instability occurred at magnetic field strengths significantly below the strength required to levitate the molten sheet. Analysis of the experimental geometry with a two-dimensional computer code (PE2D) found that the mismatch of the electrical conductivity between the stainless steel and the liquid tin resulted in a significantly larger levitation force exerted at the sides of the tin. The magnitude of the force was sufficient to cause the instability.

The use of a copper window frame resulted in the maximum levitational force applied at the center of the sheet, and the magnetic field could be brought up to levitational strength before the instability occurred. This time, the instability appeared along the front or back edge of the sheet. Analysis with the PE2D computer code showed that this instability was associated with the vertical component of the current as it expanded from a relatively small skin depth in copper to a much larger skin depth in the tin. Present experiments are being conducted with a Monel metal window frame, because the electrical conductivity of Monel is very similar to that of liquid tin.

The power supply used for these experiments had a low frequency (10 kHz) and low power output (30 kW). Results indicate that stable levitation of a liquid tin sheet in the horizontal mode may not be possible with this power supply. A higher frequency and increased power output would substantially improve the chances of achieving stable levitation.

In other experiments, a solid sheet of copper was successfully levitated using our test magnet and the 30-kW power supply. The copper sheet had a mass of 292 g and was 0.15-cm thick (11-cm wide and 13.5-cm long). The front and back of the copper sheet were bent down to form "legs" that were placed in troughs filled with a low melting point metal and formed the liquid metal electrical connections necessary to complete an eddy-current return loop. The sheet was surrounded by a copper window frame. There was a clearance of 6 mm between each side of the copper sheet and window frame. As the magnetic field strength below the sheet was increased, the sheet was elevated within the window frame. A plastic probe was used to perturb the position of the levitated sheet and thereby demonstrate its stability. The experiment was repeated several times. The experiment successfully demonstrated the bulk stability of the field configuration, which depends upon magnetic flux compression. Also, theoretically predicted parameter changes associated with inductance stabilization were verified in these experiments. The use of inductance stabilization appeared to improve the stability of the levitated copper sheet.

2. Electromagnetic Design

Various magnet geometries have been investigated with the PE2D computer code. These design analyses resulted in a conceptual design for a bench-scale horizontal caster that has the cross section schematically represented by Fig. IV-2. This window-frame-type magnet should yield a very uniform horizontal field ($\pm 0.2\%$). Special features of the caster design are the copper shield and the side guards.¹ The frequency of the AC field is chosen such that it penetrates less than one-third the thickness of the liquid steel sheet. Longitudinal eddy

Fig. IV-2. Cross Section of Conceptual Horizontal Caster

¹J. Hull et al., "Horizontal Electromagnetic Casting of Thin Metal Sheet," U.S. Patent No. 4,678,0244 (July 7, 1987).

currents, generated by the AC field, flow normal to the direction of the field. The magnetic force produced by the interaction of the eddy currents and the field levitates the steel. The space above the liquid steel is made nearly field free by arranging a copper conductor (shield), for the eddy-current return path, above the levitated steel. Below the steel sheet is space for cooling equipment and for a heat shield to protect the magnet excitation coil and the ferrite core. A small magnetic field above the levitated steel sheet provides suppression of waves and may improve surface quality.

The magnetic field concept that has evolved for vertical casting uses large-aspect-ratio solenoid coils with a vertical axis. The solenoid coil produces a stationary high-frequency field that provides containment of the molten metal. The containment forces are due to the interaction of the solenoid field with peripheral eddy currents induced in the molten metal by the stationary field. Effects of gravity are controlled with vertically traveling waves. Preliminary analysis shows that the caster design has sufficient flexibility to generate a nearly uniform levitation force over the width of the sheet, including the sheet edges.

3. Feed System Development

The EM caster requires a liquid metal feed system. The primary function of the feed system (which includes a tundish, an EM pump, refractory nozzles, and flow controls) is to provide a suitable feed stream from the liquid metal source (ladle) to the EM caster.

In the initial plans, we assumed that a conventional liquid metal feed system would provide the required liquid metal stream to the bench-scale casters. This system would operate in the batch mode and have a capacity of about 100 kg of liquid metal. One feed system design that appeared, at first, to be simple and yet adequate for the bench-scale casters was a relatively shallow tundish designed to eliminate most of the turbulence created at the inlet before the fluid reached the outlet. The fluid would enter a rectangular nozzle and then be delivered into the caster in the form of a stream having suitable shape and flow parameters. However, preliminary analysis showed that shallow tundishes are not suitable for liquid steel. Tundishes for liquid steel must have low turbulence levels so that they achieve good stream quality and steady-state flow, as well as good inclusion removal and minimal heat loss. These requirements call for a relatively deep tundish with precise fluid head and flow control.

A parametric study by numerical simulations of the fluid flow in a tundish under different geometric conditions was performed. These simulations examined some important parameters and their impact on the resulting flow. The simulations used a three-dimensional computer code (COMMIX) developed at Argonne and were performed for the tundish design shown in Fig. IV-3. The following conclusions were reached: (1) the effect of the entry depth diminishes as the fluid flows away from the point of entry and is completely eliminated by the time the fluid approaches the outlet nozzle; (2) the fluid velocity distribution at the tundish outlet is similar for different inlet widths, which do not affect the residence time; (3) the fluid velocity distribution at the tundish outlet is not significantly different with or without Baffle A; (4) an increase in turbulence occurs with the addition of weirs and dams; and (5) the location of Baffle B has the largest effect on the final velocity distribution for the fluid at the tundish outlet nozzle.

Fig. IV-3. Schematic Representation of Recirculating Feed System

During 1987, experiments related to feed system development were conducted to investigate (1) wave formation and suppression at a gas/liquid-metal interface and (2) water flow through open- and closed-channel nozzles of high-aspect ratio under small effective liquid heads.

Test results from the first series of experiments indicated that the presence of a magnetic field could damp out waves produced on a liquid metal (Indalloy 136) surface by a nitrogen gas stream. Wave suppression occurred when the waves were already present and the magnetic field was increased; alternatively, with a constant magnetic field, the critical velocity for the onset of waves was raised. Gas velocities as high as 18-20 m/s were observed with substantial wave suppression in the strongest part of the magnetic field. At higher velocities, the surface of the liquid metal was disrupted at the fringe of the magnetic field and a venturi-type instability appeared to dominate. At low gas velocities (≤ 10 m/s), the experimental results appeared to verify the theory developed earlier of Kelvin-Helmholtz type instability.

The second series of experiments (water model) indicated that the nozzle geometrical factors that influence the shape and velocity distribution of the emerging liquid stream include (1) the aspect ratio of the nozzle cross section, (2) the area contraction ratio from inlet to exit, (3) the length of straight section, and (4) the corner curvatures of the exit cross section.

To determine the effects of these geometrical factors and to compare fluid flow between open- and closed-channel nozzles, eleven Plexiglas nozzles of various geometries were built and tested with water. The following preliminary observations have been made: (1) immediately on leaving a rectangular nozzle,

the liquid stream begins to accelerate downward under the influence of gravity and starts to form a "dog-bone" shape; (2) because of gravitational acceleration, the width of the liquid stream starts decreasing and the thickness starts increasing as the stream moves farther away from the nozzle; and (3) the free surface roughness increases as the velocity and turbulence increase and as the straight section of the nozzle increases. To obtain further design information, an experimental feed system for recirculating liquid tin was designed and fabricated. This system is being used to investigate the flow of molten metal through rectangular open- and closed-channel nozzles of various shapes and sizes and to help design and evaluate devices for control of a stream shape and turbulence. The facility is operated in a nitrogen atmosphere to minimize surface contamination. We have also constructed nomograms to cover a wide range of possible design parameters for the feed system. They should aid in the design of tundishes for bench-scale, laboratory-scale, and prototype casters.

4. Heat Transfer Analysis

A key element in the development of the EM casting process for sheet is a coolant system able to remove a large amount of heat in a short time. This development is complicated by the additional heat imposed by the induced eddy currents. Radiative cooling is insufficient to meet the requirements and must be augmented with convective cooling. In addition, there are restrictions on the upper boundary of the coolant mass flow rate (velocity and density) because of the possible detrimental effect of the coolant flow on the stability of EM levitation. These restrictions, which result in poor heat transfer coefficients, make the design of a coolant system more difficult. Consistent with these operating conditions, work is being directed toward (1) parametric investigations for establishing the cooling requirements in terms of casting speed, magnet length, coolant mass flow rate, and degree of heat transfer augmentation, (2) experiments to obtain supporting data on heat transfer augmentation, and (3) development of nomograms for studying the effect of various operating parameters on the EM casting process.

For the parametric investigations, a set of reference conditions (given in Table IV-1) was established as a basis for calculating heat transfer requirements and as an aid in determining methodologies to obtain the required cooling. In addition to the reference conditions, options at higher velocity, emissivity, and pressure have been included for comparison. Since it may be feasible to develop a mechanical support system for a partially solidified strip, an exit temperature of 1455°C (2650°F) may be an overly conservative value. The emissivity (ϵ) of 0.4 for steel is low, even for ultrapure surfaces. Hence, $\epsilon = 0.6$ was also examined because the emissivity will increase owing to surface contamination and the formation of a solid skin. Higher coolant velocity (40 m/s) and pressure (210 kPa) options were included to examine the effects of some evolution in technology.

The heat transfer coefficients estimated from empirical equations are shown in Table IV-2 for nitrogen coolant. The heat transfer coefficients that are required to meet the operating conditions of Table IV-2 are graphically presented in Fig. IV-4 for emissivity values of 0.4 and 0.6. Comparison of the required heat transfer coefficients (Fig. IV-4) with the feasible ones (Table IV-2) clearly shows that some heat transfer augmentation is necessary for magnets less than 10-m long.

Table IV-1. Reference Operating Parameters for Heat Transfer Requirements

Mean Outlet Temp., °C	1455
Strip Thickness, ^a cm	0.6
Casting Speed, cm/s	30
Coolant Press., kPa	140 (210) ^b
EM Heat Flux, W/cm ²	50
Emissivity of Steel	0.4 (0.6) ^b
Coolants	N ₂ , CO ₂
Coolant Velocity, m/s	30 (40) ^b
Magnet Length, m	4, 6, 8, 10
Coolant Channel Height, cm	10-13

^aFor any width.^bNumbers in parentheses are higher pressure, emissivity, and velocity options.Table IV-2. Estimated Heat Transfer Coefficients for N₂ Coolant

Case ID	Operating Conditions		Heat Trans. Coeff. for N ₂	
	Pressure, kPa	Velocity, m/s	Heat Trans. Coeff. for N ₂	
			W m ⁻² K ⁻¹	Btu h ⁻¹ ft ⁻² °F ⁻¹
A	140	30	85	15
B	140	40	108	19
C	210	30	120	21
D	210	40	148	26

Figure IV-5 illustrates the required augmentation factors for the four different cases in Table IV-2 as a function of magnet length at $\epsilon = 0.4$. As shown in Fig. IV-5, Case A requires an augmentation factor of three for a 10-m magnet, whereas Case D requires an enhancement factor of only two for a magnet length of about 6.5 m. For 10-m magnets, Cases B, C, and D require a heat transfer augmentation factor of less than two, which should be easily achievable. Similar calculations for $\epsilon = 0.6$ show that the required magnet length for Case A is reduced to about 8 m for an enhancement factor of two. For Cases C and D, it is feasible to design an EM casting device that is less than 10-m long and does not require heat transfer augmentation.

Review of the literature showed that there is a wide selection of techniques and devices that would yield enhancement factors of two or three. For example, augmentation of heat transfer by adding fine droplets of a liquid (e.g., water) to a gaseous coolant greatly increases the cooling potential of inherently

Fig. IV-4.

Required Heat Transfer Coefficients (HTC) as a Function of Magnet Length

Fig. IV-5.

Required Augmentation Factors as a Function of Magnet Length ($\epsilon = 0.4$)

poor gaseous coolants. Therefore, by applying a mist coolant over a partially solidified strip within the EM confinement, the total length of the magnet could be significantly reduced without deleterious effect. An experimental apparatus has been constructed to determine the amount of heat transfer augmentation achieved for gaseous coolants by the addition of fine droplets of a liquid (e.g., water) to a carrier gas.

In another effort, extensive parametric analyses have been conducted to identify the interactions of various parameters related to heat transfer in the EM casting process. These analyses provide information needed as a first step in the design of a cooling system for the EM casting process. Further, they help determine the feasibility of the EM casting process from a heat transfer consideration.

5. Sensors and Process Control

The primary objective of this effort is to develop the sensors and control systems required for on-line process monitoring and automatic control of the EM casting process. The sensors and controls should permit safe and efficient operation of the caster. Current efforts are focused on the sensors and control systems needed for the horizontal casting magnet and liquid metal feed system.

In the past year, a wave detector based on capacitance change was developed for quantifying and characterizing the surface-wave formation caused by a flow of coolant gas over a pool of liquid metal. The capacitance between the liquid metal surface and a small wire hung above and parallel to the surface changes when a wave of liquid propagates underneath the wire. The change in capacitance produces a change of charge on the electrodes if a DC voltage is applied between the electrodes. This device was successfully used in the experiments to determine effects of the magnetic field on wave suppression (Sec. IV.A.3). In addition, a spectrophotometer was modified and fitted with fiber optic light guides for on-line measurement of tracer concentrations and water-jet thickness variation. This device is being used in the water model experiments (Sec. IV.A.3).

A review of sensor needs, requirements, and commercial availability for the EM casting process was initiated. The feed-system sensors and controls, in particular, were examined. Feed-system sensors that are commercially available appear to be usable; however, the special characteristics and geometry of the casting system would require, in most cases, research and development in adapting the available sensor technology to the EM casting process.

6. Future Work

Work on this project was discontinued in January 1988 because of the decision by the steel industry not to participate. A final report will be prepared.

B. *Steel Scrap Beneficiation*

The objective of this research effort is to develop processing schemes that will produce high-quality, deep-drawing steels from low-grade ferrous scrap in an efficient and cost-effective manner. The current inventory of ferrous scrap in the United States is estimated by the Institute of Scrap Iron and Steel to be approximately 750 million tons.² This scrap inventory continues to grow, even though more iron units are derived from scrap than from ore in the domestic production of steel. A major impediment to greater use of scrap in the production of high-quality steel is the presence of undesirable residual elements, such

²S. M. Kaplan, "Closing the Black Hole in the Scrap Cycle," *Phoenix Quarterly* 17(2), 8-10 (1985).

as copper and tin. The carryover of these elements into finished products can seriously degrade product quality. We are investigating schemes for removing these elements.

1. Removal of Copper from Scrap Steel

In common ferrous scrap, copper is present at a concentration of 0.6 wt% in No. 2 Bundles and at 0.2 wt% in shredded and No. 1 High Melting scrap. However, the allowable level for copper in deep-drawing steel is ≤ 0.1 wt%. For tube and pipe steel, a somewhat higher copper level of 0.2 wt% is acceptable, while the lower grade rebar steel may contain 0.3 wt% or more of copper. Thus, to produce high-grade steel from low-grade scrap, the copper content must be reduced by a factor six or more.

With the common steel-making slags in an electric arc furnace, all of the copper present in the charge is retained in the melt phase. To remove copper from the melt, one must formulate a slag chemistry such that copper forms a more-stable phase in the slag than in the melt. Sulfides are thermodynamically the most favorable compound for this purpose. Further, the reaction

can be driven to the right by a slag that provides a low Cu_2S activity coefficient and a relatively high FeS activity coefficient. By analogy with oxides and halides, the activity coefficient of Cu_2S should be low in a polyvalent sulfide slag, e.g., a slag comprised of Al_2S_3 and FeS.

Figure IV-6 shows schematically how the copper would distribute itself between the slag and melt phases. Distribution factors were measured in laboratory experiments using carbon-saturated iron. Figure IV-7 shows the effect of iron in the slag phase on the measured ratio of percent copper in the slag phase to that in the melt at temperatures of 1365-1455°C. The filled and open circles in Fig. IV-7 show the results for slag-melt systems containing Al, C, Cu, Fe, and S; the effect of the presence of small amounts of Ca or Mg in the system is shown by the filled and open squares. The presence of Ca or Mg did not appear to have a significant effect on the copper distribution factors; the calcium yielded somewhat higher, and the magnesium somewhat lower, copper distribution factors.

Fig. IV-6.

Schematic Representation of
Copper Distribution between
Metal and Slag Phases

Reaction at Slag/Melt Interface:

Fig. IV-7.

Distribution Factors of Copper between Metal and Slag Phases

In our experiments, copper distribution factors as high as 30 were obtained. Values of ~7 have been reported in the literature for sodium sulfide slags. The higher distribution factor implies a lower quantity of slag necessary for treating the melt. However, even with a copper distribution factor of 30, decreasing the copper content of the molten scrap by an order of magnitude in a single treatment would require equilibrating the melt with an almost equal volume of the slag. A greater distribution factor is desirable to further reduce the slag quantities needed for the treatment.

A schematic process for the reduction of copper in the electric arc steel-making process is shown in Fig. IV-8. The scrap is first melted in the electric arc furnace in the conventional way. The molten steel is then treated with a sulfidic slag, which removes copper (and some other elements, such as manganese) but adds sulfur to the steel. This sulfur is removed in a follow-on step to yield the desired clean steel. In a variant of this process, the spent slag is recovered using scrap aluminum.

Fig. IV-8. Flowsheet for Production of Low-Impurity Liquid Steel from High-Impurity Ferrous Scrap

2. Removal of Tin and Other Tramp Elements from Scrap Steel

Another significant impurity in ferrous scrap is tin, which is present at 0.05 wt% in No. 2 Bundles and 0.02 wt% in shredded and No. 1 High Melting

scrap. The permissible level for tin is 0.01 wt% in deep-drawing steel, 0.02 wt% in tube and pipe steel, and 0.03 wt% or higher in rebar steel. Thus, to produce high-grade steel from low-grade scrap, tin removal by a factor of five or greater is required.

Electropositive metals, such as calcium, chemically complex many electronegative elements, e.g.,

Research conducted elsewhere has shown that calcium can be used successfully to remove sulfur and tin from steels (e.g., Ref. 3). We have conducted preliminary experiments with calcium generated electrochemically *in situ*. The results to date have been promising. For the removal of tin (or other electronegative elements), the calcium can be added as Ca or as CaF_2 , CaC_2 , CaSi , etc.

3. Economics of Copper Removal from Scrap Steel

Preliminary economic analyses were conducted to compare the anticipated costs of producing high-quality steel from scrap by the proposed techniques versus the costs of producing liquid steel from iron ore by the conventional process involving coke ovens, blast furnaces, and basic oxygen furnaces. The results of the economic analyses showed that the process of Fig. IV-8 could produce liquid steel at a potential savings of ~20%; if the spent slag is reprocessed and reused, savings of ~30% are possible. The process could be even more effective in removing copper from a mixture with solid ferrous materials (rather than an alloy), such as copper wire in automotive scrap. However, a potentially significant cost factor not included in these evaluations is the cost of disposal of the spent sulfidic slag; on the other hand, this slag may represent a credit because of the relatively high copper and manganese contents.

In addition to the economic considerations, this concept offers a number of attractive features: (1) the production of low-impurity steel without the need for ore pelletizing plants, sintering plants, coke ovens, or blast furnaces; (2) increased utilization of ferrous scrap, an abundant U.S. resource; and (3) possible integration with advanced scrap-based or scrap-intensive steel-making processes under development.

4. Future Directions

Further work in this area is planned in collaboration with commercial partners in the steel industry. Some additional laboratory work will have to be conducted prior to demonstration of the processing steps in an industrial setting. Discussions have been initiated with several interested companies.

³K. Kitamura, T. Sakurai, T. Takenouchi, and Y. Iwanami, "Removal of Impurities from Carbon Steel by the Addition of CaC_2 ," Fifth Int. Iron and Steel Congress, Proc. 69th Steelmaking Conf., Washington, D.C., April 6-9, 1986, pp. 269-275.

V. MUNICIPAL AND HAZARDOUS WASTE

This effort involves research into the thermochemical conversion of municipal solid waste into gaseous and liquid fuel and the development of methods for treating hazardous waste.

A. *Energy from Municipal Waste*

Past attempts at producing an economical fuel from municipal solid waste (MSW) or biomass have not been successful. The fuels produced have been of inadequate yield and very poor quality. Before commercial processes can be developed, more information is needed about the basic mechanisms, kinetics, and chemistry of MSW pyrolysis. The overall objective is to develop a scientific data base that will support the development of economic engineering processes for the thermochemical conversion of MSW into clean gaseous and liquid fuels.

As part of this effort, we are performing laboratory-scale tests to determine how different operating parameters influence the product compositions and yields of MSW pyrolysis. In these tests, a fixed bed of MSW feedstock is heated to temperatures of 200 to 700°C in a quartz tube and then the products (gases, tars, and chars) are analyzed. The test apparatus is operated in the nonisothermal mode with heat-up rates of up to ~30°C/min. Tests under isothermal reaction conditions are run in a similar apparatus.

Several types of MSW feedstocks were used in the tests completed in 1987. The emphasis was on cellulosic material, although some polyethylene samples were also examined. The cellulosic materials were newsprint, glossy newsprint, kraft paper, cardboard, and maple wood chips. Sample sizes ranged from 5 to 50 g.

The results of the nonisothermal tests indicate little dependence of product yield on heat-up rate. Data were compared for the tar and char yields from the isothermal experiments with those from the nonisothermal experiments for newsprint and kraft paper pyrolysis (Table V-1). Tar yields for the newsprint pyrolysis were slightly lower for the isothermal experiments. These results are interesting, since the heating rate in the nonisothermal experiments did not affect the tar yields appreciably. The lower tar yield in the isothermal pyrolysis may be attributed to two possible factors: cracking of the tars on the reactor walls and incomplete pyrolysis. Incomplete pyrolysis might also explain the higher char yields obtained for isothermal pyrolysis. Although there are differences, the product yields for newsprint pyrolysis are not significantly affected by the isothermal conditions. In contrast, the kraft paper results show significantly higher tar

Table V-1. Yields from Isothermal and Nonisothermal Pyrolysis Experiments for Newsprint and Kraft Paper

	Newsprint Yields, wt%			Kraft Paper Yields, wt%	
	Iso.	Noniso.		Iso.	Noniso. at 5°C/min
		5°C/min	30°C/min		
Tar	26.64	29.18	29.50	33.09	26.48
Char	27.86	23.64	22.89	32.08	25.68

and char yields for the isothermal runs. This may be due, in part, to insufficient drying of the tars and incomplete pyrolysis of the chars.

Figure V-1 shows the infrared spectra of tars produced at 450 and 700°C from kraft paper as the only feedstock. Comparison of the two spectra shows very interesting differences. The secondary tars obtained at 700°C contain strong, sharp bands of aromatic C-H stretches at 3011, 3022, and 3045 cm^{-1} . Bands in the 800 to 900 cm^{-1} region can be assigned to the out-of-plane bending modes of aromatic C-H. These bands do not appear in the tars obtained at 450°C, suggesting the absence of aromatic species. The other major difference between these two spectra is the disappearance of the 1725 cm^{-1} band for the 700°C spectrum, suggesting the absence of carbonyl in these tars. The results indicate that, at high temperatures, either the kraft paper radicals undergo aromatization, or that the lignin component of the kraft paper decomposes. Investigation to determine which of the above reasons is leading to the highly aromatic condition is underway. The production of aromatics from MSW may be a useful process.

Fig. V-1.

Fourier Transform Infrared Spectra
of Kraft Paper Tars Obtained at
(a) 450°C and (b) 700°C

Several pyrolysis runs were made using kraft paper (KP), kraft paper/polyethylene (KPP), kraft paper/polyethylene/aluminum (KPPA), and kraft paper/polyethylene/aluminum/boric acid (KPPAB). The aluminum was added to the cellulosic/plastic mixture to test for catalytic effects. Boric acid (9 wt%) was used as a representative protic acid. Protic acids are often added to wood and wood products as flame retardants. Sample weight was 30 g. In the pyrolysis runs, the temperature of the test apparatus was raised from ambient to 700°C at a rate of 20°C/min.

Table V-2 shows the properties of tars obtained from the different feed mixtures. As seen in Table V-2, the KPP, KPPA, and KPPAB mixtures yielded tars that were less dense than those obtained from kraft paper only. In addition, the KPP and KPPA mixtures produced tars that were less viscous than the kraft-paper-only tars. The presence of boric acid during pyrolysis of the KPPA mixture produced very viscous tars similar to those from kraft paper only. These results imply a high degree of hydrogen bonding caused by the low pH of the material. Significant intermolecular and intramolecular hydrogen bonding would cause the molecules to become less free to move, which, in turn, would increase the viscosity in the liquid.

Table V-2. Properties of Pyrolysis Tars^a and Chars

Sample ^b	Tar Specific Gravity	Tar Viscosity, Centistokes	Caloric Value, J/kg x 10 ³	
			Tar	Char
Kraft paper	1.24	257.0	22,595	33,038
KPP	1.03	78.5	21,394	29,883
KPPA	1.08	19.8	21,227	32,485
KPPAB	1.06	287.7	21,249	29,544

^aTars dried over MgSO₄.

^bAbbreviations defined in text.

Analysis by Fourier transform infrared (FTIR) spectroscopy of the tars produced from the above mixtures indicated that the addition of polyethylene and aluminum to the kraft paper produces tars containing fewer hydrogen-bonded constituents. Furthermore, determination of the caloric values of the chars produced from the mixtures, along with FTIR analyses of the tars, suggests that the kraft paper/polyethylene mixture undergoes significant reaction only in the presence of aluminum. However, the boric acid significantly decreased the caloric value of the KPPA char. Additional work with composite mixtures and actual refused-derived fuel samples will be performed during the upcoming year to verify these initial observations.

There is a continuing interest as part of our overall effort to develop kinetics and reaction models for cellulose decomposition. We developed a kinetics model in which cellulose pyrolysis is assumed to occur via three competitive reactions. As cellulose is heated in a nonreactive environment, it decomposes homogeneously by a first-order process to various pyrolysis products: chars, tars, and gases. The scission of 1,4 glucosidic bonds is responsible for the tar formation, and the scission of 1,5 acetal bonds leads to the formation of chars. Gases can arise from either of these reactions. Although our three-reaction model may not accurately reflect the actual pyrolysis mechanism, it is a powerful mathematical tool capable of predicting various product yields. This three-reaction model applies over the entire temperature range of cellulose pyrolysis (250-360°C). However, at temperatures below 280°C, the cellulose pyrolysis mechanism can be better represented by a modified Kilzer-Broido model.¹ The procedure for

¹F. J. Kilzer and A. Broido, *Pyrodynamics* 2, 151 (1965).

determining the parameters from the Arrhenius equation with the modified Kilzer-Broido model should be helpful to the biomass pyrolysis community in visualizing the complex pyrolysis reactions.

Work will continue on modeling the chemical degradation of cellulose under various pyrolytic conditions. Experimental data will be acquired as needed in support of this effort.

B. *Hazardous Waste Treatment*

Efforts are underway to develop methods for treating reactive metal and hazardous organic wastes.

1. Reactive Metal Wastes

The objective of this effort is to develop an integrated process for the conversion of hazardous reactive metals into a stable waste form, such as a glass, for disposal. The process is "integrated" in that the reactive metal, along with its radioactive contaminants, is borne by an N_2 stream into a reactor at the same time as an air stream (which contains a glass-forming material, e.g., SiO_2) is introduced to oxidize the sodium. Thus, the conversion of the metal to the oxide occurs in the same step as the glass is formed.

For this study, sodium was selected as the reactive metal. The main consideration that determines the acceptability of a sodium waste form is its chemical reactivity with water (liquid or vapor), oxygen, and carbon dioxide. A secondary concern is the effect of groundwaters at the disposal site with regard to the solubility of the sodium waste and the leachability of its trace contaminants. Although relatively water-soluble but stable chemical forms of sodium (such as sodium carbonate) are considered acceptable, a low-solubility waste form, such as a glass, is considered more desirable.

In 1986, we developed a conceptual design for an integrated process to convert sodium to a soda-silica-lime glass form. In this concept, solid reactants are introduced to a drop cyclone reactor as a suspension in combustion air for sodium. Liquid sodium is injected into the reactor using nitrogen as an aspirator and atomizer. The reactions occur primarily at the walls of the cyclone reactor, and the product glass is withdrawn from the bottom of the reactor. The metal containment of the reactor is lined with glass-type refractories. Preliminary material and energy flows are shown in Fig. V-2.

There were limited funds for this task during FY 1987. The primary efforts were to refine the conceptual design and prepare a report of work completed to date.² Financial support is available for FY 1988, and experimental work is proceeding.

2. Hazardous Organic Waste

The purpose of this research is to investigate the technical feasibility of a microwave-assisted chemical process for detoxification (i.e., conversion into

²J. B. Rajan, R. Kumar, and D. R. Vissers, *Improved Treatment/Disposal of Reactive Metals*, Argonne National Laboratory Report DOE/HWP-29, ANL-87-39 (October 1987).

Fig. V-2.

Schematic Diagram of the Cyclone Reactor for Converting Sodium to Glass

harmless products) of hazardous organic waste such as trichloroethylene, trichloroethane, polychlorobiphenyls, chlorobenzene, and methyl ethyl ketones. Microwaves provide rapid and uniform heating in materials with high dielectric loss. Since heat can be transferred to reactants *in situ*, chemical reactions can be conducted without heating the entire reaction vessel. Thus, energy use is expected to be more efficient with the microwave-assisted process than with traditional thermal heating.

Earlier experiments investigated the oxidative degradation of trichloroethylene over active carbon in an air stream with microwave *in situ* heating.³ The carbon bed was tested with and without copper and chromium catalysts. The results of this study established that trichloroethylene in a vapor stream can be adsorbed on active carbon beds loaded with copper and chromium catalysts at room temperature. Once this bed is heated by microwave radiation to moderate (<400°C) temperatures while a moist air stream is passed through it, the trichloroethylene is readily converted into less-noxious products such as HCl, CO, CO₂, and trace C₂H₂Cl₂. Conversions greater than 80% for a single pass were observed. Furthermore, it was shown that the spent carbon bed could be regenerated.

Subsequent experimental runs investigated detoxification of trichloroethane (TCE) by a single pass with a TCE-air stream over a SiC bed heated to 500-580°C in a microwave oven. A 6-kW microwave heating assembly was designed, fabricated, and set up to conduct these detoxification experiments. It has a cavity with dimensions of ~0.6 x 0.6 x 1.2 m, which can accommodate

³M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 78 (1987).

two 72-cm-long quartz reaction tubes. The composition of the gases from the reaction in each run was determined by mass spectrometry. The total hydrochloric acid (HCl) produced in each run was absorbed in aqueous NaOH and measured quantitatively.

The clear advantage of microwave-assisted oxidation of TCE over thermal heating is illustrated in Fig. V-3. The results showed that TCE is almost completely detoxified (~98-99%) by the microwave-assisted process at $>500^{\circ}\text{C}$. The products of this conversion were HCl, CO_2 , and CO. We are currently investigating trace constituent products that may be present in the exit gas stream in the concentration range of parts per million to parts per billion. The single-pass detoxification with thermal heating resulted in only partial conversion. The principal products of oxidation were dichloroethylene ($\text{C}_2\text{H}_2\text{Cl}_2$) and HCl. The percent chlorine recovered as HCl was extremely low (~27-36%).

Our results to date indicate that the microwave-assisted process has considerable promise for detoxifying liquid hazardous organic wastes at moderate temperatures. Future experiments will demonstrate the technology for other waste streams.

Fig. V-3.

Detoxification of Trichloroethane
by Microwave and Thermal
Heating

VI. NUCLEAR TECHNOLOGY

This CMT effort involves (1) investigating processes for the extraction, separation, and recovery of transuranic elements in nuclear waste streams, (2) developing an electrochemical process for forming uranium deposits, (3) developing a reprocessing method for the core fuel and blanket material of a sodium-cooled fast reactor, and (4) examining waste-package performance in potential high-level waste repositories located in tuff and basalt.

A. Separation Science and Technology

The Division's work in separation science and technology consists of four projects. Three of these projects are concerned with removing and concentrating actinides from waste streams contaminated by transuranic (TRU) elements. The objective is to recover valuable TRU elements and lower disposal costs of nuclear waste. The major project in this area involves development of a generic data base and modeling capability for the TRUEX (TRansURanic EXtraction) solvent extraction process. This capability will allow us to design flowsheets for specific waste streams and to predict the cost and space requirements for implementing a site- and feed-specific TRUEX process. It will also be useful as a tool for plant operators to vary, monitor, and control the process once it is in place. The second project entails development of the TRUEX process for removing americium and plutonium from waste generated by the Hanford Plutonium Finishing Plant (PFP) while recovering a purified plutonium stream. In the third project, a PUREX/TRUEX flowsheet is being developed for removing plutonium from concentrated HCl/brine waste streams. The fourth project, which is unrelated to the first three, is concerned with examining the feasibility of substituting low-enriched uranium for the high-enriched uranium currently used in the production of fission product ^{99}Mo . Technetium-99m, the daughter of ^{99}Mo , is widely used in medical diagnosis.

1. TRUEX Technology Base Development

The TRUEX process extracts, separates, and recovers TRU elements from solutions containing a wide range of nitric acid and nitrate salt concentrations. The extractant found most satisfactory for the TRUEX process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide, which is abbreviated CMPO. This extractant is combined with tributyl phosphate (TBP) and a diluent to formulate the TRUEX process solvent. The diluent is typically a normal paraffinic hydrocarbon (NPH) or a nonflammable chlorocarbon such as carbon tetrachloride (CCl_4) or tetrachloroethylene (TCE). The TRUEX flowsheet includes a multistage extraction/scrub section that recovers and purifies the TRU elements from the waste stream and multistage strip sections that separate TRU elements from each other and the solvent. Our current work is focused on facilitating the implementation of TRUEX processing of TRU-containing waste and high-level defense waste, where such processing can be of financial and operational advantage to the DOE community. The largest part of this effort has been in developing a generic data base and model to predict solvent extraction behavior of important waste constituents and to generate TRUEX flowsheets for specific feeds. Development of centrifugal contactors for evaluating various TRUEX flowsheets is another large part of this effort.

a. Data-Base Collection

In this effort, we collected all the data necessary to begin modeling the TRUEX process for high-level defense waste and other nitrate-based TRU-containing waste. This data base includes extraction behavior for all important feed components over a range consistent with compositional variations of these waste streams.

The objective was met by acquiring data from the literature and our own laboratory measurements. The bulk of the literature data was generated in TRUEX-related work performed by the ANL Chemistry and Chemical Technology Divisions over the past five years. Other data on equilibria for aqueous-phase acid dissociation and complexation and on activity effects in media of high ionic strength were from work done throughout the world. Data that were measured in our laboratory include the extraction behavior of actinides [UO_2^{2+} , Np(IV), Np(V), Pu(IV), and Am(III)]; rare earth fission products (La, Ce, Pr, Pm, Eu, and Sm); other fission products (Tc, Ru, Zr, and Y); and important inert elements and species (Fe, Al, NO_3^- , SO_4^{2-} , F^- , PO_4^{3-} , and $\text{C}_2\text{O}_4^{2-}$). We also determined the effects on extraction behavior of variations in the TRUEX solvent composition, aqueous-phase acidity, aqueous-phase complexation agents, temperature, aqueous-phase nitrate concentration (mixed electrolytes), and contact times between the organic and aqueous phases. Figures VI-1 through VI-3 are representative of the data that have been collected and are discussed below.

Figure VI-1 illustrates the dependence of the distribution of uranyl ion $\{D_U = [\text{U}]_{\text{org}}/[\text{U}]_{\text{aq}}\}$ on the aqueous-phase composition. The uranyl ion extractability is increased by the presence of nitrate (NaNO_3) because of the equilibrium:

where the bar represents an organic-phase species. As indicated by Fig. VI-1, the presence of aqueous-phase complexants (sulfate, fluoride, oxalate, and phosphate) decreases uranyl ion extractability by decreasing the concentration of the free uranyl species in the aqueous phase.

Figure VI-2 illustrates another phenomena associated with the aqueous-phase composition. In this example, the concentration of a rare-earth cation, Nd(III), increases the extractability of the anionic species pertechnetate. In a solution of nitric acid alone, pertechnetate is extracted in the form of an acid, HTcO_4 . In the presence of a significant concentration of neodymium, technetium appears to be extracted as a neodymium salt. Depending on the relative aqueous-phase activities of pertechnetate and nitrate, pertechnetate will substitute for one to three nitrate ions in the organic-phase neodymium species:

Fig. VI-1. Distribution Ratios for Uranium with TRUEX-NPH at 25°C

Fig. VI-2. Distribution Ratios for Pertechnetate with TRUEX-NPH

Fig. VI-3. Iron Extraction by TRUEX-NPH at 25°C

Figure VI-3 illustrates a less common but extremely important facet of extraction by the TRUEX solvent. Although the extraction of most species is extremely rapid, there are a few metal ions (ferric ion being the most important because of its high concentration in many waste streams) whose measured distribution ratio is not based solely on equilibria but is also based on the contact time and the degree of mixing of the two phases. Figure VI-3 shows the iron distribution ratio for different contact times. Most species reach equilibrium within 15 s from an initial condition of all the species present in the aqueous phase (forward extraction) or in the organic phase (back extraction). However, in the case of Fe(III), at low nitric acid concentrations ($<1 \text{ M HNO}_3$), forward and back distribution ratios are still quite different after 300 s of contact.

Information for the data base will continue to be collected in support of the model-development effort.

b. Modeling Development

The generic TRUEX model can be looked at as having two sections: the Spreadsheet Algorithm for Stepwise Solvent Extraction (SASSE) and the Spreadsheet Algorithms for Speciation and Partitioning Equilibria (SASPE). To calculate stage and effluent compositions for a particular flowsheet, SASSE must have information from SASPE and other information such as the number of sections (extraction, scrub, strip), the number of stages per section, and the relative flow rates of the incoming streams. Input to SASPE is the composition of each incoming stream, temperature, and any feed preparation steps. Based on this information, SASPE calculates the thermodynamic activities of aqueous feed species that influence the partitioning of all species between the aqueous and organic phases (e.g., nitrate, fluoride, hydrogen, oxalate ions). Aqueous-phase activities and concentrations and the organic-phase composition are used to calculate the speciation of each feed component in each phase and, therefore, the distribution ratio of each component. This information is used by SASSE to generate the flowsheet and to estimate space and cost requirements for installing it in a specific facility. Relationships used to calculate aqueous-phase activities are being derived from established methods found in the literature. Speciation equilibria are being developed from modeling batch extraction data measured as part of this effort and collected from the literature.

Figure VI-4 is a plot of the distribution ratio of americium (D_{Am}) between a solution of 0.25 M CMPO in TCE and aqueous nitric acid vs. the nitric acid concentration of the aqueous phase. Curve A shows the fit of a simple equation where three nitrate ions and three molecules of CMPO are associated with the Am^{3+} in the organic phase. This equation fits the data up to about 1 M HNO_3 . Because CMPO is a good extractant for nitric acid, as the aqueous-phase concentration of nitric acid increases, so does the extraction of nitric acid by CMPO. With the increase of the $CMPO \cdot HNO_3$ species and the decrease in HNO_3 -free CMPO, the extraction of americium becomes more and more dominated by the $CMPO \cdot HNO_3$ species; terms that include the association of one to three molecules of HNO_3 are added to the equation represented by curve B. This equation fits the data to about 6 M HNO_3 . Above this nitric acid concentration, the extraction of two molecules of nitric acid by one molecule of CMPO begins to become important; a term for the association of four molecules of nitric acid with each $Am^{3+}CMPO$ complex becomes necessary to fit

the entire data range (curve C). The equation also contains terms that take into account the aqueous-phase complexing of Am^{3+} by nitrate anions and the dehydration of the cation as it is extracted into the organic phase. This approach is being used to fit all the accumulated distribution ratio data.

Fig. VI-4.

Modeling of the Effect of Nitric Acid Concentration on the Extraction of Americium. (Curves A, B, and C are described in the text.)

c. Centrifugal Contactor Development

As a part of our effort in 1987, an eight-stage centrifugal contactor with a 4-cm dia rotor was designed for operation in either a glove box or in a shielded-cell facility with manipulators and a viewing window. This contactor is a tool for demonstrating the recovery of nuclear materials using various solvent extraction flowsheets. It will be used in the base technology work to evaluate various TRUEX flowsheets. The contactor design, after it is fully tested, will also be available to others in the DOE community for use in the development of specific TRUEX flowsheets.

This remote-handled contactor builds on earlier designs that use off-the-shelf motors, improved support frames, closed extraction chambers, high-level liquid detectors, and clamping nuts to hold the motors to the rotors. Additional features were added to allow ease of use in a glove box or fully remote facility. They include modifications so that the interstage lines, the high-level liquid detectors, the purge-air lines, and the motor/rotor assembly can all be installed and removed easily. In addition, special handles were put on the bottom drain valves so that they can be operated easily, and the clearance below the valves was increased so that the liquids can be readily drained from each contactor stage. The contactor is now being tested in a mockup of a remote facility. All functions can be carried out very well using standard manipulators.

2. Process Development for Hanford

In 1987, we continued the process development work needed to implement the TRUEX process at the Hanford Plutonium Finishing Plant. The main liquid waste from this plant, designated "PFP waste," is a TRU waste because of the americium and plutonium it contains. This PFP waste is the raffinate from a TBP-based solvent extraction process used to remove uranium and plutonium from dissolved waste generated during the production and processing of plutonium. By use of the TRUEX process, the raffinate will be converted to a nonTRU waste, and the TRU elements will be recovered separately for recycle or converted to a solid TRU waste with greatly reduced volume.

Working in conjunction with the ANL Chemistry Division, we completed a preliminary reference flowsheet for processing PFP waste, including solvent cleanup. The reference flowsheet was evaluated further using SASSE and some of the data obtained under the technology base development program (Sec. VI.A.1). From this effort, we determined a final reference flowsheet, which will be the basis for subsequent process development and implementation at Hanford.

A four-stage prototype centrifugal contactor (10-cm dia rotor) was built and tested mechanically and hydraulically. It is now fully operational. Using 24 contactor stages of this design and the reference flowsheet at Hanford will allow processing of the PFP waste at the same rate as its production. The prototype contactor, which includes the latest design features developed at ANL, is small enough that 24 stages would fit easily in a glove box that is 0.9-m wide, 1.5-m high, and 7.2-m long. This prototype unit has been shipped to Westinghouse Hanford for further testing and evaluation.

Operation of the ANL contactors during solvent cleanup has been the subject of some concern because the dispersion formed during solvent cleanup does not always break readily. With the aid of our dispersion number test,¹ we found a mode of contactor operation that would work even when the dispersion formed during solvent cleanup did not break readily. This was successfully demonstrated using our 4-cm dia contactor. It was further demonstrated that typical solvent made from CMPO manufactured to more stringent purity levels does not have a problem with the coalescence of the dispersion formed during solvent cleanup.

We assisted Westinghouse Hanford in making the first TRUEX process tests using actual PFP waste in 4-cm dia contactors. This assistance included adapting the process flowsheet to the contactor stages then available at Westinghouse Hanford and providing instruction in the use of SASSE to model the process. The initial Hanford tests have gone quite well. There have been no problems with either operating the contactors or implementing the TRUEX flowsheet.

Using the SASSE worksheet, we identified key parameters for monitoring and controlling the TRUEX process as it runs in the centrifugal

¹R. A. Leonard, G. J. Bernstein, R. H. Pelto, and A. A. Ziegler, *AIChE J.* **27**, 495 (1981).

contactors. As shown in Fig. VI-5, one of the key parameters is the CMPO concentration in the solvent. Because of the high density of the diluent (in this case, TCE), the solvent density can be used by the process operator to maintain control of the CMPO concentration. To facilitate this, the solvent density was correlated with CMPO concentration, TBP concentration, TCE concentration, temperature, and contact with specific aqueous phases that are pertinent to the TRUEX process applied to the PFP waste.

Fig. VI-5.

Effect of CMPO Concentration in Solvent on Americium Concentration in Each Stage of Solvent Extraction Process. (Feed introduced, stage 5; scrubbing, stages 6-7; Am and Pu strip, stages 8-11 and 12-14.)

Overall, the transfer of the TRUEX and contactor technologies for processing PFP waste at Westinghouse Hanford is essentially complete. Further work on TRUEX processing of the PFP waste will be done as needed on a consulting basis.

3. Solvent Extraction Processing of Chloride Salt Waste

In 1985 work was begun on the development of a solvent extraction process to remove plutonium and americium from chloride salt wastes being stored at Los Alamos National Laboratory (LANL). These wastes are generated from the pyrometallurgical processing of plutonium, e.g., Direct Oxide Reduction (DOR), Electrowinning (ER), and Molten Salt Extraction (MSE). The goals of this process are three-fold: (1) to recover plutonium and remove other transuranic elements from these chloride salt wastes, which have a wide range of compositions, (2) to produce a plutonium product containing <1000 ppm total of other metals, with none exceeding 100 ppm; and (3) to produce an aqueous waste yielding <100 nCi of alpha-activity per gram of solid. A two-part flowsheet was proposed in 1985 to meet these objectives.² In this flowsheet, Pu(IV) was recovered in a PUREX-TCE cycle (25 vol % tributyl phosphate in

²M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1985*, Argonne National Laboratory Report ANL-86-14, p. 82 (1986).

tetrachloroethylene), then the americium and other transuranic elements were removed from the salt wastes in a TRUEX-TCE cycle (0.5 M CMPO in TCE), thereby leaving the raffinate as a discardable, nonTRU waste.

Solvent extraction measurements completed during 1987 include

- (1) distribution ratios for selected metal ions [Pu(IV), Fe(III), Zn(II), Am(III), Ca(II)] and HCl between PUREX-TCE and acidic chloride solutions as functions of the aqueous- and organic-phase compositions and the temperature and
- (2) distribution ratios for Am(III) and HCl between TRUEX-TCE and acidic chloride solutions as functions of the aqueous-phase composition and temperature.

The results acquired to date have permitted refinement of the earlier two-part flowsheet. Figure VI-6 is a schematic of this revised flowsheet. The chloride salt waste to be processed is initially dissolved in 6 M HCl. The Pu(III) is then oxidized to the IV state by the addition of an aqueous solution of NaClO_2 at a chlorite-to-plutonium mole ratio >1 . The aqueous feed solution is now ready to enter the extraction stage of the PUREX part of the flowsheet. After the loaded organic phase is scrubbed with 6 M HCl to remove impurities such as zinc, it is stripped of the plutonium product with <3 M HCl. If iron and gallium are suspected of being present at high concentrations, the loaded organic is stripped of the plutonium product with 3.5 to 4 M HCl. This step will leave most of the iron and gallium in the organic phase. The iron and gallium are stripped out of the organic phase with dilute HCl before the solvent is recycled. An alternative way to achieve a high-purity plutonium product from a feed solution containing iron and gallium is to add a head-end cycle where these impurities are extracted by TBP before oxidation of the Pu(III). The plutonium in the raffinate from this head-end cycle is then oxidized and

Fig. VI-6. PUREX-TRUEX Process Flowsheet for Recovery of Plutonium and Americium from Acidic Chloride Salt Wastes

extracted as described above. Cleanup for the TBP solvent is accomplished by scrubbing with 0.25 M Na_2CO_3 and filtering it with a discardable filter. However, cleanup may not be necessary since any acidic degradation products formed will not extract from the highly acidic aqueous phases used. Before the solvent is recycled, it may be necessary to add TCE because of losses from evaporation.

The raffinate from the PUREX cycle is processed by the TRUEX cycle. The chloride activity of the feed solution is adjusted to at least 30 (on the molal scale) so that the americium distribution ratio is >10 when the solution is contacted with the CMPO solvent, leaving the raffinate with less than 0.01% of the initial americium and other TRU elements (based on four extraction stages with an organic-to-aqueous phase ratio of 1). After the loaded organic phase is scrubbed with 6 M HCl, it is stripped of americium and other TRU elements with 1 M HCl. Solvent cleanup may be unnecessary here also, owing to the high acidities of the aqueous phases, but addition of TCE will probably be necessary.

During 1987, contactors for processing chloride salt waste by the PUREX process were placed in operation at LANL. Their performance was reviewed and recommendations were made to improve their performance. Overall, the use of the contactors with the PUREX-TCE cycle is going well. In particular, ER wastes are being processed as fast as they are produced. It is likely the TRUEX cycle of the process will come on line in the coming year.

Some corrosion of the contactor rotor and body, fabricated from Hastelloy C276, has occurred in the presence of 6 M HCl and NaClO_2 . This corrosion was not entirely unexpected and was accepted as a reasonable risk to get the contactors into production at LANL as soon as possible. Development and fabrication of contactors from more-resistant materials (e.g., Kynar or other fluorocarbon materials) are now needed.

4. Separation and Purification of ^{99}Mo

Technetium-99m (used for medical purposes) is a decay product of ^{99}Mo , which is produced in nuclear reactors by the fissioning of ^{235}U or from the neutron capture of ^{98}Mo . Presently, most of the world's supply of fission-product ^{99}Mo is produced in targets of high-enriched uranium (HEU, 93% ^{235}U). The U.S. is considering prohibiting the export and internal commercial use of HEU because of its potential use in nuclear weapons. The purpose of this study is to assess the technical feasibility of substituting low-enriched uranium (LEU, $<20\%$ ^{235}U) for HEU in targets for production of fission-product ^{99}Mo .

Work in FY 1987 was centered on determining the effects of LEU substitution on the processing of ^{99}Mo from these targets and investigating the dissolution (by bases) of uranium silicide targets followed by separation and purification of ^{99}Mo .

a. Processing of Uranium Silicide Fuels

Because of their higher densities, LEU silicides (U_3Si and U_3Si_2) can be substituted for the uranium aluminide and uranium-aluminum alloy in present targets without affecting the fission yield of ^{99}Mo . However, the

substitution of uranium silicides will require modifications in current processing steps because of the insolubility of uranium silicides in alkaline solutions and the presence of significant quantities of silicate in solution. The current processing of HEU aluminide targets is likely to include dissolving the cladding and meat of the irradiated target in 2-5 M NaOH. In this step, uranium and many of the fission products precipitate as hydroxides; other species, including molybdenum, are solubilized in the aqueous solution. The acidified solution is then run through an alumina column, where molybdenum is sorbed. Molybdenum is subsequently eluted from the column and further purified.

The U_3Si and U_3Si_2 materials appear insoluble in concentrated NaOH (3-6 M) and 3 M NaOH/4 M $NaNO_3$ but can be dissolved in a 1:1 solution of 3 M NaOH/30% H_2O_2 . Hydrogen peroxide then complexes the uranium and must be destroyed to allow precipitation of uranium (thus separating it from the soluble molybdenum) and to prevent complications in downstream processing of the molybdenum. This can be accomplished by the addition of small quantities of acidic ferric nitrate solution or nickel metal powder to catalyze the auto-degradation of peroxide, followed by the addition of potassium permanganate to complete the destruction of H_2O_2 .

Experiments were run to measure the effect of the concentrations of hydrogen ion, uranium, and silica on molybdenum adsorption by alumina columns. Hydrogen ion concentration in the loading solution exhibited a large effect on the sorption of molybdenum, the lowest concentration studied (0.1 M HNO_3) having the best sorption. Concentrations greater than 0.5 M HNO_3 showed a significant decrease in sorption; therefore, increases in solution acidity above 0.1 M necessitate longer columns. Both uranium and $Si(OH)_4$ have an adverse effect on molybdenum sorption; however, under conditions envisioned for processing LEU-silicide targets (i.e., essentially complete precipitation of uranium and $[Si] < 0.1$ M), the concentrations of these species will allow satisfactory sorption of molybdenum on alumina columns.

b. LEU Metal Targets

In our continuing effort to measure the effect of LEU substitution on current target processing, we studied separation of molybdenum from ^{103}Ru , an important fission-product impurity. The patent literature describes two methods for separating ^{99}Mo from the bulk of the fission products and uranium: α -benzoinoxime precipitation and adsorption of silver-coated activated charcoal (ACAC) columns. Our tests with these two separation techniques using natural molybdenum and ^{103}Ru showed that the ACAC columns were not as effective as the precipitation method.

Further studies were performed to improve ACAC column recovery of molybdenum. Even though yields and separation factors have been improved, separations from uranium are still not as good or as consistent as those attainable by the precipitation method, especially with uranium concentrations equivalent to those encountered by a first molybdenum separation step for processing of either LEU or HEU targets. Stripping of silver from the column material was observed for feeds containing high uranium concentrations and occurred with evolution of gas bubbles, which tended to destroy column effectiveness. As

reported earlier,³ ACAC column separations are useful as a polishing step, after most of the uranium is removed by α -benzoinoxime precipitation of molybdenum, not as a primary U/Mo separation.

Future work in target processing will employ low-burn-up LEU mini targets, which will be irradiated in the ANL JANUS reactor. The purpose of these studies will be to demonstrate the processing of LEU targets under more realistic conditions and to attain results applicable to the processing of full-size, fully irradiated targets in FY 1989.

B. Uranium Metal Electrodeposition

This effort is directed toward development of an electrochemical process for forming uniform and dendrite-free deposits of uranium metal from molten salt systems. Application of this technology includes the fabrication of LEU targets for the production of ⁹⁹Mo (see Sec. VI.A.4.b) and the formation of hollow, free-standing, hemispherical shells of uranium for nuclear application. The LEU targets will be formed on the inner surfaces of a stainless steel or Zircaloy cylinder (3.2-cm dia and 45.7-cm length) and will consist of a 0.3-mm-thick uranium deposit bonded to the substrate surface. On the other hand, the hemispherical uranium shells (10-cm dia and 0.75-cm thick) will be formed on a conductive mandrel. With both applications the uranium must be uniform, dense, and dendrite free.

The largest problem in the development of this electroplating process is the avoidance of dendrites that normally form when uranium is electroplated. Theoretical considerations suggest the key elements that control deposit morphology are the exchange current density of the plating process, the overpotential developed at the metal surface during plating, and the uranium metal-iron concentration gradient at the plating surface. Since the exchange current density is fixed for uranium plating, our experimental efforts were directed toward minimizing the overpotential and the concentration gradient. We examined plating of uranium onto various substrates with direct current and with pulse current under galvanostatic and potentiostatic control. Experiments were carried out at 440°C with a LiCl-KCl eutectic electrolyte containing 20 wt% uranium trichloride.

Direct current plating on nickel substrate materials was conducted at current densities of 5, 10, and 20 mA/cm² and plating times of 2.75 to 13.0 h. The results indicated that, at higher current densities (20 mA/cm²), there was a greater tendency to form dendrites (2-3 mm in length) in the deposit. At lower current densities (5 mA/cm²) and long plating times, the electrodeposit was less dense, with significant areas free of deposit. We concluded that a current density of 10 mA/cm² is near optimal for constant-current plating. The uranium deposits formed at 10 mA/cm² had excellent bonding and should be adequate for fabrication of uranium targets for ⁹⁹Mo production.

Experiments were also conducted to determine the effect of plating potential and pulse duration on the formation of dendrites on nickel substrate. The best plating regime selected from these experiments involved cycling between a pulse at

³M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 96 (1987).

-65 mV for 0.1 ms followed by a zero potential pulse for 1 ms. We then determined the effectiveness of this plating regime in electrodepositing uranium metal films on various substrate materials (stainless steel, tantalum, carbon steel, Zircaloy, nickel, and copper). Preliminary results indicated that dendrite-free deposits were being formed. However, deposit uniformity across the surfaces was poor, even though the substrate surfaces had been polished and pretreated with acid. To enhance the uniformity of the deposits, a nucleation pulse and a preanodization step were evaluated.

The final results of our pulse plating studies indicated that the best deposits were formed on the nickel and tantalum substrates. The quality of these deposits was improved by substrate preanodization and use of a nucleation pulse. A typical well-bonded uranium deposit on nickel is shown in Fig. VI-7. The sample was prepared by use of a preanodization step of 5 coulombs at 1.35 V, followed by a nucleation pulse of -706 mA/cm^2 for 2 s, and then a 21-h deposition.

Further studies are needed to reduce plating times and to improve the uniformity of the uranium deposit. In the latter case, studies are needed to optimize the nucleation pulse and preanodization step. Work is also needed to design and test the plating cell for the fabrication of cylindrical targets.

Fig. VI-7. Uranium Deposit Formed on Nickel Coupon

C. *The Integral Fast Reactor Pyrochemical Process*

The Integral Fast Reactor (IFR) is an advanced reactor concept proposed by, and under development at, ANL. Its distinguishing features are that it is a sodium-cooled, pool-type reactor (i.e., all the major components, reactor core,

pumps, and heat exchangers are in a large sodium-filled pot); it employs a metallic fuel (an alloy of U, Pu, and Zr clad with a stainless steel-type alloy); and it has an integral fuel cycle (discharged core and blanket materials are reprocessed and refabricated in an on-site facility). The advantages of this concept are an exceptionally high degree of passive safety, resulting from use of a metallic fuel with a sodium coolant, and competitive economics, resulting from low costs for reactor construction and fuel recycle.

The CMT Division has the responsibility of developing the on-site process for recovering plutonium and uranium from the core and blanket, removing fission products from them, and reenriching the core alloy with plutonium bred in the blanket.

1. Flowsheet Development

The IFR reference flowsheet in last year's report⁴ was based on two key steps: (1) electrorefining for separating fuel cladding and fission product elements and (2) halide slagging for enriching plutonium bred in the blanket to a concentration sufficient (30 to 40 wt% plutonium in uranium) to enrich the driver fuel. An alternative process concept that required only electrorefining to achieve the above two objectives was also presented. This process is based on the use of a solid cathode mandrel for selective removal of uranium and a liquid cadmium cathode for electrodeposition of both uranium and plutonium.

In this past year, the use of a liquid cadmium cathode, shown schematically in Fig. VI-8, was found to be chemically feasible. Conditions can be arranged to deposit, first, fairly pure uranium (>99%) into a liquid cadmium cathode, and then uranium and plutonium together into another cadmium cathode. In the uranium-plutonium deposit, a plutonium-to-uranium ratio higher than about one cannot be achieved. From the standpoint of deterring weapons proliferation, this is advantageous.

Different benefits are associated with removing uranium by use of a solid cathode mandrel or liquid cadmium. For a two cadmium-cathode concept, the pattern of uranium-plutonium transport is shown in Fig. VI-9. The initial transport of a relatively pure uranium fraction requires maintaining the uranium concentration in the anode at or near saturation. In contrast, deposition of uranium on a solid cathode provides a nearly plutonium-free deposit, down to very low uranium concentrations in the anode. In addition, uranium dendrites sheared from a solid cathode along with adhering electrolyte salt require melting of the product to consolidate the uranium dendrites and to permit separation of the overlying electrolyte salt. In the case of a cadmium cathode, the cadmium must first be evaporated, after which the uranium-plutonium residue can be consolidated by melting. The two uranium-deposition options are still being evaluated.

Another important process option is dissolving the fuel in liquid cadmium at 500°C. This can be done by (1) direct dissolution in the cadmium pool or (2) anodic dissolution in which uranium and plutonium in a compact

⁴M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 98 (1987).

Fig. VI-8. Schematic Representation of Electrorefining Operation with Liquid Cadmium Cathode. (N.M. FPs are noble metal fission products.)

Fig. VI-9. Pattern of Transport of Uranium and Plutonium for Two Cadmium-Cathode Concept

basket of chopped fuel pins are transported electrochemically to a liquid cadmium pool. This latter method is the reverse of uranium product deposition on a cathode mandrel; that is, the mass of uranium pins is used as the anode and the liquid cadmium pool temporarily becomes the cathode. Both options have advantages and are discussed further in Sec. VI.C.2.

Regardless of which process option is used, fission products are removed in three process streams: (1) fission product gases, xenon and krypton, which are released during pin-chopping and fuel-dissolution operations; (2) the molten salt electrolyte, in which iodine, bromine, and the highly electropositive fission products such as cesium, strontium, and the rare-earth elements accumulate; and (3) the anode cadmium phase, in which electronegative elements such as ruthenium, molybdenum, and zirconium (a fission product and an alloying element) accumulate. The fuel pin shells will be a part of the metal waste stream. The rare earth elements are the most difficult to separate from the plutonium (a decontamination factor of 5 to 10 is expected) and will probably limit the overall fission product decontamination factor to about 50. Actinide elements such as americium and curium will largely accompany plutonium through the process.

The process is designed to achieve an overall recovery of plutonium of about 99%. The chemical feasibility of the process has been established, and development work is now moving into an engineering-scale demonstration stage.

2. Fuel Dissolution

Two methods of fuel dissolution in an electrorefiner are being investigated: (1) direct dissolution in the cadmium anode of the cell and (2) anodic dissolution in the cell electrolyte.

With the direct dissolution method, a batch of fuel (blanket or core) as chopped fuel-pin segments retained in a basket is dissolved in cadmium at 500°C. The segment length is about 1/4 in. (~0.6 cm). The cladding is not attacked by cadmium, and the pin shells are sent to waste. Experimental studies of fuel dissolution were conducted with single-pin segments. The individual pins were loosely fit into a steel holder that had holes for access by liquid cadmium. The holder was rotated slowly in liquid cadmium. The solution-rate coefficient, expressed as gram-atoms uranium divided by [(minutes)(square centimeters of interfacial area)(grams uranium/grams cadmium)], was calculated from data on weight loss versus time. With blanket-type fuel (U-12 wt% Zr), the solution-rate coefficient was found to be 1.5, which is lower than the value of 2.4 found in earlier work⁵ in which bare uranium pins were dissolved in a vigorously stirred cadmium bath.

Simulation of dissolution of actual clad fuel pins, i.e., at the ends only, was done by fitting pins snugly into the holes of the holder with the exposed end of the pin flush with the surface of the holder. Access to the pin by liquid cadmium was limited to the exposed end of the pin. The rate coefficient

⁵R. D. Pierce and S. A. Miller, in *Chemical Engineering Summary Report, October-November 1962*, Argonne National Laboratory Report ANL-6648, pp. 86-88 (1962).

in this case was about one-quarter of that of the unclad U-12 wt% Zr pin. Based on this information, the time to leach a U-12 wt% Zr alloy from a batch of fuel pins would be acceptable (greater than 15 h, but probably less than 24 h). The final uranium concentration would be 70% of the saturation concentration, but the cadmium would be saturated with zirconium at 0.24% during dissolution. A core fuel alloy (U-19 wt% Pu-10 wt% Zr) is expected to dissolve faster than the U-Zr blanket alloy.

Experiments of anodic dissolution were also done with single pins. In one pin, the average rate of removal of fuel through the open end of the cladding was 0.05 in./h (0.13 cm/h). The overall depth of penetration was 0.57 in. (1.45 cm), at which point all of the fuel had been removed. For 1/4-in. (~0.6-cm) pin segments, this indicates that anodic dissolution of the fuel should be complete within 2.5 h. It is not necessary that an electrical connection be made directly to each segment of fuel. In the anodic process, U^{3+} in the electrolyte may be driven to U^{4+} . When this happens in the vicinity of a metallic uranium surface, the U^{4+} is chemically reduced back to U^{3+} by oxidation of the metallic uranium. Thus, it should be possible to anodically dissolve chopped fuel pins in a basket. Continued investigation of anodic dissolution of fuel materials is planned.

3. Electrorefining Studies

As mentioned earlier, two types of cathodes for the collection of product material, uranium or a uranium-plutonium mixture, are under consideration: a solid metal mandrel (e.g., steel, molybdenum, or zirconium) and liquid cadmium. Electrotransport of uranium onto a solid steel mandrel is straightforward, but plutonium deposition (along with uranium) onto a solid mandrel is difficult. Deposits have been amorphous, fine grained, and non-adherent. Therefore, over the past year, the use of a liquid cadmium cathode for deposition of uranium and plutonium has been investigated.

For demonstrating codeposition of uranium and plutonium, we arranged conditions in a small-scale electrorefiner (principally, the relative amounts of uranium and plutonium) to simulate the plutonium transport portion of the theoretical transport curves shown in Fig. VI-9. To concentrate plutonium and uranium in the cathode as much as possible, it is desirable to deposit uranium and plutonium in the cathode cadmium in excess of their solubilities. Volume-weight properties for cadmium cathodes were estimated and are shown in Fig. VI-10. In core fuel material, the uranium-plutonium ratio is 3.5. If sufficient cadmium is provided in the cathode to give 0.1 weight fraction plutonium in the cadmium, the cathode volume needed per kilogram of heavy metal (uranium plus plutonium) is about 0.3 L; the volume percent of solids in the cathode would be about 34%.

Deposition of uranium into a cadmium cathode after the saturation concentration has been reached is accompanied by a pronounced tendency of deposited uranium to form dendrites, which grow out of the surface of the cadmium. Formation of uranium dendrites must be avoided because they will eventually short circuit the electrorefining cell. Their formation can be prevented by using a stirrer or cutter blade that sweeps the entire cadmium surface.

Fig. VI-10. Calculated Properties for Uranium and Plutonium in Cadmium Cathode

Uranium, which has a density of 19 g/cm^3 , should sink to the bottom of the cadmium cathode. (The density of cadmium is 7.8 g/cm^3 .) The success of this procedure is shown by the 300-g cadmium cathode ingot (Fig. VI-11) into which 87 g of uranium had been deposited.

In contrast, PuCd_6 crystals of plutonium, which have a density of about 9.3 g/cm^3 , tend to remain suspended in the liquid cadmium. As the cadmium surface is swept, the PuCd_6 crystals tend to pile up in front of the blade and be plowed out of the cathode crucible. The stirrer blades were withdrawn from the crucible before lifting the cathode assembly out of the electrolyte. The total uranium and plutonium in the cathode components were 50.7 and 48.7 g, respectively. These values are in agreement with the inventory differences in cell anode and electrolyte before and after electrolysis. This experiment proved that plutonium will codeposit with uranium into a liquid cadmium cathode.

Similar results were obtained in a confirmatory experiment. In this experiment, the plutonium content of the cadmium product phase was 14.5%. Reference to Fig. VI-9 for a uranium-to-plutonium ratio of 0.75 (about what is needed in the product) shows the solids content of the product ingot to be 45%. The large solids content probably results in a slurry too thick to be stirred. Further work is needed to determine the capacity limit of the electrode and the best means of providing agitation. The goal is to obtain a cadmium ingot with a clean interface between the top surface of the metal ingot and the electrolyte.

Fig. VI-11. Photograph of Metal Ingot Formed in Electrorefining Studies

In the IFR process, decontamination of the plutonium product will be controlled by rare earth elements. That is, the only fission product elements expected to accompany plutonium to any extent through the process are the rare earths. The rare earths with high fission yields are cerium and neodymium. Information on the behavior of cerium and neodymium was obtained in two plutonium-transport experiments (designated ENG 20 and 21). Decontamination factors were calculated from Nd/Pu and Ce/Pu ratios in the cathode product and comparison with the same ratios in discharged IFR fuel (given in Table VI-1). The decontamination factors for neodymium were 5.8 and 3.1 for ENG 20 and 21, respectively. The cerium decontamination factor was 5.3 for ENG 21. These are on the low side, but acceptable. Additional information on rare earth behavior must be obtained. If necessary, the process can be modified to give greater assurance of adequate rare earth removal, e.g., a larger fraction of electrolyte could be removed after processing a batch of fuel.

In the two plutonium-transport experiments, the americium-to-plutonium ratio in the cathode product was essentially the same as in the anode prior to electrorefining. This indicates that americium transported with the plutonium. Curium and neptunium are expected to behave similarly, but additional experiments to confirm this and to verify the observed behavior of americium are required. If, as expected, Am, Cm, and Np accompany plutonium through the process, they will be recycled to the reactor in the core fuel, where they will be consumed by fission. Burning most of the actinide elements in the reactor, rather than dealing with them in various waste streams, would be advantageous.

Table VI-1. Decontamination of Plutonium from Neodymium and Cerium in Experiments ENG 20 and 21

Experiment	Ratio	IFR Discharged Fuel	Cathode Product Ingot	Decontamination Factor
ENG 20	Nd/Pu	0.069	0.012	5.8
ENG 21		0.069	0.022	3.1
ENG 20	Ce/Pu	0.045	Not obtained	--
ENG 21		0.045	0.0085	5.3

4. Waste Management

Methods of converting solid wastes generated by processing IFR fuel to disposable forms are being developed. The principal high-level wastes are spent anode baskets containing cladding hulls and cadmium, chloride electrolyte from the electrorefining cell, plenum cladding, and various ceramic materials from fuel-melting operations. Most of the fission products are contained in the anode baskets and chloride salt. The alkali metal, alkaline earth, rare earth, and halide elements are in the salt, and the zirconium and noble metal elements are in the cadmium. Each phase is likely to contain small amounts of actinides.

Although some consideration has been given to alternative waste treatment methods, the main effort has been on the reference process shown in Fig. VI-12. In this process, the actinides and most of the rare earth fission products are extracted from the waste salts into a liquid Cd-Li alloy. By lowering the alpha activity below the 100 nCi/g limit permitted in low-level waste, the salt is converted to a material that may be suitable for disposal in a near-surface repository. However, because Cs, Sr, and I will remain in the salt, the waste form will be greater than Class C. Disposal of such wastes in a near-surface repository will require engineered barriers and licensing by the Nuclear Regulatory Commission. The treated salt is dispersed in a portland cement mortar, which is cast into corrosion-resistant metal containers for disposal.

Cadmium is removed from the anode baskets (assuming fuel is dissolved directly in the cadmium anode) and the alloy used to extract actinides from the salt by retorting. Most of this cadmium is returned to the process, but a portion, equivalent to the CdCl_2 added in the process, must be disposed of. The metallic residues from retorting, the excess cadmium, and the crushed ceramic wastes are mixed with copper metal powder and packed into a copper alloy canister. The mixture is then compacted into a dense copper matrix by hot isostatic pressing. For ultimate disposal, the copper canister is sealed in a corrosion-resistant secondary container and placed in a civilian geologic repository.

A key step in the waste treatment process is the extraction of actinides from the electrolyte to produce a nonTRU waste. We assumed previously that essentially all of the americium in the spent fuels would be in the electrolyte, but recent data from electrorefining experiments have shown that more than 90% of the americium will be returned to the reactor with the plutonium. Measurements of curium distribution between chloride salts and

Fig. VI-12. Schematic for Treatment of Solid Pyroprocess Wastes

Cd-U-Pu alloys strongly suggest that most of the curium will also be recycled to the reactor. These findings greatly reduce estimates of the alpha activity in the electrolyte and, thus, make the extraction of actinides from the salt considerably easier. Measurements are being made of the distributions of U, Pu, Am, and Cm between chloride salts and Cd-Li alloys.

Preliminary studies on the possibility of separating transuranic elements from all IFR process wastes were started. The actinides would be returned to the reactor and consumed. This concept is attractive primarily because the nonTRU wastes produced can be more easily disposed. This concept has been explored many times in the past, but one of the difficult problems has been the separation of rare earth and TRU elements, especially the separation of americium from rare earths. Interest in this concept was renewed by recent data obtained from the electrolyte refining experiments. These data indicate that the actinide elements (Cm, U, and Pu) behave quite differently from rare earth elements (Ce and Nd) in chloride salt/Cd-U metal systems. The rare-earth distribution coefficients were about an order of magnitude larger than the coefficients of transuranic elements over a wide range of uranium distribution coefficients (0.1 to 100). These data suggest that transuranic elements in a chloride salt can be separated from rare earths in the salt by extraction with a Cd-U alloy.

Portland cement-based materials are being investigated for use in containment of waste salt. The treated salt will be mixed with cement, water, and various additives to produce a fluid grout that can be pumped into waste canisters. Only moderate compressive strengths will be required because the cemented waste will be cast into strong metal canisters. The mortar matrix must inhibit leaching of the chloride salts by groundwater, although the metal

containers are the primary barrier against dispersal into the environment. The metal containers are required to remain intact for about 200 years, at which time ^{90}Sr and ^{137}Cs will have decayed below Class C levels.

Experiments are being conducted to identify a mortar formulation that has favorable properties, especially a mix that has a low leach rate of chloride salts. The tests have been made primarily with mixtures containing Type I portland cement, low CaO fly ashes (Class F), and up to 10% of a salt mixture (CaCl_2 -33 wt% NaCl) simulating a quaternary electrolyte used in electrorefining. Salt added to mixtures of 40% cement, 30% fly ash, and 30% water has produced grouts with sufficient fluidity to be pumped and with adequate set times. Calcium chloride reduces set times, but fly ash additions were found to lengthen set times sufficiently to permit the grout to be cast in canisters. Compressive strengths after only three days of curing have been in the range of 21-34 MPa (3000-5000 psi), which is judged to be adequate for this waste form. After 56 days of curing, the strengths generally exceed 68 MPa (10,000 psi).

Leaching tests are being performed on mortar specimens (20-mm dia, ~25-mm long) that have been cured in moist air at room temperature for up to 113 days. The samples are suspended in about 200 mL of deionized water at room temperature in plastic bottles. Periodically, the samples are removed and placed in a new volume of water. The leachates are analyzed for chloride.

The percentage of chloride leached from a sample was found to be proportional to the square root of time up to 20 to 25% removal of the chloride. This finding indicates that the leaching rate is limited by diffusion within the solid sample.

Our preliminary goal is to develop a mortar with a chloride leach rate of less than $5 \times 10^{-6} \text{ cm}^2/\text{h}$. Mortars consisting of 40 to 50% cement, 15 to 30% fly ash, and 30% water with up to 8% salt added have shown leach rates of $2 \times 10^{-5} \text{ cm}^2/\text{h}$ when cured at room temperature for at least 113 days. Similar mortars with salt contents of 3 to 4% had leach rates of about $9 \times 10^{-6} \text{ cm}^2/\text{h}$, but leach rates were about ten times higher for mortars containing 10% or more salt. Mortars with 8% salt and cured for 56 days had leach rates around $5 \times 10^{-5} \text{ cm}^2/\text{h}$.

Future work on immobilization of salt wastes in cement will use the LiCl-KCl mixture that is the reference electrorefining electrolyte. The search for mortar formulations that contain 8 to 10% salt and have low leach rates will continue. Since the waste from IFR processing will be heated by fission product decay to 100-200°C, the effects of curing mortars at these temperatures will be studied. In addition, studies of the effects of ionizing radiation on this waste form will be initiated.

5. Large-Scale Demonstration of Electrorefining

A large-scale electrorefining facility (20 kg of uranium) was constructed to demonstrate the electrolytic transport of uranium at plant-scale levels and also to measure the dissolution rate of clad segments of uranium-zirconium alloy contained in a dissolution device. The initial experiment will consist of

demonstrating that 10 kg of depleted uranium dissolved in a molten cadmium anode can be electrodeposited onto a single steel cathode mandrel. Follow-on experiments will be more prototypic of an actual reprocessing situation, including a U-10 wt% Zr alloy in chopped, clad pin segments as feedstock; a pin segment dissolution device; and a stirred, liquid cadmium cathode. Work with plutonium in the large-scale electrorefining facility is prohibited because the amounts required far exceed the laboratory and building security limits.

After checkout for safety and operational readiness, the electrorefiner is now judged suitable for testing the electrotransport of kilogram quantities of uranium and for measuring the dissolution rates of clad pin segments of a uranium-zirconium alloy. Electrotransport operations were started in December 1987.

D. High-Level Waste/Repository Interactions

In this effort, CMT is investigating the performance of materials under projected repository conditions to provide input to the licensing of the nation's first high-level waste repository. Over the past year work has included (1) the testing of glass and spent fuel in contact with water to measure radionuclide release rates and to establish the mechanism of reaction and (2) the development of ultra-sensitive laser-based techniques to study the speciation of actinides in groundwater.

1. Glass Reaction in Unsaturated Environment

Investigation of the volcanic tuff beds of Yucca Mountain, Nevada, as a potential site for a high-level waste repository is a function of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project. As part of this study, the NNWSI Unsaturated Test has been developed as a method to obtain data on the release of waste components from the waste package in the NNWSI repository environment under conditions currently envisioned after the 300/1000-year containment period has elapsed. Specifically, the test will provide information to be used by the NNWSI project in licensing the NNWSI repository site. The test method will provide (1) data that describe the release of radionuclides from a specifically designed glass/container assemblage under strictly controlled test conditions and (2) information concerning synergistic effects that may occur between waste package components. The test results can be used to determine interactions that are important when glass leaching occurs in an environment of air, water vapor, and liquid water.

a. Experimental

The apparatus used in the Unsaturated Tests is shown schematically in Fig. VI-13. This apparatus provides for collection and containment of liquid and support of the waste package. The waste package assemblage (WPA) consists of the waste form (borosilicate glass doped with radionuclides) and a metallic holder consisting of perforated retainers (one above the waste form, the other below) welded to two pins. A solution feed system injects test water (EJ-13 well water) into the test apparatus. The tests are performed at 90°C.

In discussion of earlier tests,⁶ we speculated that variability in materials interactions was caused by different degrees of sensitization in the weld-affected regions of the waste form holder. Hence, in recent tests, the metallic waste form holder has been presensitized by heating at 550°C for 24 h, then slowly cooling to room temperature.

In the Unsaturated Tests, the WPA is contacted intermittently by small measured amounts (drops) of repository water that has been preequilibrated with tuff rock at 90°C. The nature and degree of radionuclide release from the assemblage are determined by collection and analysis of the water that has contacted the package and by surface analysis of the assemblage components. Materials interactions are noted, and secondary alteration products that influence the nuclide release from the assemblage are identified.

The test schedule involves batch and continuous testing. In the batch mode, tests are terminated at 13-week intervals up to 52 weeks. The test apparatus is disassembled, and analyses of both the solution and components are performed. In the continuous mode, the WPA (including liquid associated with the assemblage) is transferred to a new test vessel at 6.5-week intervals, and the test is continued. Analyses are done on the solution in the old vessel. With continuous testing, replication of solution analysis can be achieved. In addition, investigation of the test components is possible at the termination points, yet the test can continue for an unspecified number of test periods or until information most useful to repository evaluation is obtained. The Unsaturated Test series designated N2 has been in progress for over 65 weeks. It includes eight batch tests and three continuous tests.

b. Analysis of Test Components

Upon examination, the test components were found to be quite similar in appearance, regardless of reaction time. Cut sections from the glass specimens were uniform in appearance and the sides were reflective and smooth. After testing, the top and bottom surfaces were noticeably reacted. Figure VI-14 shows the glass top and associated retainer section. Reaction products had accumulated in the regions where the glass had not been contacted by metal. The majority of the reaction products surrounded the circumference of the holes in the retainer top. This is where standing water was observed to exist in some of the tests upon opening the test apparatus. The reaction products were identified by X-ray diffraction as FeOOH and ferrihydrate ($5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$). Silicate phases rich in either Fe, Cr, Ni, or Mn were also observed but were not as prevalent as the iron oxide phases. Other phases identified on the surface (by X-ray diffraction and scanning electron microscopy/energy dispersive X-ray spectroscopy) included gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), cristobalite, orthoclase (KAlSi_3O_8), and possibly a sodium feldspar ($\text{NaAlSi}_3\text{O}_8$). Many other accumulations of reaction products were identified, often with nonuniform compositions. These groups were amorphous and consisted of Si, Ti, Ca, Mg, Cl, and S in varying amounts.

The regions of glass/metal contact showed little evidence of coverage by reaction products, except in some localized cases where channels appeared to exist between open areas (Fig. VI-14a). The extent of coverage by

⁶M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1985*, Argonne National Laboratory Report ANL-86-14, p. 77 (1986).

Fig. VI-13.

Schematic Diagram of Unsaturated Test Apparatus

the rust-colored reaction products appeared to increase between 13- and 26-week samples, but was fairly constant thereafter. The metal in contact with glass was covered with an amorphous mat rich in aluminum and silicon. Several unique phases were observed on the metal, including a solid solution of the calcite-type structure $\text{Ca}_{.74}(\text{Mn,Mg})_{.26}\text{CO}_3$. Other products were too small ($<50 \mu\text{m}$) to identify by X-ray diffraction.

Although the side surfaces of the glass retained their reflective appearance, they were covered with random watermarks. This appearance suggests that some water flowed over the sides, but that the strong interactions present on the top and bottom surfaces did not occur on the sides. During the sampling and test termination periods, water was observed standing at the interface between the glass bottom and the associated metal retainer. Only in a few samples was water observed on the top section of the waste form holder. It is believed that water collects in this area during the test but evaporates during the cool-down period before the test apparatus is opened. Condensed water is always observed on the inner sides and tops of the apparatus.

The pre-test appearance of the sensitized waste form holder ranged from a uniform deep blue to a mix of blue and gold. After testing, the top and bottom retainers were discolored in the glass contact region, attaining a dark brown to rust-colored appearance. The interface where the glass contact ended was clearly marked by a buildup of precipitates (Fig. VI-14b). However, visual examination indicated that the extent of precipitate coverage did not increase during the 52-week testing period. This observation agrees with the measured weight gains of the top and bottom retainers, which are constant throughout the 52-week test period.

After surface analyses, the metal retainers were acid stripped to remove actinides, cross sectioned, epoxy mounted, polished, and subjected to an oxalic acid etch to determine the extent of sensitization that had been imparted

(a)

(b)

Fig. VI-14. Micrograph of (a) Top Section of Glass Showing Circular Regions of Iron Oxide and Hydroxide Formation (19 X) and (b) Associated Retainer Section (120 X)

during the heat treatment. Two distinct levels of sensitization were imparted to the metal samples. In all the metal samples studied, carbide precipitation at the grain boundaries was evident in the sample interior. However, in the 13- and 26-week tests, the sensitization proceeded to within 10 μm of the surface of the steel, while in the 39- and 52-week tests the sensitization was within 40 μm of the surface.

c. Analysis of Test Solution

At the end of a test in the batch mode, the WPA was rinsed with high purity water, and the solution was analyzed. All elements except silicon showed a net release from the glass. Silicon showed a net release in two 26-week batch tests and one 39-week batch test, but was abstracted from solution in the remaining tests. Normalized release values $[(\text{NL})_i]$, in units of grams per square meter were calculated to compare the release behavior of different elements. Figure VI-15 gives $(\text{NL})_i$ values for Li, Na, and B. The results indicate an apparent trend of increasing reaction for the 13- to 26-week tests. However, in the 39- and 52-week tests, the release values for lithium and sodium are similar to the 26-week values, while the glass reaction as measured by boron release and weight loss is actually less than for the 26-week results. Table VI-2 gives the normalized release values for the actinide elements in the analyzed solution ("Solution Only" columns). These values, as well as those for boron, are lower than the normalized release values for lithium and sodium.

Fig. VI-15.

Normalized Release of Lithium (triangles), Sodium (squares), and Boron (circles) and Glass Weight Loss (diamonds) for the N2 Batch Tests

These $(\text{NL})_i$ values were calculated based on the total surface area of the glass and on the measured amount of each element released from the WPA after rinsing. However, if the amount of Pu, Am, and U remaining with the metal components of the WPA is measured after complete stripping of the metal and it is assumed that the release of these elements is associated mainly with the end sections of glass that contacts metal, then higher $(\text{NL})_i$ values are calculated (Table VI-2).

Table VI-2. Normalized Release of Actinides from Unsaturated Test

Test Period, weeks	Solution Only ^a				Solution + Acid Strip ^a	
	(NL) _{Np}	(NL) _{Pu}	(NL) _{Am}	(NL) _U	(NL) _{Pu}	(NL) _{Am}
13	0.2	0.008	0.008	0.01		
13	0.4	0.015	0.018	0.06	0.3	0.4
26	1.3	0.024	0.022	0.21		
26	2.0	0.028	0.028	0.19	0.7	1.1
39	1.3	0.024	0.020	0.42		
39	0.4	0.008	0.008	0.04	0.5	0.7
52	0.6	0.014	0.012	0.18		
52	0.8	0.026	0.015	0.12	0.6	0.7

^aThe entire surface area of the glass was used to calculate (NL)_i for the solution-only results, while only the surface area of the end sections of the glass was used in the solution + acid strip calculations.

In the continuous tests, the components are not rinsed before the solution in the test apparatus is analyzed. For these tests, several elements, including Ca, Mg, Na, and Si, were depleted in the analyzed solution compared with the starting EJ-13 water. Normalized release values for lithium in three continuous tests are plotted in Fig. VI-16. While these values will be slightly lower than those for the batch tests owing to the lack of a rinse, it can be seen that lithium is continuously being released from the glass through the 65-week test period.

Fig. VI-16.

Normalized Release of Lithium for Three Continuous Tests in the N2 Series

d. Discussion

The data collected from this series of tests and earlier Unsaturated Tests suggest that sensitized metal interacts strongly with glass in the presence of small volumes of repository water. This strong interaction results in matrix breakdown of the glass, thereby increasing elemental release up to ten

times the amount observed without the interaction. However, the matrix breakdown does not necessarily result in equal release to solution of all the actinide elements. Neptunium is released to solution without interacting significantly with either reaction products or metal components. However, uranium interacts moderately with the reaction products and forms unique stable phases, which decrease its release to solution. The release of plutonium and americium to solution is reduced even further because these elements strongly interact with reaction products and metal components in the WPA.

The Unsaturated Tests are still in progress and will be continued to gain additional information regarding glass/metal/water interactions under unsaturated conditions. Also under investigation is the effect of radiation-induced reactions on the environment of a basalt repository.

2. Actinide Speciation Studies Using Laser-Based Techniques

The current strategy for disposal of high-level nuclear waste involves immobilizing radionuclides in glass, enclosing the glass in a metal canister, and burying the canister in deep cavities below the land surface. The major concern of such procedures is the possible dissolution of the radionuclides from the waste package and their eventual introduction into the ecosystem. Models based on experimentally determined thermochemical properties of actinides, such as solubility and sorption coefficients, are being used to make predictions of repository performance. These predictions, however, are only as good as the data that have been generated regarding actinide geochemistry.

Aqueous geochemistry of transuranic elements is a particularly challenging area of research because of the large number of chemical equilibria involved. In near-neutral environments, actinides readily hydrolyze and form hydroxides whose solubilities limit concentrations to submicromolar levels. The complexation of ligands such as carbonate, chloride, fluoride, and sulfate and the formation of colloids compete for the variety of metal ions present in order to increase their solubility. These reactions, in turn, depend upon the oxidation state of the transuranic ion, which is a property of the redox properties of the environment. In addition, equilibria are temperature dependent, and this factor must be taken into consideration since the repository is anticipated to exceed 150°C during the isolation period.

Optical absorption methods offer a convenient means by which to characterize actinide complexes in solution because of the "fingerprint" character of their absorption spectra. Unfortunately, the transitions are unusually weak, augmenting the already existing difficulty associated with detecting trace levels of the species. Conventional absorption spectrometers, which rely on pronounced differences in light absorption, lack the sensitivity required to reach anticipated solubility concentrations. While extrapolations from concentrated solutions are useful, they are compromising at best, since many actinides are likely to form polynuclear species at concentrations amenable to conventional absorption spectrometers. It is evident that accurate assessment of the repository will require the detection of concentrations comparable to those present.

Recently, we have applied the ultra-sensitive detection method known as laser photoacoustic spectroscopy (LPAS) to the speciation of actinides in

simplified groundwater solutions at temperatures up to 90°C. The technique relies on the detection of acoustic signals generated by thermally induced pressure variations in a medium due to radiationless relaxation mechanisms from an optically prepared state of the ion. The photophysical response is an acoustic wave; thus the detector is a highly sensitive microphone. Neglecting saturation effects, the acoustic signal, S , is given by

$$S = C N_i \sigma_{ik} \Delta x P_L \beta \nu_a S_m (1 - n_k) / C_p$$

Here, S is related to the density of absorbing species, N_i , undergoing the transition from a lower level to an excited level; the absorption cross section, σ_{ik} ; the path length, Δx ; the velocity of the acoustic wave, ν_a ; the heat capacity, C_p ; the thermal expansivity, β , of the medium; the laser power, P_L ; the sensitivity of the microphone, S_m ; and parameters associated with the cell design, C . Since the signal results from radiationless relaxation, it decreases with increasing quantum efficiency, n_k ; thus LPAS complements fluorescence detection, an alternative method which we are also pursuing.

To accommodate radioactive samples and to house the LPAS system, a laser facility was constructed within a shielded area in CMT. This facility has an excimer pumped dye laser capable of producing energies in excess of 25 mJ from 300 nm to 1 μ m. The output of the laser is used to excite aqueous actinide samples enclosed in thermostated sample compartments of a differential (blank vs. sample) photoacoustic spectrometer. This arrangement increases the dynamic range of the measurement by subtracting out the absorption caused by the solvent (i.e., water). Signals generated following the absorption are detected at right angles by a piezoelectric transducer that is in acoustic contact with the sample cells but thermally isolated from them by a quartz rod. Differentially amplified signals are averaged using a boxcar averager and normalized to the laser intensity. Scanning of the wavelength of the dye laser thus produces a normalized LPAS absorption spectrum of the analyte.

Laser photoacoustic spectra were recorded for a number of Am, Pu, and Np samples in order to establish the sensitivity of the apparatus. Initial studies were performed with carbonate solutions because of carbonate ubiquity in natural waters. Dilution curves were found to be linear to absorbances of $\sim 5 \times 10^{-7}$ per centimeter of solution. This translates to a detection limit (signal-to-noise ratio = 1) of $\sim 10^{-9}$ M and 10^{-8} M for the Am^{3+} and Pu^{4+} carbonate complexes, respectively. The spectra exhibited considerable redshifts from the uncomplexed ion spectra, thus demonstrating the speciation capabilities of the instrument. Measurements at up to 90°C verified the theoretical predictions of signal enhancement with increased temperature, thus establishing the applicability of LPAS to repository relevant conditions. When the solutions were neutralized, the spectra exhibited broad, featureless bands indicative of colloid generation.

The most useful data that can be obtained from sensitive measurements of actinide absorption spectra will undoubtedly be that which generates accurate solubility and stability constants for the various species present. For Am^{3+} in groundwater, mixed complexes and colloids of hydroxide, carbonate, and humic or fulvic acids are expected to predominate. Unlike americium, which remains trivalent under the pH and Eh conditions of natural waters, plutonium can be in

different oxidation states owing to redox and disproportionation reactions. Thus, for plutonium, additional information is needed for the various oxidation states that may coexist. The paucity of literature data suggests that systematic spectroscopic determinations of simplified actinide groundwater solutions are necessary to establish extinction coefficients for the various species present. From this library of data, deconvolution of spectra taken of groundwater samples containing several actinide elements will be possible.

Future developments in this area include applications of the complementary technique, laser induced fluorescence. Compilation of reference optical spectra using these methods will ultimately be used to facilitate the accurate and complete speciation of transuranic ions in groundwaters typical of those encountered in the near-field environment of proposed nuclear waste repositories.

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. *Fission Product Chemistry*

The objective of this effort is to understand 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 transport, condensation, revaporization, and deposition of fission products in the primary reactor system, (2) the release of fission products during the interaction of molten fuel with the concrete basemat, and (3) the reactions between fission product compounds under the conditions expected in the primary system.

1. Downstream Behavior of Volatile Fission Products

During a loss-of-coolant accident, the temperature of the fuel will rise above its normal operating temperature and lead to a rupture of the cladding and the release of fission products. We are investigating the interaction between these fission products in a flowing steam/hydrogen mixture. The objective of these studies is to characterize the chemical and physical processes that determine the downstream behavior of the mixture of fission products and steam.

In earlier laboratory experiments, we injected CsOH, CsI, Te, or mixtures of these substances into a flowing superheated steam/hydrogen stream at 1273 K (1000°C). This mixture flowed down a reaction duct (9.4-cm ID, 3.6-m long) on which a temperature gradient [from 1273 K (1000°C) to 473 K (200°C)] had been imposed. The reaction duct was lined with twelve removable liners. The amount of the injected substance deposited on each liner was determined by chemical analyses. Results from these experiments were given in last year's report.¹

Analysis of the experimental data has shown that the downstream behavior can only be understood when the chemical interactions between the different fission products are taken into account. The downstream behavior of iodine is dependent upon its reaction with cesium and steam, and the behavior of tellurium is dependent on its reaction with cesium. The modeling of the behavior of iodine, cesium, or tellurium without taking into account their chemical interactions with each other will lead to gross errors in the predicted source terms.

Concerns have been expressed regarding the stability of cesium iodide with respect to reaction with stainless steel. Analysis of the results from our first two experiments, in which CsI alone was injected into the reaction duct, yielded some information on this question. In these experiments, the duct liners were leached with hot water, and the iodine and cesium content of the leachants was determined. The weight ratio of iodine to cesium for the second experiment is shown in Fig. VII-1. Two of the samples had ratios that significantly deviated

¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 112 (1987).

Fig. VII-1.

Weight Ratio of Iodine to Cesium
in CsI Deposition Experiments

from the theoretical value for CsI (dashed line in figure). The low value of the ratio for liner 8 and the high value for the condenser are consistent with a small amount of decomposition of CsI in the high-temperature regions of the duct. The amount of cesium over that required for CsI in the deposits in the duct and the tail pipe indicated that about 0.3% of the CsI could have decomposed. The extra iodine in the condensate indicated that 0.08% of the CsI decomposed. These estimates must be viewed with caution since the liners were only leached with hot water; cesium strongly bound to the corrosion layer may not have been recovered. Since CsI is a relatively stable compound compared to the cesium compounds that may be formed with stainless steel, its interaction with stainless steel is not expected to be extensive. The small amount of decomposition observed may be due to the gas-phase hydrolysis of CsI,

and the reaction of the gaseous CsOH produced with the oxide corrosion layer. Our experiments in which CsOH alone was injected showed a small amount of reaction of gaseous CsOH with stainless steel in the high-temperature regions of the duct. From the calculated equilibrium constant for Eq. 1 and the amount of reaction observed in our CsOH experiments, we estimated that about 0.08% of the CsI could react with the stainless steel by the suggested mechanism.

The deposition of tellurium was found to be significantly affected by CsOH. The difference in the deposition with and without CsOH present is shown in Fig. VII-2. Approximately 50% of the tellurium injected was deposited in the duct when CsOH was absent, while only about 15% was deposited when CsOH was present. These differences are due to a change in the deposition mechanism.

When CsOH is absent, the gaseous tellurium species are Te_2 , TeO_2 , and H_2TeO_3 , with the composition depending on the oxidation potential. The

Fig. VII-2. Observed Tellurium Deposition for Gas Mixture with and without CsOH

computed deposition pattern, based on the vapor condensation of these species, is not in agreement with the deposition observed in the high-temperature region of the duct. This result is not unexpected since gaseous tellurium reacts with stainless steel at high temperatures to form a telluride (Fe_2Te_2). The rate of this reaction is only limited by the mass transfer rate of tellurium to the stainless steel surface. When it is assumed that reaction of Te_2 with stainless steel occurs, then the computed and observed deposition patterns are in better agreement, as shown in Fig. VII-3.

When CsOH is present, the amount of tellurium deposited is greatly reduced, not only in the high-temperature region in which gaseous reaction with the stainless steel dominated, but also in the lower temperature region in which

Fig. VII-3. Observed Tellurium Deposition and That Calculated Assuming Reaction of Te_2 with Stainless Steel

vapor condensation occurred. The presence of CsOH markedly reduced the amount of gaseous Te_2 in the system. The formation of cesium tellurite (Cs_2TeO_3) could be responsible. To test this hypothesis, the vapor pressure of Cs_2TeO_3 was calculated from estimated values of the thermodynamic properties of gaseous Cs_2TeO_3 . The deposition pattern was computed assuming that all of the tellurium injected formed the gaseous tellurite and that only vapor condensation and aerosol deposition occurred. The results of these computations are shown along with the observed pattern in Fig. VII-4. It can be seen that a significant fraction of the high-temperature deposition may be explained by vapor condensation of Cs_2TeO_3 . The reaction forming Cs_2TeO_3 probably does not go to completion, and a small quantity of unreacted Te_2 remains in the gas stream. This would help account for the differences between the computed and observed patterns.

Fig. VII-4. Observed Tellurium Deposition and That Calculated Assuming Formation of Cs_2TeO_3

The results of these studies of tellurium deposition are a good example of the complex chemical interactions that must be considered if accurate predictions of the downstream behavior of volatile fission products are to be made. During the coming year, the analysis of the remaining experimental data will be completed and a final report prepared.

2. Fission Product Release from Core-Concrete Melts

The objective of this study is prediction of the release of refractory fission products--strontium, barium and the rare earths--from the molten core-concrete mixtures that would form if a molten core penetrated the bottom of a reactor vessel in a severe accident. The vaporization of the core-concrete mixtures is being measured using a transpiration method. The materials tested are stainless steel, concrete (limestone or basaltic), and urania doped with 1 mol% La_2O_3 and SrO , 0.4 mol% BaO , and 2 mol% ZrO_2 . These materials (alone or mixtures of all three) are vaporized at 2150-2400 K from a zirconia crucible into He-6% H_2 gas flowing at a rate of 100 cm^3/min or 200 cm^3/min over the sample surface. Up to 600 ppm H_2O is added to the gas in order to fix the partial

molar free energy of oxygen in the range -420 to -550 kJ. The fraction of the sample that is vaporized is determined by weight change and by chemical analyses (inductively coupled plasma/atomic emission spectroscopy and fluorescence spectroscopy) of the condensates, which are collected in a molybdenum condenser tube.

The data obtained from the experimental runs are being compared with calculations made with the SOLGASMIX computer code.² This computer code is used to calculate equilibrium conditions for 17 elements in the gas, the liquid, and the solid phases of the core-concrete melts. The number of gas-phase species (elements, oxides, hydroxides) included in the calculations is 100. There are also 74 solid or liquid species included in metallic and oxide phases. The thermodynamic data are obtained from the literature. Computer codes similar to SOLGASMIX are being used for prediction of refractory fission-product release from core-concrete mixtures in a severe reactor accident. Comparison of the experimental results and the calculations provides a test of the thermodynamic data base and the underlying assumptions of the computer codes.

In the runs with a mixture of stainless steel, limestone concrete, and doped urania, the amount of material transported was 98 mg at 100 cm³/min and 129 mg at 200 cm³/min. The closeness of these two amounts suggests that gas saturation had been achieved. Analytical chemistry data from the two runs (Table VII-1) indicated that the major limestone-concrete components (Mg and Ca) had achieved saturation. However, the major steel components (Fe, Cr, and Ni) showed transport factors of three to ten lower than in runs with steel alone; gas saturation by the steel components was achieved in runs with steel alone.

To search for the cause of the low transport rate for the steel components, we cross-sectioned the zirconia crucible from the run at 100 cm³/min.

Table VII-1. Calculated and Measured Transport by He-6% H₂-0.006% H₂O Gas (15.2 L) in Runs at 2150 K with Stainless Steel, Limestone Concrete, and Doped Urania

	Amount Added, mg	Calculated Transport, mg	Measured Transport, mg	
			200 cm ³ /min	100 cm ³ /min
La	33	0.013	<0.002	<0.005
Ba	6	0.006	0.018	0.028
Sr	12	0.003	0.006	0.012
U	2648	0.062	0.047	0.028
Fe	2470	44.0	1.26	1.52
Cr	628	32.0	1.64	1.36
Ni	277	3.0	0.08	0.04
Mn	50	30.0	15.4	9.7
Zr	2056	0.0	0.009	<0.005
Ca	974	0.29	0.2	0.22
Mg	143	17.0	40.0	39.0
Si	118	1.1	2.9	—
Al	32	31.0	0.0	0.2
Mo ^a	—	—	314.0	371.0

^aThe molybdenum is from the condenser tube.

²G. Erickson, Chem. Scr. 8, 100 (1975).

The solidified mass of concrete, urania, and steel occupied the bottom third of the crucible and had evidently been liquid during the run. The concrete-urania phase, which had wet the zirconia crucible, had a pronounced meniscus. In addition, the thickness of the zirconia-crucible wall had been reduced by roughly 40% in the wetted area (the bottom third of the crucible). The steel phase was approximately spherical and was embedded within the solidified concrete-urania mixture. Evidently, the steel could not equilibrate with the gas phase in this geometry. We plan to eliminate the steel phase from future runs since we cannot obtain good measurements with two-phase mixtures of this type. With the steel omitted, a tungsten or molybdenum crucible can be used and the problem of zirconia dissolution can also be circumvented.

The "amount added" column in Table VII-1 includes our estimate of zirconia dissolution from the beaker. This amount is a factor of 100 higher than was added as a dopant to the urania. According to our SOLGASMIX calculations, the zirconia suppresses vaporization of the alkaline earth oxides by forming zirconates. With the zirconia addition, reasonable agreement was obtained between the calculations and the measurements for transport of Ba, Sr, Ca, and Mg (see Table VII-1). We were less successful in modeling the very low vaporization of lanthanum. It is likely that zirconia is suppressing the lanthanum vaporization by forming the compound $\text{La}_2\text{Zr}_2\text{O}_7$ (mp, 2573 K). However, thermodynamic data are not available for this compound, so we are not yet able to include its effects in the SOLGASMIX code.

The transpiration experiments appear to be capable of yielding useful data with which to check the computer codes now being used to predict release during a severe accident. However, the experiments are difficult to interpret due to complex chemical and physical effects. The results obtained to date have indicated a need for inclusion of more complex species, such as the alkaline earth zirconates, in the calculations. With additional work, we hope to be able to derive activity coefficients for the elements of interest (Ba, Sr, and the rare earths).

3. Fission Product Behavior in Reactor Accidents

In an earlier CMT experimental program, CsI and CsOH vapors were studied separately and together in flowing steam under a temperature gradient (from 1273 to 500 K).³ In the current experimental effort, we investigated the iodide-hydroxide (CsI-CsOH) vapor species over a liquid solution of CsI and CsOH.

A quadrupole mass spectrometer was used to determine the partial pressures of vapor species over liquid CsOH (622-772 K), liquid CsI (917-1035 K), and liquid solutions of the two salts (809 to 927 K) held in a silver Knudsen cell. The ions formed by ionization of gas over CsOH are Cs^+ , believed to be a fragment of the CsOH(g) monomer; the parent ion CsOH^+ ; and Cs_2OH^+ , a fragment of $\text{Cs}_2(\text{OH})_2(\text{g})$. The CsOH(g) and $\text{Cs}_2(\text{OH})_2(\text{g})$ pressures were calculated from the CsOH^+ and Cs_2OH^+ ion peaks in the mass spectra. In the mass spectrometric study of cesium iodide vapor, the ion intensities for Cs^+ , CsI^+ , and

³M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1985*, Argonne National Laboratory Report ANL-86-14, p. 91 (1986).

Cs_2I^+ were measured. The Cs^+ ion is a fragment of the CsI(g) monomer, CsI^+ is the parent ion, and Cs_2I^+ is a fragment of $\text{Cs}_2\text{I}_2(\text{g})$. The CsI^+ and Cs_2I^+ ion intensities were then used to calculate CsI(g) and $\text{Cs}_2\text{I}_2(\text{g})$ pressures. In these measurements, the ion intensities of the four gases [i.e., CsI(g) , $\text{Cs}_2\text{I}_2(\text{g})$, CsOH(g) , and $\text{Cs}_2(\text{OH})_2(\text{g})$] were measured continuously with time and temperature.

To convert ion intensities (I) to pressures (P), we used the formula,

$$P = K I T \quad (2)$$

where K is a constant, and T is the temperature of the vaporized material in degrees Kelvin. For the conditions of our experiments, the values of the constants were approximately $K_{\text{CsOH}} = 10^8 \text{ atm A}^{-1}\text{K}^{-1}$ and $K_{\text{CsI}} = 10^9 \text{ atm A}^{-1}\text{K}^{-1}$. These values indicate that the ionization cross section of CsOH(g) is about ten times higher than the cross section of CsI(g) .

Equation 2 was used to calculate pressures of CsOH , $\text{Cs}_2(\text{OH})_2$, CsI , and Cs_2I_2 gas over liquid CsOH and CsI . The calculated values are plotted as a function of temperature in Fig. VII-5. Third-law calculations for the heat of vaporization ($\Delta H_{\text{vap}} 298$) yielded $152.00 \pm 1.874 \text{ kJ/mol}$ for CsOH(g) , $155.64 \pm 0.519 \text{ kJ/mol}$ for $\text{Cs}_2(\text{OH})_2(\text{g})$, $188.44 \pm 1.318 \text{ kJ/mol}$ for CsI(g) , and $234.01 \pm 2.171 \text{ kJ/mol}$ for $\text{Cs}_2\text{I}_2(\text{g})$, where the uncertainty is one standard deviation. Our CsOH partial pressures are substantially lower than those calculated with JANAF data, but are in general agreement with the transpiration results of Cummings et al.⁴ Our cesium iodide pressures are in good agreement with literature data.

Fig. VII-5.

Partial Pressures of Cesium Hydroxide and Iodide Gases as Function of Temperature

⁴J. C. Cummings, R. M. Elrick, and R. A. Sallach, *Status Report on the Fission-Product Research Program*, Sandia National Laboratories Report NUREG/CR-1820, SAND80-2662 R3 (1982).

In the mass spectrometry measurements, we attempted to detect $\text{CsI}\cdot\text{CsOH}^+$ (at mass 410) without success. Since the alkali halide polymers lose a halide atom and alkali hydroxide polymers lose OH during ionization to produce fragments of the parent molecules, $\text{CsI}\cdot\text{CsOH}(\text{g})$ should lose either I or OH during ionization. The problem here is that the two possible fragments are indistinguishable from those of $\text{Cs}_2\text{I}_2(\text{g})$ and $\text{Cs}_2(\text{OH})_2(\text{g})$.

By taking advantage of the relation between the CsOH or CsI concentration in liquid solution and its partial pressure and the relation between the monomer and dimer pressures, one can establish conditions where the concentration of the fragment of the $\text{CsI}\cdot\text{CsOH}$ complex is larger than either fragments of the Cs_2I_2 or $\text{Cs}_2(\text{OH})_2$. By making measurements with solutions poor in CsOH or poor in CsI, we can lower the activity and partial pressure of CsOH or CsI, respectively. Since the dimer pressures are proportional to the square of the monomer pressures, the partial pressures of the dimers for the low-activity species will be substantially reduced, while those for the complex will be reduced much less. From our previous measurements of the pressures for $\text{CsI}(\text{g})$ and $\text{Cs}_2\text{I}_2(\text{g})$ over liquid CsI and of $\text{CsOH}(\text{g})$ and $\text{Cs}_2(\text{OH})_2(\text{g})$ over liquid CsOH, we calculated the relation between the two gases for dimerization.

Measurements of the Cs_2I^+ ion over CsI-CsOH solutions with low CsI concentrations produced intensities expected for fragments of $\text{Cs}_2\text{I}_2(\text{g})$, eliminating Cs_2I^+ from consideration as a fragment of $\text{CsI}\cdot\text{CsOH}$. Calculations using spectroscopic measurements of CsI-CsOH solutions with an initial mole fraction of 0.135 CsOH showed that the fragmentation of the $\text{CsI}\cdot\text{CsOH}$ produces Cs_2OH^+ rather than Cs_2I^+ . For a composition range between 0.122 and 0.053 mol fraction CsOH, the ion intensity of the Cs_2OH^+ varied from 18- to 378-fold higher than calculations suggested this value would be if it were only a fragment of $\text{Cs}_2(\text{OH})_2(\text{g})$. This established Cs_2OH^+ as the fragment of $\text{CsI}\cdot\text{CsOH}(\text{g})$.

The partial pressure of the $\text{CsI}\cdot\text{CsOH}$ complex is calculated from the total ion fragment intensity minus that computed from the calculated pressure of $\text{Cs}_2(\text{OH})_2(\text{g})$. The ion fragment intensity attributed to $\text{CsI}\cdot\text{CsOH}$ is converted to pressure with the constant in Eq. 2 and the relative ionization cross sections. The ionization cross section for the complex is assumed to be the sum of the cross sections for $\text{CsI}(\text{g})$ and $\text{CsOH}(\text{g})$. From our data, the equilibrium constant (K_{eq}) for the reaction of $\text{CsI}(\text{g})$ and $\text{CsOH}(\text{g})$ to form $\text{CsI}\cdot\text{CsOH}(\text{g})$ was determined to be

$$K_{\text{eq}} = \exp(19240/T - 15.79) \quad (3)$$

This equation was derived with estimated entropies for the complex as a function of temperature.

It is known that fission product cesium is more than an order of magnitude more abundant than fission product iodine. The principal forms of these two fission products are CsI for iodine and CsOH for cesium. These two molecules are expected to condense on reactor system surfaces after release from the fuel pins and form a solution that will be heated by radioactive decay. Our results indicate that revolatilization from a solution consisting of 0.1 CsI-0.9 CsOH would produce nearly equal partial pressures of $\text{CsI}(\text{g})$ and $\text{CsI}\cdot\text{CsOH}(\text{g})$. Our

research has also provided some evidence for the existence of the $\text{CsI}\cdot\text{CsOH}$ complex molecule. The existence of this complex molecule can lead to a doubling of the iodine released from the reactor containment.

B. Metal Fuels Properties

Development of the Integral Fast Reactor (see Sec. VI.C) requires understanding of fuel behavior for wide temperature and composition ranges. Much of the needed information is not available, and our ongoing program is designed to provide the essential thermophysical and chemical property data. These efforts are coordinated with R&D efforts on fuel performance, design, and safety to be certain that fuels properties of primary concern are examined. Our effort involves experimental and analytical work. In the experimental work, we are measuring the thermal expansion, thermal conductivity, and phase transition temperatures of alloys of interest. Chemical reaction studies are also being performed to gain an understanding of fuel-cladding interaction. In the analytical work, phase diagram calculations are performed to reduce uncertainties in solidus-liquidus temperatures, provide self-consistent phase diagrams, improve understanding of fuel-cladding compatibility, and help explain fuel segregation. Thermodynamic calculations of chemical equilibrium are also performed in connection with the chemical reaction studies of fuel-cladding interaction. In the following report, we present progress on thermal expansion measurements, thermal conductivity measurements, and phase diagram calculations.

1. Thermal Expansion

Thermal expansion measurements are being performed for selected alloys of interest to the IFR project. A push-rod dilatometer was installed in a helium-atmosphere glove box for this work. Calibrations were performed using a tungsten thermal expansion standard from the National Bureau of Standards (NBS). In addition, independent temperature calibrations were performed at the melting points of high-purity gold and aluminum. Thermal expansion data are typically obtained at heating and cooling rates of 1 K/min for many heating/cooling cycles over the temperature range of interest. To date, measurements have been made on four fuel alloys (U-8.4 wt% Zr, U-20 wt% Pu-1.3 wt% Zr, U-19 wt% Pu-10 wt% Zr, and U-26 wt% Pu-10 wt% Zr) and two cladding alloys (D9 and HT9).

Thermal expansion measurements on U-20 wt% Pu-1.3 wt% Zr alloys indicated that, at low temperatures (~ 800 K), the values obtained on heating differed significantly from those obtained on cooling. Differential thermal analysis (DTA) studies were performed to clarify this effect. The DTA curve obtained on heating showed a slight indication of a transition at about 840 K, which corresponded to a change in slope in the thermal expansion curve. On cooling, that transition was not detected in the DTA curve. However, a small peak in the cooling curve indicated a transition at about 620 K coinciding with the beginning of an upturn in the thermal expansion data. The phase transition involved is probably $\xi + \alpha \rightarrow \xi + \beta$, which occurs at 833 K. This delayed phase transition is responsible for the difference between the heating and cooling curves for thermal expansion. Because the inlet coolant temperature for the IFR is above 620 K, fuel will not transform on cooling during reactor operation.

In subsequent thermal expansion measurements, the ternary sample was heated to 1150 K and then cycled between about 1150 and 650 K. That is,

after the initial heating, the sample was maintained above the 620 K transition. After the initial heating, the cooling and heating thermal expansion curves were similar. When the sample was finally cooled to room temperature at the conclusion of the experiment, the 620 K transformation occurred. It is clear that, when the fuel is maintained above about 620 K, the heating and cooling expansion curves are the same. Only if the fuel is cooled below about 620 K will the transformation occur.

The thermal expansion of the cladding alloy HT9 (a ferritic-type steel) was measured up to about 1200 K. Six heating/cooling cycles were performed at a rate of 1 K/min. The first three were performed from room temperature to about 925 K and the second three from room temperature to 1200 K. This was done because of an anticipated phase transformation in this alloy above 925 K. The linear thermal expansion data from the measurements to 925 K showed good agreement between heating and cooling cycles and agreed well with the values found on heating for the cycling to 1200 K. The data clearly indicated a phase transition (probably $\alpha \rightarrow \gamma$) in this alloy at about 1075 K. Moreover, the alloy did not transform on cooling until a very much lower temperature, even at 1 K/min. The cladding alloy D9 (an austenitic-type steel) does not show such a transition. This transformation may be the cause of mechanical differences between D9 and HT9 with respect to fuel compatibility at 1073 and 1153 K.

2. Thermal Conductivity

We determined the thermal conductivity of U-8.4 wt% Zr, D9, and HT9. The technique used in the conductivity measurements is based on a comparative method. A cylindrical alloy sample is positioned in a vertical column between two reference alloys having known thermal conductivity. Longitudinal heat flow through the column is established by heaters placed above and below the column. Radial heat losses are minimized by surrounding the column with a guard furnace in which the thermal gradient is matched to that of the column and by filling the annular space with foamed-yttria granules. Of particular interest were the conductivity results for HT9, which showed the effects of the phase transition mentioned above. Considerable difficulty was experienced in obtaining reproducible values for HT9 because the phase transition is slow. While the variation in thermal conductivity is fairly small over the temperature range studied, the phase transition clearly influences the thermal conductivity.

3. Phase Behavior

Both experimental and calculational efforts are focused on clarification of the phase behavior of IFR fuel alloys. Initial emphasis has been on determination of solidus and liquidus temperatures, but increasing attention is now being devoted to clarification of the solid-state transitions in the U-Pu-Zr system. The solid-state transitions have important implications for zirconium redistribution on fuel and for fuel-cladding interactions. As previously reported,⁵ the U-Pu-Zr alloys reacted with beryllia crucibles, and all subsequent work has been performed using yttria crucibles.

We present here some of the experimental work carried out on one alloy, namely, U-26 wt% Pu-10 wt% Zr. We have completed numerous

⁵M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 123 (1987).

heating/cooling cycles with this alloy at rates ranging from 0.5 to 12.5 K/min. At low rates (0.5 to 2 K/min), good resolution of the solid-state transitions was obtained, but the solidus and liquidus transitions could not be distinguished. At high rates (10 to 12.5 K/min), the solidus and liquidus were readily observed, but the solid-state transitions were not well resolved. At intermediate rates, all transitions could be seen. The melting transitions were obtained at heating/cooling rates of 5 to 12.5 K/min. Generally, solidus temperatures are more reliably determined on heating, and liquidus temperatures more reliably determined on cooling. At low rates, these temperatures are not readily obtainable from the DTA traces because of the broadness of the peaks. For the solid-state transitions, however, two very sharp peaks (designated transitions 1 and 2) are observed. The lower temperature transition, trans. 1, appears at the same temperature (843 K) for heating/cooling rates from 0.5 to 12.5 K/min. For the higher temperature transition, trans. 2, significantly lower transition temperatures are found on cooling than on heating at rates greater than about 1 K/min. The mean transition temperature for trans. 2 at 0.5 and 1 K/min is 915 K. Comparison of the transitions with the ternary diagram led to tentative assignment of trans. 2 with the reaction $\gamma + \beta \rightarrow \alpha + \xi$, reported by O'Boyle and Dwight at 923 K.⁶ Transition 1 is probably $\gamma + \alpha \rightarrow \delta + \xi$, reported by O'Boyle and Dwight at 868 K. Another possible reaction is $\gamma + \xi \rightarrow \delta + \eta$, reported by O'Boyle and Dwight at about 823 K.

In a calculational effort in collaboration with researchers from the University of Montreal,⁷ we are developing a computer model for the solidus and liquidus surfaces of the phase diagram for the U-Pu-Zr system. In addition, we have begun developing a model to describe the solid-state transitions in that system. This work involves a computer-coupled thermodynamic/phase diagram analysis by a methodology that has been well documented. When applied to the computation of an unknown ternary phase diagram, this methodology begins with the critical evaluation and analysis of all relevant phase diagram and thermodynamic data for the three binary subsystems with a view of obtaining mathematical expressions for the thermodynamic properties of all binary phases as functions of composition and temperature. Following this, interpolation techniques based upon solution models are used to estimate the thermodynamic properties of the ternary phases from the properties of the binary phases. The ternary phase diagram is then calculated from the estimated ternary Gibbs energy surfaces.

As a result of the DTA measurements of melting temperatures, some of the model assumptions have been reassessed. In our earlier work, we found that the enthalpy of fusion of uranium recommended by the International Atomic Energy Agency (IAEA)⁸ was inconsistent with its recommended U-Pu solidus.⁹

⁶D. R. O'Boyle and A. E. Dwight, "The Uranium-Plutonium-Zirconium Ternary Alloy System," Proc. of the Fourth Int. Conf. on Plutonium and Other Actinides, Santa Fe, NM, October 5-9, 1970, p. 720 (1970).

⁷C. W. Bale, A. D. Pelton, and W. T. Thompson, "F*A*C*T* Users' Instruction Manual," McGill University/Ecole Polytechnique, Montreal (1979-84).

⁸F. L. Oetting, M. H. Rand, and R. J. Ackerman, *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part I, Int. Atomic Energy Agency, Vienna (1986).

⁹P. Chiotti, V. V. Akhachinskij, I. Ansara, and M. H. Rand, *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part 5, Int. Atomic Energy Agency, Vienna (1981).

Our initial decision was to accept the U-Pu solidus and reject the recommended enthalpy of fusion of uranium. This was based, in part, on the fact that earlier studies¹⁰ had reported roughly the same U-Pu solidus as IAEA and that there was a reasonable experimental determination of the enthalpy of fusion of uranium,¹¹ which was ignored by the IAEA but which was consistent with the reported U-Pu solidus. Our decision led to calculated solidus temperatures that were much lower than those which we subsequently measured. Our new experimental information indicates that a better choice would be to reject the U-Pu solidus and accept the IAEA enthalpy of fusion. The revised model gives better agreement with the available ternary solidus and liquidus data and better agreement with the fragmentary data for the U-Zr system as well. We believe that the U-Pu system should be reinvestigated experimentally.

C. Fusion-Related Research

A critical element in the development of the fusion reactor is the blanket for breeding tritium fuel. We are conducting several studies with the objective of determining the feasibility of using lithium-containing ceramics as breeder material. We are also conducting design studies of methods for improving fusion reactor performance and neutron dosimetry and damage analysis of fusion materials in neutron facilities.

1. Characteristics of the LiAlO₂-H₂O System

Accounting for the tritium inventory in the tritium breeding blanket of a fusion reactor requires, among other things, knowledge of (1) the adsorption-desorption characteristics of tritium-containing species on the breeder surface, (2) the solubility of tritoxide and tritide in the bulk breeder, and (3) the kinetics of various processes that transport tritium out of the breeder. An experimental study on LiAlO₂ is in progress to provide information on the thermodynamics of adsorption of H₂O(g) and dissolution of OH⁻ and on the kinetics of the evolution of H₂O(g).

a. H₂O Surface Adsorption and OH⁻ Solubility

Adsorption measurements were made by the frontal analysis technique of gas chromatography,¹² also known as the breakthrough technique. The method is to inject a gas stream (in this case, helium) with a known flow rate and partial pressure of H₂O(g) into the inlet of a packed column of the sample at a known time. A Beckman H₂O analyzer measures the H₂O(g) level in the effluent gas. Because the adsorption process is rapid, the response of the analyzer remains at the preinjection level until the surface of the sample reaches the degree of coverage that is thermodynamically required by the prevailing temperature and partial pressure of H₂O(g). At that time, water vapor emerges at the end of the column (breakthrough occurs) and the analyzer records a sharp

¹⁰F. H. Ellinger, R. O. Elliot, and E. M. Cramer, *J. Nucl. Mater.* **3**, 233 (1959).

¹¹H. Savage and R. D. Seibel, *Heat Capacity Studies of Uranium and Uranium-Fissium Alloys*, Argonne National Laboratory Report ANL-6702 (1963).

¹²J. R. Conder and C. L. Young, *Physicochemical Measurement by Gas Chromatography*, John Wiley & Sons, New York, pp. 6, 124, 354 (1979).

rise in water level in the effluent gas. A similar technique has been used to study surface adsorption of H_2O on Li_2O .¹³

Figure VII-6 presents the isotherms obtained for adsorption of $\text{H}_2\text{O}(\text{g})$ on the LiAlO_2 surface at 673 and 773 K. The value of θ (the fraction of surface covered) is based on the measured surface area and on the approximation that the size of one adsorption site is 10^{-15} cm^2 . This approximation is based on observations by DeBoer et al.¹⁴ that the water monolayer capacity on alumina corresponds to $1.1 \times 10^{15} \text{ sites/cm}^2$. The linear regression equations representing the adsorption isotherms for 673 and 773 K are, respectively,

$$\log(\theta) = (-1.590 \pm 0.691) + (0.497 \pm 0.064)\log(\text{p}_{\text{H}_2\text{O}}) \quad (4)$$

and

$$\log(\theta) = (-1.112 \pm 0.061) + (0.497 \pm 0.052)\log(\text{p}_{\text{H}_2\text{O}}) \quad (5)$$

where $\text{p}_{\text{H}_2\text{O}}$ is the partial pressure of $\text{H}_2\text{O}(\text{g})$ in Pascals.

Fig. VII-6.

Surface Adsorption Isotherms for
 $\text{LiAlO}_2\text{-H}_2\text{O}(\text{g})$ System at 673 and
773 K

¹³H. Yoshida, S. Konishi, H. Takeshita, T. Kurasawa, H. Watanabe, and Y. Naruse, J. Nucl. Mater. **122-123**, 934 (1984).

¹⁴J. H. DeBoer, J. M. H. Fortuin, B. C. Lippens, and W. H. Meijs, J. Catal. **2**, 1 (1963).

Both isotherms are of the Freundlich type. Freundlich adsorption isotherms are generally indicative of surface heterogeneity, such as the presence of more than one kind of surface site for adsorption.¹⁵ This heterogeneity arises from differences among O^{2-} , Li^+ , and Al^{3+} sites as well as from dislocations, ledges, etc. on the surface. Different energies of adsorption are expected from such chemical and physical differences. Different kinds of sites can dominate in different measurements involving different ranges of surface coverage.

Figure VII-7 presents the isotherms for the solubility of OH^- in $LiAlO_2$ at 673 and 773 K. The linear regression equations for 673 and 773 K, respectively, are

$$\log(x_{OH}) = (-4.667 \pm 0.096) + (0.309 \pm 0.088)\log(p_{H_2O}) \quad (6)$$

and

$$\log(x_{OH}) = (-4.899 \pm 0.079) + (0.499 \pm 0.063)\log(p_{H_2O}) \quad (7)$$

where x_{OH} is the mole fraction of OH^- .

Fig. VII-7.

Isotherms for Solubility of Hydroxide in $LiAlO_2$ at 673 and 773 K

¹⁵D. O. Hayward and B. M. W. Trapnell, *Chemisorption*, Butterworths, London, p. 174 (1964).

For the $\text{H}_2\text{O}(\text{g})$ partial pressure range of these measurements, the slopes of the solubility curves suggest that LiAl_5O_8 is soluble in LiAlO_2 at 673 K but not at 773 K, an example of retrograde solubility. It is also possible that OH^- behaves differently above and below 744 K, the melting point of LiOH . The two isotherms bracket this temperature.

Although the hydroxide solubility for a given H_2O partial pressure appears to decrease at higher temperature, the fractional surface coverage between 673 and 773 K appears to increase. However, preliminary results from a few measurements at 873 K indicate that the degree of surface adsorption decreases at this higher temperature. Low temperature chemisorption that becomes reversed at higher temperature is one way to understand the results. Without more closely spaced isotherms, it is impossible to determine at which temperature the maximum adsorption occurs. However, if the equations for θ are extrapolated to a condition of 1 ppmV $\text{H}_2\text{O}(\text{g})$ in a sweep gas of 10^5 Pa total pressure, then $\theta = 0.0082$ and 0.025 for 673 and 773 K, respectively. Reactor blanket conditions might fall into such a range.

b. Post-Run Heatup Results

Following completion of $\text{H}_2\text{O}(\text{g})$ evolution in several runs, we raised the temperature to about 923 K. The curve for the subsequent $\text{H}_2\text{O}(\text{g})$ evolution with time under this condition often showed up to three peaks. The relative heights of these peaks were variable. A detailed interpretation of them has not been made yet. However, their occurrence is consistent with the Freundlich view that the adsorption process involves sites of different properties and energies. Under conditions of constant partial pressure of $\text{H}_2\text{O}(\text{g})$, the overall adsorption/solubility was found to decrease as temperature increased. Thus, the overall process is exothermic. In contrast, endothermic behavior for solubility was observed for Li_2O by Tetenbaum et al.¹⁶ and by Norman and Hightower.¹⁷

c. Kinetics of $\text{H}_2\text{O}(\text{g})$ Evolution

To determine the reaction order for the $\text{H}_2\text{O}(\text{g})$ evolution process, a generalized rate equation was used:

$$dx_{\text{OH}}/dt = k_g(a - m_{\text{OH}})^n \quad (8)$$

where dx_{OH}/dt is the rate of water loss expressed in terms of hydroxide; k_g is the generalized rate constant; a is the amount of hydroxide present in the system at zero time for the start of the kinetic analysis; m_{OH} is the amount of hydroxide that has been lost (as H_2O) at time t ; and n is the kinetic order of the process. With this equation, the reaction order was found to be 2.22 ± 0.17 for 673 K and 1.95 ± 0.17 for 773 K. The activation energy derived from second-order rate constants is 14.7 ± 1.9 kcal (61.5 ± 7.9 kJ).

¹⁶M. Tetenbaum, A. K. Fischer, and C. E. Johnson, *Fusion Technol.* **7**, 53 (1985).

¹⁷J. H. Norman and G. R. Hightower, *J. Nucl. Mater.* **122-123**, 913 (1984).

Adherence to a rate equation that is second order in the hydroxide content of the system is consistent with a rate-determining bimolecular process. This process is taken to be the combination of two surface OH^- groups to split out a molecule of $\text{H}_2\text{O}(\text{g})$ with an activation energy of 14.7 kcal (61.5 kJ). (An intervening, but faster desorption step, $\text{H}_2\text{O}(\text{ads}) \rightarrow \text{H}_2\text{O}(\text{g})$, is possible.) For a system containing small amounts of tritium and relatively large amounts of protium, as in a blanket, the kinetic behavior would be pseudo-first order in tritoxide. A report by Kudo¹⁸ on the kinetics of thermal decomposition of LiOH [$\text{H}_2\text{O}(\text{g})$ evolution] indicated that the rate-limiting step follows first-order kinetics and that the activation energy is 29.5 ± 1.1 kcal (123.4 ± 4.6 kJ).

To relate Kudo's data to the present work, we note that removal of H_2O from LiOH results in a two-phase system of $\text{LiOH-Li}_2\text{O}$. If the main processes to consider are desorption from the surface and surface combination of OH^- , then a comparison of our results for LiAlO_2 with those of Kudo for $\text{LiOH-Li}_2\text{O}$ suggests some differences for the two systems. Because the slow step for LiAlO_2 is bimolecular combination of OH^- , it appears that unimolecular desorption is faster than combination of OH^- groups on LiAlO_2 . For $\text{LiOH-Li}_2\text{O}$, Kudo's results suggest the reverse relationship between the two processes. Furthermore, the overall evolution process is easier from LiAlO_2 because the activation energy is lower. Kudo et al.¹⁹ also reported that the evolution of HTO from neutron-irradiated Li_2O followed first-order kinetics with an activation energy of 18.8 ± 1.3 kcal (78.7 ± 5.4 kJ). A conclusive explanation for the difference in his values was not given. However, our activation energy for $\text{H}_2\text{O}(\text{g})$ release from LiAlO_2 is lower than either of the values for the Li_2O or LiOH^- systems. On this basis, tritium release from LiAlO_2 is expected to be easier than from Li_2O .

d. Future Work

An additional isotherm (for 873 K) for the $\text{LiAlO}_2\text{-H}_2\text{O}$ system is being measured. This will be followed by measurements of the effect of $\text{H}_2(\text{g})$ in the helium gas stream. There are indications that the rate of release of $\text{H}_2\text{O}(\text{g})$ is accelerated under these conditions, and earlier calculations²⁰ had indicated that low oxygen activities ($<10^{-15}$) affect hydroxide solubility. Concurrent efforts will include measurements on the Li_2ZrO_3 system analogous to those on LiAlO_2 .

2. Modeling of Tritium Transport in Ceramic Breeders

The objective of this work is to develop a computer model that will predict tritium behavior in ceramic breeder materials. When complete, the model will enable one to compare the relative contributions of the different transport processes (such as bulk diffusion, grain boundary diffusion, desorption, permeation, and trapping) to the total tritium inventory and to the tritium release kinetics.

¹⁸H. Kudo, J. Nucl. Mater. 87, 185 (1979).

¹⁹H. Kudo, K. Tanaka, and H. Amano, J. Inorg. Nucl. Chem. 40, 363 (1978).

²⁰A. K. Fischer, J. A. McDaniel, and C. E. Johnson, J. Nucl. Mater. 141-143, 344 (1986).

Until recently, the tritium release from ceramic breeder materials was interpreted as controlled by either diffusion²¹⁻²³ or desorption.^{24,25} Models based on these processes were unable to satisfactorily account for much of the data obtained in tritium release experiments. In addition, the inappropriate use of the simple diffusional release model has resulted in a large variation in reported tritium diffusivities, especially for ceramics such as LiAlO_2 . We have developed a diffusion-desorption model that is a significant improvement over previous models.

Our diffusion-desorption model leads to the following expression for the tritium flux (R_t) as a function of time for a spherical grain after a temperature change occurs:

$$R_t = \left(1 - \frac{3}{Ga} K_d C_1\right) \left[\frac{Ga}{3} - 2h^2 a G \sum_{n=1}^{\infty} \frac{\exp(-D\alpha_n^2 t)}{\alpha_n^2 [a^2 \alpha_n^2 + ah(ah - 1)]} \right] + K_d C_1 \quad (9)$$

where

- G = generation rate/unit volume
- a = grain radius
- K_d = effective desorption rate constant
- C_1 = concentration of tritium at the surface prior to the temperature change
- D = tritium diffusivity
- $h = K_d/D$
- α_n = roots of $a\alpha \cot(a\alpha) = 1 - ah$

Using this equation and previously determined values, we calculated the *in situ* tritium release from a sample of Li_2SiO_3 . As shown in Fig. VII-8, the results are in good agreement with experimentally observed release for the LISA experiment under conditions of pure helium purge gas.²⁶ Next, tritium release was calculated using both a pure-diffusion model and our diffusion-desorption model for a second Li_2SiO_3 sample from the LISA experiment. The diffusion model did a very poor job of predicting the observed tritium release behavior when the diffusion coefficients calculated by Werle²⁶ were used. When the diffusion coefficients were optimized to fit the data, the fit was fair (Fig. VII-9) but not as good as that for our diffusion-desorption model.

²¹R. G. Clemmer et al., *The TRIO Experiment*, Argonne National Laboratory Report ANL-84-55 (1984).

²²K. Okuno and H. Kudo, *J. Nucl. Mater.* **138**, 210 (1986).

²³T. Kurasawa, H. Watanabe, G. W. Hollenberg, Y. Ishi, A. Nishimira, H. Yoshida, Y. Naruse, M. Aizawa, H. Ohno, and S. Konishi, *J. Nucl. Mater.* **141-143**, 265 (1986).

²⁴M. Dalle Donne, *Fusion Technol.* **9**, 503 (1983).

²⁵T. Tanifuji, K. Noda, S. Nasu, and K. Uchida, *J. Nucl. Mater.* **95**, 108 (1980).

²⁶H. Werle, J. J. Abassin, M. Briec, R. G. Clemmer, H. Elbel, H. F. Hafner, M. Mason, P. Sciers, H. Wedemeyer, *J. Nucl. Mater.* **141-143**, 321 (1986).

Fig. VII-8.

Calculated and Observed Tritium Release from First Li_2SiO_3 Sample. Calculated curve obtained from diffusion-desorption model.

Fig. VII-9.

Calculated and Observed Tritium Release from Second Li_2SiO_3 Sample. Calculated curve obtained from pure-diffusion model with optimized diffusional parameters.

Predictions of the tritium release for two other samples of Li_2SiO_3 were calculated with the diffusion-desorption model and were also in good agreement with the experimental data. There were some regions in the observed tritium release profiles where the diffusion-desorption model did not accurately predict the tritium release. This indicates that the values used for the diffusivity and the desorption rate constant in the calculations may be in error, or that a third mechanism may be important in determining tritium release in these regions.

Work is in progress to develop a more-sophisticated model that will take into account other processes that affect tritium release besides diffusion and desorption. Processes under investigation include grain boundary diffusion, surface reactions, and permeation.

3. Design of Blanket Processing System

The requirements of tritium technology in a fusion reactor are centered in three main areas: fuel processing, tritium extraction from the breeder blanket, and tritium containment. The Tritium Systems Test Assembly (TSTA) now in operation at Los Alamos National Laboratory is dedicated to developing and demonstrating the technology for fuel processing and tritium containment. The TSTA is the only fusion fuel processing facility that can operate in a continuous, closed-loop mode. Its inventory of tritium is restricted to 100 g; however, it has the capability to process tritium at the rate of 1000 g/day. The initial TSTA proposal included a system to simulate the processing of the tritium gas stream from the breeder blanket. This system was not constructed because of budget limitations and limited information on blanket systems at that time. Interest in such a system has again surfaced in an agreement between the U.S. and Japan to upgrade the TSTA.

We have initiated a study to define a blanket processing mockup for TSTA. The first step of the work was to determine the condition of the gaseous tritium stream from the blanket with respect to the total gas throughput, the hydrogen-to-tritium ratio, the corrosive chemicals, and the radionuclides. The blanket chosen for initial study was self-cooled liquid lithium. The key discoveries were as follows:

- (1) The total throughput of the blanket gas stream is a factor of 500 higher than the plasma exhaust stream of TSTA because this stream is a dilute product in the gas.
- (2) The protium-to-tritium ratio is about 1. The implication of this is that the blanket stream may require modification of the present isotopic separation system.
- (3) The corrosion chemicals are halides; the radionuclides are mainly ^{14}C , ^{32}P , and ^{35}S ; and there is a high level of nitrogen contamination in the blanket stream. A method of reducing these species to acceptable levels will be needed.

Future work will define the blanket processing system needed to clean up this stream and will also define its interface with TSTA. Similar work for an aqueous solution blanket and helium-cooled Li_2O blanket will be done.

4. Tritium Oxidation Experiment

Tritium losses due to permeation from fusion breeder blanket systems can be severe. These permeation losses could be reduced if the tritium is retained in the oxidized (T_2O) rather than the reduced (T_2) form. We are undertaking a series of experiments to evaluate tritium oxidation as a means of converting the permeating tritium to tritiated water. The overall objective is to determine (1) if tritium permeating through a stainless steel component can be oxidized to tritiated water, (2) what conditions will optimize the yield of tritiated water, and (3) if competing reactions that use oxygen are important.

We are examining tritium oxidation in a double-walled tube made of stainless steel. A tritium/helium gas mixture is circulated through the inner tube, and an oxygen/helium gas mixture is circulated through the outer tube. An ethylene glycol trap collects the tritiated water formed by oxidation in the steel tube. The other reaction product, molecular tritium, is converted to tritiated water in a copper oxide bed and collected in another ethylene glycol trap. A metal oxide coating is produced on the steel surface in the course of an experiment.

The experimental parameters which we assumed to be important are oxygen concentration, temperature, presence of excess gaseous protium in the oxygen/helium gas, and tritium concentration. Four types of experiments were planned to study tritium oxidation. The first is a series of runs at <0.01 ppm oxygen and temperatures of 350 – 550°C . The second is a series of runs at 550°C with 15 ppm protium and an oxygen level of 1 to 1000 ppm. The third is a repeat of the second series but without the protium. The fourth is a series of runs in which temperature, tritium concentration, and oxygen concentration are randomly varied. We completed the first two series in 1987.

In the first series, the yield of tritiated water was $<50\%$, ranging from 35.5% at 350°C to 41.9% at 550°C . At the low oxygen level used for these runs (<0.01 ppm), we expected competition between the oxidation of the stainless steel surface and the oxidation of the tritium. The respective free energies of formation of chromium oxide, iron oxide (FeO), and tritiated water for each mole of oxygen at 500°C are -920 , -219 , and -203 kJ/mol, respectively. Since the free energies of formation of iron oxide and tritiated water are similar, the reaction product could depend on the kinetics. For iron oxide, we calculated the need for oxygen assuming a metal oxide growth rate independent of the tritium present. Metal oxide growth could incorporate all the oxygen at a 10 ppm level. However, we found that up to 41.9% of the tritium was converted to tritiated water at <0.01 ppm oxygen. Therefore, tritium oxidation appears to be kinetically favored. Nevertheless, the water yield at this low oxygen level is not high enough to minimize permeation losses.

The second series of experiments consisted of runs at 1, 40, and 912 ppm oxygen, all at 550°C with 15 ppm gaseous protium in the oxygen/helium gas. We hoped in this series to observe the combined effect of increased oxygen concentration and added protium on the tritiated water yield. We found a steady increase in the yield of tritiated water as we increased the oxygen level. The maximum yield was 97.2% at 912 ppm oxygen.

We calculated the permeation loss in a heat exchanger similar to the test apparatus in the 912 ppm run. Assuming a surface area of 2052 m^2 and a

wall thickness of 0.005 m, the expected permeation loss would be ~60 Ci/d. This tritium loss, although above the present design goal of 10 Ci/d, would probably be environmentally acceptable for a commercial fusion reactor. Therefore, if oxygen concentrations of 1000 ppm are acceptable, the oxidation of tritium may be a useful technique to achieve low permeation losses.

Although our experimental results are limited, we have speculated on the reactions that influence the yield of tritiated water. We believe there are five major reactions. These are the diffusion of tritium through the oxide, the oxidation of metal species by means of oxygen, the oxidation of tritium, the reduction of the metal oxide, and the oxidation of metal species by means of the tritiated water. This latter reaction has been reported in catalytic studies²⁷ and may be particularly significant when the tritiated water yield exceeds 90%. We hope to elucidate the importance of each of these reactions by means of the third and fourth series of experiments.

5. Dosimetry and Damage Analysis

The purpose of this effort is to collect nuclear data and develop techniques for the measurement of the neutron flux and energy spectrum in fusion-materials irradiation facilities, including fission reactors and accelerator-based neutron sources. This information is then used to calculate radiation damage parameters, such as atomic displacements and gas production. The goal is to provide data for the correlation of materials property changes, regardless of the irradiation facility, and to predict materials performance in fusion reactors.

Dosimetry support is being provided for U.S. and Japanese materials irradiations, primarily in the High Flux Isotopes Reactor (HFIR) at Oak Ridge National Laboratory and the Omega West Reactor at Los Alamos National Laboratory. Neutron measurements are made by the multiple foil activation technique, wherein integral activities from various nuclear reactions with different energy thresholds are used to adjust the neutron flux spectrum. Flux gradients are also measured throughout the materials irradiation assemblies so that neutron fluences and radiation damage can be precisely determined for each specimen. Since these techniques require well-known neutron activation cross sections, recent research has focused on the measurement and testing of such nuclear data.

In collaboration with Rockwell International, we have measured helium-production cross sections for a wide range of elements and alloys in irradiation facilities. Helium production is considered important because 14-MeV fusion neutrons produce considerably more helium than fission neutrons. The iron samples were especially interesting. Analyses of iron samples irradiated up to 10^{27} n/m² in HFIR indicated more helium than was expected from fast neutron reactions at high neutron fluences. The helium excess increased systematically with neutron exposure, suggesting a transmutation-driven process. The extra helium may be produced in two different ways: either by fast neutron reactions on the transmuted isotopes of iron or by a thermal neutron reaction with

²⁷G. A. Somoraji and M. Salmeron, "Surface Properties of Catalysts, Iron, and Its Oxides: Surface Chemistry, Photochemistry and Catalysis," in *Homogeneous and Heterogeneous Photocatalysis*, eds. E. Pelizzetti and N. Serpone, D. Reidel Publishing, Holland, pp. 445-477 (1986).

the radioactive isotope ^{55}Fe . Radiometric and mass spectrometric measurements established that the thermal-neutron total absorption cross section of ^{55}Fe is 13.2 ± 2.1 b and that the thermal-helium cross section is less than 18 mb.

These results indicate that helium production in ferritic materials during irradiations can be increased in mixed-spectrum reactors by isotopically enriching the samples. If a thermal neutron mechanism is operative for ^{55}Fe , then we can generate fusion-like helium levels (300 appm) in a one-year irradiation in HFIR. Without a thermal effect, we can still increase the helium production up to a factor of six by doping with ^{55}Fe , or a factor of two or three by doping with ^{54}Fe or ^{57}Fe . Further work is needed to clarify the reaction mechanisms and helium-production cross sections.

New cross section measurements have been reported for the production of long-lived radioisotopes near 14.8 MeV. Such data are needed to assess activity levels in fusion reactor materials for maintenance and waste disposal applications. High-fluence irradiations were performed at the Rotating Target Neutron Source II of Lawrence Livermore National Laboratory. Following chemical separations to remove unwanted activities, we used X-ray spectrometry to determine the production rates of ^{91}Nb from ^{92}Mo , as well as ^{93}Mo and $^{93\text{m}}\text{Nb}$ from ^{94}Mo . There are no previously reported measurements of these reactions. Our data suggest that the half-life of ^{91}Nb is only about 350 y, which is shorter than the previous value (680 ± 130 y); the cross section for ^{91}Nb is about 40% higher than calculations; and the production of ^{93}Mo is only about one-third of previous estimates. Further work is in progress to measure production rates for ^{14}C (5730 y), ^{53}Mn (3.7×10^6 y), ^{93}Zr (1.5×10^6 y), and ^{92}Nb (3.7×10^6 y).

Neutron activation cross sections are also being measured at lower neutron energies, primarily to improve our fission reactor dosimetry. Integral measurements have been made for ten different reactions using a Be(d,n) accelerator-based neutron source with a deuteron energy of 7 MeV. Differential measurements were performed at selected neutron energies between 1 and 10 MeV, especially for the $^{55}\text{Fe}(n,\alpha)^{51}\text{Cr}$ and $^{93}\text{Nb}(n,n')^{93\text{m}}\text{Nb}$ reactions. The latter reaction is of particular interest for long reactor irradiations due to the long half-life (16.8 y) of $^{93\text{m}}\text{Nb}$. The low neutron energy threshold (30 keV) also makes the reaction particularly well-suited for indicating radiation damage in materials, which is generally only significant above 100 keV. For these reasons, considerable effort is being expended to assess this reaction for monitoring damage to reactor pressure vessels. Our data are expected to have much lower uncertainties (3-5%) than previous measurements and should resolve existing discrepancies between differential and integral measurements.

VIII. BASIC CHEMISTRY RESEARCH

Basic chemistry research is being pursued in many different areas: catalytic chemistry for converting small molecules to desired products; materials chemistry for liquids and vapors at high temperatures; interfacial processes of importance to corrosion science, catalysis, and high-temperature superconductivity; thermochemical properties of minerals having major importance to nuclear waste storage investigations, as well as "high-tech" materials; and the geochemical processes involved in water/rock interactions occurring in active hydrothermal systems.

A. *Fluid Catalysis*

This research is designed to determine reaction mechanisms and to explore catalytic chemistry for converting small molecules to desired products. Currently under investigation are nucleophilic hydrogen activation processes that occur in the presence of soluble oxide complexes. Catalytic chemistry is being investigated using a combination of kinetic and spectroscopic techniques, in addition to theoretical (molecular orbital) methods. Also explored are (1) synthetic methods designed to obtain stable phthalocyanine catalysts for homogeneous reactions that occur at high temperatures and pressures and (2) alternative techniques for adapting multinuclear magnetic resonance spectroscopy to high-pressure kinetic studies.

1. Soluble Oxide Chemistry

Several types of hydrogen activation occur with transition metal complexes in solution, e.g., the oxidative addition reactions:

where ϕ = phenyl. These are relatively common processes in homogeneous catalysis and have been extensively investigated with solution-phase spectroscopic and kinetic techniques. In contrast, the nucleophilic activation of hydrogen that occurs with oxides in the solid state, e.g.,

is an extremely important process in heterogeneous catalysis, but solution-phase counterparts are relatively rare and little studied.

We are exploring the solution-phase catalytic chemistry of metal complexes that contain oxide or oxo ligands. We have already reported a mechanism for homogeneous oxide catalysis of carbon monoxide hydrogenation¹

¹J. W. Rathke and R. J. Klingler, "Soluble Oxide Chemistry at High Pressures," presented at the Sixth DOE Catalysis and Surface Chemistry Research Conf., Gaithersburg, MD, October 14-16, 1987.

and have begun efforts to extend the scope of our work to other types of solution-phase processes. We have found that relatively simple nucleophilic oxo complexes catalyze reactions that heretofore had been the domain of transition metal complexes. Thus, alkali metal formates and hydroxides catalyzed the water-gas-shift reaction in triethylene glycol solutions. Figure VIII-1 shows the first-order dependence on sodium formate composition for the water-gas-shift reaction:

Fig. VIII-1.

First-Order Rate Dependence on
[NaO₂CH] for Water-Gas Shifting

The presence of small amounts of extraneous catalytic species in these experiments was ruled out by use of gold-plated or glass-lined reactors. We suspect that the mechanism for catalysis in this system includes decarboxylation of formate to yield CO₂ and, perhaps, an unstable adduct of hydrogen with hydroxide anion

followed by production of hydrogen and hydroxide

and carbonylation of the hydroxide with regeneration of formate

The presumed hydroxide adduct of H_2 in Eqs. 5 and 6 warrants further investigation. One possibility is that it exists as a solvated hydride anion, $\text{H}_2\text{O}\cdot\text{H}^-$. Whatever its true structure, the adduct seems to have a remarkable potential for catalytic chemistry. As demonstrated in Fig. VIII-2, NaOH equilibrates the water-gas-shift reaction (in this case, starting from the right-hand side in Eq. 4), catalyzes the hydrogenation of ethylene, and shows some activity for the hydrogenation of N_2 . The N_2 hydrogenation result should be regarded as, at best, preliminary, since the amount of NH_3 actually produced was very small. Nevertheless, we suspect that sodium-hydroxide-catalyzed N_2 hydrogenation is not unreasonable in view of our other results.

Fig. VIII-2.

Nucleophilic Activation of Hydrogen
by NaOH Catalyst at 300 atm and
180-250°C

Future efforts will involve an investigation into the role that the metal center plays in catalysis of reactions involving the nucleophilic activation of hydrogenation. Early results indicate that, at least for the water-gas-shift reaction, coordination by the metal center is counterproductive, since water-gas-shift rates decrease in the series: $\text{Cs}^+ > \text{Na}^+ > \text{Li}^+$ (thus, the formate salt of the least-binding cation, Cs^+ , has the highest rate). We will also investigate the properties of more nucleophilic anions in less acidic solvents. For example, NH_2^- in liquid NH_3 may be much more reactive for nitrogen hydrogenation than OH^- in triethylene glycol.

2. Homogeneous Phthalocyanine Chemistry

Our interest in metallophthalocyanines began with the observation that ZnPc (Pc = phthalocyanine) catalyzes many of the reactions involved in our

studies even at the low concentrations (near 10^{-5} M) achievable with its limited solubility. This phthalocyanine catalyzes the disproportionation of trimethylsilyl formate and the addition of carbon dioxide to metal hydrides. Beyond our current interests, phthalocyanine catalytic chemistry is expected to parallel that of the porphyrins in enzymes and enzyme model systems. However, in comparison to porphyrins, the phthalocyanines are generally much more stable. For example, ZnPc does not undergo measurable decomposition when heated for two weeks in the presence of H_2 and CO (350 atm) at $250^\circ C$. Similar experiments with zinc tetraphenylporphyrin result in its extensive decomposition within one hour. We expect that the high stabilities of the metallophthalocyanines could result in new homogeneous catalysts for reactions that occur at high temperatures and pressures. Efforts in this area during the past year were focused on synthetic methods designed to incorporate (1) substituents into the phthalocyanines that will impart maximal solubility in organic solvents or (2) structural features that might ultimately be useful in constructing shape- or size-selective catalysts.

We have recently discovered that the ring carbons in phthalocyanines can be efficiently metalated. This might allow us (because of the extreme versatility of lithium and magnesium reagents in organic synthesis) to incorporate a variety of structural features into phthalocyanines. Isotopic labeling studies using Li_2Pc as the substrate, 1-deuteriotetramethylpiperidine as the electrophile, and lithium tetramethylpiperidide as the metalation reagent indicate that metalation occurs with stereospecific substitution of the inner ring protons of the peripheral benzene rings of the phthalocyanines. The 1H NMR spectra in Fig. VIII-3 indicate the complex AA'BB' pattern of the ring protons in Li_2Pc . Confirming substitution at the inner ring positions, deuterated samples show a decrease in the intensity of the low field multiplet of the inner ring protons. The high field multiplet, arising from the outer ring protons, appears as a singlet in deuterated samples because of loss of spin-spin coupling from the inner protons.

In future studies, we plan to use this method to prepare soluble metallophthalocyanine complexes for catalytic studies at high temperatures and pressures.

Fig. VIII-3.

1H NMR Spectra Obtained at 80 MHz for Li_2Pc in Dimethyl Sulfoxide. (TMS = tetramethylsilane, TMP = tetramethylpiperidide, and PPM = parts per million)

Labeling indicates:

3. High-Pressure NMR Studies

Obtaining representative samples from reacting systems at high pressures is difficult because the concentrations of transient species or equilibrium values tend to change upon cooling and depressurization. *In situ* spectroscopic methods solve this problem by allowing observation of the system at true reaction conditions. We are designing a high-pressure multinuclear magnetic resonance cell suitable for *in situ* kinetic studies that would complement or replace some of our autoclave equipment and sampling methods. For our purposes, a new cell design is necessary because current designs do not possess gas-liquid mixing capabilities adequate for kinetic studies involving gaseous reactants or because the materials used in cell construction are not readily machinable; are reactive toward hydrogen, which is commonly used in our studies; have tensile strengths too low to withstand the required pressure (300 atm) on adequate sample sizes; or have such high magnetic susceptibilities that high-resolution spectra cannot be obtained. A design that meets our requirements is shown in Fig. VIII-4. This cell, constructed from sapphire and an aluminum copper alloy (C642), is similar to a sapphire/titanium alloy cell described by Roe² except that our design provides a tested mechanism for gas-liquid mixing, uses materials that are not attacked by hydrogen, and makes use of a compression fitting that connects the ceramic to metal in place of an epoxy glue seal. Because of its fixed gas connections, the new cell is not rotatable but will provide ample signal resolution and will run safely. Gas-liquid mixing is accomplished by means of a magnetically driven solenoid actuator (not shown in figure), which has been demonstrated by Vander Velde and Jonas³ to provide rapid mixing. Further efforts will involve the construction and operational testing of the new cell.

Fig. VIII-4.

Schematic of High-Pressure NMR Cell

²D. C. Roe, J. Magn. Reson. **63**, 388-391 (1985).

³D. G. Vander Velde and J. Jonas, J. Magn. Reson. **71**, 480-484 (1987).

B. *High-Temperature Materials Chemistry*

Our goal in this effort is to perform experimental and theoretical studies that lead to a basic understanding of materials chemistry at high temperature. Our focus is on superconducting oxides and associated and ordered solutions, such as chloroaluminates, silicates, and "ionic" alloys.

1. Measurements on Superconducting Oxides

The characterization of phases and phase transformations in the new superconducting oxides is important for the development of optimized synthesis and fabrication procedures. We have initiated experiments that use emf measurements to more clearly elaborate phase transformation behavior and derive the thermodynamic properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ as a function of temperature and oxygen pressure. The advantages of the emf technique are its precision and the large range of oxygen pressures that can be easily investigated.

In this work, we employ the following galvanic cell

with air as the reference electrode. Oxygen is introduced or removed from the superconductor sample compartment by means of a coulometric titration, and the oxygen activity is determined by measuring the cell potential after equilibration of the sample.

Several coulometric titrations have been carried out at 1023 K (750°C) and oxygen pressures of ~ 0.21 to 10^{-4} atm. The results show a phase transformation occurring at low oxygen partial pressure, 10^{-3} - 10^{-4} atm, at a stoichiometry of about $\text{YBa}_2\text{Cu}_3\text{O}_{6.1-6.2}$. This phase transformation was irreversible. X-ray examination of a residue after slowly cooling to room temperature showed the tetragonal phase; the starting material was orthorhombic. The results to date suggest the possibility that the important orthorhombic structure can exist over an extended composition range, namely, $0 < \delta < \sim 0.9$.

2. Ordered and Associated Solutions

Obtaining a theoretical understanding of ordered and associated solutions presents many difficulties and challenges. Most concepts of such solutions are still intuitive: experiments often produce unexpected results, which lead to substantial modifications in the modeling approaches. The exploration of the relationship between ordering or association and the thermodynamic, transport, electrical, and physical properties should ultimately provide a basis for developing scientifically meaningful theories.

Some of the solutions under study include molten salts such as chloroaluminates and cryolite-based melts; "ionic" alloys such as Na-Sb, K-Pb, and Rb-Au; silicates; and metal/molten-salt systems. All of these high-temperature solutions are ionically and/or electronically conducting; and coulomb interactions, as well as electronic effects, are important in determining their structure and energetics. The solutions containing metals are usually involved in

metal-to-nonmetal transitions. These characteristics, coupled with the observed ordering and association, lead to striking properties. The thermodynamic properties are often characterized by inflections in chemical potentials and very large deviations from additive densities. Intermediate- to fairly long-range order is found in some cases. Large changes in electrical conductivities as a function of composition are found in many ordered alloys. Some appear to contain unusual structural groups, which impart surprising properties to the solutions. All these phenomena underscore the unusual nature of many of these solutions and raise a range of scientific questions for which there are only partial answers. In addition to their scientific significance, such solutions have major technological importance in energy-intensive industries such as steel, aluminum, and copper production and for high-temperature and room-temperature batteries.

We are examining a variety of alloys in which one intuitively expects a range of different types of bonding (covalent, ionic, etc.), and where the composition and characteristics of the transitions are likely to vary. In addition, we are developing theories and concepts about ionic ordered solutions with the aim of describing their properties with a minimum of information. Theories of multi-component systems are under investigation to develop the means for predicting their properties from those of lower order systems.

a. Quantum Mechanical Calculations of Molten-Salt Complexes

The structures of Al_2F_7^- and Al_2Cl_7^- are being investigated using *ab initio* molecular orbital theory and the STO-3G and 6-31G* basis sets.^{4,5} The STO-3G basis set was used for mapping out the potential energy surface, while the 6-31G* basis set, which includes polarization functions, was used to obtain final energy points in important parts of the surface. These species are part of the series of ionic structures of increasing size that characterize the ordering in fluoroaluminate and chloroaluminate solutions. The existence of Al_2Cl_7^- in chloroaluminate melts has been the subject of numerous experimental and theoretical studies, but some question remains as to the linearity of the Al-Cl-Al bond. The results of our calculations indicate that, in the absence of any cations, the Al_2Cl_7^- anion has a bent bridge with an Al-Cl-Al angle of about 131° and a barrier to inversion of 4 kcal/mol, as shown in Fig. VIII-5. Three different bent bridge structures for Al_2Cl_7^- , all related by internal rotation, differ by less than 0.4 kcal/mol in energy. In contrast, the Al_2F_7^- anion has a linear or nearly linear Al-F-Al bridge with, at most, a very small barrier to inversion (less than 0.2 kcal/mol). The preference for a linear bridge in Al_2F_7^- is attributed to increased Al-Al repulsion and smaller anion polarizability compared to those in Al_2Cl_7^- . Edge- and face-bridged structures are predicted to be much less stable than the corner-bridged structures for both Al_2F_7^- and Al_2Cl_7^- . Results also indicate that the introduction of an alkali cation into Al_2Cl_7^- reduces the Al-Cl-Al bond angle further. These results are consistent with our recent molecular dynamics calculations on MAX_4 melts (see Sec. VIII.B.2.b), which indicate that inclusion of polarizable anions results in bent Al-X-Al bridges. Smaller cations were found to have a larger effect on the Al-Cl-Al bond angle, in agreement with experiment.⁶

⁴W. J. Hehre, R. F. Stewart, and J. A. Pople, J. Chem. Phys. **51**, 2657 (1969).

⁵P. C. Hariharan and J. A. Pople, Theoret. Chim. Acta **28**, 213 (1973).

⁶J. Hvistendahl, P. Klaeboe, E. Rytter, and H. Øye, Inorg. Chem. **23**, 706 (1984).

Fig. VIII-5. Potential Energy vs. Al-Cl-Al Bond Angle in the Chloroaluminate Ion, Al_2Cl_7^- at the STO-3G and 6-31G* Basis Set Levels

Silicon hydrides are important in the chemical vapor deposition of silicon in the manufacture of microelectronic devices and solar energy cells, while their ions are important for detailed modeling of plasma etching of silicon surfaces. Reliable thermodynamic data for many of these short-lived radical and ionic species are either not available or have large uncertainties. For example, the values for the heat of formation of the SiH_2 radical range from 58 to 69 kcal/mol. We have used new theoretical methods based on *ab initio* molecular orbital theory to provide a reliable set of thermochemical data for the silicon hydride species that are accurate to ± 2 kcal/mol. For example, the heat of formation of SiH_2 is predicted to be 63.9 kcal/mol. Several recent experimental studies have confirmed this value.^{7,8} Also, an unusual Jahn Teller distortion in SiH_4^+ , which has significant implications for its thermodynamic properties, has been discovered. This distortion means that the ionization potential of SiH_4 is lower by 0.6 eV than the observed value⁹ so that the heat of formation of SiH_4^+ has to be revised by 14 kcal/mol downward. The new theoretical methods have also been used to predict thermodynamic properties of a series of other hydrides.

b. Molecular Dynamics Calculations of Ordered Ionic Melts

In collaboration with researchers at the University of Minnesota, we have completed molecular dynamics calculations of MAX_4 melts with polarizable anions for the case in which A^{3+} cations are four coordinated by X^- anions

⁷J. G. Martin, M. A. Ring, and H. E. O'Neal, Int. J. Chem. Kin. 19, 715 (1987).

⁸J. M. Jasinski, J. Phys. Chem. 90, 555 (1986).

⁹A. W. Potts and W. C. Price, Proc. R. Soc. London A326, 165 (1972).

and the interionic distances are similar to those in the ordered melt of NaAlCl_4 . The computations are the first to incorporate anionic polarizability in such a system. We used values of the polarizability given by Tessman et al.¹⁰ Our aim in this effort is to investigate the kinds of structures associated with the ordering phenomenon. Prior calculations by us¹¹ and experimental measurements by many others suggest that the ordered state is characterized by a series of anions, such as AlCl_4^- and Al_2Cl_7^- .

In addition to the predominant AX_4^- tetrahedra, our calculations, surprisingly, lead to doubly bridged A_2X_6 species similar in structure to the known vapor molecules Al_2Cl_6 and Al_2Br_6 and to a molecule that has been postulated to exist in acid chloroaluminate melts (e.g., NaCl-AlCl_3 mixtures high in AlCl_3). The double A-X-A bridges connect two AX_4 tetrahedra that share two X^- anions. The angular distributions of these A-X-A bridges peak at about 71° , close to the complement of the tetrahedral angle of the X-A-X triplets. The M^+ cations appear to be located largely at positions perpendicular to the faces of the AX_4^- tetrahedra.

Although such structures are likely to exist in real melts, their calculated stability is significantly higher than that in real systems. One possible reason is that polarization of the anions is not likely to be a linear function of polarizabilities up to the large field intensities near A^{3+} cations in our calculations. Consequently, the effective polarizability is probably lower than that used in our calculations, and a lower value is needed to better represent real systems. With a lower polarizability, we should achieve results that are close to real systems where intermediate-range ordering can be described in terms of the presence of a series of anionic species (AX_4^- , A_2X_7^- , $\text{A}_3\text{X}_{10}^-$, etc.) as well as the neutral species A_2X_6 . In any case, our method provides a unique capability for exploring structures in ordered ionic systems, and this initial calculation is a good starting point for such studies.

c. Neutron Diffraction Studies of Ordered Alloys

In collaboration with ANL's Materials Science Division and Intense Pulsed Neutron Source, we have undertaken neutron diffraction experiments on equiatomic K₂Pb liquid alloys. This alloy was chosen because of anomalous electrical and thermodynamic properties previously reported by Meijer et al.¹² and by us.¹³ The electrical conductivity and its temperature derivative exhibit a well-pronounced extremum at the 50:50 composition; the entropy of mixing and the heat capacity present features similar to those observed in ordered liquids. The magnitude of the heat capacity and its temperature dependence are unusual for metallic alloys and even for ionic solutions.

The neutron diffraction experiments were carried out at 870, 900, and 930 K. Our results for the three liquid temperatures, shown in Fig. VIII-6, exhibit a well-structured $S(Q)$. A distinctive first sharp diffraction peak (FSDP)

¹⁰J. Tessman, A. Kahn, and W. Shockley, *Phys. Rev.* **92**, 890 (1953).

¹¹M.-L. Saboungi, A. Rahman, and M. Blander, *J. Chem. Phys.* **80**, 2191 (1984).

¹²J. A. Meijer, W. Geertsma, and W. van der Lugt, *J. Phys. F: Met. Phys.* **15**, 899 (1985).

¹³M.-L. Saboungi, S. R. Leonard, and J. Ellefson, *J. Chem. Phys.* **85**(10), 6072 (1986).

Fig. VIII-6.

Total Structure Factor $S(Q)$ of Liquid KPb Alloy at 870, 900, and 930 K. Circles are measured values; solid curve in lower panel is calculated $S(Q)$.

at $0.96 \text{ \AA}^{-1}$ is present at all three temperatures and the first main peak is at $2.18 \text{ \AA}^{-1}$. With the exception of the height of the FSDP, which decreases with an increase in temperature, the main features in $S(Q)$ remain unaltered as the temperature is varied. The change in the FSDP height is related to the heat capacity, which decreases very sharply in the same temperature interval. The pronounced FSDP and the molecular character of solid KPb led us to carry out model calculations based on the known structural units in the KPb crystal structure, e.g., nearly regular Pb_4 tetrahedra surrounded by K_4 tetrahedra oriented in the opposite direction. Calculations based on these units gave excellent fits with experimental data, as shown in Fig. VIII-6.

The structures of similar alloys (e.g., NaPb and CsPb) will be investigated to determine whether an FSDP is present and to investigate the chemical bonding in these liquids. Inelastic scattering experiments are also contemplated to investigate the dynamics of these liquids and to further identify

molecules via their vibrational spectra. Finally, we are investigating the feasibility of using other molecular theories, such as RISM (Reference Interaction Site Model), to interpret our diffraction results. In any case, most of the anomalous properties in the liquid are probably related to the presence of the structural units containing tetrahedra of K and Pb and to the increasing dissociation of these units with an increase in temperature.

3. Calculation of Complex Gas/Condensed-Phase Equilibria in Coal Combustion

Our recently developed computer program, based on geometric programming, is being used to calculate the condensed and gaseous products chemistry in the combustion and gasification of high-sulfur Illinois #6 coal. This work is done in collaboration with ANL's Materials and Components Technology Division.

To start, we defined condensed liquid solutions that are close to ideal in their behavior and are also illustrative of the chemical properties. Our calculations revealed the following. Under both oxidizing and reducing conditions, the condensed phases are saturated with silica, and the major gaseous carriers of Na and Cl are NaCl and HCl, respectively. However, the concentration of NaCl is almost one order of magnitude higher under reducing conditions than under oxidizing conditions.

Under oxidizing conditions and temperatures above 1600 K, the liquid condensates are mostly silicates with traces of sulfates, which increase in concentration with a decrease in temperature. At equilibrium, the liquid solution disappears at ~1390 K before the solution becomes rich in sulfate. However, with a reasonable constraint on the kinetics of reaction of liquid with solids, a corrosive sulfate-rich liquid with traces of silicates forms in the temperature range of 1260-1350 K.

Under reducing conditions, sulfides are present in the solution phase. Above 1600 K, the liquid condensates are mostly silicates with a small amount of sulfide, which increases with decreasing temperature. The solution phase is present below 1100 K under nonequilibrium conditions, and even under equilibrium conditions, a sulfide-rich solution phase exists down to temperatures as low as 1260 K.

Our calculations for these very complex chemical systems include a large number of chemical species (300), and our method provides us with the capability for deducing the chemistry of corrosion in coal combustion and conversion. Our computer program has proved particularly suited for such problems. Our plans are to extend our present capabilities for realistically calculating similar complex chemical equilibria in corrosion, energy conversion, pyrometallurgy, vapor deposition, and other processes.

C. *Interfacial Materials Chemistry*

This research embodies a family of experimental and theoretical studies that focus on interfacial processes of importance to corrosion science, catalysis, and high-temperature superconductivity. 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 gas chromatographic studies of the chemistry of species adsorbed on molecular sieve materials, and (3) the characterization of high-critical-temperature (T_c) superconducting oxides and fabrication of functional embodiments employing high- T_c materials. Paralleling semiempirical and *ab initio* theoretical research is carried out to support and extend the experimental findings.

1. Aqueous Corrosion Research

The corrosion of metals and alloys in aqueous media has been studied extensively. While interest in the mechanisms of aqueous corrosion has been long-standing, concerns about corrosion problems with both austenitic and nickel-base alloys in light water reactors have given a renewed impetus to research in this field. Although progress has been made in alleviating some of the conditions that cause stress corrosion cracking and pitting corrosion, a fundamental understanding of the factors involved in such corrosion is lacking. For example, little is known about the effect of impurities on crack tip propagation and pit growth in high-purity water at high temperatures and pressures. The overall goal of this research is to provide an experimental data base against which theoretical models of aqueous corrosion can be tested over a wide range of temperatures and pressures. To reach this goal, we are undertaking studies that employ coupled spectroscopic and electrochemical measurements, transient electrochemical techniques, and modeling/theoretical calculations. Results during the past year in each aspect of this research are summarized below.

a. Spectroelectrochemical Studies of Aqueous Corrosion

This research involves the combined use of electrochemical and spectroscopic techniques to investigate the corrosion of metals in aqueous media. The electrochemical behavior of nickel in 7×10^{-4} M Na_2SO_4 was studied using cyclic voltammetry and AC impedance techniques. Nickel was found to exhibit both primary and secondary passivity states, which persisted up to about 100°C ; at higher temperatures only active anodic dissolution behavior was observed, with pitting corrosion in evidence above 250°C . The composition of the extremely thin (~ 50 to 200 Å) corrosion film in the region of secondary passivity was determined by laser Raman spectroscopy to correspond to that of "hydrous" NiO_2 . Alternating-current impedance measurements on nickel up to 210°C showed that the polarization resistance (which varies inversely with the corrosion rate) decreases as the time and temperature increase.

Studies of the spectroelectrochemical behavior of nickel in other solution media are in progress. Preliminary results for nickel in 0.1 M Na_3PO_4 and 0.1 M K_2CrO_4 showed that the anions of these solutions are incorporated in the corrosion film formed on the nickel in the potential region of secondary passivity.

Cyclic voltammetry and laser Raman spectroscopic studies are also being performed on iron as a function of pH in phosphate solutions. In alkaline solution of 0.1 M Na_3PO_4 ($\text{pH} = 11.8$), iron was found to passivate both in the presence and absence of dissolved O_2 . The corrosion films, however, appeared to be extremely thin and attempts to obtain Raman spectra were not successful.

In acidic 0.1 M NaH_2PO_4 ($\text{pH} = 4.4$), iron could be passivated at 0.4 V vs. a standard carbon electrode. In aerated solution, a dark gray film was formed, which took on a bluish color when the sample was left in air for long periods. *In situ* Raman spectra of the film showed a band at 954 cm^{-1} , while *ex situ* measurements yielded a strong band at 1010 cm^{-1} . These two bands are both attributed to the PO_4^{3-} group; the difference between the two spectra is believed to be caused by sample oxidation.

Future work will include studies of the corrosion/passivation behavior of chromium, stainless steels, and nickel alloys at high temperature and pressure. Corrosion inhibition by inorganic and organic substances will also be investigated.

b. Electrode Kinetic Studies of Aqueous Corrosion

Research in this area involves the elucidation of the effect of temperature on the kinetics and mechanism of charge transfer reactions. In addition to its importance to high-temperature aqueous corrosion, the issue of charge transfer has a wider significance in electrochemistry. Only a limited number of electrode kinetic studies have ever been carried out above the boiling point of water, even though the temperature dependence of electrode reactions is a central issue in emerging theories of charge transfer. This section contains a description of the experimental effort to measure charge transfer rates as a function of temperature; Sec. VIII.C.1.c discusses the application of advanced theoretical techniques to the study of electron transfer mechanisms.

We chose a simple model reaction to conform with the limitations of the theoretical techniques. This reaction consists of a single charge transfer step and is not complicated by the making/breaking or rearranging of chemical bonds. For the initial studies, the reaction selected was the ferrous/ferric redox process in a noncomplexing medium (perchloric acid) on an inert gold electrode. In the future, these studies will be extended to more complex reactions, such as the reduction of hydrogen ions or water; to more complex surfaces, such as oxides; and finally to metal dissolution reactions that simulate actual corrosion processes.

High-temperature/high-pressure measurements of the kinetics of the ferrous/ferric redox electrode reaction in perchloric acid solutions at a gold electrode surface are in progress. Two series of kinetic measurements were carried out in the temperature range from 25 to 125°C . The anodic Tafel slopes of the reaction were independent of temperature within the error of our measurements and had values of 0.46 ± 0.04 and 0.46 ± 0.02 for the two series. (Results for the first series are shown in Fig. VIII-7.) The actual rates of the reaction were about two to three times higher in the first series than in the second series; similarly, the calculated activation energies were different for the two series, with respective values of 5.7 and 4.6 kcal/mol. The residence time of the electrolyte in the cell was the only experimental variable in the two series. It seems that, with long residence times, an impurity accumulates in the electrolyte and decreases the efficiency of our chloride desorption procedure, resulting in the higher rate constants. This observation has been tied to traces of copper and titanium in the feed water to the cell. We are investigating both removal of the source of these impurities and the effect of copper and titanium on the $\text{Fe}^{2+}/\text{Fe}^{3+}$ electrode reaction.

Fig. VIII-7.

Rate Constants for Ferrous/Ferric
Redox Reaction at 25-125°C

A study was carried out to test the effect of neglect of the double-layer structure on the electrochemical determination of aqueous corrosion rates of metals. Present data-evaluation methods completely ignore the effects of the double-layer structure on the kinetics of the partial electrode reactions comprising the corroding system. Our results show that, while the error caused by neglect of the double layer depends on many parameters, the two dominating factors are the solution concentration and the potential of the corroding metal with respect to the potential of zero charge (pzc). The error was found to be negligible (<10%) if the solution concentration is at least 0.1 molar or the corrosion potential is at least ± 0.25 V from the pzc. The error can be very large (many hundreds or thousands of percents) unless at least one of the above conditions is met, and the polarization curves give no clear indication of the reliability of the measurement. Under these conditions, the electrochemical measurements should be supplemented with other types of corrosion rate determinations, or an appropriate correction should be made if the double-layer parameters are known.

c. Theoretical Studies of Electron Transfer Processes

This research involves the development of microscopic models for electron transfer processes at the electrode-electrolyte interface to facilitate the study of reaction kinetics at electrodes and the mechanism of metallic corrosion in aqueous solutions over a wide range of temperatures. Present charge transfer theories cannot explain the temperature dependence of many heterogeneous charge transfer reactions. The reasons for this include the fact that fundamental aspects of electron transfer associated with thermal activation and solvation changes are not well understood. By coupling recent advances in computer technology, molecular dynamics, and molecular orbital theory, we can now study the kinetics of charge transfer from the metal surface to a solution species and the molecular

structure in the interfacial layer. The ferrous-ferric electron transfer process at a gold electrode was chosen for an initial study aimed at the development of a theoretical model that can readily be compared with experiment. (This work is being conducted in collaboration with researchers at the University of Minnesota.)

During the past year, progress has been made in a number of areas. The work of the prior year on three-body interaction energies for Fe^{2+} and Fe^{3+} interactions with H_2O has been extended to include four-body and many-body effects. While the size of the four-body interaction energy is still significant in the clusters considered, it is smaller and of opposite sign than the three-body interaction energies. In addition, relative stabilities of the clusters from the many-body total are close to those from the two-body empirical potential that is being used in molecular dynamics simulations for electron transfer models. This is illustrated by Fig. VIII-8.

Fig. VIII-8. Binding Energies (E) of $\text{Fe}^{3+}(\text{H}_2\text{O})_n$ as Function of Cluster Size (n). Curves are derived from two-body empirical potentials (filled circles) and *ab initio* calculations on the full clusters (open circles), including many-body (1,2,3,... n) effects.

Potentials for Cu^+ and Cu^{2+} interacting with a water molecule have been derived using a minimal basis set reported by Huzinaga.¹⁴ This basis set had given reasonable results for the Fe^{2+} and Fe^{3+} interactions with water. Calculation of three-body terms indicates that nonadditivity will be important for Cu^{2+} simulations in water. However, for Cu^+ in water, the results indicate that a pair potential should give reasonable simulations of the aqueous ionic system.

¹⁴S. Huzinaga, *Gaussian Basis Sets for Molecular Calculations*, Elsevier-Science, Amsterdam (1984).

2. Research on Molecular Sieve Materials

Recent advances in the synthesis of novel molecular sieve materials have opened new vistas for product-selective catalysis of fuels and chemical feedstocks. This research is focused on studies of the mechanisms of sieve formation in gel media and the catalytic properties of the framework structures produced therefrom.

a. Theoretical Studies of Molecular Sieve Synthesis

The use of organic bases such as tetraalkylammonium hydroxides has greatly enhanced the scope of gel/solution synthesis routes for producing microporous materials such as zeolites.¹⁵ The role of these organic components, however, continues to be a topic of considerable debate. In collaboration with researchers at ANL's Materials Science Division and Intense Pulsed Neutron Source, we have been using molecular orbital theory and incoherent inelastic neutron scattering (INS) spectroscopy to study the torsional frequencies and barriers for tetraalkylammonium ions. The effects of the zeolite framework on the torsional force constant and rotational barrier of tetramethylammonium (TMA) ion have been modeled using *ab initio* molecular orbital theory. In general, interaction with negative sites tends to lower the barrier, while interaction with positive sites tends to raise the barrier. This is consistent with INS results for the torsional frequencies of TMA in a zeolite cage.¹⁶ *Ab initio* and atom-atom potential calculations are also being carried out on the energetics of the conformational rearrangements required for tetrapropylammonium (TPA) ion to template the zeolite ZSM-5.

b. Studies of Catalysis by Molecular Sieve Materials

In this research effort, we seek to develop new understanding of the catalytic activity and product selectivity demonstrated by synthetic molecular sieve cage networks of medium pore size (4 to 6 Å). Diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy is used in conjunction with gas chromatography (GC) to provide detailed information on structure-composition-reactivity relationships for a variety of light hydrocarbon reactions on selected aluminosilicate and aluminophosphate framework systems. Molecular sieve materials studied during the past year have included ZSM-5, offretite, silicon-substituted AlPO-34 (SAPO-34), and cobalt-substituted AlPO-34 (CoAPO-34). Reactivity of H-ZSM-5 and H-offretite was determined by DRIFT/GC with dimethyl ether (DME) as a probe molecule. Although H-offretite exhibits more features than H-ZSM-5 in the O-H stretching region, the application of subtraction procedures to spectra recorded after exposure of each zeolite to DME revealed that the accessible O-H site character of H-offretite is nearly identical to that of H-ZSM-5. This similarity is explained by the fact that all O-H sites of H-ZSM-5 are accessible to, and hence perturbed by, the probe molecule, while certain sets of hydroxyl groups in H-offretite are located in the inaccessibly small hexagonal prisms and cancrinite cages of the H-offretite structure and, hence, are not perturbed by the probe molecule.

¹⁵B. M. Lok, T. R. Cannan, C. A. Messina, *Zeolites* **3**, 282 (1983).

¹⁶T. O. Brun, L. A. Curtiss, L. E. Iton, R. Kleb, J. M. Newsam, R. A. Beyerlein, and D. E. W. Vaughan, *J. Am. Chem. Soc.* **109**, 4118 (1987).

The interaction between light alcohols and the Bronsted acid site of H-ZSM-5 has been investigated using $(\text{CD}_3)_2\text{CHOH}$ as the probe molecule. To augment this work, samples of the cesium- and potassium-substituted forms of H-ZSM-5 (Cs-ZSM-5 and K-ZSM-5) were also investigated. For the reaction of deuterated isopropanol (DIP) on H-ZSM-5 at 150°C , DRIFT spectra showed several features that are indicative of reactivity: loss of Bronsted site intensity, evidence for formation of H_2O (due to dehydration of the alcohol), spreading of the C-H and C-D band envelopes, and appearance of the C-D analogs of protonated framework sites (indicating that C-D bond breaking is occurring). The DRIFT spectra obtained after exposure of Cs-ZSM-5 and K-ZSM-5 to DIP at 150°C showed none of the above features. Instead, these spectra revealed that the Bronsted site was populated with protons cleaved from the OH group of DIP, and that the isopropoxide anion was present in the zeolite pores and channels. In essence, the DIP reacted with the alkali-substituted ZSM-5 to produce the acid form H-ZSM-5, with Cs^+ or K^+ and $(\text{CD}_3)_2\text{CHO}^-$ ions in the zeolite framework and with no evidence of hydrocarbon products. This important result provides evidence that metal cations can inhibit the catalytic process in H-ZSM-5 pores and channels even when the Bronsted site is occupied by protons and reactive organic fragments are present.

The catalytic properties of AlPO-34 structures synthesized with silicon (SAPO-34), cobalt (CoAPO-34), and mixtures of the two (CoAPSO-34) in framework positions are being studied by a combination of spectroscopic and chromatographic techniques (in collaboration with ANL's Materials Science Division). The electronic structure of cobalt in CoAPO-34 and CoAPSO-34 has been probed by electronic absorption spectroscopy. We found some cobalt present as Co^{2+} in a tetrahedrally coordinated crystal field, as would be expected for Co^{2+} ions occupying framework positions. Diffuse reflectance infrared spectroscopy is being used to study (1) the creation of acid sites during calcining of the templated form of each molecular sieve and (2) the C-H bands of organic fragments produced following exposure of the calcined 34-series structures to selected light alcohols ($\text{C}_{\leq 5}$). Analysis with DRIFT/GC revealed variations in the C-H vibrations that are correlated with the type of reactant, rate of reaction, and light olefin product mix. Connections were also found between acid site character and the isomeric species that are formed.

Future work will focus on gaining an understanding of the variations in acid site character exhibited by divalent- and tetravalent-metal-substituted AlPO-34s with the objective of unraveling the product-selectivity properties of this novel structure.

3. Research on High- T_c Materials

The discovery that certain types of perovskite crystal structures have exceptionally high T_c has stimulated much interest and spurred a variety of new research activities at ANL. In close collaboration with ANL's Materials Science Division, we have been engaged in the following activities: (1) measurements and analysis of the vibrational density of states of high- T_c materials and related compounds; (2) *ab initio* and semiempirical molecular orbital studies of the electronic and vibrational properties of $(\text{Cu-O})_n$ clusters similar to those found in high- T_c structures; (3) synthesis of high- T_c phases by oxidation of metallic precursors (alloys, sintered metal mixtures, etc.); and (4) X-ray diffraction studies of single-crystal high- T_c phases. Progress in and future plans for work in each of the above areas are summarized below.

a. Phonon Density of States of Superconducting Phases

Infrared, Raman, and group theoretical methods are being used to investigate the vibrational density of states of a variety of perovskite-type structures, including ones that have exceptionally high T_c . The predicted number of phonons (at zero wave vector, $k = 0$) and their activities in the Raman and infrared spectra were compared with experimental observations. The results of these comparisons identified the frequency range of phonons having the type of symmetry and eigenvector that could contribute to the high T_c . Reorganization of the vibrational density of states associated with phase transformations, e.g., orthorhombic to tetragonal, was correlated with observed changes in the infrared and Raman spectra of the respective phases. Several of the $k = 0$ phonons of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ have been observed and unambiguously assigned to appropriate symmetry species of the corresponding space group. A number of phonons that are sensitive to oxygen stoichiometry and temperature have been identified. Several recurring bands, particularly ones appearing in Raman spectra, were found to be due to impurity phases such as BaCuO_2 , Y_2BaCuO_5 , and $\text{Ba}(\text{OH})_2$. Some progress has been made in modeling the vibrational density of states of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ by use of an approximate valence bond-type force field.

b. Theoretical Studies of Superconductivity

Molecular orbital calculations are being carried out on copper oxide clusters representing the new high- T_c superconducting materials $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. From these calculations, we have been able to deduce the likely valence states of the different Cu sites in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The Cu's in the CuO_3 "chains" have a valence of 2.5-3.0, while the Cu's in the CuO_2 dimpled planes have a valence of 2.0-2.5. These results are supported by bond valence arguments. The calculations also reveal that the presence of mixed valence states in the CuO_3 "chains" and the CuO_2 planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ give rise to charge fluctuations from oxygen displacements in the breathing vibrational mode. The same holds true for the CuO_2 planes of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$. This may be related to the mechanism for superconductivity in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ materials. Finally, the calculations indicate that the presence of half-divalent and half-trivalent Cu's in the "chains" results in a double minimum potential well for oxygen displacement in the "chains." This may give rise to an instability around an oxygen stoichiometry of 6.75. Based on these results, we have postulated a phase change occurring at 6.75, which implies that the superconducting phase for $T_c = 94$ K is characterized by an oxygen stoichiometry near 7.0. There is some experimental evidence to support this idea.

c. Preparation of Perovskite Surface Layers

Attempts are being made to fabricate high- T_c superconducting ceramic materials in bulk and coating form by controlled oxidation of crystalline, glassy, or sintered metallic phases consisting of the required constituent metals in the proper stoichiometric ratios. In one experiment, a stoichiometric melt containing 62 at.% La-5 at.% Sr-33 at.% Cu (the metallic composition of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$) was quenched in an inert atmosphere. A portion of the quenched metal phase was then oxidized in air at 800°C for a 24-h period. A second melt containing 5 at.% La and 0.5 at.% Sr (balance Cu) was also prepared, quenched, and oxidized in a manner similar to that used for the stoichiometric melt. The experiment carried out on the 62 at.% La alloy produced

oxides which powdered easily, whereas the oxide that formed on the surface of the Cu-rich alloy appeared to be an adherent film. Both oxide phases showed X-ray diffraction lines that correspond to the orthorhombic perovskite phase of $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$. Unfortunately, because of the similarity of the orthorhombic and tetragonal perovskite diffraction patterns, we could not determine whether the tetragonal phase was also present as a minor constituent. Scanning electron microscopy (SEM) and backscatter electron imaging (BEI) revealed multiple phases in both the alloys and the corresponding oxides. Energy dispersive X-ray (EDX) analysis confirmed variations in composition in the various phases. An important finding was the formation of an adherent oxide layer in the case of the Cu-rich alloy. The BEI analysis clearly showed an $\sim 80\text{-}\mu\text{m}$ thick oxide layer attached to this alloy. When layers thicker than $200\text{ }\mu\text{m}$ were allowed to form, they tended to break away from the metal.

Based on results obtained thus far, we believe that superconducting films can be fabricated on metal precursors by careful adjustment of metal phase composition and morphology, oxygen partial pressure, reaction time, and temperature. The possibility of preparing other types of compositions and/or structures from appropriate alloys (e.g., Y-Ba-Cu) with oxygen or other oxidants (e.g., S, Cl_2 , F_2) also exists and is currently being explored.

d. X-ray Diffraction Studies of Single Crystal High- T_c Phases

A single crystal of $\text{Ba}_2\text{YCu}_3\text{O}_{6.8}$ has been examined by X-ray diffraction to probe morphological characteristics which might be connected with high- T_c superconductivity. The results were as follows: (1) irregular crystal growth appears to occur from dislocations or impurities, which prevent uniformity of the unit cell over all regions of the crystal; (2) bulk twinning appears to be present; (3) the crystal contained many inclusions of small crystallites, some random and some oriented; and (4) very small crystals, unprotected from the atmosphere, can break into smaller fragments. Future experiments will involve the examination of high-quality crystals that have been subjected to thermal shock. The effect of humidity on the crystals will also be studied by X-ray techniques.

D. *Thermochemistry*

In the United States, the chosen system for disposal of nuclear waste is deep burial in a repository in a suitable geological formation. In the selection of a site for the high-level nuclear waste repository, host rock mineralogy is one of the most important factors in determining the limits of potential radionuclide transport.

The primary mineralogy has a direct effect on radionuclide transport at a distance from the repository. In addition, since all materials in the vicinity of the emplaced waste (both host rock and engineered backfill) will be subject to the resulting temperature excursion and the effects of groundwater, a complex set of reactions will occur, producing a secondary mineralogy. These alteration products can affect radionuclide transport in a number of ways (for example, through effects on sorption, rheology, and temperature profile).

To demonstrate the reliability of the disposal system, quantitative predictions of repository behavior must be available. However, because of the great time span and complexities involved in these systems, such predictions lie beyond the domain of direct experimentation, and mathematical modeling must be used.

The successful development and validation of appropriate models depend greatly on the accuracy and precision of thermodynamic information available for the mineral assemblages involved. Our thermochemical work has been directed toward addressing these needs for the Nevada Nuclear Waste Site Investigations Project (see Sec. VI. D).

1. Thermodynamics of Uranium Compounds: Schoepite and Dehydrated Schoepites

When reacted with H_2O , amorphous UO_3 yields crystalline substances that have variously been referred to as hydrates, hydroxides, and, because of their amphoteric properties, acids; most modern structural evidence indicates that they should be regarded as hydrated or anhydrous hydroxides, for example, $UO_2(OH)_2 \cdot H_2O$.¹⁷ However, for the sake of compactness, we shall use the generic formula $UO_3 \cdot xH_2O$. Three compounds in (uranium trioxide + water) are quite well defined: schoepite, with $x = 2$; dehydrated schoepite, with $1 > x > 0.75$; and a composition with $x \approx 0.5$. With schoepite as starting material, the other compounds are formed progressively with loss of water.

Our current technical interest in schoepite, $UO_3 \cdot 2H_2O$, arises from modeling studies connected with the burial of nuclear waste. Specifically, the question being addressed is the fate of dissolved uranium in contact with concrete at ambient temperatures. Under such conditions, and on the basis of existing thermodynamic values, schoepite is calculated to be the phase that would limit the uranium activity in solution.¹⁸

In the present research, we used high-precision calorimetry to obtain the following molar thermodynamic properties of a single specimen of pure schoepite: the standard enthalpy of formation ($\Delta_f H_m^\circ$) at $T' = 298.15$ K; the low-temperature heat capacity ($C_{p,m}^\circ$) and, by derivation, the standard entropy (S_m°); and the enthalpy increments relative to T' , up to the limit of stability of the material. The following values were obtained for schoepite at T' : $\Delta_f H_m^\circ = -(1825.4 \pm 2.1)$ kJ mol⁻¹, $C_{p,m}^\circ = (172.07 \pm 0.34)$ J K⁻¹ mol⁻¹, and $S_m^\circ = (188.54 \pm 0.38)$ J K⁻¹ mol⁻¹. The enthalpy increments are given by the equation ($T' < T < 400$ K):

$$H_m^\circ(T) - H_m^\circ(T') = -38209.0 + 84.2375 T + 0.1472958 T^2 \quad (8)$$

where the enthalpy is J mol⁻¹ and the temperature is degrees Kelvin. The heat capacity is given by

$$C_{p,m}^\circ(T) = 84.238 + 0.294592 T \quad (9)$$

where the heat capacity is J K⁻¹ mol⁻¹ and the temperature is degrees Kelvin. For $UO_3 \cdot 0.9H_2O$ at T' , we also obtained $\Delta_f H_m^\circ = -(1506.3 \pm 2.1)$ kJ mol⁻¹, and estimated $S_m^\circ = (125 \pm 2)$ J K⁻¹ mol⁻¹.

¹⁷E. H. P. Cordfunke, *The Chemistry of Uranium*, Elsevier-Science, Amsterdam, pp. 109-112 (1969).

¹⁸T. J. Wolery, D. J. Isherwood, K. J. Jackson, J. M. Delany, and I. Puigdomenech, *EQS/6: Status and Applications*, Lawrence Livermore National Laboratory Report UCRL-91884 (1984).

One of the principal uses to which the present thermodynamic information is expected to be put is the calculation of solubilities of uranium-containing solids, and the modeling of aqueous-phase equilibria in various nuclear-repository scenarios. For such applications, standard molar Gibbs energies of formation ($\Delta_f G_m^\circ$) and, by implication, $\Delta_f H_m^\circ$ and S_m° are required for the chemical species of interest. Table VIII-1 lists these values for compounds in (uranium trioxide + water). Earlier we determined a complete set of thermodynamic quantities for schoepite.¹⁹ However, there are no experimental values as yet for $S_m^\circ(\text{UO}_3 \cdot x\text{H}_2\text{O}, T')$ with $x < 2$, and so those quantities have had to be estimated.

For the decomposition reaction

we use the relation:

$$\log_{10}(p/p^\circ) = -2568.9 T^{-1} + 6.843 \quad (11)$$

from which it follows that $\Delta_r S_m^\circ = 144 \text{ J K}^{-1} \text{ mol}^{-1}$. Here p denotes the equilibrium decomposition pressure, and p° is the standard pressure of 101.325 kPa. We have also used this relation to estimate $\Delta_r S_m^\circ$ for the dehydration reactions of schoepite to $\text{UO}_3 \cdot \text{H}_2\text{O}$ and $\text{UO}_3 \cdot 0.85\text{H}_2\text{O}$. For the generic dehydration,

our calculations and estimates are consistent with $\Delta_r S_m^\circ/(2 - y) = (133 \pm 3) \text{ J K}^{-1} \text{ mol}^{-1}$, and we use this relation to estimate $\Delta_r S_m^\circ$ for the dehydration of $\text{UO}_3 \cdot \text{H}_2\text{O}$ to $\text{UO}_3 \cdot 0.648\text{H}_2\text{O}$ and $\text{UO}_3 \cdot 0.393\text{H}_2\text{O}$.

Table VIII-1. Thermodynamic Values for $\text{UO}_3 \cdot x\text{H}_2\text{O}(\text{cr})$
($T' = 298.15 \text{ K}$, $p^\circ = 101.325 \text{ kPa}$)

	$\Delta_f H_m^\circ$, kJ mol ⁻¹	S_m° , J K ⁻¹ mol ⁻¹	$\Delta_f G_m^\circ$, kJ mol ⁻¹
$\text{UO}_3 \cdot 2\text{H}_2\text{O}$	-1826.4 ± 2.1	188.5 ± 0.4	-1637.0 ± 1.7
$\text{UO}_3 \cdot \text{H}_2\text{O}$	-1533.2 ± 2.0	$137 \pm 2^*$	-1397.9 ± 2.5
$\text{UO}_3 \cdot 0.9\text{H}_2\text{O}$	-1506.3 ± 2.1	$125 \pm 2^*$	-1374.4 ± 2.6
$\text{UO}_3 \cdot 0.85\text{H}_2\text{O}$	-1491.4 ± 2.0	$123 \pm 2^*$	-1362.3 ± 2.5
$\text{UO}_3 \cdot 0.648\text{H}_2\text{O}$	-1424.6 ± 2.1	$118 \pm 2^*$	-1308.1 ± 2.6
$\text{UO}_3 \cdot 0.393\text{H}_2\text{O}$	-1347.9 ± 2.1	$103 \pm 2^*$	-1244.6 ± 2.6

*Estimated uncertainty.

¹⁹I. R. Tasker, P. A. G. O'Hare, B. M. Lewis, G. K. Johnson, and E. H. P. Cordfunke, Can. J. Chem., in press.

The $\Delta_r S_m^\circ$ values derived in this way are shown in Table VIII-2, along with the corresponding $\Delta_r G_m^\circ$, and (p/p°) . Now, with $\Delta_r S_m^\circ$, $S_m^\circ(\text{UO}_3 \cdot 2\text{H}_2\text{O}, \text{cr}, T') = (188.54 \pm 0.38) \text{ J K}^{-1} \text{ mol}^{-1}$, and $S_m^\circ(\text{H}_2\text{O}, \text{g}, T') = (188.72 \pm 0.04) \text{ J K}^{-1} \text{ mol}^{-1}$,²⁰ the S_m° values given in Table VIII-1 are calculated. Combination of those values with S_m° for U,²¹ H₂,²⁰ and O₂²⁰ and with $\Delta_f H_m^\circ$ yields $\Delta_r G_m^\circ$ (Table VIII-1). The salient features of the thermodynamic quantities in Table VIII-2 appear to be as follows. For the dehydration of schoepite according to Eq. 12, $\Delta_r H_m^\circ/(2 - y)$ is fairly reproducible at 49 to 51 kJ mol⁻¹, and the equilibrium pressures are relatively high, with $(p/p^\circ) + 1$ at 373.15 K consistent with experimental observation. We also determined the solubilities in acid of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ and $\text{UO}_3 \cdot 0.9\text{H}_2\text{O}$ as a function of temperature (Table VIII-3).

Table VIII-2. Thermodynamic Values for Decomposition Reactions of Solid $\text{UO}_3 \cdot x\text{H}_2\text{O}$ ($T' = 298.15 \text{ K}$, $p^\circ = 101.325 \text{ kPa}$)

Reaction	$\Delta_r H_m^\circ(T')$ kJ mol ⁻¹	$\Delta_r S_m^\circ(T')$ J K ⁻¹ mol ⁻¹	$\Delta_r G_m^\circ(T')$ kJ mol ⁻¹	(p/p°)	
				298.15 K	373.15 K
$\text{UO}_3 \cdot 2\text{H}_2\text{O} = \text{UO}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}(\text{g})$	51.4	137	10.6	1.4×10^{-2}	0.91
$\text{UO}_3 \cdot 2\text{H}_2\text{O} = \text{UO}_3 \cdot 0.9\text{H}_2\text{O} + 1.1\text{H}_2\text{O}(\text{g})$	54.1	144	11.2	1.7×10^{-2}	0.90
$\text{UO}_3 \cdot 2\text{H}_2\text{O} = \text{UO}_3 \cdot 0.85\text{H}_2\text{O} + 1.15\text{H}_2\text{O}(\text{g})$	56.9	152	11.6	1.7×10^{-2}	0.95
$\text{UO}_3 \cdot \text{H}_2\text{O} = \text{UO}_3 \cdot 0.648\text{H}_2\text{O} + 0.352\text{H}_2\text{O}(\text{g})$	23.5	45	10.1	1.0×10^{-5}	2.1×10^{-3}
$\text{UO}_3 \cdot \text{H}_2\text{O} = \text{UO}_3 \cdot 0.393\text{H}_2\text{O} + 0.607\text{H}_2\text{O}(\text{g})$	38.5	80	14.6	5.9×10^{-5}	1.0×10^{-2}
$\text{UO}_3 \cdot \text{H}_2\text{O} = \text{UO}_3(\text{cr}, \gamma) + \text{H}_2\text{O}(\text{g})$	67.6	148	23.5	7.7×10^{-5}	1.9×10^{-2}
$\text{UO}_3 \cdot \text{H}_2\text{O} = \text{UO}_3(\alpha, \beta) + \text{H}_2\text{O}(\text{g})$	71.1	148	27.0	1.9×10^{-5}	6.0×10^{-3}
$\text{UO}_3 \cdot \text{H}_2\text{O} = \text{UO}_3(\text{am}) + \text{H}_2\text{O}(\text{g})$	83.1				

2. Thermochemistry of Zeolites and Silicates

We determined the thermodynamic properties of the silicate minerals clinoptilolite, dehydrated clinoptilolite, tobermorite, and four synthetic faujasites.

Clinoptilolite is a mineral of major importance to nuclear waste storage investigations, particularly for the Nevada site. It is a silica- and alkali-rich member of the heulandite group. This group of minerals has received extensive investigation owing to their excellent sorptive properties for many radionuclide cations, excellent mechanical properties, and apparently good thermal stability. An important factor in considering the Yucca Mountain site in Nevada as a possible location for the repository is that the strata being examined for the repository horizon overlie vitric to zeolitized nonwelded tuffs containing significant quantities of clinoptilolite (with minor quantities of heulandite), which could provide an important natural barrier to radionuclide migration.

²⁰CODATA recommended key values, J. Chem. Thermodyn. 10, 903 (1978).

²¹F. L. Oetting, M. H. Rand, and R. J. Ackermann, *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part 1, "The Actinide Elements," International Atomic Energy Agency, Vienna (1976).

Table VIII-3. Thermodynamic Values for Dissolution of $\text{UO}_3 \cdot x\text{H}_2\text{O}$ ($p^\circ = 101.325 \text{ kPa}$)

$\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{cr}) + 2\text{H}^+(\text{aq}) = \text{UO}_2^{2+}(\text{aq}) + 3\text{H}_2\text{O}(\text{aq})$								
T, K	298.15	300	320	340	360	380	400	423.15
$\Delta_r G_m^\circ(T)$, kJ mol ⁻¹	-27.3	-27.2	-25.7	-24.3	-23.0	-21.7	-20.5	-19.2
$\log_{10} K^\circ(T)^a$	4.78	4.74	4.19	3.73	3.33	2.98	2.68	2.37
$\text{UO}_3 \cdot 0.9\text{H}_2\text{O}(\text{cr}) + 2\text{H}^+(\text{aq}) = \text{UO}_2^{2+}(\text{aq}) + 1.9\text{H}_2\text{O}(\text{aq})$								
T, K	298.15	350	400	450	500	550	600	
$\Delta_r G_m^\circ(T)$, kJ mol ⁻¹	-29.0	-24.6	-20.6	-16.7	-13.0	-9.4	-5.9	
$\log_{10} K^\circ(T)^a$	5.08	3.67	2.69	1.94	1.36	0.89	0.51	

^a K° is the equilibrium constant.

The clinoptilolite used in this investigation was a natural sample from the Succor Creek area of Malheur County, Oregon. Its formula, based on extensive chemical analyses, was $(\text{Sr}_{0.036}\text{Mg}_{0.124}\text{Ca}_{0.761}\text{Mn}_{0.002}\text{Ba}_{0.062}\text{K}_{0.543}\text{Na}_{0.954})(\text{Al}_{3.450}\text{Fe}_{0.017})\text{Si}_{14.533}\text{O}_{36.000} \cdot 10.922\text{H}_2\text{O}$. Before the analyses and experiments, the mineral was equilibrated with an atmosphere of 50% relative humidity, and corrections were subsequently made for the vaporization of the water. The heat capacities in the range 5 to 350 K were measured using our low-temperature adiabatic calorimeter.

The enthalpy of reaction of clinoptilolite with 24.4 mass % hydrofluoric acid was determined by solution calorimetry. We also performed auxiliary measurements of the enthalpies of reaction with $\text{HF}(\text{aq})$ of $\text{Al}(\text{OH})_3$, SiO_2 , NaF , and KF , which were needed to complete the Hess cycle. A portion of the calorimetric specimen was dehydrated, and the enthalpy of formation of the dehydrated clinoptilolite was determined. The enthalpy increments $[H_m^\circ(T) - H_m^\circ(T')]$ of clinoptilolite to 500 K and dehydrated clinoptilolite to 750 K were measured using the drop-calorimetric system. The following equations were derived from the experimental results by the method of least squares:

$$H_m^\circ(T) - H_m^\circ(T') = -257056.1 + 50.155 T + 3.182229 T^2 - 1.538538 \times 10^{-3} T^3 \quad (T' < T < 500 \text{ K}) \quad (13)$$

for clinoptilolite and

$$H_m^\circ(T) - H_m^\circ(T') = -92532.6 - 478.070 T + 3.455199 T^2 - 3.010290 \times 10^{-3} T^3 + 9.7545077 \times 10^{-7} T^4 \quad (T' < T < 750 \text{ K}) \quad (14)$$

for dehydrated clinoptilolite. The complete thermodynamic properties of clinoptilolite from 5 to 500 K and a partial list of thermodynamic properties of dehydrated clinoptilolite from T' to 750 K have been derived from the present measurements.

Similar calorimetric measurements have been completed on a sample of synthetic "11Å" tobermorite, a phyllic calcium silicate hydrate having the tentative composition $\text{Ca}_{4.389}\text{Si}_{6.252}(\text{OH})_{1.784}\text{O}_{16}\cdot 5.2866\text{H}_2\text{O}$. In addition to being a member of the suite of possible hydrothermal alteration products, tobermorite is an important constituent of cements that may be abundant in the sealed repository, and as such may influence the composition of final alteration products through its effect on groundwater composition. We are currently measuring the vapor pressure of water over tobermorite as a function of temperature in order to make corrections to the heat capacities and enthalpy increments.

One of the recurrent problems in the application of thermodynamic information to practical geochemical problems involves variations in the compositions of zeolites. The main criterion for choice of sample is purity of material; as a result, the zeolite samples that are studied are not always representative of site-relevant assemblages. Moreover, we must anticipate the possibility of wide variations in the composition of secondary minerals, which will depend upon the varying chemistry of the groundwater. Examples of compositional variability in zeolites are differences in the Si-to-Al ratios, in the substituted cations (i.e., Ca^{2+} for 2Na^+), and in the nature and amount of the zeolitic water.

We began by determining $\Delta_f H_m^\circ$ for the following four faujasites (in the hydrated and dehydrated forms): $\text{Na}_{0.011}\text{Al}_{0.011}\text{Si}_{7.987}\text{O}_{16}\cdot 1.795\text{H}_2\text{O}$ (I), $\text{Na}_{2.803}\text{Al}_{2.803}\text{Si}_{5.917}\text{O}_{16}\cdot 5.835\text{H}_2\text{O}$ (II), $\text{Na}_{2.320}\text{Al}_{2.320}\text{Si}_{5.680}\text{O}_{16}\cdot 9.885\text{H}_2\text{O}$ (III), and $\text{Na}_{3.583}\text{Al}_{3.583}\text{Si}_{4.417}\text{O}_{16}\cdot 9.202\text{H}_2\text{O}$ (IV). The average binding energy of the zeolitic H_2O in these faujasites is (7.20 ± 5.4) , (17.51 ± 1.42) , (18.35 ± 0.85) , and (24.68 ± 0.99) kJ mol^{-1} . For comparison, the average binding energy is 40.9 kJ mol^{-1} in analcime, 29.7 kJ mol^{-1} in mordenite, and, as calculated from the results given above, $23.4 \pm 1.7 \text{ kJ mol}^{-1}$ in clinoptilolite. We see that the binding energy of water is highly variable, even within a family of structurally similar zeolites; therefore, at our present level of knowledge, a simple means of describing the effects on $\Delta_f H_m^\circ$ of varying water composition is beyond reach. This problem warrants more investigation since there will be varying levels of water saturation in the Nevada repository environment, and moisture absorbed by zeolite-bearing rocks affects their grain density, a parameter important in site evaluation. For the present time, we will concern ourselves only with the anhydrous forms in trying to answer the other questions of the effect of compositional variation on thermodynamic properties.

We may now address the earlier question: what influence does the variation of the Si-to-Al ratio have on the basic thermodynamic properties of zeolites? If we consider the four anhydrous faujasites to be composed of NaAlO_2 and SiO_2 units, we can show that the enthalpy of formation is best represented by the equation:

$$\Delta_f H_m^\circ (\text{Na}_x\text{Al}_x\text{Si}_y\text{O}_{16}) = -1159.6x - 902.0y \quad (15)$$

To test the validity of this equation, we have used it to calculate the enthalpies of formation of the four faujasites as well as those of the anhydrous forms of analcime, mordenite, and clinoptilolite. The differences between calculated and

measured values for the faujasites are 0.036% for [I], 0.083% for [II], -0.18% for [III], and 0.064% for [IV]. In addition, the differences are -0.54% for clinoptilolite, -0.57% for analcime, and 0.12% for mordenite. Thus the average deviation for the four faujasites, on which Eq. 15 is based, is 0.09% and it is 0.41% for the other three minerals. The conclusion we reach is that an expression such as Eq. 15 probably cannot be used to predict enthalpies of formation with any degree of reliability. However, when used to calculate the effect on $\Delta_f H_m^\circ$ of small changes in Si-to-Al ratios, the equation will suffice.

3. Thermodynamics of "High-Tech" Materials

Thermodynamic properties are being determined for "high-tech" materials that have uses in electronics, tribology, corrosion, and catalysis, as well as thin-film, battery, and other technologies. The measurement technique used is, in general, fluorine-combustion calorimetry. We shall briefly describe recent studies of vanadium monosulfide, tungsten diselenide, and black phosphorus.

Vanadium monosulfide is used as a catalyst and plays an important role in the mechanical and other properties of stainless steels. The standard molar enthalpy of formation $\Delta_f H_m^\circ(\text{VS}_{1.043})$ determined by us was found to be $-(230.3 \pm 2.2) \text{ kJ mol}^{-1}$, which differs by as much as 60 kJ mol^{-1} from earlier high-temperature results. Part, but by no means all, of this large disagreement is attributed to the use by previous investigators of erroneous high-temperature thermodynamic properties for vanadium monosulfide.

The importance of WSe_2 as a high-temperature lubricant, and the chaotic state of the published thermodynamic properties of this compound²² prompted the present study. Our value for $\Delta_f H_m^\circ(\text{WSe}_2)$ very strongly suggests that the high-temperature vaporization of the selenide does not lead to the exclusive formation of $\text{Se}_2(\text{g})$, as many investigators have stated, nor $\text{Se}(\text{g})$, as others have suggested. A careful, systematic high-temperature study of $(\text{W} + \text{Se})$ is highly desirable.

The energy of combustion in F_2 of the semiconductor black phosphorus, combined with similar earlier measurements²³ on α -white phosphorus, gave a value of $-(21.2 \pm 2.1) \text{ kJ mol}^{-1}$ for the enthalpy of transition of the α -white to black allotropes of phosphorus. This research also indicates that the black allotrope is the most stable form of phosphorus, at least at T' and atmospheric pressure.

4. Preliminary Calorimetric Studies of Superconducting Mixed Oxides

The objective of this work is to determine $\Delta_f G_m^\circ$ as a function of temperature for a number of superconducting and related phases. The thermodynamic work will involve, at a minimum, measurements of $\Delta_f H_m^\circ(T')$ by solution calorimetry and of enthalpy increments by drop calorimetry. The $\Delta_f G_m^\circ(T)$ values are expected to be of particular usefulness in connection with fabrication procedures for the superconducting materials. A promising technique has been devised for the solution-calorimetric studies. These measurements will be started as soon as well-characterized materials become available. These studies are being carried out in collaboration with the Materials and Components Technology Division.

²²P. A. G. O'Hare, J. Chem. Thermodyn. 19, 675 (1987).

²³P. A. G. O'Hare and W. N. Hubbard, Trans. Faraday Soc. 62, 2709 (1966).

E. *Geochemistry of Natural Hydrothermal Systems*

The objective of this project is to gain a better understanding of the geochemical processes involved in water/rock interactions that occur in active hydrothermal systems in the Earth's crust. The approach being taken is to investigate specific problems through detailed chemical and isotopic analyses of rock, mineral, water, and gas sampled from natural hydrothermal systems. These data are interpreted in terms of the processes governing rock alteration and element redistribution in hydrothermal systems. We are investigating the rates and mechanisms of element redistribution, the time scale of rock alteration and element redistribution, water/rock ratios, and the relations between hydrothermal activity and local tectonomagmatic events. Potential applications of this work are in nuclear waste isolation, geothermal energy exploration and development, and mineral exploration. Highlights of the progress during 1987 are described.

1. Uranium-Series Disequilibrium Studies

The extent of radioactive disequilibrium among members of the ^{238}U decay series can be exploited for many applications in the earth and environmental sciences. We have been investigating the redistribution of actinides and the time scale of hydrothermal activity with U-series methods in several active hydrothermal systems that are under study as part of the Continental Scientific Drilling Program. These systems are located at Yellowstone (Wyoming), Valles (New Mexico), and Long Valley (California).

During 1987, we collected large-volume thermal water samples from 13 hot springs and geysers in Yellowstone National Park for analysis of Ra, Th, and U isotopes. These analyses are being performed to investigate the geochemical behavior of these isotopes, as well as their potential applications as tracers and as indicators of groundwater flow rates, in active hydrothermal systems. Large-volume water samples from the VC-2A drill hole (located in Valles Caldera, New Mexico) were also obtained for this purpose. Fresh travertine from active travertine-depositing springs at Yellowstone was sampled to investigate the applicability of the Ra/Th dating method for travertine; these results will be analyzed in conjunction with our previous results for Th/U studies of travertine from the Y-10 drill core in Yellowstone. The Ra content of the previously studied travertine samples is also being determined. In addition, new samples of hydrothermal vein minerals were obtained from the Hoho (Japan) and Platanares (Honduras) geothermal systems, for collaborative Th/U geochronologic studies with the Japan Geological Survey and Los Alamos National Laboratory, respectively. The components of an α -spectrometry system to be devoted to geoscience applications were purchased this year.

2. Fluid Inclusion Analyses

A new technique was developed (in collaboration with scientists at the University of California, Berkeley) for microanalysis of fluid inclusions trapped in minerals. Noble gases are released from pre-selected fluid inclusions in polished mineral chips with a laser and analyzed in a high-sensitivity noble gas isotope ratio mass spectrometer. Before analysis, the mineral samples are subjected to neutron irradiation to produce isotopes of Ar, Kr, and Xe from selected elements such as K, Ca, Cl, Ba, Br, U, and I, which can then be analyzed together with the naturally occurring gases in the same inclusions.

Simultaneous analysis of noble gases (Ar, Kr, and Xe) and halogens (Cl, Br, and I) in fluid inclusions could greatly increase our ability to resolve questions about past fluid reservoirs and their interactions in ancient hydrothermal systems. Ratios among elements (such as Xe/Ar, Kr/Ar, Br/Cl, I/Cl, and Ar/Cl) may be used to determine likely fluid sources and to distinguish among processes such as fluid mixing or boiling. Other ratios (such as $^{40}\text{Ar}/^{36}\text{Ar}$, K/Ca, and Ba/Ca) may be used as indicators of fluid-rock interactions. Relative abundances of noble gases and halogens, distinct from those of likely contaminants, were measured in 10^{-10} to 10^{-9} L of fluid inclusion water. Preliminary data from irradiated CO_2 -rich fluid inclusions in vein quartz (110 million years old) from the Sierra Nevada indicate that the trapped fluids contain excess radiogenic ^{40}Ar , which could not have been produced by *in situ* decay of ^{40}K . The $^{40}\text{Ar}/^{39}\text{Ar}$ isochron lines in Fig. VIII-9a indicate the effects of *in situ* ^{40}K decay. The results also indicate that the $^{40}\text{Ar}/^{36}\text{Ar}$ ratios of the fluid inclusions probably have not changed significantly since they were trapped in the quartz about 110 million years ago. Figure VIII-9b indicates that the K/Cl mole ratios of the fluid inclusions apparently were variable, but the average values are consistent with independent determinations based on mineral equilibria and analysis of salt extracts.

Fig. VIII-9. Argon Isotope Ratios in Irradiated, Laser-Decreepitated Vein Quartz from Alleghany, California: (a) $^{40}\text{Ar}/^{36}\text{Ar}$ versus $^{39}\text{Ar}/^{36}\text{Ar}$ and (b) $^{39}\text{Ar}/^{36}\text{Ar}$ versus $^{38}\text{Ar}/^{36}\text{Ar}$. The x's are for inclusion-free quartz. Other symbols (circles, squares, etc.) are fluid-inclusion data for different samples. Crosses indicate error bars. The abbreviation "ma" represents million annum.

The fluid inclusions have Br/Cl ratios similar to those of seawater and most geothermal fluids, but they have much higher I/Cl ratios (~1000 times that of seawater). The fluid inclusions have krypton isotope ratios, xenon isotope

ratios, and Kr/Ar ratios similar to those of air and most analyzed groundwaters, but they appear to be anomalously enriched in xenon. These data seem to support the hypothesis that surface-derived (meteoric) water participated in medium-grade metamorphic reactions at depths >5 km, where they acquired CO₂ and then carbonated rocks and precipitated precious metals as they ascended deep fault zones. Excess quantities of ⁴⁰Ar, I, and Xe could have been acquired from various rocks (including marine sediments) along the fluid flow paths. Significant variations in the observed ratios of halogens and noble gases in the fluid inclusions within and between samples suggest that mixing and/or vapor phase separation occurred, but more detailed studies are needed to interpret these variations.

To refine the microanalysis technique quantitatively, we have prepared synthetic fluid inclusions (in collaboration with scientists at the University of Chicago) containing salt solutions with known compositions. Synthetic inclusions are made by annealing fractures in clean quartz crystals in a supercritical aqueous solution. These crystals will be processed along with natural samples as standards.

Other types of minerals from a variety of hydrothermal environments are being prepared for analysis. We have entered an agreement to begin analyzing 20 million-year-old fluid inclusions from Creede, Colorado, one of the primary targets of the Continental Scientific Drilling Program.

3. Relation Between Hydrothermal Activity and Volcanism

The hydrothermal system of the Nevado del Ruiz volcano (Colombia) has been under investigation since its catastrophic eruption in November 1985. Our study of the hydrothermal activity at Nevado del Ruiz is being conducted in collaboration with colleagues from Louisiana State University and from several Colombian organizations. In this report period, the sulfur isotope ratio was determined for various types of volcanic and hydrothermal sulfur species, including gaseous SO₂ from the volcanic vapor plume and dissolved SO₄²⁻ from acidic hot springs on the slopes of the volcano. The isotopic data suggest that the vapor plume contains SO₂ that emanates from a body of magma beneath the volcano; the dissolved SO₄²⁻ in the acidic hot springs probably forms through disproportionation of magmatic SO₂ by reaction with water within the volcanic hydrothermal system. This interpretation for the origin of the dissolved SO₄²⁻ implies that the acidity of the hot springs is related directly to the emission of magmatic SO₂. A direct magmatic origin for the SO₂ emission from the volcano is consistent with the high ³He/⁴He ratio measured in the fumaroles and acidic hot springs on the volcano.

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 analytical chemistry support 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 handles a wide range of analytical problems, from routine standard analyses to unique problems that require significant development of methods and techniques.

The ACL is administratively within the CMT Division, the principal user, but provides technical support for all the technical divisions and programs at ANL. The ACL has three technical groups--Chemical Analysis, Instrumental Analysis, and Organic Analysis--which together include 46 technical staff members.

The Chemical Analysis Group performs wet chemical analyses and instrumental analyses; does spectrochemical analyses and coal analyses; and provides specialized analytical support--separations, preparations, advice, etc. The Instrumental Analysis Group uses nuclear-decay counting techniques; performs mass spectrometric and gas chromatographic analyses of gases; analyzes solids with X-ray techniques; and does remote analysis of radioactive samples, 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 ACL technical accomplishments are contained in previous sections of this report and in similar reports of other ANL divisions. Selected accomplishments are also summarized here.

DOE Environmental Survey

The DOE has initiated a program designed to identify current and/or potential environmental problems and areas of environmental risk at DOE facilities. Over 40 sites nationwide will be surveyed. Argonne is currently staffing one of the six field sampling teams in the program, and the ACL is providing organic, inorganic, and radiological analyses for the Argonne field sampling team and for sampling teams from the other participating laboratories. Idaho National Engineering Laboratory (INEL), Oak Ridge National Laboratory (ORNL), and Battelle--Columbus Division (BCD) are also involved in field sampling and analysis. The Oak Ridge Gaseous Diffusion Plant (ORGDP) is providing additional analytical support. The U.S. Environmental Protection Agency (Environmental Monitoring Systems Laboratory--Las Vegas) is providing an independent quality assurance overview; Environmental Monitoring Services, Inc., a consulting firm, is conducting third-party audits; and Nuclear Utilities Services, a consulting firm, is providing DOE with technical advice in developing site-specific sampling and analysis plans.

The ACL role includes consulting with and advising the ANL field sampling team on analysis problems, providing analyses and associated quality assurance/quality control using methods selected for the program, and developing methodology suitable for the program in cases where the sample is atypical and/or the type of analytical data required is unique. The methodologies for the organic,

inorganic, and radiological analyses are coordinated with ORNL, ORGDP, INEL, and BCD to ensure a consistent and uniform application of methods and data treatment.

In FY 1987, the ACL efforts involved analysis of environmental samples from the Feeds Materials Production Center in Fernald, Ohio; the Y-12 Plant in Oak Ridge, Tennessee; the Portsmouth Uranium Enrichment Complex in Piketon, Ohio; and the Kansas City Plant in Kansas City, Missouri. In addition, inorganic and organic analysis support was provided to INEL for the sampling and analysis effort at the Hanford site in Washington, and inorganic analysis support was provided to BCD for the sampling and analysis at the Pinellas Plant in Florida.

Measurement of ^{126}Sn Half-Life

The ACL has cooperated in a study by Argonne physicists to measure the half-life of ^{126}Sn with the Argonne Tandem Linac Accelerator System. Our contribution involved the separation and isolation of purified ^{126}Sn . Dissolver solutions of high-burnup uranium fuel were used as a source of ^{126}Sn . A separation procedure was developed and used to produce a solution containing $\sim 10^{15}$ atoms of ^{126}Sn essentially free from transuranics, uranium, and fission product nuclides, especially ^{106}Ru , ^{125}Sb , ^{137}Cs , and ^{155}Eu .

Chemical Analysis of Dew Collected on Natural Surfaces

The dry deposition of SO_2 onto a grassy surface located at ANL was studied. Among other things, the presence of dew on natural surfaces may have a significant effect on the uptake of SO_2 , depending on the chemical composition of the dew. The effects of surface wetness on dry deposition of SO_2 were studied by collecting dew samples from the natural surface (grass) and from an artificial surface above the grass. Preliminary results suggest a chemical difference between the dew collected on natural and artificial surfaces. Apparently, dew leaches material from the grass so that the uptake of SO_2 is enhanced on the natural surface relative to the artificial surface. This work relates to DOE acid rain studies. The chemical analysis performed by ACL included determinations of SO_4^{2-} , NO_3^- , NH_4^+ , Na^+ , K^+ , Cl^- , Ca^{2+} , Mg^{2+} , and F^- by liquid-ion chromatography and SO_3^{2-} by colorimetry.

Pyrochemical Processes for IFR Fuels

In the electrorefining of uranium and plutonium fuels for the Integral Fast Reactor (IFR), metallic fuel pins (U, Pu, Zr) are dissolved in a molten cadmium anode, and the actinide elements are electrochemically transported through a halide-salt electrolyte to the cell cathode, where they are collected as a metallic deposit. Engineering-scale studies of this electrorefining process are being carried out at ANL (Sec. VI.C) to develop models that describe recovery of the uranium and plutonium metals and their decontamination from fission-product elements and process materials. The ACL has contributed to this effort by determining each element of interest in samples of the cadmium anode, the halide-salt electrolyte, and the cathode product.

The utilization of a new "hot" inductively coupled plasma/atomic emission spectrometer (ICP/AES) has virtually eliminated the tedious separation procedures for removing actinides before analysis for cations such as Ba, Ca, Sr, Ce, Nd, Na,

Li, Y, Cd, and Zr. With this capability, procedures have also been developed to determine uranium and plutonium in samples where high accuracy (uncertainty <1%) is not needed. The precise determination of both uranium and plutonium is being done by mass spectrometric isotope dilution assay after spiking with ^{233}U and ^{244}Pu and extracting into hexone. Large amounts of waste and scrap generated in the IFR reprocessing experiments were also dissolved and analyzed for uranium and plutonium content. These analyses were necessary for subsequent disposal of the material. Analyses were also performed to determine ^{241}Am and ^{244}Cm . During FY 1987, approximately 240 samples were analyzed.

Treatment of IFR Process Waste

The waste electrorefining salts generated by IFR fuel reprocessing will be contacted with Cd-Li-K alloy to remove essentially all of the actinides. The treated salt will be immobilized in mortar for disposal as an intermediate-level waste. Formulations of mortar are being developed that will yield radioactive waste with high compressive strength and low leachability. The leach tests are performed by a standard procedure. Leachates are submitted for analysis to the ACL. Ion chromatography is being used to measure the amount of Cl^- present, which determines the leach rate from the grout.

Requalification of Low-Enrichment Fuel Pins

Low-enrichment-uranium fuel pins that were fabricated for the Special Power Excursion Reactor Test (SPERT) Program several decades ago are stored in several locations around the United States. These pins represent a potentially valuable resource for use in refueling university research reactors, which are now required to operate with reduced-enrichment fuels. A batch of SPERT fuel pins was examined at ANL to provide data for requalifying the fuel pins after several years of storage. The ACL determined the gas pressure and the composition of fill gas contained in selected pins and estimated the void volumes in corresponding pins. Fuel and cladding components were also analyzed. The fill-gas parameters were determined by first puncturing the pin cladding with a specially designed saddle-valve device and then measuring the gas pressure at standard volume. The collected gas was analyzed by mass spectrometry. Uranium in the fuel was assayed by isotope dilution, and its isotopic composition was determined by thermal ionization mass spectrometry. Impurities in the fuel and cladding were determined by ICP/AES.

Thermal Degradation Studies of Engine Fluid

The engine fluid RC1 is a mixture of 60 mol% pentafluorobenzene and 40 mol% hexafluorobenzene. It was initially reported to have excellent properties as a high-temperature working fluid for organic Rankine-cycle engines. The objective of this study was to thermally degrade it under controlled conditions at 427, 480, and 538°C (800, 900, and 1000°F). The liquid was then chemically characterized both qualitatively and quantitatively.

Identifications were made by gas chromatography/mass spectrometry (GC/MS) and GC/Fourier transform infrared spectroscopy (FTIR). Quantitation was done with multidimensional GC (MDGC). The MDGC was essential because most of the degradation products were isomers, and the higher resolution was required to separate them.

At 427°C (800°F), degradation was relatively minor but the degradation products were highly corrosive; stoichiometry indicates that both hydrogen fluoride and fluorine, or their reaction products, were given off. At 480°C (900°F), degradation was more marked. Most degradation products were dimers and trimers of the starting material. Correspondingly greater amounts of HF and fluorine were evolved. At 538°C (1000°F), degradation was so severe that only 7% of the starting material remained. The product was a black solid consisting of polymers of the starting material. The study proved that RC1 is inappropriate for use in a Rankine-cycle engine at the temperatures studied.

Degradation of 2-Methylpyridine

In this effort, 2-methylpyridine mixed with water was studied at 274, 302, and 329°C (525, 575, and 625°F). Degradation products were quantitatively analyzed by GC and identified by GC/MS and GC/FTIR.

Degraded fluid with a large number of isomers was difficult to resolve chromatographically in capillary columns. Analysis was first made using a non-polar column, which resolved the high-boiling fraction. The lower boiling fraction was resolved using a polar (DX4) column.

The fluid was found to be much less stable than toluene, which was studied previously.¹ The 2-methylpyridine degraded by ring cleavage adjacent to the nitrogen. Ring fragments either reacted with other molecules of fluid or were hydrolyzed. The fluid itself degraded upon standing at room temperature, even though it was stored in the dark in airtight containers.

Method Development for Dioxin Analysis

A cleanup technique using gel permeation chromatography was developed at ACL for removing unwanted coextractants that interfere with measurements of targeted compounds from soil extracts.² This technique has been tested further. It was found to be more effective in producing an extract amenable to GC/MS quantitation than EPA Region VII methodology (the serial application of five sulfuric acid washes followed by acid-modified silica and alumina column cleanups). The ability to replicate good recoveries from soil extracts has been demonstrated.

At least a dozen different cleanup techniques are available for soil extracts, some preferred more than others. Each provides some degree of coextractant removal. The effect that some of the preferred techniques have on the extract was determined by gas chromatography with flame ionization detection by observing the chromatogram before and after the application of a particular cleanup. This work provided the means to make knowledgeable selections of the most effective cleanups.

¹D. W. Green et al., *Analytical Chemistry Laboratory Progress Report for FY 1986*, Argonne National Laboratory Report ANL/ACL-86-2, p. 15 (1986).

²M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory ANL-87-19, p. 171 (1987).

Analysis of Dioxins from Municipal Waste Incineration

A cooperative effort is underway with the National Bureau of Standards (NBS) to monitor emissions from municipal waste incineration. The NBS team has been concerned with the construction of a small-scale incinerator, development of sampling capability, and organization of samples for burning. The preparation of samples requires the use of several compounds as binders to hold the waste material in pellets. The ACL has been analyzing both the waste materials that will be combusted and the binders for background chlorinated benzene content. These data are needed prior to combustion of the samples.

FTIR Analysis of Complex Mixtures and Stack Gases

A methodology was developed to analyze mixtures of common industrial solvents using a long-path vapor cell. The objective was to determine the feasibility of using FTIR as an analysis tool in determining whether workers had been exposed to high concentrations of industrial solvents present in the atmosphere. The new methodology for analysis was combined with new software by Nicolet Analytical Instruments and proved successful in qualitatively and quantitatively analyzing the solvent mixtures. It is anticipated that this technology will be developed into an inexpensive means of determining worker exposure to hazardous compounds.

Fourier transform infrared spectroscopy was also investigated as a tool to identify surrogates and combustion products found in hazardous waste incinerators. New variable-pathlength, heatable cells were purchased and modified for this experiment.

A library of potential components of interest was assembled and mixtures of simulated stack gases were tested. Results were excellent, with most variations within 10% of the values for prepared stack-gas components that varied in concentration from 0.4 to 50 ppm. Results were good even when high-concentration components not in the library were mixed with gases that were in very low concentration. The results were equally encouraging when actual incinerator stack gases were studied. The chloroform concentration agreed well with the GC/MS analyses used for a trial burn in a hazardous-waste incinerator under the Resource Conservation and Recovery Act (RCRA). This new technique could greatly reduce the cost and analysis time for permitting hazardous waste incinerators compared with current EPA procedures.

Source Term Experiments Project

The Source Term Experiments Project (STEP) consisted of a series of four experiments that focus on characterizing the source term associated with a postulated light water reactor accident. The experiments were conducted at the ANL Transient Reactor Test Facility in Idaho and were designed to capture representative fission products from fuel pins that have degraded in a steam environment. The experimental sample system is designed such that aerosol and volatile fission products can be determined through detailed post-test examination and analysis.

Several samples obtained from the second set of experiments, STEP-2, have been analyzed for cesium. Cesium was determined by analyzing a sample for its isotopic content and normalizing to a known quantity of either ^{134}Cs or ^{137}Cs .

The isotopic composition of the samples was determined by thermal ionization mass spectrometry, and the ^{134}Cs and ^{137}Cs disintegration rates were determined by absolute gamma-ray spectrometry. The cesium concentrations were then used to normalize other fission product concentrations that were determined at Oak Ridge National Laboratory by spark-source mass spectrometry. The compositions of the released aerosols determined from these data were compared with calculated compositions. For the most part, relatively good agreement was obtained between the measured and calculated compositions. However, the spectrometry results indicated that releases of barium, strontium, and ruthenium are markedly less than calculated using current release models.

Analysis of $\text{Na}_2\text{S-Al}_2\text{S}_3$

The $\text{Na}_2\text{S-Al}_2\text{S}_3$ system has been studied with X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX). Four new phases were confirmed by XRD, and with the aid of SEM-EDX analysis, three of the phases were given the provisional stoichiometries of $\alpha\text{-Na}_3\text{AlS}_3$, $\beta\text{-Na}_3\text{AlS}_3$, and Na_5AlS_4 . These results were a by-product of a study on the corrosion of aluminum in Na_2S_3 at high temperatures.³ Because this system is very unstable in air, the study was conducted under inert atmosphere conditions, in this case helium.

The XRD powder spectrum for Na_3FeS_3 was noted to have a characteristic pattern similar to that obtained for $\alpha\text{-Na}_3\text{AlS}_3$. A computer program⁴ that can generate the XRD powder spectrum from known crystal data was used to replace the iron with aluminum and to calculate an XRD spectrum for " Na_3AlS_3 ." The results indicated that the Na_3FeS_3 structure is a good model for $\alpha\text{-Na}_3\text{AlS}_3$, although further refinement should be done with single-crystal data. The results of this study have been published.⁵

Recently, single-crystal results for Na_5FeS_4 have been reported.⁶ Thus, the powder spectrum for " Na_5AlS_4 " was calculated using Na_5FeS_4 atom coordinate data and again substituting aluminum for iron. This computer-generated pattern for the Na_5AlS_4 data showed reasonably good agreement with Na_5FeS_4 data. However, interatomic distance calculations indicated that some bond distances were slightly out of line with expected distances. Thus, if possible, the proposed model should be further supported by single-crystal data.

LiAlO_2 Characterization

A series of high-fired lithium aluminate samples has been assayed for lithium and aluminum. In addition, the isotopic composition of the lithium was measured. The analytical methodology was developed by the ACL in support of a program that developed a process for fabrication of these materials. The materials were very refractory and were not amenable to ordinary acid attack.

³A. P. Brown, J. Electrochem. Soc. **134**, 2506 (1987).

⁴D. K. Smith and M. Holomany, "A Fortran IV Program for Calculating X-Ray Powder Diffraction Patterns--Version 7," The Pennsylvania State University (April 1978). Note: latest update is Version 10.

⁵A. P. Brown and B. S. Tani, Mater. Res. Bull. **22**, 1029 (1987).

⁶K. O. Klepp and W. Bronger, Z. Anorg. Allg. Chem. **532**, 23 (1986).

A specialized technique for dissolution was required. Weighed samples were sealed in quartz tubes with HCl and heated at high temperature ($\sim 300^\circ\text{C}$) for 24 h. The tubes were contained in an atmosphere of carbon dioxide in a stainless steel pressurized shell to avoid bursting of the tube. After dissolution, the samples were transferred to weighed flasks and diluted to volume. Weight aliquots of the solution were analyzed for lithium and aluminum. Lithium was determined to 0.2% relative by a mass spectrometric isotope dilution method. This determination yielded values for the total weight percent and isotopic composition. Aluminum was determined gravimetrically to 0.3% relative with 8-hydroxyquinoline.

The Argonne Premium Coal Sample Program

In FY 1987, three coals were processed through the Premium Coal Sample Preparation Facility, which is designed to provide the coal research community with coal samples that are homogeneous, stable, and well characterized. Homogeneity of mixing for the crushed coals was monitored with the neutron activation technique and high-resolution gamma spectroscopy. Approximately 160 coal samples were irradiated and counted for isotopes of Na, K, As, La, and Sc. Each sample was counted a minimum of six times to obtain reliable statistical results. The total number of analyses for all three coals was 4800. This effort concluded the preparation of eight premium coals for the program over the last two years.

The cover gases from 50 glass vials containing samples of coal from the Argonne Premium Coal Sample Program were also analyzed this year. Each vial was enclosed in a stainless-steel cylinder, which was evacuated and degassed. The vial was broken in vacuum, and the cover gas admitted to a mass spectrometer for analysis. The vials were originally sealed in a nitrogen atmosphere, and the principal gas detected was N_2 , with lesser amounts of H_2 , CH_4 , H_2O , C_2H_6 , and CO_2 , depending on the coal. The intention is to analyze samples for each coal at regular intervals to determine if the relative amounts of the smaller components are changing (increasing) with time.

Americium Certified Reference Materials

The New Brunswick Laboratory (NBL) is presently responsible for preparing, certifying, and distributing reference materials related to nuclear safeguards measurements in the United States; the U.S. National Bureau of Standards (NBS) no longer provides these services. Among its current projects, NBL is working toward producing a certified reference material (CRM) for ^{243}Am and a $^{241}\text{Am}/^{243}\text{Am}$ isotopic CRM.

The ACL has been contracted by NBL to carry out the dissolution of the ^{241}Am and ^{243}Am metals, to perform precise assays of the americium in each solution, and to prepare accurately weighed aliquots of the solution for subsequent dilution and dispensing into CRM ampoules. During FY 1987, the ACL effort was directed toward demonstrating a precise method for the americium assays and adapting the method for use in a glove-box facility. The titration procedure, which used ethylenediaminetetracetic acid as a titrant and a mercury pool electrode to indicate the endpoint, performed poorly because of variable sample contamination by trace amounts (up to $\sim 20\ \mu\text{g}$) of iron (rust) from corrosion in the glove box. A new instrument, a Brinkman Instruments (Model PC800) Dipping Probe Colorimeter, was purchased for this work to permit our using

colorimetric rather than potentiometric detection of the endpoint under conditions that are less sensitive to contamination effects.

Isotopic Analysis of Highly Irradiated Iron Samples

Materials damage resulting from helium production during intense neutron irradiation is of serious concern to fusion reactor engineers. A collaborative study between ANL and Rockwell International Corp. has found more helium than expected in iron wire samples that were irradiated in the High Flux Isotope Reactor at ORNL (Sec. VII.C.5). These researchers proposed two different ways in which the extra helium may be produced: (1) fast-neutron reactions of the transmuted isotopes of iron or (2) a thermal neutron reaction with the radioactive isotope ^{55}Fe . To aid in distinguishing between these possibilities, the ACL investigated the isotopic characterization of highly irradiated iron samples. The abundance of the radioactive ^{55}Fe isotope was measured by liquid scintillation counting after chemical separations were done to remove interfering radioactive species such as ^{51}Cr , ^{54}Mn , ^{57}Co , and ^{58}Co . The stable iron isotopes were found to be ^{54}Fe , ^{56}Fe , ^{57}Fe , and ^{58}Fe by thermal ionization mass spectrometry. This technique also identified the isotope ^{55}Fe after procedures were developed to eliminate interference from its ^{55}Mn decay daughter. Both liquid scintillation counting and thermal ionization mass spectrometry resulted in values for ^{55}Fe that agreed within the experimental errors for each method.

Methods for Analyzing Organics in Solid Waste

The objective of this program is to use advanced separation and instrumental techniques to characterize those organics in solid wastes that cannot be analyzed by GC/MS. Even with a high-resolution capillary column coupled to a mass spectrometer, identification of organics in the wastes is often difficult because of the incomplete resolution of many of the peaks in the complex mixtures typically found in these wastes. A second problem that arises in GC/MS analysis is that the mass spectrum of a GC peak does not always lead to a positive identification of the peak. For example, phenanthrene and anthracene have indistinguishable spectra, as do the eight isomeric dimethyl naphthalenes and three isomeric xylenes. Also, there are many cases in which the mass spectrum does not contain a molecular ion, that is, one corresponding to the molecular weight of the compound. The molecular weight is probably the most important piece of information in a mass spectrum, and, without it, identification is difficult. Typically, spectra for alcohols, carboxylic acids, and esters do not show molecular ions.

Mixtures that could not be analyzed directly by GC/MS were subjected to high-performance liquid chromatography (HPLC) to convert the very complex mixtures into four simpler mixtures that showed sufficient resolution of peaks for GC/MS analysis. To look at those compounds whose mass spectra do not lead to positive identification, the technique of gas chromatography/matrix isolation infrared spectroscopy (GC/MIIR) was investigated. The GC/MIIR technique was found to have sufficient sensitivity, of the order of GC/MS, and was useful for differentiating between the eight isomeric dimethyl naphthalenes, the three isomeric xylenes, and phenanthrene and anthracene. Each of these compounds gave unique infrared spectra. The sharpness of the peaks in the fingerprint region (as is characteristic of MIIR spectra) was paramount to obtaining positive identification of the compounds.

Organics in Solid and Sludge Wastes

The organics in solid and sludge wastes from the processes of emerging energy technologies (such as coal gasification and liquefaction, and the extraction of oil from shale) were analyzed to characterize them by narrow-bore capillary column GC/MS and to determine their potential for leaching from these wastes after disposal. With a knowledge of the organics in these wastes and their potential for leaching, strategies for treatment of the waste before disposal can be formulated.

Twenty waste samples were analyzed, including feed coals, pulverized feed coal, equalization tank sludge, pitch, tar, and heavy distillates. Two types of analyses were done on each of these samples. The first type was a direct analysis in which the samples were extracted, typically with methylene chloride, and then analyzed by GC/MS. In the second, the samples were leached according to an extraction procedure developed by the EPA, and the leachates were extracted with methylene chloride and analyzed by GC/MS. The leaching procedure is expected to simulate what can take place in the real world. The types of compounds found in the wastes include alkanes, benzenes, naphthalenes, polynuclear aromatic hydrocarbons, and phenols.

Plastic Pipe Program

The objective of the Plastic Pipe Program of the Gas Research Institute is to analyze and characterize the chemical and molecular properties of polyethylene (PE) resins and to determine the effect of these properties on the mechanical strength of commercial PE pipe presently used for gas distribution.

In ^{13}C nuclear magnetic resonance studies, the type of branches and groups on the PE backbone was determined. Four types of branching were found: ethyl, n-butyl, n-pentyl, and long (>n-hexyl). Generally, pipes with n-butyl branching performed best, as determined by the mechanical test used in these studies--the constant tensile load (CTL) test. From the analytical data, the number of methyl and vinyl end groups was determined. The number of end groups was discovered to be related to the average length of the polyethylene molecules and, therefore, to the number-average molecular weight.

In X-ray diffraction studies on 15 pipe samples, the PE crystallites were larger on the inner surface than the outer surface, with the exception of one sample that had been processed in an unusual way. (Of these samples, 14 had not been in field use, but no differences have been observed or are expected because of field use.) This phenomenon is probably due to the rapid cooling of the outer surface relative to the inner surface during extrusion of the pipe. In the one pipe in which cooling was uniform, there was little variation in the crystallite size.

With gel permeation chromatography studies, the best pipes exhibited a wide distribution of molecular weights of polyethylene. Mechanical strength was correlated with increasing weight-average molecular weight and decreasing number-average molecular weight.

With GS/MS, a relationship was found between the concentration of low-molecular-weight polyethylenes (n-alkanes and n-alkenes) and the strength of the

PE pipe as measured by the CTL test. As the concentration of the very low-molecular-weight polyethylenes increased, the mechanical strength increased. In the case of a pipe that had particularly poor mechanical strength (in fact, so poor that the relative strength could not even be measured by the CTL test), there was an extremely low concentration of low-molecular-weight polyethylenes. Gas chromatography has been found to be useful for "fingerprinting" PE pipes and resins. It can be used to identify the source of the pipe, resin manufacturer, compounded resin manufacturer, additives manufacturer, and pipe processor.

X. COMPUTER APPLICATIONS

The Computer Applications Group provides assistance to Division staff 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) computer operating system maintenance, (7) small and large computer system networking, (8) procurement of equipment, 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 11/785 central computing facility and (2) hardware maintenance of various small systems and peripherals, including the Division's terminal communications system.

Utilization of personal computers both for data acquisition/control and modeling has continued to increase. During the past year, assistance has been given to the Separation Science and Technology Group in computerizing its generic TRUEX model (Sec. VI.A.1.b). The generic TRUEX model will be used to design and optimize flowsheets for processing waste streams by the TRUEX process. The model will consist of a user interface and three spreadsheet sections: Spreadsheet Algorithm for Stagewise Solvent Extraction (SASSE), Spreadsheet Algorithms for Speciation and Partitioning Equilibria (SASPE), and Spreadsheet Algorithms for Space and Cost Estimation (SASCE). Work so far has primarily been done on the SASSE portion of the model.

The SASSE began as a Microsoft Excel spreadsheet for one specific TRUEX flowsheet. To expedite the creation and modification of SASSE spreadsheets, the formulas in the original SASSE spreadsheet were generalized. Currently, SASSE consists of two Excel macros. The first macro generates the SASSE spreadsheet based on user inputs of the number of stages and sections (extraction, scrub, strip) in the process. Additional information such as the aqueous and organic flow rates to each section is then entered directly into cells on the spreadsheet. In a future version, a user interface will allow data entry through the use of a series of forms that will guide the user through the required data input and will provide error checks. HyperCard software by Apple Computer will be used to simplify the creation and modification of a user interface. The second macro allows the user to modify the number of stages and/or sections in an existing spreadsheet without losing any existing data. Work on the user interface and SASSE will continue in the next year, and development of SASPE and SASCE will begin.

Installation of a voice/data PBX at ANL was completed in November 1987. This system brings improved data communications to the Laboratory by providing the capability for high-speed terminal-to-host and host-to-host data links, including Laboratory-wide Ethernet capability. Computer systems outside CMT, which were previously limited to transmission speeds of 19.2 kilobaud, are now able to communicate to the VAX 11/785 and to each other at speeds up to 1 megabaud. The Lab-wide Ethernet has facilitated the implementation of personal computer networks, which not only allow the VAX to be used as a file server but also permit VAX applications to manipulate the stored data. The VAX is also connected to the National Magnetic Fusion Energy Computing Center (NMFEC) at Livermore National Laboratory.

The VAX 11/785 continues to be used for a wide variety of applications including post-analysis of experimental data, theoretical calculations in basic energy science, graphics, electronic mail, and other office automation and management functions. Major enhancements to the VAX during 1987 include the addition of two Vaxstation 2000 workstations as part of a local area VAX cluster. In addition to providing an excellent environment for software development for our systems programmers, these workstations permit some of the VAX's overload to be shifted to the Vaxstations in a manner transparent to the end-user. Additional improvements to accommodate CMT's growing workload are being planned. The use of sophisticated laser printers has virtually replaced other printing systems in the Division. Access to a typesetting system at ANL now permits CMT users to obtain extremely high-resolution output when needed. At present, the VAX is being utilized by over 250 members of the division and other related ANL personnel.

The High-Temperature Materials Group (Sec. VIII.B) continues to run intensive theoretical calculations on its MicroVAX-II. This system, which provides approximately 90% of the computational power of a VAX 11/780, is connected to CMT's Ethernet to provide access to various peripherals and computer networks. The addition of a high-speed Vaxstation with a twofold performance increase is planned for FY 1988.

A block diagram of the Divisional computing configuration is shown in Fig. X-1.

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

XI. ADDENDUM.**CHEMICAL TECHNOLOGY DIVISION
PUBLICATIONS--1987**

The Division's publications and oral presentations for 1987 were entered into a bibliographic data base. The pages that follow are a printout of this information sorted into six categories: (1) journal articles, books, and book chapters, (2) patents, (3) ANL progress and topical reports, as well as contributions to reports published by organizations other than ANL, (4) abstracts and papers published in proceedings of conferences, 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.

CHEMICAL TECHNOLOGY DIVISION
PUBLICATIONS -- 1987

A. Journal Articles, Books, and Book Chapters

Transport and Reaction Kinetics at the Gel:Glass Solution Interface Region: Results of Repository-Oriented Leaching Experiments

T. A. Abrajano and J. K. Bates

Scientific Basis for Nuclear Waste Management X, eds. J. K. Bates and W. B. Seefeldt, Materials Research Soc., Vol. 84, pp. 533-546 (1987)

The Effect of Gamma Radiation on Groundwater Chemistry and Glass Leaching as Related to NNWSI Repository Site

T. A. Abrajano, J. K. Bates, W. L. Ebert, and T. J. Gerding

Adv. Ceram. 20, 609-618 (1987)

Hydrogen Speciation in Hydrated Layers on Nuclear Waste Glass

R. D. Aines, H. C. Weed, and J. K. Bates

Scientific Basis for Nuclear Waste Management X, eds. J. K. Bates and W. B. Seefeldt, Materials Research Society, Vol. 84, pp. 547-558 (1987)

Wastage of In-Bed Heat Transfer Surfaces in the Pressurised Fluidised-Bed Combustor at Grimethorpe

J. S. Anderson, E. L. Carls, P. J. Mainhardt, W. M. Swift, J. M. Wheeldon, S. Brooks,

A. J. Minchener, and J. Stringer

J. Eng. Gas Turbines Power 109, 298-304 (1987)

Scientific Basis for Nuclear Waste Management X

J. K. Bates and W. B. Seefeldt, eds.

From Materials Research Society Symp. Proc., Boston, MA, December 1-4, 1986, Vol. 84 (1987)

Thermodynamic Properties of Molten Salt Solutions

M. Blander

Molten Salt Chemistry, An Introduction and Selected Applications, eds. G. Mamantov and R. Marassi, D. Reidel Publishing Co., Dordrecht, Holland, pp. 17-62 (1987)

Thermodynamic Analysis of Binary Liquid Silicates and Prediction of Ternary Solution Properties by Modified Quasichemical Equations

M. Blander and A. D. Pelton

Geochim. Cosmochim. Acta 51, 85-95 (1987)

Business Graphics Made Easy (EDTGRAF—An Easy Way to Use DISPLA)

I. Bloom

The DEC Professional 6(7), 60-66 (1987)

Chemical Stability of $\text{Na}_2\text{O-ZrO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ Glasses in Sodium, Sodium Polysulfides, and Sulfur

I. Bloom, J. Bradley, and M. F. Roche

J. Electrochem. Soc. 134(9), 2102-2106 (1987)

The Corrosion Behavior of Molybdenum and Hastelloy B in Sulfur and Sodium Polysulfides at 623 K

A. P. Brown

J. Electrochem. Soc. **134**(8), 1921-1925 (1987)

The Corrosion of Aluminum in Sodium Polysulfides and Sulfur at 350°C

A. P. Brown

J. Electrochem. Soc. **134**, 2506-2507 (1987)

Powder X-Ray Diffraction Identification of Some New Phases in the $\text{Na}_2\text{S}-\text{Al}_2\text{S}_3$ System

A. P. Brown and B. S. Tani

Mater. Res. Bull. **22**, 1029-1037 (1987)

Inelastic Neutron Scattering from Tetramethylammonium Cations Occluded within Zeolites

T. O. Brun, L. A. Curtiss, L. E. Iton, R. Kleb, J. M. Newsam, R. A. Beyerlein, and D. E. W. Vaughan

J. Am. Chem. Soc. **109**, 4118 (1987)

Phonon Dispersion Curves for $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$

T. O. Brun, M. H. Grimsditch, K. E. Gray, R. Bhadra, and V. A. Maroni

Phys. Rev. B **35**(16), 8837-8839 (1987)

Raman and ^{67}Zn NMR Studies of the Structure of Zinc(II) Solutions in Concentrated Aqueous Potassium Hydroxide

K. J. Cain, C. A. Melendres, and V. A. Maroni

J. Electrochem. Soc. **134**(3), 519-524 (1987)

Homologation of Methanol Catalyzed by Manganese Carbonyl in Alkali-Metal Formate-Methanol Solutions

M. J. Chen and J. W. Rathke

Organomet. **6**, 1833-1838 (1987)

Corrosion in Batteries and Fuel-Cell Power Sources

W. R. Cieslak, A. P. Brown, V. K. Dantam, B. D. Lichter, S. R. Shah, W. W. Paden, S. F. Pensabene, and P. N. Ross, Jr.

Metals Handbook (Corrosion), Ninth Ed., Vol. 13, American Society for Metals, Metals Park, OH, pp. 1317-1323 (1987)

A Theoretical Study of the Inversion Barrier in NF_3^+

L. A. Curtiss

Chem. Phys. Lett. **136**(6), 566-570 (1987)

Nonadditivity of *Ab Initio* Pair Potentials for Molecular Dynamics of Multivalent Transition Metal Ions in Water

L. A. Curtiss, J. W. Halley, J. Hautman, and A. Rahman

J. Chem. Phys. **86**(4), 2319-2327 (1987)

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L. A. Curtiss, E. Kraka, J. Gauss, and D. Cremer

J. Phys. Chem. **91**, 1080-1084 (1987)

Comparison of Correlation Effects on the Inversion Barriers in CF_3 and NF_3^+ from Perturbation Theory and Configuration Interaction

L. A. Curtiss and J. A. Pople

Chem. Phys. Lett. 141(3), 175-178 (1987)

Lifetime of Supported Liquid Membranes: The Influence of Interfacial Properties, Chemical Composition and Water Transport on the Long-Term Stability of the Membranes

P. R. Danesi, L. Reichley-Yinger, and P. G. Rickert

J. Membrane Sci. 31(2-3), 117-145 (1987)

Conductivity of Porous $\text{Ni}/\text{ZrO}_2\text{-Y}_2\text{O}_3$ Cermets

D. W. Dees, T. D. Claar, T. E. Easler, D. C. Fee, and F. C. Mrazek

J. Electrochem. Soc. 134(9), 2142-2146 (1987)

Experimental Observations of Free-Convection Mass Transfer to a Horizontal Surface with a Micromosaic Electrode

D. W. Dees and C. W. Tobias

J. Electrochem. Soc. 134(2), 369-377 (1987)

Mass Transfer at Gas Evolving Surfaces: A Microscopic Study

D. W. Dees and C. W. Tobias

J. Electrochem. Soc. 134(7), 1702-1713 (1987)

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M. M. Dextader, V. A. Maroni, and J. V. Beitz

Scientific Basis for Nuclear Waste Management X, eds. J. K. Bates and W. B. Seefeldt, Materials Research Soc., Vol. 84, p. 173 (1987)

The Effects of Gamma Radiation on Groundwater Chemistry and Glass Reaction in a Saturated Tuff Environment

W. L. Ebert, J. K. Bates, T. J. Gerding, and R. A. Van Konynenburg

Scientific Basis for Nuclear Waste Management X, eds. J. K. Bates and W. B. Seefeldt, Materials Research Soc., Vol. 84, pp. 613-622 (1987)

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L. R. Greenwood

Influence of Radiation on Materials Properties, eds. F. A. Garner, C. H. Henager, and N. Igata, American Society for Testing of Materials, STP 956, pp. 743-749 (1987)

Production of ^{91}Nb , ^{94}Nb , and ^{95}Nb from Mo by 14.5-14.8 MeV Neutrons

L. R. Greenwood, D. G. Doran, and H. L. Heinisch

Phys. Review C 35(1), 76-80 (1987)

Formation of Perovskite Surface Layers by Oxidation of Cu-La-Sr Alloys

D. M. Gruen, W. F. Calaway, V. A. Maroni, B. S. Tani, and A. R. Krauss

J. Electrochem. Soc. 134(6), 1588-1589 (1987)

Method for Determination of Oxygen-18 of Hydrogen Peroxide in Rainwater

Ben D. Holt and R. Kumar

Anal. Chem. 59, 995-999 (1987)

Characterization of Selected Nuclear Fuel Cycle Materials by Column Extraction Chromatography and ICP-AES

E. A. Huff

Spectrochim. Acta **42B**(1-2), 275-283 (1987)

Kinetics of the Ferrous/Ferric Electrode Reaction in the Absence of Chloride Catalysis

N. C. Hung and Z. Nagy

J. Electrochem. Soc. **134**(9), 2215-2220 (1987)

Heat Capacity of Liquid Equiatomic Potassium-Lead Alloy: Anomalous Temperature Dependence

G. K. Johnson and M.-L. Saboungi

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Thermodynamic Properties of Silicalite SiO_2

G. K. Johnson, I. R. Tasker, D. A. Howell, and J. V. Smith

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Use of Electronic Worksheets for Calculation of Stagewise Solvent Extraction Processes

R. A. Leonard

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The Standard Molar Enthalpy of Formation at 298.15 K of $\text{VS}_{1.043}$ by Combustion Calorimetry in Fluorine

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On the Structure of the Higher Oxide Forms of Nickel

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B. Misra and G. D. Morgan

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Z. Nagy, M. Minkoff, G. K. Leaf, and R. H. Land

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Performance of Materials in Fluidized-Bed Combustors

K. Natesan, S. A. Miller, and W. F. Podolski

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Inorganic Chalcogenides: High-Tech Materials, Low-Tech Thermodynamics

P. A. G. O'Hare

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Calorimetric Measurements on High-Purity ScI_3

P. A. G. O'Hare, G. K. Johnson, I. R. Tasker, H. E. Flotow, and C. W. Struck

J. Chem. Thermodyn. 10, 77-88 (1987)

The Energy Difference Between the Crystalline and Vitreous Forms of Germanium Diselenide as Determined by Combustion Calorimetry in Fluorine. The Ge-Se Bond Energy

P. A. G. O'Hare, S. Susman, and K. J. Volin

J. Non-Cryst. Solids 89, 24-30 (1987)

A Fluorine-Combustion Calorimetric Study of Two Molybdenum Selenides: MoSe_2 and Mo_5Se_8

P. A. G. O'Hare, I. R. Tasker, and J. M. Tarascon

J. Chem. Thermodyn. 19, 61-68 (1987)

Ion and Neutral Atomic and Cluster Sputtering Yields of Molybdenum

M. J. Pellin, W. Husinsky, W. F. Calaway, J. W. Burnett, E. L. Schweitzer, C. E. Young, B. Jorgensen, and D. M. Gruen

J. Vac. Sci. Technol. B5, 1477-1481 (1987)

Sensitive, Low Damage Surface Analysis Using Resonance Ionization of Sputtered Atoms

M. J. Pellin, C. E. Young, W. F. Calaway, J. W. Burnett, B. Jorgensen, E. L. Schweitzer, and D. M. Gruen

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Detection of Mercury Coordination Numbers Greater Than Two for Organomercurials Using Chlorine-35 Magnetic Resonance

J. J. Pesek and J. F. Schneider

Inorg. Chem. 26, 3064-3065 (1987)

Integrated Testing of the SRL-165 Glass Waste Form

D. L. Phinney, F. J. Ryerson, V. M. Oversby, W. A. Lanford, R. D. Aines, and J. K. Bates

Scientific Basis for Nuclear Waste Management X, eds. J. K. Bates and W. B. Seefeldt, Materials Research Soc., Vol. 84, pp. 433-446 (1987)**Investigation of Alternative MCFC Cathode Materials at Argonne National Laboratory**

R. D. Pierce, J. L. Smith, and G. H. Kucera

Progress in Batteries and Solar Cells, U.S. Office of Electrochem. Soc. of Japan, Cleveland, OH, Vol. 6, pp. 159-164 (1987)**Theoretical Thermochemistry. 3. A Modified Procedure for Ionization Energies of AH_n Species**

J. A. Pople and L. A. Curtiss

J. Phys. Chem. 91(13), 3637-3639 (1987)

Modeling of Sulfide Capacities of Silicate Melts

R. G. Reddy and M. Blander

Metall. Trans. B 18B, 591-596 (1987)

Synthesis of ^{13}C -Labeled Polychlorinated Biphenyls

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On the Conformal Ionic Solution Theory—Principles and Applications

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M.-L. Saboungi, R. Blomquist, K. J. Volin, and D. L. Price

J. Chem. Phys. 87(4), 2278-2281 (1987)

The Coordination Cluster Theory: Extension to Multicomponent Systems

M.-L. Saboungi, D. Caveny, I. Bloom, and M. Blander

Metall. Trans. A 18A, 1779-1783 (1987)

High-Resolution Computed Tomography for Flaw Detection in Advanced Thin-Layer Ceramics for Fuel Cells

B. D. Sawicka, W. A. Ellingson, and C. C. McPheeters

Ceram. Eng. Sci. Proc. 8, 7-8 (July-August 1987)

Agenda for Advancing Electrochemical Corrosion Science and Technology: Report of the Panel on Electrochemical Corrosion

W. H. Smyrl, T. R. Beck, and M. Blander et al.

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Thorium-Uranium Disequilibrium in a Geothermal Discharge Zone at Yellowstone

N. C. Sturchio, C. M. Binz, and C. H. Lewis III

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Reply to Comment by Greiling and El Ramly on "Mapping of Serpentinities in the Eastern Desert of Egypt by Using Landsat Thematic Mapper Data"

M. Sultan, R. Arvidson, and N. C. Sturchio

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M. Sultan, R. Arvidson, N. C. Sturchio, and E. Guinness

Geol. Soc. Am. Bull. 99, 748-762 (1987)

Quantum Percolation Thresholds and Random Walk Fractal Dimensions

S. W. Tam and C. E. Johnson

J. Phys. A: Math. Gen. 20, L471-L477 (1987)

Phase Relations for Reactions of Hydrogen with Sodium Oxide Between 500 and 900°C

E. Veleckis and L. Leibowitz

J. Nucl. Mater. 144, 235-243 (1987)

Pyrochemical Extraction of Transition Metals from Pacific Ocean Deep Sea Nodules**S. von Winbush and V. A. Maroni****Sep. Sci. Technol. 22(2&3), 1135-1148 (1987)****Laser-Based Secondary Neutral Mass Spectroscopy: Useful Yield and Sensitivity****C. E. Young, M. J. Pellin, W. F. Calaway, B. Jorgensen, E. L. Schweitzer, and D. M. Gruen****Nucl. Instrum. Meth. Phys. Res. B27, 119-129 (1987)**

B. Patents**Refractory Lining for Electrochemical Cell**

M. Blander and G. M. Cook

Patent No. 4,687,564, issued August 18, 1987

Bipolar Battery with Array of Sealed Cells

T. D. Kaun and J. A. Smaga

Patent No. 4,687,717, issued August 18, 1987

Molten Carbonate Fuel Cell

T. D. Kaun and J. L. Smith

Patent No. 4,714,661, issued December 22, 1987

Electrochemical Cell with High Conductivity Glass Electrolyte

P. A. Nelson, I. Bloom, and M. F. Roche

Patent No. 4,659,637, issued April 21, 1987

Radioactive Waste Processing Apparatus

R. E. Nelson, A. A. Ziegler, D. F. Serino, and P. J. Basnar

Patent No. 4,666,676, issued May 19, 1987

Catalyst for Producing Lower Alcohols

J. W. Rathke, R. J. Klingler, and J. J. Heiberger

Patent No. 4,656,152, issued April 7, 1987

Device for Equalizing Molten Electrolyte Content in a Fuel Cell Stack

J. L. Smith

Patent No. 4,643,954, issued February 17, 1987

Molten Carbonate Fuel Cell Reduction of Nickel Deposits

J. L. Smith and S. A. Zwick

Patent No. 4,643,955, issued February 17, 1987

Coated Ceramic Breeder Materials

S. W. Tam and C. E. Johnson

Statutory Invention Registration No. H259, issued 1987

Electrode-Active Material for Electrochemical Batteries and Method of Preparation

R. Varma

Patent No. 4,687,598, issued August 18, 1987

C. Reports**Hydrogen Speciation in Hydrated Layers on Nuclear Waste Glass**

R. D. Aines, H. C. Weed, and J. K. Bates

Lawrence Livermore National Laboratory Report UCRL-95961 (1987)

Tiber II/ETR, Nuclear Performance Analysis Group Report

C. C. Baker, M. A. Abdou, P. A. Finn, et al.

ANL/FPP-87-3 (September 1987)

Lithium/Iron Sulfide Batteries: Development and Demonstration

G. Barlow and A. A. Chilenskas

EPRI-EM-5183 (1987)

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J. K. Bates, T. J. Gerding, D. F. Fischer, and W. L. Ebert

Lawrence Livermore National Laboratory Report UCRL-15991 (1987)

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G. F. Berry, C. S. Wang, and U. S. Choi

ANL-MHD-86-1 (September 1987)

A Study of Natural Glass Analogues as Applied to Alteration of Nuclear Waste Glass

C. D. Byers, M. J. Jercinovic, and R. C. Ewing

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Tokamak Power Systems Studies—FY 1986: A Second Stability Power Reactor

D. Ehst, C. Baker, P. A. Finn, et al.

ANL/FPP/86-1 (March 1987)

Adsorption, Solution, and Desorption Characteristics of the $\text{LiAlO}_2\text{-H}_2\text{O}$ System

A. K. Fischer and C. E. Johnson

Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1987, DOE/ER-0313/2, p. 247 (September 1987)

Final Report for the Light Water Breeder Reactor Proof-of-Breeding Analytical Support Project

D. G. Graczyk, J. C. Hoh, F. J. Martino, R. E. Nelson, J. Osudar, and N. M. Levitz

ANL-87-2 (May 1987)

Analytical Chemistry Laboratory Progress Report for FY 1987

D. W. Green, R. R. Heinrich, K. J. Jensen, M. D. Erickson, et al.

ANL/ACL-87-2 (December 1987)

Characterization of the NLTNIF Facility in the BSR

L. R. Greenwood

Fusion Reactor Materials Semiannual Progress Report for the Period Ending September 30, 1986, DOE/ER-0313/1, pp. 12-16 (June 1987)

Dosimetry and Damage Analysis for the HFIR-CTR-47/48 Experiments**L. R. Greenwood****Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1987, DOE/ER-0313/2, pp. 38-40 (September 1987)****Dosimetry and Damage Analysis for the Omega West Reactor****L. R. Greenwood****Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1987, DOE/ER-0313/2, pp. 34-37 (September 1987)****International Dosimetry Standardization Activities****L. R. Greenwood****Fusion Reactor Materials Semiannual Progress Report for the Period Ending September 30, 1986, DOE/ER-0313/1, p. 39 (June 1987)****Measurements for the JP2, JP6, and JP7 U.S./Japanese Experiments in HFIR****L. R. Greenwood****Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1987, DOE/ER-0313/2, pp. 31-33 (September 1987)****Cross Section Measurements for Long-Lived Isotopes****L. R. Greenwood and D. L. Bowers****Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1987, DOE/ER-0313/2, pp. 26-30 (September 1987)****Production of Long-Lived Activities in Fusion Reactors****L. R. Greenwood and D. L. Bowers****Fusion Reactor Materials Semiannual Progress Report for the Period Ending September 30, 1986, DOE/ER-0313/1, p. 35 (June 1987)****Pyrolysis of Municipal Solid Waste: Annual Report, July 1985-June 1986****J. E. Helt, R. K. Agrawal, and K. M. Myles****ANL/CNSV-62 (October 1987)****Model of Tritium Transport in Ceramic Breeder Materials****J. P. Kopasz and C. E. Johnson****Fusion Reactor Materials Semiannual Progress Report for the Period Ending March 31, 1987, DOE/ER-0313/2, p. 291 (September 1987)****Tests to Produce and Recover Carbon Dioxide by Burning Coal in Oxygen and Recycled Flue Gas; Black Hills Power and Light Company Customer Service Center Boiler No. 2, Rapid City, South Dakota****R. Kumar, T. Fuller, R. Kocourek, F. G. Teats, Y. E. Young, K. M. Myles, and A. Wolsky****ANL/CNSV-61 (December 1987)****Measurement of Stibine and Arsine Generation from the Exide 3100-Ah Lead-Acid Module****J. J. Marr and J. A. Smaga****ANL-87-1 (January 1987)****Post-Test Analyses of Aqueous Batteries Developed for Electric Propulsion: Summary Report for January 1985-September 1986****J. F. Miller, J. J. Marr, and J. A. Smaga****ANL-87-33 (July 1987)**

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K. Natesan, S. A. Miller, and W. F. Podolski

ANL-86-42 (February 1987)

Atmospheric Fluidized-Bed Cogeneration Air Heater Experiment: 1000-h Laboratory Test A

K. Natesan and W. F. Podolski

ANL/FE-87-2 (April 1987)

Computerized Operating Procedures for Shearing and Dissolution of Segments from LWBR Fuel Rods

J. Osudar, P. G. Deeken, D. G. Graczyk, J. E. Fagan, F. J. Martino, J. E. Parks, N. M. Levitz, R. W. Kessie, and J. M. Leddin

ANL-87-17 (May 1987)

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D. L. Phinney, F. J. Ryerson, V. M. Oversby, W. A. Lanford, R. D. Aines, and J. K. Bates

Lawrence Livermore National Laboratory Report UCRL-94688 (1987)

Improved Treatment/Disposal of Reactive Metals

J. B. Rajan, R. Kumar, and D. R. Vissers

DOE/HWP-29, ANL-87-39 (October 1987)

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L. Redey, J. A. Smaga, J. E. Battles, and R. Guidotti

ANL-87-6 (April 1987)

A Study of the Permeability of Polyethylene Pipe by Organic Compounds

J. F. Schneider and L. Harty

ANL/ACL-87-1 (December 1987)

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Monolithic Fuel Cell Development

D. C. Fee, P. E. Blackburn, D. Busch, T. Claar, D. W. Dees, J. Dusek, T. Easler, W. Ellingson, B. Flandermeyer, R. Fousek, J. J. Heiberger, T. Kraft, S. Majumdar, C. C. McPheeters, F. C. Mrasek, J. Picciolo, R. Poppel, and S. Zwick

Presented at the 1987 Summer National Meeting of the American Institute of Chemical Engineers, Minneapolis, MN, August 16–19, 1987

Processing and Waste Disposal of Fusion Blanket Systems

P. A. Finn and S. Vogler

Presented at the Symp. on Waste Disposal and Treatment for Fusion Reactor Systems, Am. Chem. Soc., Denver, CO, April 5–10, 1987

Thermodynamic and Kinetic Observations on LiAlO_2 : Adsorption, Dissolution, and Evolution of Water Vapor

A. K. Fischer and C. E. Johnson

Presented at the Int. Conf. on Fusion Reactor Materials, Karlsruhe, Federal Republic of Germany, October 4-8, 1987

Tritons as the Diffusing Species in Ceramic Tritium Breeders

A. K. Fischer and C. E. Johnson

Presented at the 89th Annual Meeting and Exposition of the Am. Ceram. Soc., Pittsburgh, PA, April 26-30, 1987

Nuclear Modules of ITER Tokamak Systems Code

Y. Gohar, J. Brooks, P. A. Finn, A. M. Hassanein, S. Willms, W. Barr, A. Bushigin, K. M. Kalyanam, and J. R. Haines

Presented at the 12th Symp. on Fusion Eng., Monterey, CA, October 12-16, 1987

Low Technology High Tritium Breeding Blanket Concept

Y. Gohar, D. L. Smith, M. C. Billone, Y. S. Cha, R. G. Clemmer, P. A. Finn, A. M. Hassanein, C. E. Johnson, Y. Liu, S. Majumdar, and R. F. Mattas

Presented at the 12th Symp. on Fusion Eng., Monterey, CA, October 12-16, 1987

Precise Chemical and Radiometric Analysis of Irradiated Fuel Rods from the Light-Water Breeder Reactor

D. G. Gracsyk

Presented at the 30th Oak Ridge Analytical Chemistry Conf., Oak Ridge National Laboratory, Knoxville, TN, October 20-22, 1987

SPECOMP Calculations of Radiation Damage in Compounds

L. R. Greenwood

Presented at the Sixth ASTM-EURATOM Symp. on Reactor Dosimetry, Jackson Hole, WY, June 1-5, 1987

Measurement of Long-Lived Isotopes in Fusion Materials

L. R. Greenwood and D. L. Bowers

Presented at the Sixth ASTM-EURATOM Symp. on Reactor Dosimetry, Jackson Hole, WY, June 1-5, 1987

Production of Long-Lived Activities in Fusion Materials and Calculation of Displacement in Compounds

L. R. Greenwood and D. L. Bowers

Presented at the Int. Conf. on Fusion Reactor Materials, Karlsruhe, Federal Republic of Germany, October 4-8, 1987

Dosimetry and Cross Section Measurements at RTNSII

L. R. Greenwood and D. W. Kneff

Presented at the U.S./Japan RTNSII Experimenters' Workshop, Monterey, CA, October 15-16, 1987

New Techniques for Enhancing Helium Production in Ferritic Materials

L. R. Greenwood, D. W. Kneff, and D. G. Gracsyk

Presented at the Int. Conf. on Fusion Reactor Materials, Karlsruhe, Federal Republic of Germany, October 4-8, 1987

Effect of Interstitial Components (O, C, N) on Interdiffusion of UPuZr and Stainless Steel Combinations

G. L. Hoffman, L. Leibowitz, E. Veleckis, R. V. Strain, and S. Merchant

Presented at the Am. Chem. Soc. Meeting, Pittsburgh, PA, April 26-30, 1987

The Determination of Technetium by ICP-AES

E. A. Huff and D. L. Bowers

Presented at the 30th Oak Ridge Analytical Chemistry Conf., Oak Ridge National Laboratory, Knoxville, TN October 20-22, 1987

Cluster Emission from a Molybdenum Surface

W. Husinsky, M. J. Pellin, W. F. Calaway, J. W. Burnett, E. L. Schweitzer, C. E. Young, and D. M. Gruen

Presented at the Second Topical Meeting on Microphysics of Surfaces Beams and Adsorbates, Santa Fe, NM, February 16-18, 1987

Ceramic Breeder Materials—Promise and Performance

C. E. Johnson

Presented at the Int. Conf. on Fusion Reactor Materials, Karlsruhe, Federal Republic of Germany, October 4-8, 1987

Chemical Site of Volatile Fission Products in Nuclear Accidents

C. E. Johnson

Presented at the US/JAPAN Seminar, National Science Foundation, University of Tokyo, Japan, June 8-12, 1987

Mass Spectrometry Studies of Fission Product Behavior. II. Gas Phase Species

C. E. Johnson and P. E. Blackburn

Presented at the US/JAPAN Seminar, National Science Foundation, University of Tokyo, Japan, June 8-12, 1987

Thermodynamics Studies of Zeolites: Clinoptilolite

G. K. Johnson and I. R. Tasker

Presented at the 42nd Annual Calorimetry Conf., Boulder, CO, July 26-31, 1987

Pyrochemical Reprocessing of Metallic Fast Reactor Fuel

I. Johnson

Presented at the US/JAPAN Seminar, National Science Foundation, University of Tokyo, Japan, June 8-12, 1987

Thermodynamic Data Needed for Pyrochemical Actinide Separation Process Development

I. Johnson

Presented at the Actinide Separations Workshop, Lawrence Livermore National Laboratory, Livermore, CA, April 1987

Comparison of Three Aerosol Sampling Techniques and the Differences in the Nitrate Determined by Each

S. A. Johnson and R. Kumar

Presented at Symp. on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 3-6, 1987

FTIR Studies of Zeolite Structures and Zeolite Catalysis

S. A. Johnson, K. A. Martin, and V. A. Maroni

Presented at the 21st Annual Great Lakes Regional Meeting, Symp. on New Advances in Fourier Transform Interferometry, Am. Chem. Soc., Chicago, IL, June 10-12, 1987

Depth of Origin of Sputtered Atoms

B. Jorgensen, M. J. Pellin, C. E. Young, W. F. Calaway, J. W. Burnett, E. L. Schweitzer, D. M. Gruen, J. W. Burnett, and J. T. Yates

Presented at the Materials Modification by High-Fluence Ion Beams, NATO Advanced Study Institute, Viano do Castelo, Portugal, August 24-September 4, 1987

Helium Production in Mixed-Spectrum Fission Reactors

D. W. Kneff, B. M. Oliver, R. P. Skowronski, and L. R. Greenwood

Presented at Sixth ASTM-EURATOM Symp. on Reactor Dosimetry, Jackson Hole, WY, June 1-5, 1987

Modeling Tritium Transport and Release in Ceramic Breeder Materials

J. P. Kopass and C. E. Johnson

Presented at the Int. Energy Agency Specialists Workshop on Modelling Tritium Behaviour in Fusion Blanket Ceramics, Chalk River, Canada, April 23-24, 1987

Modeling of Tritium Behavior in Ceramic Breeder Materials

J. P. Kopass, S. W. Tam, and C. E. Johnson

Presented at Int. Conf. on Fusion Reactor Materials, Karlsruhe, Federal Republic of Germany, October 4-8, 1987

Modifying FMS-11 to Provide Read-With-Timeout and Video Attribute Control

J. E. Kulaga

Presented at the Digital Equipment Computer Users Society Symp., Anaheim, CA, December 7-11, 1987

Experience in the Measurement of Alkali Vapors in PFBC Process Stream by Ames On-Line Alkali Analyser

S. H. D. Lee, K. M. Myles, W. J. Haas, Jr., and D. E. Eckels

Presented at the Alkali Research Seminar, Morgantown Energy Technology Center, Morgantown, WV, August 10, 1987

Thermophysical Properties of Metallic Fuel Systems

L. Leibowitz, E. Veleckis, and R. A. Blomquist

Presented at the 89th Annual Meeting and Exposition of the Am. Ceram. Soc., Pittsburgh, PA, April 26-30, 1987

Solidus and Liquidus Temperatures in the Uranium-Plutonium-Zirconium System

L. Leibowitz, E. Veleckis, R. A. Blomquist, A. D. Pelton, and C. E. Johnson

Presented at US/JAPAN Seminar, National Science Foundation, University of Tokyo, Japan, June 8-12, 1987

Electronic Worksheets—A McCabe-Thiele Solution for the 80's

R. A. Leonard

Presented at Application of Microcomputers in Chem. Eng., Chicago Section of AIChE, Chicago, IL, May 29, 1987

Modeling Americium Separations in Staged Solvent Extraction

R. A. Leonard

Presented at the 11th Actinide Separations Conf., Lawrence Livermore National Laboratory, Livermore, CA, June 1-4, 1987

Modeling New Process Chemistry Using the SASSE Worksheet

R. A. Leonard

Presented at Conf. on Plutonium/Uranium Recovery Operations, Richland, WA, October 12-15, 1987

Recent Advances in Centrifugal Contactor Design

R. A. Leonard

Presented at the Fifth Symp. on Separation Science and Tech. for Energy Applications, Oak Ridge National Laboratory, Knoxville, TN, October 26-30, 1987

Characterizing Coals for the Argonne Premium Coal Sample Program

P. C. Lindahl

Presented at the 21st Annual Great Lakes Regional Meeting, Symp. on Electrochemical Engineering and Technology, Am. Chem. Soc., Chicago, IL, June 10-12, 1987

Sample Analysis for the DOE Environmental Survey

P. C. Lindahl, D. K. Knight, J. R. Barker, J. E. Gebhart, J. S. Jessup, L. W. McMahon, and B. R. Clark

Presented at the 30th Oak Ridge Analytical Chemistry Conf., Oak Ridge National Laboratory, Knoxville, TN, October 20-22, 1987

Theoretical and Experimental Investigations of the Phonon Density of States of High T_c Superconducting Phases

V. A. Maroni, T. O. Brun, S. A. Johnson, M. H. Grimsditch, and C. A. Melendres

Presented at the 194th Am. Chem. Soc. Meeting, New Orleans, LA, August 30-September 4, 1987

Blanket Module Testing in TIBER

R. F. Mattas, C. C. Baker, Y. Cha, P. A. Finn, S. Majumdar, B. F. Picologlou, D. K. Sze, H. Stevens, M. A. Abdou, A. Hadid, R. Raffray, M. S. Tillack, M. Youssef, E. Cheng, R. L. Creedon, B. A. Engholm, K. Schultz, C. P. C. Wong, L. Deutsch, J. Gordon, S. Piet, R. Puigh, D. Steiner, and Y. Watanabe

Presented at the 12th Symp. on Fusion Eng., Monterey, CA, October 12-16, 1987

Tape-Casting Process Parameters for Control of Yttria-Stabilized Zirconia Properties

C. C. McPheeters and S. A. Willis

Presented at the 89th Annual Meeting and Exposition of the Am. Ceram. Soc., Pittsburgh, PA, April 26-30, 1987

High Temperature Laser Raman Spectroelectrochemical Studies of Pb and Ni in Dilute Sulfate Solutions

C. A. Melendres

Presented at the DOE/BES Contractors Meeting, Traverse City, MI, September 3-5, 1987

High Temperature *In Situ* Laser Raman Spectroelectrochemistry

C. A. Melendres, J. J. McMahon, and W. Ruther

Presented at the Gordon Research Conf. on Electrochemistry, Santa Barbara, CA, January 19-23, 1987

***In-Situ* Laser Raman Spectroscopy of Corrosion Films in High Temperature Aqueous Environments**

C. A. Melendres, J. J. McMahon, and W. Ruther

Presented at the 14th DOE Surface Studies Conf., Sandia National Laboratory, Albuquerque, NM, June 2-4, 1987

Interim Technology Assessment of Research and Development Modules from Energy Research Corporations' Nickel/Cadmium Battery Contract

T. P. Mulcahey, J. F. Miller, C. E. Webster, and C. C. Christianson

Presented at the DOE EHP Contractors Coordination Meeting, Las Vegas, NV, December 1-2, 1987

Measuring System for High Temperature/High Pressure Electrode Kinetic Studies

Z. Nagy

Presented at the DOE/BES Corrosion Contractor's Meeting, Traverse City, MI, September 3-4, 1987

Recent Advances and Applications of Fast Relaxation Techniques

Z. Nagy and N. C. Hung

Presented at the Gordon Research Conf. on Electrochemistry, Santa Barbara, CA, January 19-23, 1987

Electrochemical Cell and Electrode Designs for High-Temperature/High-Pressure Kinetic Measurements

Z. Nagy and R. M. Yonco

Presented at the Third Int. Symp. on Environmental Degradation of Materials in Nucl. Power Systems-Water Reactors, Traverse City, MI, August 30-September 3, 1987

An Assessment of Performance of Materials for FBC Air Heater Applications

K. Natesan, S. A. Miller, and W. F. Podolski

Presented at the National Association of Corrosion Engineers, Corrosion/87 Conf., San Francisco, CA, March 9-13, 1987

Thermochemical Studies of Chalcogenides

P. A. G. O'Hare, B. M. Lewis, S. Susman, K. J. Volin, J. G. Edwards, and B. Parkinson

Presented at the 42nd Annual Calorimetry Conf., Boulder, CO, July 26-31, 1987

System Analysis for Material Control and Accountancy Technology

P. J. Persiani, T. A. Daly, R. G. Bucher, A. B. Rothman, B. C. Cha, L. E. Trevorow, and W. B. Seefeldt

Presented at the Third Int. Conf. on Facility Operations-Safeguards Interface, Am. Nucl. Soc., San Diego, CA, November 29-December 4, 1987

Fluidised Bed Combustion

W. F. Podolski

Presented at the Direct Combustion of Coal Workshop, Sponsored by Delta-H Institute, Vancouver, B.C., Canada, July 6-8, 1987

Pressurized Fluidized Bed Combustion

W. F. Podolski

Presented at the FBC Technology Workshop, Sponsored by Delta-H Institute, Palo Alto, CA, January 28-30, 1987

Integrated Oxidation-Glass Formation Process for Waste Sodium Disposal

J. B. Rajan, R. Kumar, and D. R. Vissers

Presented at the Winter Meeting of the Am. Nucl. Soc., Los Angeles, CA, November 15-19, 1987

Integrated Oxidation/Vitrification of Reactive Metals

J. B. Rajan, R. Kumar, and D. R. Vissers

Presented at the Energy Research Conf. on Radioactive Waste Management, Processing and Disposal, Baton Rouge, LA, September 17-18, 1987

The Use of Gas Chromatography/Matrix Isolation Infrared Spectroscopy (GS/MIIR) and Supercritical Fluid Chromatography (SFC) for Waste Characterization

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

Presented at Advanced Research Technology Development Utilization Contractor Review Meeting, October 14-16, 1987

Soluble Oxide Chemistry at High Pressure

J. W. Rathke and R. J. Klingler

Presented at the Sixth DOE Catalysis and Surface Chemistry Research Conf., Gaithersburg, MD, October 14-16, 1987

Sulfide Capacities of MnO-SiO₂ Slags

R. G. Reddy and M. Blander

Presented at the Annual Meeting of the Metallurgical Soc., Am. Inst. Mechanical Engineers, Denver, CO, February 24-27, 1987

Ultra-High Performance Li-Alloy/FeS₂ Batteries for Pulse-Power Applications

L. Redey and T. D. Kaun

Presented at the U.S. Army Workshop on Capacitors and Batteries for Pulse Power Applications, Ashbury Park, NJ, November 17-18, 1987

Effect of Gamma Radiation of Moist Air Systems

D. T. Reed and R. A. Van Konynenburg

Presented at the Fall Meeting of Materials Research Soc., Boston, MA, November 30-December 4, 1987

Supported Liquid Membranes for the Separation and Recovery of Metal Ions

L. Reichley-Yinger and P. R. Danesi

Presented at the Actinide Separations Workshop, Lawrence Livermore National Laboratory, Livermore, CA, June 1-4, 1987

Partitioning of Pu and Other Metals Between TBP in Tetrachloroethylene and Aqueous Chloride Solutions

L. Reichley-Yinger and G. F. Vandegrift

Presented at the Actinide Separations Workshop, Lawrence Livermore National Laboratory, Livermore, CA, June 1-4, 1987

PUREX-TRUEX Recovery of Plutonium and Americium from Chloride Salt Wastes

L. Reichley-Yinger and G. F. Vandegrift

Presented at the Fifth Symp. on Separation Science and Tech. for Energy Applications, Oak Ridge National Laboratory, Knoxville, TN, October 26-29, 1987

Core-Concrete Chemistry: Fundamental Studies

M. F. Roche, J. L. Settle, L. Leibowitz, and C. E. Johnson

Presented at LACE/ACE Technical Advisory Committee Meeting, Argonne National Laboratory, Argonne, IL, July 21-24, 1987

The EPRI Laboratory Experiments at ANL

M. F. Roche, J. L. Settle, L. Leibowitz, C. E. Johnson, and R. L. Ritsman

Presented at Workshop on Chemical Processes and Products in Severe Reactor Accidents, National Research Council, Captiva Island, FL, December 9-12, 1987

A. Molecular Alloy: The K-Pb System

M.-L. Saboungi

Presented at NATO Advanced Study Institute on Alloy Phase Stability, Maleme, Crete, June 13-27, 1987

Anomalous Behavior of Some Unusual Liquid Alloys

M.-L. Saboungi

Presented at Chemistry Department, Purdue University, West Lafayette, IN, September 30, 1987

Anomalous Structure and Thermodynamic Properties of Liquid Alkali-Lead Alloys

M.-L. Saboungi

Presented at Argonne National Laboratory, Argonne, IL, April 23, 1987

Especies Moleculaires Dans Des Alliages Liquides

M.-L. Saboungi

Presented at Ecole Polytechnique, University of Montreal, Montreal, Canada, November 20, 1987

Molten Salt Solutions and Their Technological Applications

M.-L. Saboungi

Presented at Short School and Workshops on Materials Science, Energy, and Development, University of the West Indies, Jamaica, March 30-April 10, 1987

Potassium-Lead: A Molecular Liquid

M.-L. Saboungi

Presented at Intense Pulsed Neutron Source Division, Argonne National Laboratory, Argonne, IL, February 26, 1987

GC/Matrix-Isolation/FTIR as a Complementary Technique to GC/MS in Characterising Organics in Waste

J. F. Schneider, L. A. Raphaelian, and M. C. Hansen

Presented at the 194th Am. Chem. Soc. Meeting, Environmental Chemistry Division Symp., New Orleans, LA, August 30-September 4, 1987

Calculation of the Chemistry of Reaction Products from Combustion of High Sulfur Illinois #6 Coal Using Geometric Programming

S. N. Sinha, K. Natesan, and M. Blander

Presented at the TSM-AIME Annual Meeting, Denver, CO, February 24-27, 1987

Experimental Method for Investigating Helium Effects in Irradiated Vanadium

D. L. Smith, H. Matsui, L. R. Greenwood, and B. Loomis

Presented at Int. Conf. on Fusion Reactor Materials, Karlsruhe, Federal Republic of Germany, October 4-8, 1987

Development of the Be(d,n) Neutron Source for Cross-Section Investigations in the 14.5-14.8-MeV Energy Range

D. L. Smith, J. W. Meadows, P. T. Guenther, and L. R. Greenwood

Presented at the Sixth ASTM-EURATOM Symp. on Reactor Dosimetry, Jackson Hole, WY, June 1-5, 1987

Application of Thermodynamics to Pyrochemical Process Design

R. K. Steunenberg and J. P. Ackerman

Presented at the Actinide Workshop, Lawrence Livermore National Laboratory, Livermore, CA, June 2, 1987

An Investigation of SO₂-NO_x Control in a Staged Cyclone Coal Combustor with Pressure-Hydrated Limestone Injection

W. M. Swift and F. G. Teats

Presented at the Second Int. Conf. on Processing and Utilization of High-Sulfur Coals, Southern Illinois University, Carbondale, IL, September 27-October 1, 1987

Solution Properties of Solid and Liquid Potassium-Indium Alloys

T. Takenaka and M.-L. Saboungi

Presented at the 172nd Electrochem. Soc. Meeting, Honolulu, HI, October 18-23, 1987

The Role of Cation Defects in Tritium Migration in Lithium Ceramics

S. W. Tam, J. P. Kopass, and C. E. Johnson

Presented at the 89th Annual Meeting and Exposition of the Am. Ceram. Soc., Pittsburgh, PA, April 26-30, 1987

Calorimetry of Geological Materials for Nuclear Waste Disposal

I. R. Tasker

Presented at the 42nd Annual Calorimetry Conf., Boulder, CO, July 26-31, 1987

Continuing Investigations for Technology Assessment of ⁹⁹Mo Production from LEU Targets

G. F. Vandegrift, J. D. Kwok, S. L. Marshall, D. R. Vissers, and J. E. Matos

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors, Buenos Aires, Argentina, September 28-October 2, 1987

Methods of Chemical Analysis for Species in Marble and Limestone Selected Surfaces Exposed to the Acidic Environment

F. L. Williams, E. A. Huff, K. J. Jensen, and C. A. Youngdahl

Presented at the Symp. for the College of Sciences, Southern University College of Sciences, Baton Rouge, LA, February 19-20, 1987

Fundamental Properties of Nickel Sulfide Positive Electrode Materials for Use in Molten-Salt Batteries

C. Woodcock and L. Redey

Presented at AMOCO/University, Naperville, IL, October 15, 1987

Separation and Desulfurization of Pure Macerals. Part B. Separation of Coal Macerals from Illinois High Sulfur Coals

J. E. Young, G. R. Dyrkacz, and D. B. Chamberlain

Presented at the Fifth Annual Contractor's Technical Meeting, Center for Research on Sulfur in Coal, Champaign, IL, July 28-30, 1987

Separation of Coal Macerals by Density in a Continuous Flow Process

J. E. Young, G. R. Dyrkacz, and P. H. Neill

Presented at the Fine Coal Cleaning and Control of Fine Coal Cleaning Processes, Eng. Foundation Conf., Santa Barbara, CA, January 25-30, 1987

Correlation of Chemical Properties of Polyethylene Pipes with Constant Tensile Load Test Strength

J. E. Young and L. A. Raphaelian

Presented at the Tenth Plastic Fuel Gas Pipe Symp., New Orleans, LA, October 27-29, 1987

An Investigation of SO_2 - NO_x Control in a Staged Cyclone Coal Combustor with Limestone Injection

B. Zauderer, E. Fleming, and W. M. Swift

Presented at the 194th Am. Chem. Soc. Meeting, New Orleans, LA, August 30-September 4, 1987

F. Papers Accepted for Publication**Dating of MORB by Palagonite Layer Thickness Measurement**

T. A. Abrajano

To be published in Proc. of the Conf. on Dating of Young Mid-Ocean Ridge Basalts

The Reaction of Reference Commercial Nuclear Waste Glasses during Gamma Irradiation in a Saturated Tuff Environment

J. K. Bates, W. L. Ebert, T. J. Gerding, and D. F. Fischer

To be published in J. Mater. Res.

Detection and Speciation of Transuranium Elements in Synthetic Groundwater via Pulsed-Laser Excitation

J. V. Beitz, D. L. Bowers, M. M. Duxtader, V. A. Maroni, and D. T. Reed

To be published in Radiochim. Acta

The Coordination Cluster Theory for Metallic Solutions

M. Blander and M.-L. Saboungi

To be published in Proc. NATO ASI on Alloy Phase Stability

Stable Isotope Investigation of Gold Quartz Veins at the Oriental Mine, Alleghany District, California

J. K. Böhlke, R. M. Coveney, Jr., R. O. Rye, and I. Barnes

To be published in the U. S. Geological Survey Open-File Report

Theoretical Studies of Copper Oxide Clusters: Prediction of an Electronically Driven Phase Separation in $\text{YBa}_2\text{Cu}_3\text{O}_7$

L. A. Curtiss, T. O. Brun, and D. M. Gruen

To be published in Proc. of the High Temp. Superconductors Symp., Mater. Res. Soc.

Valence Fluctuations in $\text{YBa}_2\text{Cu}_3\text{O}_7$

L. A. Curtiss, T. O. Brun, and D. M. Gruen

To be published in Inorg. Chem.

Theoretical Enthalpies of Formation of SiH_n and SiH_n^+ ($n = 1-4$)

L. A. Curtiss and J. A. Pople

To be published in Chem. Phys. Lett.

Theoretical Thermochemistry 4. Ionisation Energies and Proton Affinities of AH_n Species ($A = \text{Li to B}$ and Na to Al): Geometries and Enthalpies of Formation of their Cations

L. A. Curtiss and J. A. Pople

To be published in J. Phys. Chem.

Processing and Waste Disposal Needs for Fusion Breeder Blanket Systems

P. A. Finn and S. Vogler

To be published in Fusion Eng. Des.

Thermodynamic and Kinetic Observations on LiAlO_2 : Adsorption, Dissolution, and Evolution of Water Vapor

A. K. Fischer and C. E. Johnson

To be published in J. Nucl. Mater.

Tritons as the Diffusing Species in Ceramic Tritium Breeders

A. K. Fischer and C. E. Johnson

To be published in *Adv. Ceram.***Production of Long-Lived Activities in Fusion Materials**

L. R. Greenwood and D. L. Bowers

To be published in *J. Nucl. Mater.***A New Technique for Enhancing Helium Production in Ferritic Materials**

L. R. Greenwood, D. G. Graczyk, and D. W. Kneff

To be published in *J. Nucl. Mater.***An Analysis of the Vibrational Characteristics of Zeolites Using Factor Group Methods**

V. A. Maroni

To be published in *Appl. Spectrosc.***Valence Force Field Treatment of the Rutile Structure at Zero Wave Vector**

V. A. Maroni

To be published in *J. Phys. Chem. Solids***Studies of Molecular Sieve Catalysis by Diffuse Reflectance Infrared Spectroscopy**

V. A. Maroni, K. A. Martin, and S. A. Johnson

To be published in the *Am. Chem. Soc. Symp. Ser. Vol. on Perspectives in Molecular Sieve Sciences****In-Situ* Laser Raman Spectroelectrochemical Study of the Corrosion of Lead in Dilute Na_2SO_4 Solution at High Temperature**

J. J. McMahon, W. Ruther, and C. A. Melendres

To be published in *J. Electrochem. Soc.***DC Relaxation Techniques for the Characterization of Fast Electrode Reactions**

Z. Nagy

To be published in *Techniques for Characterization of Electrodes and Electrochemical Processes*, John Wiley & Sons/The Electrochemical Society**Electrochemical Cell and Electrode Designs for High-Temperature/High-Pressure Kinetic Measurements**

Z. Nagy and R. M. Yonco

To be published in the *Proc. of the Third Int. Symp. on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors***An Assessment of Performance of Materials for FBC Air Heater Applications**

K. Natesan, S. A. Miller, and W. F. Podolski

To be published in *J. Mater. Energy Syst., Am. Soc. Met.***Robert Boyle: Pioneer of Experimental Chemistry**

P. A. G. O'Hare

To be published in *Books at Iowa*—The University of Iowa Libraries, Iowa City, IA

Standard Molar Enthalpy of Formation of Tungsten Diselenide (WSe_2) by Fluorine Combustion Calorimetry. Thermodynamics of the High-Temperature Vaporization of WSe_2 . Revised Value of the Standard Molar Enthalpy of Formation of Molybdenite (MoS_2)

P. A. G. O'Hare, B. M. Lewis, and B. A. Parkinson

To be published in J. Chem. Thermodyn.

Thermodynamic Stability of Orthorhombic Black Phosphorus

P. A. G. O'Hare, B. M. Lewis, and I. Shirotani

Thermochimica Acta, in press.

A Least Squares Optimization Technique for the Analysis of Thermodynamic Data in Ordered Liquids

A. D. Pelton and M. Blander

To be published in CALPHAD J.

Thermodynamic Properties of Liquid K-Bi Alloys by Electromotive Force Measurements

A. Petric, A. Pelton, and M.-L. Saboungi

To be published in J. Phys. F: Met. Phys.

Voltammetry of Uranium and Plutonium in Molten $\text{LiCl-NaCl-CaCl}_2\text{-BaCl}_2$. I. Reduction of U(III) to Uranium Metal

D. S. Poa, Z. Tomczuk, and R. K. Steunenbergh

To be published in J. Electrochem. Soc.

The Use of Gas Chromatography/Matrix Isolation Infrared Spectroscopy (GS/MIIR) and Supercritical Fluid Chromatography (SFC) for Waste Characterization

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

To be published in Proc. of the Advanced Research and Technology Development (AR&TD) Direct Utilization and Contract Meeting for METC

Liquid Potassium-Antimony Alloys - Investigation of Some Thermodynamic Properties

M.-L. Saboungi, J. Ellefson, G. K. Johnson, and W. Freyland

To be published in J. Chem. Phys.

Liquid Alloys—New Perspectives and Challenges

M.-L. Saboungi, S. R. Leonard, G. K. Johnson, and D. L. Price

To be published in Proc. NATO ASI on Alloy Phase Stability

Uranium-Series Age Determination of Calcite Veins, VC-1 Drill Core, Valles Caldera, New Mexico

N. C. Sturchio and C. Bins

To be published in J. Geophys. Res.

Thermochemistry of Uranium Compounds. XVI. Calorimetric Determination of the Standard Molar Enthalpy of Formation at 298.15 K, Low-Temperature Heat Capacity, and High-Temperature Enthalpy Increments of $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ (Schoepite)

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