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CHEMICAL TECHNOLOGY DIVISION
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1989

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CHEMICAL TECHNOLOGY DIVISION
ANNUAL TECHNICAL REPORT
1989

ABSTRACT

Highlights of the Chemical Technology (CMT) Division's activities during 1989 are presented. In this period, CMT conducted research and development in the following areas: (1) electrochemical technology, including high-performance batteries (mainly lithium/iron sulfide and sodium/metal chloride), aqueous batteries (lead-acid and nickel/iron), and advanced fuel cells with molten carbonate and solid oxide electrolytes; (2) coal utilization, including the heat and seed recovery technology for coal-fired magnetohydrodynamics plants and the technology for fluidized-bed combustion; (3) methods for recovery of energy from municipal waste and techniques for treatment of hazardous organic waste; (4) nuclear technology related to a process for separating and recovering transuranic elements from nuclear waste and for producing ^{99}Mo from low-enriched uranium targets, the recovery processes for discharged fuel and the uranium blanket in a sodium-cooled fast reactor (the Integral Fast Reactor), and waste management; and (5) 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 superconducting oxides and associated and ordered solutions at high temperatures; interfacial processes of importance to corrosion science, high-temperature superconductivity, and catalysis; and the geochemical processes responsible for trace-element migration within the earth's crust. The Division continued to be administratively responsible for and the major user of the Analytical Chemistry Laboratory at Argonne National Laboratory (ANL).

SUMMARY

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

1. *Electrochemical Technology*

The CMT Division is engaged in a variety of activities related to the development of advanced batteries (lithium/iron sulfide and sodium/metal chloride), aqueous batteries (lead-acid and nickel/iron), and advanced fuel cells with molten carbonate and solid oxide electrolytes. These activities include research, performance and lifetime testing, post-test examinations, modeling, and technical management of industrial contracts from the Department of Energy (DOE). Another effort involves electrochemical investigation into anomalous heat effects reported for deuterated metals in an electrolysis cell.

The research effort on the Li/FeS₂ cell has resulted in several advances in the technology. Small-scale monopolar cells with overcharge protection by a lithium-shuttle mechanism have been tested with MgO powder electrode separators. This separator, which requires operation of the cell in an electrolyte-starved condition, has the potential for lower cost and greater thermodynamic stability compared with the BN felt previously used. These electrolyte-starved cells with MgO powder separators have demonstrated comparable performance to that of flooded cells with BN felt separator. Overcharge tolerance tests indicated that a 3-mA/cm² trickle charge (where 15% more coulombs than the rated capacity are charged into the electrode) was tolerated without positive electrode polarization. Such cells have been operated over 200 cycles with high performance and stable overcharge tolerance. In other work, we have developed hermetic ceramic sealants for peripheral seals in bipolar cells and feedthroughs in monopolar cells. A small-scale bipolar cell with the hermetic peripheral seal was operated for 175 cycles with high performance.

The research on the sodium/metal chloride cell has focused on increasing the performance of the NiCl₂ electrode. A new method for electrode fabrication was developed in 1989. In tests of an electrode fabricated by this method (containing 18 vol % Ni), the area specific impedance was 0.50 Ω cm² at 300 °C, which is a significant improvement over that of state-of-the-art cells (1.0-1.5 Ω cm²). Also being investigated is use of a composite electrolyte based on β"-alumina and a suitable glass as an alternative to the β"-alumina ceramic currently used. Such composites would allow fabrication of cells with high-surface-area prismatic electrolytes, which would reduce voltage losses. Composites have been produced with excellent resistivity values of 30 Ω cm at 250 °C, which is even better than the target value of 75 Ω cm at 250 °C.

The Analysis and Diagnostic Laboratory (ADL) in CMT includes a test laboratory to conduct battery evaluations under simulated application conditions and a post-test analysis laboratory. In the test laboratory, cells and modules of four battery technologies (Na/S, Li/FeS, Ni/Fe, and lead-acid) fabricated by various industrial firms underwent performance and lifetime testing during 1989. Two of these technologies (Na/S and Ni/Fe) were also subjected to post-test analysis. Causes of cell failure were determined to be glass seal problems in the Na/S cells and iron particulate contamination of the nickel plates in the Ni/Fe cells. The information gained from the performance and lifetime tests and the post-test evaluations provides a measure of the technical progress made by the battery developers and identifies specific areas where changes in design or the materials of construction would improve battery performance.

In 1989, the CMT Division continued to provide DOE with technical management support of industrial contracts for development of lead-acid and Ni/Fe batteries, phosphoric acid fuel cell/battery system, and proton exchange membrane fuel cells for transportation applications.

A study was initiated to address claims of anomalous heat in the palladium-deuterium electrochemical system ("cold fusion"). Two series of experiments were performed: (1) differential temperature analyses of identical light- and heavy-water electrochemical cells and (2) calorimetric measurements of operating heavy-water electrochemical cells. For the first series, it proved to be impossible to maintain identical electrochemical conditions in both cells. Thus, the results from this kind of experiment are too ambiguous for evaluating the occurrence of

excess heat, as has been reported by others. In the second series, no significant excess heat was detected.

Two advanced fuel cells are being studied at CMT: the solid oxide fuel cell and the molten carbonate fuel cell. In the solid oxide fuel cell development, an effort is underway to develop a monolithic fuel cell design which employs the same thin ceramic components used in other oxide fuel cells but in a strong, lightweight honeycomb structure of small cells. In this effort for 1989, the effect of fuel composition (H_2O partial pressure and CO/CO_2 ratio) on the anode/electrolyte interfacial resistance was determined. It was concluded that an oxygen-rich species in the fuel is necessary to assist the transfer of charge from the oxide ion to the electrons in the electrodes of the fuel cell.

A project was recently initiated to develop new materials which permit operation of ceramic solid-state fuel cells at lower temperatures ($500\text{--}800^\circ\text{C}$ vs. 1000°C currently required). Our approach is to start with a search for a new electrolyte. Materials with perovskite and scheelite structures have been evaluated.

The work on molten carbonate fuel cells is focused on finding improved materials for the cathode and anode and testing them in cells. The material Li_2MnO_3 is being considered as an alternative cathode material to the present NiO . It was determined that Zn , Al , and Nb dopants all improved the conductivity of Li_2MnO_3 to the extent believed necessary for a fuel cell cathode. In anode materials studies, an MnO structure that is thermodynamically stable in the anode environment was prepared. This material showed a resistivity of $20\ \Omega\ \text{cm}$ at 650°C (cell operating temperature), which is within the range that might be applicable for cell use.

Cell testing was done with an undoped LiFeO_2 anode. The test results indicated that the anode performance is near that for the presently used nickel at low current densities ($<50\ \text{mA}/\text{cm}^2$), but that the performance decays with time at higher current densities. The anode test also indicated that the solubility of iron in the anode conditions is higher than that in the cathode conditions. This is a very promising result for use of LiFeO_2 as a cathode, but not necessarily for its use as an anode. Tests on a variety of cathode materials showed that the cathode surface area has a greater effect on performance than material conductivity over a fairly wide range of conductivity.

2. *Fossil Fuel Research*

The fossil fuel program in CMT includes research on fluidized-bed combustion (FBC) technology, heat and seed recovery for coal-fired magnetohydrodynamics (MHD), and multiphase flow systems.

The FBC projects include (1) measurement and control of alkali vapor in the off-gas from a pressurized fluidized-bed combustor (PFBC), (2) testing and evaluation of Illinois char as fuel for a PFBC, (3) materials testing for a cogeneration air-heater application in an atmospheric fluidized-bed combustor (AFBC), (4) investigation of metal wastage of FBC heat exchanger surfaces, and (5) studies of chaotic behavior in fluidized beds.

For several years, CMT has been investigating the use of sorbents for the removal of alkali metal vapor compounds from the PFBC off-gas. Previous tests in a bench-scale PFBC/alkali sorber with an Ames on-line alkali analyzer had indicated that the sampling and analysis of the alkali vapor compounds were complicated by the interaction of these compounds with the stainless steel sampling line. The problem was overcome by using an analytical technique (atomic absorption spectrometry analysis of sections from a sorber bed exposed to the PFBC off-gas) that does not require use of a sampling line. This technique is being employed to develop a regenerable activated bauxite sorber alkali monitor (RABSAM) for field application. The RABSAM will use commercially available activated bauxite, which contains some clay impurities; therefore, a technique for deactivating these impurities (i.e., NaCl solution impregnation of the bauxite followed by heat treatment) was developed.

Bench-scale PFBC experiments were also carried out using both an Illinois No. 6 coal and char which had been prepared from the coal. The objective of these tests was to evaluate the suitability of the char as a fuel for a PFBC system. For both char and coal combustion, the alkali vapor concentration in the PFBC off-gas was measured to be more than five times greater than the 0.024 ppm currently suggested alkali limit for an industrial oil-fired gas turbine.

Argonne is managing a project to assess materials and process performance of in-bed air heaters for cogeneration of electricity and hot air in an AFBC. About 1700 h of testing in the large-scale AFBC unit at Rockwell International has been completed. Argonne and Westinghouse Corp. are performing data analysis and an assessment of the heat exchanger performance.

Argonne and seven other organizations are participating in a cooperative research and development venture directed at the problem of metal wastage of heat exchanger surfaces in fluidized-bed combustors. The objective of the effort is to develop hydrodynamic and erosion computer models that will be used to generate guidelines for the design and operation of FBCs that will minimize metal loss. As part of this effort, ANL has developed two-dimensional computer models incorporating hydrodynamics of the solids and bubble motion and the erosion of tubes resulting from the impaction and abrasion of particles. These models have been partially validated with experimental results obtained by other research organizations participating in this project. A workshop was held at ANL in October 1989 to demonstrate the hydrodynamic and erosion computer codes for the project participants and to provide them with hands-on experience in using the codes.

Measurements of pressure, voidage, and gas and solids velocities made in fluidized beds usually show rapid fluctuations. Analyses of experimental time series data obtained from pressure fluctuations of a fluidized bed were undertaken to determine if the data exhibit only stochastic features, or if they have characteristics of deterministic chaos. The results indicate the presence of a nonrandom component in the process underlying the time series data.

In work on the technology for heat and seed recovery in an MHD plant, experiments were performed to determine the corrosion of candidate steam superheater alloys exposed to MHD conditions (metal temperature, 840 K; gas temperature, 1480 K) for 2000 h. The austenitic

alloys (304H, 316, 310, 321, and 800H) exposed to superheater test conditions showed negligible corrosion. Acceptable materials for the intermediate-temperature air heater for an MHD plant are still being sought.

During 1989, detailed design of a small-scale one-dimensional flow reactor for the investigation of nitrous oxide decomposition kinetics under radiant boiler temperature conditions in an MHD plant was initiated. Experimental data from the flow reactor will be used to provide further validation of the available nitrous oxide decomposition kinetics codes.

A collaborative effort was initiated with Ohio State University to study the interfacial phenomena and dynamics of bubble wakes in three-phase (gas-liquid-solid) fluidized beds. The overall objectives are to study the local hydrodynamic behavior of gas bubbles and their wakes in gas-liquid-solid flow systems and to determine how such behavior affects the scaleup criteria for optimum design of three-phase flow systems.

3. *Municipal and Hazardous Waste Technologies*

The CMT effort on municipal and hazardous waste technologies involves research into the thermochemical conversion of municipal solid waste (MSW) and the development of methods for treating hazardous waste.

A model is being developed to simulate the MSW combustion process and the formation of products not only during combustion but also during cooling of the combustion products in the heat recovery and gas cleanup system. In this model, we have assumed that MSW is composed of pseudo components (such as cellulose, plastics, etc.), which pyrolyze through numerous pathways to yield fuel gases, ash, and char. The model equations were solved to generate the temperature and mass flow profiles along the length of the MSW bed. The results revealed that there is a well-defined "feasible operating range" of variation in the solids feed rate for a given air flow rate. This feasible range is sharply bounded by inadequate fuel gas generation at one end and incomplete volatilization of the solids at the other end. Parametric studies showed that the air flow rate is the most important operating variable in MSW combustion because it affects both the flame and bed temperatures.

The research on hazardous waste treatment includes an investigation of a one-step process for conversion of reactive metal (primarily sodium) to a glass for disposal. Our earlier work had identified suitable glass compositions for disposal of waste sodium. In this report period, process energy requirements to convert waste sodium to several different glass compositions were determined for temperatures of 900-1600 °C. Work is also underway on determining the technical feasibility of employing a microwave-induced plasma for detoxification of chlorinated hydrocarbons.

An effort has been initiated to develop a process for separating the organic and inorganic constituents of the red-water waste stream generated in production of 2,4,6-trinitrotoluene. The ANL conceptual process for red-water treatment consists of separating the inorganic salts from the organic nitrosulphonic acids before the latter are biodegraded to nonhazardous compounds. This separation, which appears necessary for biodegradation of the

organics, is accomplished by a biphasic solvent extraction process. Research to date has concentrated on the polyethylene glycol (PEG)/Na₂SO₄ system. At room temperature, a concentration of 7.5% PEG and 6% Na₂SO₄ forms an aqueous two-phase system. Increasing temperature to 80 °C results in biphasic formation at significantly lower salt and PEG concentrations. During the next year, a bench-scale demonstration of aqueous biphasic solvent extraction is planned.

4. *Nuclear Technology*

Separation Science and Technology. The Division's work in separation science and technology is mainly concerned with developing a process for removing and concentrating actinides from waste streams contaminated by transuranic (TRU) elements. The objective is to recover the valuable TRU elements and lower disposal costs by use of the TRUEX (TRAnsUranic EXtraction) solvent extraction process developed at ANL. The extractant used for this process is octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO).

The Generic TRUEX Model was developed to design flowsheets for specific feed streams and to predict cost and space requirements for implementing a site- and feed-specific TRUEX process. Versions of the model are now available for use with Macintosh and IBM-compatible personal computers. A more powerful and faster second-generation Generic TRUEX Model will be available in 1990. Improvements will include the ability to calculate flowsheets and predict space and cost requirements for any type of solvent extraction equipment, including pulsed columns, and to estimate solvent degradation during processing caused by radiolysis and hydrolysis of the extractant (CMPO). Generation of experimental extraction data using an ANL-design centrifugal contactor with multiple feed and exit points continues to be an important part of the model development effort. These data and literature data are being collected in a computer data base for easy access and documentation. In addition, experiments with sixteen-stage 4-cm contactors are underway to verify the species extraction behavior predictions and flowsheet calculations with the Generic TRUEX Model.

Centrifugal contactor development continues as an important part of TRUEX process development. A spreadsheet-based model was developed for predicting motor/rotor vibration characteristics to allow the continued use of inexpensive, off-the-shelf motors for the ANL centrifugal contactor. A 2-cm minicontactor was built and tested and is ready for routine laboratory use. Since the minicontactor requires only 1 L of feed solution instead of the 10 L needed for the 4-cm contactor, it is useful in those cases where more feed may be difficult and expensive to prepare, or cannot be accommodated in the test facility, or is simply unavailable. In other contactor work, a sixteen-stage 4-cm unit was built and installed at the Y-12 plant (Oak Ridge, TN) to help in development of new solvent extraction processes. Design of a centrifugal contactor for use with molten salts and metals (the "pyrocontactor") was begun in support of development of waste treatment processes for the Integral Fast Reactor.

Another project is concerned with examining the feasibility of substituting low-enriched uranium for the high-enriched uranium currently used in the production of fission product ⁹⁹Mo. Technetium-99m, the daughter of ⁹⁹Mo, is used widely in medical applications. A conceptual process was designed for recovering ⁹⁹Mo from U₃Si₂ targets.

High-Level Waste/Repository Interactions. The proposed site for the first repository for storage of nuclear waste in the United States is the tuff beds of Yucca Mountain, Nevada. This CMT effort mainly concerns the interaction between the host repository environment at Yucca Mountain and emplaced high-level nuclear waste and spent fuel. The repository site is characterized as hydrologically unsaturated with free air exchange, and several experimental methodologies have been developed to assess the behavior of glass and spent fuel in limited volumes of water. Several CMT experimental programs, in support of the Yucca Mountain Project, are in progress to characterize the reaction of borosilicate nuclear waste glasses and spent fuel with repository groundwater, the irradiation of moist air and groundwater, and the speciation of released radionuclides.

Tests are in progress wherein simulated nuclear waste glasses are reacted in water vapor, reacted in liquid water, reacted sequentially in vapor and then in liquid water, or intermittently contacted by small volumes of liquid water. These tests provide information regarding the long- and short-term durabilities of various waste glass compositions and the behavior of glass in limited volumes of water. In these tests, glass reaction with water vapor was found to occur in a small volume of condensed water, which became highly concentrated after a small amount of glass had reacted. The formation of secondary phases was found to increase the reaction rate and so must be accounted for when projecting glass durabilities to long times. The leach tests, which were performed at various glass surface area/leachant volume (SA/V) ratios, indicated that the leach rate is directly proportional to SA/V, provided that the solution pH does not change significantly and no secondary mineral phases form. The experimental alteration of natural materials, i.e., basalt glass and obsidian, in water vapor is being investigated in support of similar experiments with simulated waste glasses.

In addition to glass studies, experiments designed to determine radionuclide release rates by exposing spent fuel to repository-relevant groundwater are being performed. Preliminary experiments with UO_2 powders and monoliths in liquid water and small amounts of dripping water have been performed in preparation for the spent fuel studies.

The effect of ionizing gamma radiation on the host environment and on waste package components has also been experimentally studied. Radiolytic yields of NO_x , ammonia, and nitrous oxide in dry and moist air have been determined at temperatures up to 200°C . The results indicated that ammonia formation under repository-relevant conditions is possible. The formation of ammonia has serious implications regarding the use of copper-based alloys for waste disposal, owing to their susceptibility to ammonia cracking. The extent of corrosion of candidate canister materials (Incoloy 825, Cu, Cu-Ni, and Al-bronze) in moist air under a radiation field was found to be sensitive to the humidity. Localized corrosion of the copper-based materials occurred at intermediate humidities (3-15% relative humidity).

Other programs are underway in support of DOE Defense Programs and the Repository Technology Program, in which the durabilities of defense glass compositions under expected repository conditions and performance assessment criteria are being evaluated. Experimental work for these programs includes the long-term testing of actual waste glass and laser photoacoustic spectroscopy analysis of dilute solutions containing radionuclides.

Experimental effort is also underway to investigate the effect of ionizing radiation on the potential for gas generation in the Waste Isolation Pilot Plant (WIPP) site. In this report period, experiments were initiated to determine the extent that nonbiodegradable plastics present in the WIPP waste canister will be radioactively converted to biodegradable material.

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, re-enriching the core alloy with plutonium bred in the blanket, and immobilizing fission product wastes in suitable media for disposal.

The reference process for initial operation of the electrorefiner in the fuel cycle facility utilizes anodic dissolution of spent binary fuel (U-10 wt % Zr) in a molten chloride electrolyte salt and collection of uranium products on a solid cathode. The anodic dissolution of binary fuel has been successfully demonstrated at the 10 kg per batch level and is now a routine operation. In addition, both single mandrel and multipin solid cathodes have been successfully used to deposit uranium at the 10 kg per batch level. Experimental research efforts included determination of parameters that control deposition rate, transport efficiency, and product composition. Additional experiments demonstrated the feasibility of using a liquid cadmium cathode for collecting a U-Pu product. Also, development work on an alternative method (direct chemical reduction) for collecting a U-Pu product was initiated. This method employs a lithium reductant to reduce PuCl_3 and UCl_3 out of the molten electrolyte and deposit the metal in the cadmium pool. Results of four experiments, with varying degrees of success, have demonstrated the potential of this method.

Experiments have been conducted to demonstrate purification and consolidation of liquid cadmium cathode products. The starting compositions for these experiments were selected to simulate the expected product in the recovery of uranium and plutonium in a liquid cadmium cathode. The results confirmed that a purified and consolidated U-Pu product can be obtained from the electrorefiner product (U-Pu-Cd-salt), and that essentially no uranium or plutonium is lost in the process.

Studies are underway to develop processes for the treatment and packaging of metal and salt wastes generated in the processing of IFR fuel so that it is suitable for disposal. In the reference flowsheet for waste treatment, the salt from the electrorefiner is first contacted with a Cd-U alloy to strip away uranium, residual TRU, and rare earths. The stripped salt, which is expected to be nonTRU, is immobilized and packaged for disposal. Indeed, laboratory tests during this report period have verified this portion of the reference flowsheet. The overall TRU decontamination of this salt treatment procedure was about 1×10^5 and total alpha activity was <10 nCi/g. Efforts are underway to characterize salt behavior in a high radiation field and to develop suitable means of encapsulating the waste salt for disposal.

The metal waste includes cladding hulls and cadmium (with noble metal fission products) from the electrorefiner. The current concept for treating and packaging this waste involves blending copper (or other suitable metals) with the waste, distilling off the excess cadmium, and then hot isostatically pressing the remaining residue into a dense monolith. Work has been initiated to develop this concept.

Plutonium Residue Recovery. The objective of this effort is to develop an effective pyrochemical method for the recovery of plutonium from intractable residues. Several solvent/reductant systems have been considered for reducing the oxide residues and making the plutonium available for further pyro or aqueous processing. In this report period, experimental results for plutonium reduction and recovery from incinerator ash heels and bomb reduction slag were obtained with Zn-Ca and Al-Ca reductant systems and CaCl_2 - CaF_2 salt. On the basis of the plutonium content in the salt phase, plutonium reduction averaged 98% after one reduction stage and 99.4% after two reduction stages for the ash heel experiments and 93.6% after one reduction stage for the slag experiments. However, analysis of the metal ingots failed to confirm the good reductions indicated by the salt analysis. This discrepancy is under investigation.

5. *Applied Physical Chemistry*

Fission Product Release from Core-Concrete Melts. The vaporization of strontium, barium, and lanthanum oxides from mixtures with urania, zirconia, and concrete was determined in a series of experiments. The objective was to obtain an estimate for the release of these refractory fission products during the core-concrete interaction phase of a degraded-core accident. The vaporization of uranium and the total mass was also determined. Three different concretes having silica contents ranging from 7 to 69 wt % were used to reflect the known range of reactor-basemat compositions. In the experiments, the mixtures were vaporized at 2400 K into flowing H_2 -0.03% H_2O gas. Our experimental data indicated that the releases of Sr, Ba, La, and U expected in a severe nuclear-reactor accident will be less than 1% for the basemat concrete of low silica content (7 wt %) and less than 0.01% for the basemat concrete of high silica content (69 wt %). These values are much lower than those reported in the literature. The total mass release (aerosol) was about 0.5% for all three concretes.

Thermophysical Properties of Metal Fuels. An earlier literature survey revealed serious shortcomings in the data available on the thermophysical properties of fuel and blanket materials for the IFR. An effort was, therefore, initiated to correct the most serious deficiencies by performing experimental and calculational studies of fuel alloy and cladding materials. A summary is given of our work on fuel-cladding compatibility, the U-Pu-Zr phase diagram, and phase relations in the U-Fe system.

As part of our investigation on fuel-cladding compatibility, differential thermal analysis (DTA) experiments were performed with mixtures of U-Pu-Zr fuel and stainless steel cladding. The DTA curves on initial heating indicated solid-state transitions in the fuel at 600-700°C and an exothermal reaction forming more stable products (probably an Fe_2Zr -like phase) at 1200°C. On subsequent cooling, the DTA curve indicated primary precipitation at 1220°C and a freezing transition at 700°C. The DTA curves were used to estimate the "onset-of-melting" temperature with an accuracy of ± 10 -20°C. Scanning electron microscopy of the residues from

these experiments indicated the following reaction sequence on heating: primary precipitation of a Fe_2Zr -like phase, followed by secondary precipitation of Fe_2U , followed by formation of $\text{Fe}_2\text{U}-\text{FeU}_6$ eutectic.

Other studies on metal fuel properties involved calculations of the Pu-U phase diagram, which will be used to refine the U-Pu-Zr phase diagram, and DTA experiments with U-Fe mixtures, which will be used to obtain a better understanding of the phase relations involved in fuel-cladding systems.

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.

In one such study, temperature programmed desorption (TPD) measurements are in progress to provide data that describe the kinetics of desorption of $\text{H}_2\text{O}(\text{g})$ and $\text{H}_2(\text{g})$ from $\text{LiAlO}_2(\text{s})$. The TPD spectra exhibited different shapes suggestive of differing and/or multiple processes taking place as $\text{H}_2\text{O}(\text{g})$ is desorbed from the solid. Another study is in progress to develop a computer model that will predict tritium release from neutron-irradiated lithium ceramics into a gas purge stream. In most previous studies, tritium desorption has been treated as occurring from one site with a single desorption activation energy. However, recent experiments have shown tritium-release behavior that could not be explained by a diffusion-desorption model with one desorption activation energy. This behavior was modeled by using a desorption activation energy that varies with surface coverage by adsorbed hydrogen.

Experiments were undertaken to investigate the transport of LiOH from a lithium oxide solid breeder with a helium purge gas stream containing water vapor (at 50 Pa). The gas velocity was varied from 50 to 2600 cm/s at 850 °C. The fractional saturation product for $\text{H}_2\text{O}(\text{g})$ diffusion from the flowing helium to the lithium oxide and $\text{LiOH}(\text{g})$ diffusion into the flowing helium was calculated from the experimental results. Our results were in general agreement with those reported by others. This work established conditions for calculating LiOH undersaturation in helium as a function of the blanket purge channel dimensions and velocity of the purge gas.

The International Thermonuclear Experimental Reactor (ITER) is an international project whose purpose is to produce a conceptual design of a tokamak reactor which can be used to test components for a prototype fusion reactor. Designs of each of the reactor systems are being generated by the ITER partners in the U.S., U.S.S.R., Japan, and the European Community. In support of this project, CMT has examined the technical requirements for an aqueous lithium salt blanket (2 M LiOH or LiNO_3) in which tritium fuel is bred. This effort included calculation of the corrosion products in an operating aqueous blanket and the design of a tritium recovery system for the aqueous blanket.

The Breeding Blanket Interface (BBI) is that system which performs the necessary processing and recycle of the tritium recovered from a fusion reactor blanket. Although considerable attention has been given to studies of tritium breeding and recovery and also many aspects of tritium processing, very little work had been done on the BBI. In this report period,

pre-conceptual designs of the BBI system were developed for two types of blankets: aqueous salt solution and solid breeder blanket. A summary of the major design features of the two BBI systems is given.

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. Our nuclear data measurements have focused on the production of long-lived isotopes in fusion reactor materials. These data are needed for the assessment of waste disposal and reactor maintenance application.

6. *Basic Chemistry Research*

Fluid Catalysis. This research is designed to determine reaction mechanisms and to explore new catalytic chemistry associated with molecular energy resources. Real-time kinetic and spectroscopic techniques at high pressures and temperatures are used to determine the chemistry of small molecules derived from coal, natural gas, and petroleum. Maximal concentrations of reactive gases are achieved by making use of their complete miscibilities with supercritical fluids. Thus, the potential energy profile for activation of dihydrogen by the commercial Oxo catalyst in supercritical CO_2 solution was determined by using high-pressure nuclear magnetic resonance (NMR) spectroscopy. These studies were facilitated by our finding that a new type of NMR detector, an elongated toroid, achieves greatly improved sensitivity in metal pressure probes for nuclei associated with organometallic systems.

In other research, solution-phase oxide catalyzed hydrogenation and water-gas shift processes that seem to parallel metal oxide surface chemistry are being explored. In this effort for 1989, a procedure was developed for synthesizing tris(trimethylsilyl)methyl zinc formate and the corresponding hydroxide complex. The tris(trimethylsilyl)methyl ligand has the potential to solubilize a range of polar metal oxide and hydroxide complexes in common organic solvents at high temperatures and gas pressures.

Also being investigated is the organometallic chemistry of extremely robust metallocphthalocyanines designed to achieve stereoselective homogeneous hydrogenation and oxidation catalyses at unusually high temperatures. A facile synthesis procedure was developed for 1,4,8,11,15,22,25-octapentylphthalocyanine (R_8PcH_2), and this procedure was used to prepare the following complexes: $\text{Co}(\text{R}_8\text{Pc})$, $\text{Rh}(\text{R}_8\text{Pc})(\text{CO})\text{Cl}$, $\text{Rh}(\text{R}_8\text{Pc})(\text{PBU}_3)\text{Cl}$, $\text{Rh}(\text{P}_8\text{Pc})(\text{PhCN})\text{Cl}$, and $\text{Rh}(\text{R}_8\text{Pc})\text{PBU}_3\text{-Cl-Rh}(\text{R}_8\text{Pc})\text{Cl}$. These complexes will be convenient starting points for the requisite cobalt and rhodium hydrides, alkyls, and metal-metal bonded species necessary for experimental work in the area of hydrocarbon activation.

High-Temperature Materials Chemistry. Solubilities of CoCl_2 in binary molten solutions of NaCl with AlCl_3 exhibit a sharp minimum at the most ordered composition of 50 mol % NaCl -50 mol % AlCl_3 . The concentration dependence of our solubility measurements in acid solutions, $X(\text{AlCl}_3) > 0.5$ mole fraction, was accurately described by the coordination cluster theory and by the solubility product principle and has provided the information necessary to predict such solubilities in all other acid chloroaluminates. The behavior of the solubilities of

two other transition metal chlorides, FeCl_2 and NiCl_2 , especially in basic melts, is important for modeling the electrochemical kinetics of the "Zebra" battery (NaCl-saturated NaCl- AlCl_3 electrolyte that is also saturated with FeCl_2) under development for automobile propulsion.

Neutron diffraction measurements were performed on a series of trivalent halides (AlBr_3 , GaBr_3 , GaI_3 , and NdCl_3) at temperatures slightly above their melting points. The cation-anion coordination numbers were 4.0 for AlBr_3 , 3.8 for GaBr_3 , and 3.7 for GaI_3 . This finding indicates that the AlBr_3 melts consist of Al_2Br_6 molecules, whereas the two gallium salts are about 70-80% dimerized. This observation was supported by comparison of the measured structure factors with model calculations using the Reference Interaction Site Model. The measured NdCl_3 structure factor was used to obtain a model structure by the reverse Monte Carlo method. The resultant structure shows a close similarity to a randomized structure of solid NdCl_3 for features up to about 6 Å, with no remnant of the solid structure present at ~8 Å.

Ab initio molecular orbital calculations on CuO clusters representing chains and planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconductors were used to determine d-d excitations of divalent copper. The results indicate that these excitations lie in the region of 1.4-1.8 eV, and that the presence of O^- has little effect on the excitation energies. Measured peaks at higher energy in the optical absorption spectra have been assigned to d-d excitations in some experimental studies. Our results suggest that these excitations are due to a different mechanism, such as charge transfer.

A method, referred to as Gaussian-1 (G1), is under development for performing accurate *ab initio* quantum chemical calculations of the energetics of clusters and molecules. This method had been shown to predict energies of species of first-row atoms to 0.1 eV and was used to predict energies of molecules for which there are no experimental data. The G1 method has helped to identify B_2H_4 and B_2H_5 for the first time. The method was extended to the calculation of the energies of compounds containing second-row atoms and shown to be accurate to 0.1 eV by comparisons with experimental data.

Structures and energies of AlX_5^{2-} and AlX_6^{3-} ($\text{X} = \text{F}, \text{Cl}$) have been calculated with molecular orbital theory. When cations are included, AlF_6^{3-} is more stable than AlF_5^{2-} in fluoroaluminate melts. With an excess of AlCl_3 , Al_2Cl_7^- is the calculated stable chloride species. These results are consistent with observations in the liquid and can be used to provide structures for modeling aluminum halide solutions.

Interfacial and Corrosion Science. The work in the area of interfacial and corrosion science has produced several important findings concerning the effect of temperature on the kinetics of aqueous corrosion processes, the catalytic activity and selectivity of some novel molecular sieve materials, and methods for fabricating useful structures from high-critical temperature (T_c) superconducting ceramics.

A major accomplishment has been the determination from first-principle theoretical calculations that the transfer coefficient for the $\text{Fe}^{2+}/\text{Fe}^{3+}$ electron transfer reaction in aqueous media is independent of temperature over the range from 25 to 275 °C. This result, obtained by a combination of molecular dynamics and *ab initio* molecular orbital methods, confirms our

experimental findings reported earlier. In related research on aqueous corrosion, the thiocyanate ion, SCN^- , has been used to determine the effect of "halide-like" anions on the corrosion and passivation of iron and copper. The corrosion currents were found to increase by up to fivefold in the presence of even small quantities of SCN^- and were correlated with specific changes in the passive film structures that were revealed by Raman measurements of the molecular vibrations of the SCN^- . The results of these spectroelectrochemical studies highlight the intrusive effects of certain types of anions during passivation and corrosion of metals in aqueous media.

Cobalt-substituted AlPO_4 -type molecular sieves were found to possess catalytic activity for direct oxidative coupling of methane to higher hydrocarbons at temperatures $< 500^\circ\text{C}$. *Ab initio* molecular orbital methods have been used to determine the likelihood of alkyl group conformational rearrangement during molecular sieve crystallization templated by the tetraethylammonium cation.

An apparatus designed for wetting substrates with liquid metallic alloy precursors of high- T_c superconducting ceramics, e.g., YbBa_2Cu_3 , has been fabricated, and its utility for producing textured high- T_c films has been demonstrated. A method based on low-temperature ($80\text{--}120^\circ\text{C}$) thermocompressive diffusion has been developed for bonding $\text{YBa}_2\text{Cu}_3\text{O}_7$ to copper. Bonded assemblies produced by this process typically exhibit very low interfacial electrical resistivities ($\leq 10^{-6} \Omega \text{ cm}^2$) and withstand pulling forces in excess of 3 MPa (500 psi).

Geochemistry. The objectives of the ongoing research in CMT are to understand (1) the geochemistry of active hydrothermal systems and (2) the thermal and chemical effects of high temperatures on hydrocarbons in the Earth's crust. The approach being taken is to investigate specific problems through detailed chemical and isotopic analyses of natural materials sampled from appropriate field areas.

One project completed this year was a study of radium isotopes in thermal waters and travertines of Mammoth Hot Springs, Yellowstone National Park, Wyoming. This was done to investigate the potential application of ^{226}Ra for age determinations of young travertines ($< 10,000$ years). Although the measured ^{226}Ra activities below the surface (to depth of 70 m) were much lower than predicted, the rate of travertine deposition ($\sim 1 \text{ cm/yr}$) was accurately estimated from the slope of the best-fit curve through the measured ^{226}Ra activity versus depth below surface.

Another project undertaken in 1989 was a study of carbon isotopes in hydrocarbon-bearing rocks from the thermal aureole of the Duluth Complex in Minnesota. The results indicated that large-scale mobilization of hydrocarbons might be associated with the formation of the Duluth Complex. Also, step combustion experiments were performed between 200 and 550°C with kerogen from the Green River Shale. The data will be used to determine the potential fractionation of carbon isotopes that may occur in high-temperature geologic environments.

7. *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 four technical groups: Chemical Analysis, Instrumental Analysis, Organic Analysis, and Environmental Analysis.

During the past year, the ACL was involved in a diverse array of activities, including the following: analyses in support of the development of the IFR pyrochemical process, analyses of environmental samples taken from DOE sites for the DOE Environmental Survey Program, development of a new method for analysis of organic samples (namely, supercritical fluid chromatography/matrix-isolation infrared spectroscopy/mass spectrometry), analyses of gases dissolved in a palladium electrode from an electrochemical cell used in cold fusion studies, analyses of samples from pressurized fluidized-bed combustors, analytical support for rare-earth characterization of metal and salt phases withdrawn from an electrorefiner system for IFR pyrochemical processing, analyses to support TRUEX flowsheet development, analyses of samples from a study of molten corium-concrete interactions during a degraded-core accident, isotopic analyses of thermal waters and minerals from Yellowstone National Park, development of a procedure for one-step separation of uranium from mixtures containing other metals, determination of organic fluid fouling in heat exchange systems, X-ray diffraction measurements on a wide variety of solids (including superconducting ceramics), measurement of radium in waters and soils, development of methods for remote detection of chemical warfare agents and related precursors and degradation products, and environmental analyses requested by various DOE sites.

8. *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 database development, computer networking, procurement of automatic data processing equipment, and advisory and consulting services. In providing technical support to CMT staff, the Computer Applications Group has assisted in the effort to develop the Generic TRUEX Model, which can be used to design and optimize flowsheets for processing waste streams by the TRUEX process developed at ANL. In addition, the group has provided software development support to the Analysis and Diagnostic Laboratory and the Analytical Chemistry Laboratory.

I. ELECTROCHEMICAL TECHNOLOGY

The electrochemical technology under investigation in this CMT program includes advanced batteries (e.g., lithium/iron sulfide, sodium/nickel chloride, sodium/sulfur), aqueous batteries (e.g., lead-acid and nickel/iron), and advanced fuel cells with molten carbonate and solid oxide electrolytes. Potential applications for this technology include electric vehicle propulsion, utility load-leveling, and other energy storage applications. Another effort involves electrochemical investigation into anomalous heat effects reported for deuterated metals in an electrolysis cell.

A. *Advanced Battery Research and Development*

Research and development is underway at CMT to attain major improvements in the performance and cycle life of two types of advanced batteries: Li/FeS₂ and Na/NiCl₂.

1. Lithium/Iron Disulfide Cell Research

This research effort is focused on development of overcharge-tolerant monopolar and bipolar cells having molten-salt electrolyte, lithium negative electrodes, and iron disulfide positive electrodes. These cells are normally operated at temperatures of 375-425 °C. In the bipolar cell, the positive and negative electrodes have a common current collector, the bipolar plate. Accomplishments in 1989 included (1) demonstration of high performance and long life in overcharge-tolerant monopolar FeS₂ cells with MgO powder electrode separators and (2) development and demonstration of ceramic sealant for peripheral seals in bipolar cells and in feedthroughs of monopolar cells.

As reported previously,¹ an improved monopolar Li/FeS₂ cell with BN-felt electrode separator has exhibited high performance and long cycle life. This cell has a low melting electrolyte, 25 mol % LiCl-37 mol % LiBr-38 mol % KPr (mp, 310 °C), and a densely loaded FeS₂-15 mol % CoS₂ electrode, which is operated only on the upper voltage (U.P.) plateau. In this report period, we sought to replace the BN felt separator with an MgO powder separator, which has the potential for lower costs and greater thermodynamic stability in overcharge-tolerant U.P. FeS₂ cells. However, the MgO powder separator, since it is not physically stable under flooded electrolyte conditions, must be operated in an "electrolyte-starved" cell configuration. In our efforts to develop an electrolyte-starved, overcharge-tolerant cell, we fabricated and tested LiAl + 10 mol % Li₅Al₅Fe₂/LiCl-LiBr-KBr/U.P. FeS₂ cells (22.5-Ah capacity) with 100-cm² MgO powder separators. These cells demonstrated performance comparable to that of the flooded cell with BN felt separator. To increase the conductivity of the electrolyte-starved cell, which is normally about 30% lower than that of the flooded cell, the electrolyte composition was shifted off-eutectic to a LiCl-rich composition (in mol %, 34 LiCl-32.5 LiBr-33.5 KBr), which has a 25% higher ionic conductivity than that of the eutectic at 425 °C. This higher ionic electrolyte conductivity approximately compensates for the reduced electrolyte content of the electrolyte-starved cell. Therefore, the area specific impedance

¹T. D. Kaun, J. Electrochem. Soc. **132**, 3063-3064 (1985).

(ASI_t) of the electrolyte-starved cells ($1.1 \Omega \text{ cm}^2$) is comparable to that of the flooded cell ($1.0 \Omega \text{ cm}^2$). The capacity utilization of the electrolyte-starved cells (>85% at discharge current density of 50 mA/cm^2) after more than 50 cycles is now slightly greater than that of the flooded cell.

One electrolyte-starved, overcharge-tolerant cell was fabricated with an electrode/MgO separator plaque that we had pressed by Westinghouse Oceanic (Cleveland, OH). The performance of this cell at 425°C was outstanding: 92% utilization at a discharge current density of 50 mA/cm^2 and an ASI_{15s} of $1.2 \Omega \text{ cm}^2$. Concurrently, overcharge tolerance tests indicated that 3-mA/cm^2 trickle charge rates were tolerated for over 10% additional charge capacity without positive electrode polarization. A near 100% coulombic efficiency was attained for normal charge-discharge cycles before and after the overcharge tolerance tests. As seen in Fig. I-1, the ASI_t curve for the positive electrode as a function of depth-of-discharge (DOD) is virtually flat out to 80% DOD. The impedance values observed at the different potential relaxation times ($t = 45 \text{ ms}$ to 15 s) indicate that approximately 50% of the electrode impedance is electronic rather than ionic. Such low cell impedance is highly desirable for power-demanding applications such as the electric vehicle. The demonstrated electrode performances support the projected specific energy of 175 Wh/kg and specific power of 200 W/kg for a 200-Ah prototype cell design.

Fig. I-1. Half-Cell Impedance Measurements of Electrolyte-Starved U.P. FeS_2 Cell Operated at 400°C and 100 mA/cm^2

The recent development of overcharge-tolerant Li/FeS and Li/FeS₂ cells was accomplished by an innovative application of a self-discharge mechanism, based on a "lithium-shuttle mechanism."^{2,3} In general, the lithium-shuttle mechanism involves diffusion of lithium metal species across the separator to chemically discharge the positive electrode. The chief controlling element of the mechanism is the lithium activity of the negative electrode, while the cell operating temperature and electrolyte composition are minor contributing factors. With this design, self-discharge rates of ≥ 2 mA/cm² develop at lithium-alloy electrode potentials of -150 to -200 mV (vs. $\alpha + \beta$ Li-Al reference electrode at 0 mV). A Li-Al₅Fe₂ alloy with a potential of -260 mV (vs. $\alpha + \beta$ Li-Al reference electrode) has been applied to engineering development of overcharge-tolerant cells.

Tests of overcharge-tolerant monopolar FeS₂ cells (25-Ah capacity) with reference electrodes (Ni/Ni₃S₂) have verified that the lithium-shuttle mechanism provides sufficient levels of overcharge tolerance and overcharge protection. Such cells have operated over 200 cycles with high performance and stable overcharge tolerance. In Fig. I-2, the electrode potentials vs. percent of capacity utilization for a U.P. FeS₂ cell [LiAl + 10 mol % Li₅Al₅Fe₂/LiCl-LiBr-KBr (MgO)/FeS₂] are given for a charge-discharge cycle. A bulk charge at 25 mA/cm² to 2.03 V was followed by a trickle charge of 3.0 mA/cm². As seen in Fig. I-2, the lithium electrode undergoes about a 200 mV transition near full-charge capacity. This is crucial to ensure cell longevity. The U.P. FeS₂ electrode indicates negligible change in potential during the overcharge period; that is, it is protected from the deleterious effects of overcharge polarization. The self-discharge rate undergoes a stepwise increase (a 20-fold increase by the lithium-shuttle mechanism) to become equal and opposite in effect to the trickle-charge rate. In this test, the trickle-charge period (8 h) charged 15% more coulombs into the electrode than the rated capacity, and the extended trickle charge did not contribute to additional capacity in the subsequent discharge. A coulometric and galvanic analysis of the overcharge-tolerant cell design indicated approximately 0% charge acceptance for a trickle charge of 3.0 mA/cm² for the U.P. FeS₂ cell at 425 °C.

Peripheral hermetic seals are required for the bipolar cell, while only a feedthrough seal is required for the monopolar cells. These hermetic seals in the Li/FeS₂ cells have certain chemical and mechanical requirements that must be met by the component materials. For long-term operation, the seal must maintain an electrically insulating, gas-tight bridge between the metal components, usually molybdenum at the positive side and steel at the negative side. Structural integrity requires coefficients of thermal expansion for ceramic and metal components to be sufficiently matched to tolerate a temperature range of 750 to 1000 °C for seal formation and room temperature to 450 °C for cell assembly and operation. Additionally, the electrically insulating component must be chemically stable in molten salts that have either high sulfur or lithium activity. We have developed new sealant materials, which are excellent electronic insulators and bond tenaciously to metals (Fe, Ni, Mo) and ceramics (MgO, BN), even after exposure to molten salt containing lithium alloy or iron disulfide at 400-450 °C.

²T. D. Kaun, T. F. Holifield, M. Nigohosian, and P. A. Nelson, "Development of Overcharge Tolerance in Li/FeS and Li/FeS₂ Cells," Extended Abstracts, 174th Electrochem. Soc. Meeting, Chicago, IL, October 9-14, 1988, Vol. 88-2, p. 69 (1988).

³L. Redey, "Chemical Overcharge/Overdischarge Protection for Li-Alloy/Transition Metal Monosulfide Cells," J. Electrochem. Soc. **136**, 1989 (1989).

Fig. I-2. Overcharge Tolerance of U.P. FeS_2 Cell Operated at 425°C and Overcharged by 15% at 3 mA/cm^2 . No polarization of U.P. FeS_2 (positive) electrode indicates overcharge safeguard.

The mechanical strength of the sealant bond to various metals was evaluated metallographically to determine adhesion and wetting angles. Three substrate materials were examined: molybdenum, steel, and TiN-coated steel. In general, good-to-excellent wetting (i.e., wetting angles from 25° to $<10^\circ$) was observed. Sealant coverage was generally $>95\%$ of the available area. Metallographic examination of the sealant/substrate interface indicated excellent wetting on steel, with wetting angles approaching 0° . Our efforts to improve sealing and bonding onto molybdenum have been quite successful. Initially, the sealant exhibited good wetting (25° wetting angle) on molybdenum, but the sealant tended to break away. A modified sealant displayed improved wetting onto molybdenum with better adhesion. The modified sealant has a thermal expansion coefficient of about $5.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, which approximates that of molybdenum.

To verify the good performance of hermetic seals formed from the new materials, we tested seals in both a Li/U.P. FeS_2 monopolar and bipolar cell. Chemical stability of the sealant materials was verified by post-test X-ray diffraction and differential thermal analysis. A feedthrough seal in a monopolar cell was successfully tested over 1000 h and 100 cycles at 400°C . During this time, the seal maintained a resistance greater than $100\text{ k}\Omega$, which is considered excellent for FeS_2 monopolar cell applications.

In the bipolar cell, the hermetic seal is formed at the periphery prior to cell assembly (Fig. I-3). Here, a ceramic ring is sealed to molybdenum on one side to form the FeS_2 electrode housing, and a steel assembly is sealed to the other side of the ring to form the lithium electrode housing. Cold-pressed pellets of electrodes and separator materials make up the cell. In tests of the hermetic peripheral seal, a LiAl + 10 mol % $\text{Li}_5\text{Al}_5\text{Fe}_2$ /U.P. FeS_2 bipolar cell (3-cm dia, 0.25-Ah capacity) has been operated over 175 cycles and 400 h and has exhibited high

performance and >99% coulombic efficiency. Following 50 short discharge cycles, the U.P. FeS_2 electrode attained >80% utilization over the next 125 deep discharge cycles. Cell capacity was limited by the negative electrode capacity. Post-test analysis of the cell confirmed the stability of the metal-to-ceramic seals after 400 h of operation. With continued success in the development of the 3-cm dia bipolar test cell, we hope to develop, fabricate, and test a 15-cm dia prototype cell.

Fig. I-3. Sealed Bipolar Cell Design for Li/FeS_x Battery. Seal is formed prior to cell assembly.

2. Sodium/Metal Chloride Cell Research

The purpose of this research is to generate the scientific and technical base of information needed to develop advanced sodium/metal chloride (Na/MCl_2) cells with high specific energy (200 Wh/kg) and power (>200 W/kg). The present cell uses a molten sodium negative electrode, a $\beta''\text{-Al}_2\text{O}_3$ solid electrolyte, and a solid metal chloride such as NiCl_2 or FeCl_2 as the positive electrode. This latter electrode uses a secondary electrolyte of NaAlCl_4 . The cell is normally operated at 260 °C. Despite the high theoretical specific energy of the Na/NiCl_2 cell (790 Wh/kg), the performance of the present single $\beta''\text{-Al}_2\text{O}_3$ tube cells is limited (~100 Wh/kg and ~100 W/kg). Our preliminary cell modeling studies suggested that, to develop high-performance Na/MCl_2 cells, one will need to increase the area of the solid $\beta''\text{-Al}_2\text{O}_3$ electrolyte, use MCl_2 electrodes that are thinner and have higher capacity density and lower resistivity, and operate at low or moderate current densities.

Our positive electrode studies have focused on increasing the performance of the NiCl_2 electrode. In these cell tests, the NiCl_2 electrode (30-40 mAh capacity) is used on the inside of the $\beta''\text{-Al}_2\text{O}_3$ -tube electrolyte in an annular configuration. We investigated the effects of (1) electrode porosity in annular electrodes (16, 18, and 20 vol % Ni), (2) sulfur additives (2 wt %), as used in the current technology, (3) cycling rates (charge and discharge rates of 2, 4, and 8 h), and (4) temperature (220, 260, and 300 °C). To improve the performance of this electrode, which represents about 50% of the cell weight, we are developing high-capacity-density electrodes, 0.50-0.55 Ah/cm³, made from a sintered mixture of Ni and NaCl (3:1 in terms of capacity). This high capacity loading is almost 50% higher than that used in the current technology.

The results of these studies clearly indicated that charge rate, sulfur addition, electrode porosity, and temperature have a marked effect on electrode utilization. Those cells that were charged quickly tended to have lower utilizations than those charged more slowly. In some cases, the effect of charge rate was more pronounced than the effect of temperature on the electrode utilization. Sulfur seemed to increase the electrode utilization at all discharge rates. In cell studies conducted at 250 °C and the 8-h charge rate, marked effects of the sulfur additive and the volume percent nickel used in the electrode were observed. For example, in the 18 vol % Ni electrode containing sulfur, there was a 95% utilization at the 2-h discharge rate, as compared to only 50% in the electrode without sulfur. Sulfur appears to improve the charge acceptance of the nickel electrode by increasing the surface area and pore diameter of the nickel metal matrix. The 16 and 20 vol % Ni electrodes did not perform as well as the 18 vol % Ni electrode, suggesting that electrode porosity is an important factor in electrode performance.

The area specific impedance of the 18 vol % Ni electrode with sulfur, which was the best-performing electrode in this study, was $1.2 \Omega \text{ cm}^2$ at 300 °C. This value is comparable to state-of-the-art cells, which have values of about 1.0-1.5 $\Omega \text{ cm}^2$. In an effort to improve the impedance characteristics of our electrodes, we decided to fabricate electrodes with larger mean pore diameters, which were obtained by altering the present fabrication procedure. Electrodes fabricated by this procedure tended to have significantly lower impedance, $<0.50 \Omega \text{ cm}^2$ at 300 °C.

We are also investigating use of a composite electrolyte based on β'' -alumina and a suitable glass as an alternative to the β'' -alumina ceramic currently used. The rationale behind the development of the composite electrolyte is that advanced cell designs require high-surface-area (multitube or prismatic) electrolytes to reduce the voltage losses. However, the current material, $\beta''\text{-Al}_2\text{O}_3$, is difficult to fabricate into these configurations. Glasses, on the other hand, are easier to fabricate but do not have as high a conductivity. A composite of the two materials could possess the desired properties of both materials and also be inexpensive to fabricate. The glass in the composite should have a high Na^+ -ion conductivity and be compatible with $\beta''\text{-Al}_2\text{O}_3$ and the active material.

Our approach was to first identify potential glasses for use in forming the composite and then to prepare and test the composite. In this effort, we determined the effect of several parameters (e.g., glass composition, glass volume fraction, sintering conditions, and particle size distribution) on the conductivity and chemical stability of the composite. Once the important parameters had been identified, an attempt was made to optimize the composite design. On the basis on these considerations, glasses in the $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ system were selected for further testing. A resistivity value of $75 \Omega \text{ cm}$ at 250 °C was set as a target for the composite.

All $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2/\beta''\text{-Al}_2\text{O}_3$ composites contained about 35 vol % glass (50 wt %). More glass was found to increase the resistivity of the composite; less glass produced a composite with very little strength. The composites were sintered at 1000 °C to lessen soda loss (which occurs at the temperatures needed to sinter $\beta''\text{-Al}_2\text{O}_3$, 1400 °C). We found that glasses with no borate and small amounts of Al_2O_3 produced better composites than glasses containing larger amounts of B_2O_3 and Al_2O_3 .

Using the above results and the proper precursor preparation, we were able to produce composites with excellent resistivity values, $\sim 30 \Omega \text{ cm}$ at 250°C . Preliminary experimental results suggest that these materials may have the needed chemical stability against sodium. Future work in this area will be directed toward further optimizing the fabrication method and determining the performance of the composite in small cell tests.

In other studies of the Na/MCl_2 system, three different cell design configurations were modeled to estimate the voltage-loss characteristics (IR drop) of these designs and, thus, their potential for high performance. The designs considered were the 100-Ah single tube design now being used in state-of-the-art cells, a multitube cell design, and a cell design using an array of flat-plate electrolyte structures that contain a number of individual square pocket electrode compartments, each of which is operated in parallel. In determining the voltage-loss characteristics of the three cell designs, we used literature values for the $\beta''\text{-Al}_2\text{O}_3$ resistivity and area specific impedance values estimated from the published cell data for NiCl_2 electrodes with $0.25\text{-}0.35 \text{ Ah/cm}^2$ loading densities.^{4,5}

The results of this analysis indicated that the voltage losses can be decreased by more than an order of magnitude by shifting from a low-surface-area single tube to a high-surface-area multitube or flat-plate compartmented design. The projected specific energy and power for such high-surface-area cells is $\sim 200 \text{ Wh/kg}$ and $300\text{-}500 \text{ W/kg}$. While this initial design analysis clearly demonstrates the potential of the system, further work needs to be carried out to refine the calculations.

3. Development of Li-Al/FeS Batteries for Transportation

Testing of a fractional-scale (36 V) Li-Al/FeS battery for electric van application was completed in 1989. This battery was designed and fabricated as a joint effort between ANL and Westinghouse Naval Systems Division (Cleveland, OH) and Meyer Tool and Manufacturing, Inc. (Oak Lawn, IL). It consisted of three 9-cell modules in a vacuum-insulated case. The test results provided validation of a conceptual van battery design under development at ANL for the past several years, as well as design and performance data for 12-V Li-Al/FeS modules and fractional-scale battery components. The most important test results can be summarized as follows:

1. Electrical performance requirements for the van application were achieved. The cells in the 36-V battery attained an energy output of $>110 \text{ Wh/kg}$ (on the SAE J227a/C driving profile) and a specific power of $>95 \text{ W/kg}$ (50% DOD, 300 A). However, battery life was limited to only 141 cycles.
2. The cause of battery life limitation was determined by allowing the battery to cycle until 12 (out of a total of 27) cells had failed. The failure mode was found to be related to the module restraint design and not to electrochemical factors.

⁴R. M. Dell and R. J. Bones, "The Sodium/Metal Chloride Battery," 22nd Intersoc. Energy Conversion Eng. Conf., August 10-14, 1987, pp. 1072-1083 (1987).

⁵J. L. Sudworth, R. C. Galloway, and D. S. Dermott, *Electric Vehicles*, 73, 14 (Autumn 1987).

A Li/FeS battery development program sponsored jointly by the DOE (Electric and Hybrid Propulsion Division) and Electric Power Research Institute (EPRI) has been initiated. Responses to a request for proposals have been evaluated, and a contractor has been selected (SAFT America) for a three-year effort leading to a test of a proof-of-concept van battery.

B. *Analysis and Diagnostics Laboratory*

The Analysis and Diagnostic Laboratory (ADL) was established at ANL in 1976 as a facility for studying advanced battery systems. It includes a test laboratory to conduct battery performance and lifetime evaluations under simulated application conditions and a post-test analysis laboratory to determine, in a protected atmosphere if needed, component compositional changes and failure mechanisms. During 1989, battery technology evaluations in the ADL were performed for both DOE and EPRI. The results of these ongoing 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.

1. Performance and Life Evaluations

The general design specifications and performance for the four technologies evaluated in 1989 (Na/S, Li/FeS, Ni/Fe, lead-acid) are given in Table I-1. The values of specific energy were derived at a 3-h discharge rate, and those of peak power were derived from driving profile discharge data at 50% DOD. The ranges projected for vehicles powered by each technology with various driving profile discharges are listed in Table I-2. These test results and others are discussed below.

Table I-1. Summary of Selected Electric-Vehicle Module Evaluations in ADL for 1989

	Na/S	Li/FeS	Ni/Fe	Ni/Fe	Pb-Acid	Pb-Acid
Mfr. ^a	CSPL	Westing.	EPI	EPI	CEVS	JCI
Designation	PB	--	NIF200	NIF220	3ET205	Flow-By
No. Cells	960	27	5	5	3	3
Weight, kg	232	95	25.1	25.3	32.8	11.0
Initial Ah Capacity	306	215	200	227	185	73
Initial kWh Capacity	18.7	7.2	1.24	1.39	1.08	0.44
Charge Procedure ^b	CI/CI	CI/CV/CI	CI/CV/CI	CI/CV/CI	CI/CI/CI	CI/CV
Overcharge	0	10-15%	>35%	>35%	15-20%	8%
Wh Efficiency, %	91	85	58	55	68	81
Spec. Energy, Wh/kg	81	70	50	55	39	40
Peak Power, W/kg	140	71	112	94	93	227
Life Cycles	225	141	>50	200	>650	18

^aAbbreviations defined as follows: CSPL = Chloride Silent Power Ltd.; EPI = Eagle Picher Industries, Inc.; Westing. = Westinghouse Naval Systems Division; CEVS = Chloride EV Systems Ltd.; JCI = Johnson Controls, Inc.

^bAbbreviations are CI = constant current and CV = constant voltage.

Table 1-2. Projected Ranges for Simulated Electric-Vehicle Driving Profiles

Battery Technology	Projected Vehicle Range,* mi (km)		
	SFUDS79	J227aD	J227aC
Na/S	148 (237)	182 (291)	135 (216)
Ni/Fe (NIF220)	76 (122)	110 (176)	93 (149)
Ni/Fe (NIF200)	87 (139)	108 (173)	102 (163)
Lead-Acid (3ET205)	47 (75)	54 (86)	65 (104)
Lead-Acid (Flow-By)	56 (90)	65 (104)	74 (118)

*Range for single discharge. The three driving profiles are as follows: a simplified version of the Federal Urban Driving Schedule for a van, the standard SAE J227aD profile for a passenger automobile, and the standard SAE J227aC profile for a van.

a. Sodium/Sulfur Technology

Three multicell modules fabricated by Chloride Silent Power Ltd. (CSPL) were tested. The largest was a one-third-size electric vehicle battery that contained 960 cells. Each cell was hermetically sealed in a chromized steel case and had a rated capacity of 10 Ah. This 300-Ah, 64-V battery came complete with charger and thermal management system and was evaluated at ADL for 241 test cycles. The thermal management system satisfactorily maintained the battery within an operating temperature range of 330-360 °C during driving profile discharges. A battery temperature limit of 370 °C was reached only after conducting a continuous hill-climbing power discharge of 50 W/kg for 1.2 h. A cell (or cells) failed on the 135th cycle, which caused a capacity loss of ~15 Ah. The battery continued to operate satisfactorily and exhibited the same gradual decline in capacity (~0.03 %/cycle rate) that was present before the cell failure. After ~225 cycles, the capacity declined to 80% of its initial level. Testing was continued for another 15 cycles to verify proper thermal management and performance during end-of-life.

Two 24-cell modules also built by CSPL were evaluated in 1989. One module was removed from test after 12 months and 339 cycles of operation and replaced with a second module that had cells of a newer, safer design. Both modules were rated at 60 Ah (480 Wh) and contained 24 cells. The first module still retained 84% of its initial capacity when life testing was voluntarily halted. The capacity of this module had declined at a rate of 0.08%/cycle during its last 200 cycles with driving profile discharges. Prior to this, it exhibited a capacity decline of only ~0.02%/cycle. The data are being reviewed and compared with those from other Na/S tests to assess any relation between capacity loss and type of discharge. At this increased rate of capacity loss, module life (capacity ≤80% of its initial 50.9 Ah) was projected to be ~420 cycles. Testing of the second 24-cell module was abruptly halted after only 100 cycles because of cell failures. These cells were found to have seal problems, which were subsequently corrected by CSPL. An improved replacement module is expected for ADL testing.

b. Lead-Acid Technology

Johnson Controls, Inc., is developing an improved lead-acid electric-vehicle battery based on the forced flow of electrolyte through the active material. As part of this program, a prototype three-cell (75-Ah) module was delivered to the ADL for testing. An abbreviated performance characterization was conducted followed by life testing. Good performance was obtained but the module had a very short life (18 cycles). Due to the rapid capacity decline ($\sim 1\%$ /cycle), reproducible data were unattainable.

Two advanced tubular lead-acid modules (3ET205 design) from Chloride EV Systems Ltd. are being evaluated. Performance tests were completed and life testing started with driving profile discharges to 100% DOD in 1988. During the life evaluation in 1989, no degradation in performance was observed with either module. One was removed from life test after completing 450 cycles, while the second continues with more than 650 cycles having been accrued to date. This module has undergone over 29,000 simulated driving miles (46,400 km) without any loss in initial performance.

A life evaluation of valve-regulated lead-acid batteries for cycling applications was started. Two technologies are being tested: (1) gelled-electrolyte modules from Johnson Controls and (2) absorbed electrolyte modules from GNB Industrial Battery Co. This study uses a matrix of operating conditions designed to vary the stress of known failure modes. In this way, the mechanisms that cause battery end-of-life are accelerated on select modules. Module operating temperature and DOD were selected as the stress factors. The primary failure mode is expected to be active material changes caused by charge-discharge cycling. Preliminary results indicate that both technologies need a daily charge return of $\geq 105\%$, and charge times of ≤ 8 h are difficult to attain due to the immobilized electrolyte. Higher charge returns ($\geq 115\%$) are also required at elevated temperatures (50°C). Charge method evaluations are being conducted.

c. Nickel/Iron Technology

Two types of advanced electric-vehicle Ni/Fe modules from Eagle-Picher Industries, Inc., are being tested. One type uses sintered-powder nickel electrodes (NIF220 and NIF200), and the other uses nickel fiber electrodes. Four NIF220 modules were tested and all exhibited a rapid capacity loss ($\sim 0.1\%$ /cycle) with cycling. Rated capacity (220 Ah) could only be achieved early in life with excessive overcharging, and a life of only 200 cycles was attainable. Post-test analyses (Sec. I.B.2) on a failed NIF220 cell showed that severe deterioration of the iron plates had contaminated the nickel plates. The causes of the iron electrode problem were corrected in the recent NIF200 design. This design is being life tested and good results have been obtained to date.

Five Eagle-Picher modules with nickel fiber electrodes were operated in 1989. The nickel fiber electrodes are attractive because of their lower nickel requirements. Tests were completed on three modules, while two continue to be evaluated. This technology has exhibited long life (>800 cycles) but low specific energy (45 Wh/kg) as compared to that of the nickel-powder electrode technology (55 Wh/kg).

d. Lithium/Metal Sulfide Technology

A 36-V Li-Al/FeS electric-van module was tested for 141 cycles (see Sec. I.A.3). After about 103 cycles, the module had reached its end-of-life because its available energy had declined to <80% (<6.32 kWh) of the initial 7.2 kWh level. Testing was continued to examine the response of the weak cells when driven into voltage reversal. At the end of testing, 12 of the 27 cells in the module were in voltage reversal.

2. Post-Test Analyses

Detailed examinations are conducted on selected cells, modules, and batteries that have completed testing either at the ADL or at other centers of battery research. The information gained from post-test analyses provides a measure of the technical progress made by the battery developers and identifies specific areas where changes in design or the materials of construction would improve battery performance. In this report period, we examined a Na/S battery and cell from CSPL and a Na/S cell and Ni/Fe module from Eagle-Picher.

In a joint CSPL/ANL effort, teardown of the 300-Ah, 64-V Na/S battery (see Table I-1) was performed to determine the predominant modes of cell failure. The battery was composed of eight banks containing 120 cells each. The highest number of cell failures occurred in the two central banks. Nine cell failures were found in each of these banks. The associated capacity loss of 90 Ah was consistent with the capacity decline observed for the battery as a whole.

The distribution of failed cells indicated that the failures were extremely temperature dependent. A temperature gradient in this battery occurred because the central banks operated at a higher temperature than the end banks. The coldest cells were adjacent to the end wall of the thermal enclosure; no failures were noted in this population of cells. Another temperature gradient arose from the fact that the heater was located beneath the cells, and excess heat was extracted from the top of the battery. No failures were detected in the top level of cells. All of the failures occurred in the three lower levels of cells, where temperatures were hotter.

Fractures through the glass seals in the cells from this battery proved to be the primary failure mechanism. These fractures propagated through the glass joint and severed the lip of the α -alumina top cap. Once a fracture was complete, direct reaction of sodium and sulfur would occur. Of the 18 cell failures in the two central banks, 17 cells failed by this mechanism. Only one cell suffered an electrolyte failure that did not involve the glass seal. The high percentage of seal failures was probably related to improper glazing procedures, but more detailed examinations of the failed seals need to be completed before this hypothesis can be confirmed.

A 30-Ah Na/S cell built and tested by CSPL was also analyzed. This cell represented a transitional state in the development of cells with safety features and had the longest operational life, 1012 cycles, of any CSPL cell examined at ADL to date. The examination confirmed that the recent CSPL design changes provided benefits in cell

performance as well as cell safety. A felt-wrapped safety can promoted low resistance by providing excellent wicking action for maximized usage of the electrolyte surface and by reducing calcium contamination of the electrolyte. The deficiencies noted for this cell stemmed from extemporized design features: a two-piece construction for the cell case impaired the quality of its chromized coating and the use of an older design glass seal (Mark IIA) led to the accumulation of corrosion products on the outer electrolyte surface. The newer design of this cell should eliminate these problems.

A 50-Ah Na/S cell built and tested by Eagle-Picher completed 854 cycles that simulated usage on a satellite in low earth orbit, after which the β'' - Al_2O_3 electrolyte fractured and caused the cell to fail. Our examination attributed the electrolyte failure to a defective glass seal between the electrolyte and the cell header. Specifically, the glass sealant was lacking in a section of the joint, and this condition resulted in a nonuniform distribution of stresses at the electrolyte interface. This cell also demonstrated appreciable corrosion of the cell case. Improvements in the quality of the chromium plating are needed to minimize the effects of corrosion product buildup on cell resistance.

A comprehensive examination was conducted on an Eagle-Picher Ni/Fe module to determine the cause of accelerated capacity decline, a condition that has troubled the performance of several modules in the NIF220 series (see Table I-1). The capacity of this module was characterized by a relatively constant decline of about 0.3 Ah per cycle over 200 cycles of operation. The results of electrical diagnostic tests and microscopic and analytical studies of the cell components indicated that deterioration of the iron plates was the underlying reason for the performance decline. Their physical degradation led to excessive contamination of the nickel plates with iron particulate, and this contamination resulted in the observed capacity decline. Test cells were constructed from electrode plates removed from the weakest cell in the NIF220 module to verify this observation. For these tests, the cut-off voltages and the charge and discharge currents were proportionately scaled downward from the module level to the plate level to replicate testing conditions as closely as possible. The best capacity from a single nickel plate was obtained after the contaminated surface was cleaned by mild abrasion. This nickel plate regained two-thirds of the lost capacity.

C. *Transportation Application Technical Support*

The CMT Division provides technical support to DOE for the development of aqueous batteries and fuel cells for transportation applications. This support includes technical assessments, system analyses, assistance in program planning, preparation of work statements for developmental contracts, and technical management of several major DOE contracts with industrial developers.

1. Fuel Cells for Transportation Applications

Fuel cells, operating on nonpetroleum fuels, can potentially provide an alternative propulsion system for transportation needs with nearly twice the fuel economy and greatly reduced emissions and noise compared with those of the internal combustion engine.

a. Fuel Cell System Analysis and Modeling

We conducted a study of the suitability of four different types of fuel cells for vehicle propulsion applications: phosphoric acid, proton exchange membrane (PEM), molten carbonate, and monolithic solid oxide (alkaline fuel cells were not included because they are not considered to be compatible with methanol fuel). Simplified flowsheets were constructed for each system in order to carry out thermodynamic analyses. All of these fuel cell systems were found to offer the potential for fuel efficiencies significantly greater than that of the internal combustion engine.⁶

Our calculations for a liquid-cooled phosphoric acid fuel cell system have shown that its net efficiency can be improved by operating at an electrochemical fuel utilization greater than the presently proposed 75% value. As the electrochemical fuel utilization is increased from 65% to 85%, the net efficiency of the system increases from 32% to 43% (efficiencies for internal combustion engines range from 18% to 30%). Our calculations for the PEM fuel cell system have shown that the system efficiency can be on the order of 37%. However, water management in the PEM fuel cell system is still a complex issue; if substantial amounts of water that are transported electro-osmotically across the membrane need to be provided to the anode in vapor form, the system efficiency would decrease significantly.

b. Fuel Cell/Battery Powered Bus System

An urban bus was selected as the initial fuel cell/battery test vehicle because its larger size can readily accommodate the packaging of a fuel-cell powered propulsion system, and because the present-day acquisition cost of fuel-cell systems can be amortized over a longer service life in a bus than in passenger cars. Methanol was selected as the fuel of choice because it can be derived from nonpetroleum sources (e.g., coal, natural gas, biomass), is readily transportable, and can be processed for fuel cell use at relatively low temperatures. The phosphoric acid fuel cell was selected for this program because it is at a more mature state of development and because its operation on reformed methanol has been demonstrated. The use of a battery in parallel with the fuel cell minimizes the size of fuel cell required. The fuel cell provides the average power required, and the battery, which is recharged by the fuel cell during bus idle periods, provides the supplemental power needed during vehicle acceleration. For maximum energy efficiency, the energy released during vehicle braking can also be used to charge the battery.

The U. S. Departments of Energy and Transportation initiated a program in 1987 to demonstrate a methanol-fueled urban bus powered by a phosphoric acid fuel cell/battery. The program is now also co-sponsored by the California South Coast Air Quality Management District. Phase I of this program is directed at demonstrating proof-of-feasibility by constructing and evaluating a half-scale propulsion system. The CMT Division provides technical management of this program.

⁶M. Krumpelt and C. C. Christianson, *An Assessment and Comparison of Fuel Cells for Transportation Applications*, Argonne National Laboratory Report ANL-89/28 (1989).

During 1989, the two industrial contractor teams each constructed, for laboratory evaluation, a half-scale propulsion system. The team of Booz-Allen & Hamilton, Inc., Chrysler Pentastar Electronics, Inc., and Fuji Electric Co. built and tested a liquid-cooled phosphoric acid fuel cell/battery power source. This 68-kW system consists of a 25-kW fuel cell and 43-kW lead-acid battery, a dc chopper to step up the fuel cell output voltage to match that of the battery, and overall system controls. The team of Energy Research Corp., Los Alamos National Laboratory, and Bus Manufacturing, Inc., completed the design of an air-cooled phosphoric acid fuel cell/battery propulsion system for a bus. Energy Research Corp. then built and tested a 62-kW power source consisting of a 32-kW fuel cell and 30-kW Ni/Cd battery, connected in parallel. In both systems, the test results verified the performance predicted by design analyses and confirmed the feasibility of the fuel cell bus concept. Based on these results, a decision was made to proceed to Phase II, which is directed at installing and testing a full-size fuel cell/battery propulsion system in a bus.

c. Proton Exchange Membrane (PEM) Fuel Cells

The PEM fuel cell, when fully developed, may offer significant advantages over the phosphoric acid fuel cell for transportation applications. These advantages include reduced size and weight, faster startup, better transient response, and potentially lower cost. The DOE (Office of Transportation Systems) has initiated programs aimed at developing a PEM fuel cell, as well as a thermo-electrochemical (TECH) system. The CMT Division is providing technical support to these DOE programs.

The TECH system uses a cation exchange membrane in an electrochemical cell with thermally regenerable reactants to convert methanol fuel or waste heat into electrical power for propulsion. In September 1989, DOE awarded a two-year (50% cost-shared) contract to the Delco Remy and Hughes Divisions of General Motors Corp. for the development of the TECH system for transportation applications. The initial activities will include a conceptual design of a TECH system for transportation applications and cost and design trade-off studies. Additional activities will include component development and the design, fabrication, and evaluation of a 5-kW demonstration unit. A major emphasis in this development effort will be on demonstrating high efficiency at a reasonable projected cost for the system.

We prepared for DOE an overall program plan and a statement-of-work for research and development on PEM fuel cells for transportation applications. The program will be divided into four phases with a go/no-go decision between each phase. Phase I, feasibility evaluation, will lead to the demonstration of a 10-kW system. Phase II, proof-of-feasibility, will be directed at proving feasibility by testing a 25-kW system. Phase III, system scale-up, will result in the laboratory evaluation of a full-scale 50-kW propulsion system. In Phase IV, proof-of-concept, this full-scale system will be installed and evaluated in a test-bed vehicle, and additional vehicles will also be fabricated.

A two-year period for Phase I is planned. Contractor selection and award of a cost-sharing contract are expected to occur in 1990. The desired outcome of the Phase I work is an evaluation of the feasibility of an electric propulsion system based on a PEM fuel cell system

and an identification of the critical problems that must be resolved in system scale-up and integration into a vehicle.

2. Aqueous Batteries for Electric Vehicles

The Division continued to provide technical support to DOE for the development of aqueous battery technologies for electric vehicles. In this capacity, CMT provided technical management of two major industrial contracts: one with Johnson Controls for the development of an advanced lead-acid battery and the other with Eagle-Picher for the development of Ni/Fe batteries.

a. Advanced Lead-Acid Battery

The work at Johnson Controls is focused on research and development of an advanced lead-acid battery based on the use of a forced electrolyte flow by the porous lead and lead dioxide electrodes to achieve an increase in the utilization of these materials. The objective of the R&D effort is to improve the performance of lead-acid batteries and develop an electric van with a range of 75 mi (120 km). During 1989, Johnson Controls fabricated and delivered two flow-by cells and a 6-V flow-by module. Test results obtained at ADL (based on initial capacity) indicated that the cells, as a result of the flowing electrolyte, are able to meet the peak power requirements of the Simplified Federal Urban Driving Schedule (SFUDS) at up to 96% DOD, whereas most other lead-acid batteries fail to meet the power requirements beyond 75-80% DOD. As a result, the 6-V module demonstrated a simulated vehicle range of 68 mi (109 km) on the SFUDS, thereby achieving over 90% of the development goal. The cycle life of these cells remains limited, however, with a life of only 130 cycles to date in the best cells tested at Johnson Controls. Efforts aimed at improving the cycle life of the technology will be continued in 1990.

b. Nickel/Iron Battery

The work at Eagle-Picher is directed toward improving the performance and reducing the cost of Ni/Fe batteries. The effort at Eagle-Picher is focused on the development of fiber-type nickel electrodes. Because nickel metal is the major cost element in the manufacture of Ni/Fe batteries, the lower nickel requirements of the fiber-type approach are expected to provide significant cost reduction for future Ni/Fe batteries. During 1989, Eagle-Picher continued to make steady progress in the development of fiber-based nickel electrodes and fabricated several fiber-based Ni/Fe modules. Testing and evaluation of these developmental modules were performed at the ADL (Sec. I.B.1), where a fiber-based Ni/Fe module successfully demonstrated over 800 charge/discharge cycles. The long life of Ni/Fe batteries developed under this program was also demonstrated by tests in electric vehicles; a Ni/Fe battery system has powered an electric van for over 50,000 mi (80,000 km) to date at the Electric Vehicle Test Facility in Chattanooga, TN. Efforts to reduce the cost of the Ni/Fe technology will be continued in 1990.

D. *Anomalous Effects in Deuterated Metals*

In March 1989 Pons and Fleischman⁷ announced that they had generated heat from a fusion reaction at room temperature in an electrolysis cell (net reaction: $2\text{D}_2\text{O} \rightarrow 2\text{D}_2 + \text{O}_2$) with a palladium cathode and deuterated water electrolyte. This announcement set the scientific community in search of "cold fusion." In the CMT Electrochemical Technology Program, a study was initiated to verify the claims of anomalous heat in the palladium-deuterium electrochemical system and to ascertain whether an electrochemical cell could be operated to produce sufficient excess heat for the production of useful energy.⁸

Excess heat has been generally defined as the heat output from the cell that is greater than the heat equivalent of the electrical energy that was put into the cell. For an open system (i.e., a cell in which the deuterium and oxygen product gases are allowed to escape without recombining), the heat equivalent from the cell is the current to the cell times the quantity of the cell voltage minus the thermal neutral voltage of the electrolysis reaction (1.53 V at 30 °C). The thermal neutral voltage times the cell current is the rate at which chemical energy is lost from the cell to the environment in the form of product gases.

Two series of experiments were performed: (1) differential temperature analysis of identical light- and heavy-water electrochemical cells and (2) calorimetric measurements of operating heavy-water electrochemical cells. The cathodes in both kinds of experiments were wrought palladium, 5.0 cm in length and 0.63 cm in diameter. The rods were placed in 3.2-cm dia glass vessels with platinum anodes.

In the first series of experiments, we monitored the temperature difference between identically constructed Pd-H/LiOH-saturated- H_2O /Pt and Pd-D/LiOD-saturated- D_2O /Pt cells. It was anticipated that the temperature difference would be close to zero until the production of excess heat, when the deuterated cell would become noticeably hotter. However, it proved to be impossible to maintain identical electrochemical conditions in both cells. For example, at identical current densities, the operating cell voltage of the D_2O cell (therefore, also the temperature) was higher, and when the current density and cell voltage were made similar, the H_2O cell became warmer ($\Delta T = 0.8$ K). We concluded that the results from this kind of experiment were too ambiguous and, thus, not suitable for evaluating the occurrence of excess heat.

In the second series of experiments, Pd-D/LiOD-saturated- D_2O /Pt cells were operated in a constant-heat-loss calorimeter that was sensitive enough to detect the levels of excess heat that had been previously reported by Pons and Fleischman,⁷ as well as others. The constant-heat-loss calorimeter was made by placing a constant temperature bath at 30 °C inside another constant temperature bath at 21 °C. The power needed to maintain the temperature of the inside bath was measured. A cell was then placed in the inside bath and operated. The heat output

⁷M. Fleischman and S. Pons, *J. Electroanal. Chem.* **262**, 301 (1989).

⁸L. Redey, K. M. Myles, D. Dees, M. Krumpelt, and D. R. Vissers, "Calorimetric Measurements on Electrochemical Cells with Pd-D and Pd-H Cathodes," Workshop on Cold Fusion Phenomena, May 23-25, 1989, Santa Fe, NM.

from the cell (for example, approximately 15 W at 500 mA/cm²) was determined from the reduction in power needed to maintain the temperature of the inside bath.

Cells were operated in the calorimeter over a wide range of current densities (12.5-500 mA/cm²) for up to 460 h. Total heat output from the cells varied with current density. Periodic weight measurements of the cathode throughout the duration of the experiment indicated that a high concentration of the deuterium in the palladium was maintained for hundreds of hours. Heavy-water consumption measurements did not detect any recombination of product gases during the experiment. The results of the energy balance measurements and calculations are given in Fig. I-4. No significant excess heat was detected during the experiment. Also, analysis of the electrolyte indicated that no significant increase in the tritium concentration had occurred.

Fig. I-4.

Excess Heat vs. Current Density for
Palladium-Deuteride Electrochemical Cell

A joint program is now being initiated with a group from Case Western Reserve University (CWRU) that has seen some evidence of excess heat in their experiments. The challenge for the future is to first reproduce CWRU's experiments in this laboratory in an attempt to confirm excess heat in the palladium-deuteride electrochemical system. Once that has been accomplished, the joint effort will focus on determining the source of the anomalous heat.

E. *Advanced Fuel Cell Research and Development*

We are developing two types of high-temperature fuel cell: one with a solid oxide electrolyte, the other with a molten carbonate electrolyte.

1. Monolithic Solid Oxide Fuel Cell Research

The solid oxide fuel cell has an oxide-ion conducting electrolyte material, yttria-stabilized zirconia (YSZ). The electrode materials are strontium-doped lanthanum manganite on

the air side and nickel-YSZ on the fuel side. The material that connects the individual cells in electrical series (bipolar plate) is strontium-doped lanthanum chromite. These components are all oxide-ceramic materials. On the fuel side, 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. On the air side, 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.

The monolithic solid oxide fuel cell (MSOFC) developed in CMT 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. The principal building blocks of the MSOFC structure are two multilayer composites: the anode/electrolyte/cathode (A/E/C) and the cathode/interconnect/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. The characteristics of the electrode/electrolyte interfaces, such as electrode porosity and the quality of the electrode-electrolyte bond, are also important to achieving good fuel cell performance.

The MSOFC development effort has focused on reducing the resistances of the electrode/electrolyte interfaces and thus improving the performance of the fuel cell. Electrode porosity, the quality of the electrode/electrolyte bond, and the fuel gas compositions have been found to be the most important parameters affecting fuel cell performance. Good cathode porosity is necessary for transfer of oxygen to the interface on the air side. A good electrode/electrolyte bond is necessary to maintain electrical continuity through the fuel cell structure. The effect of the fuel composition on the interfacial resistance is illustrated by Figs. I-5 and I-6. The A/E/C composites designated C-787 and METC 16-18 were operated at 1000 °C with fuels having a range of H_2C/H_2 and CO/CO_2 compositions. These figures show that a certain percentage of H_2O in hydrogen fuel (or CO_2 in CO fuel) must be maintained to reduce the anode/electrolyte interfacial resistance. An oxygen-rich species (H_2O or CO_2 in these cases) seems to be necessary to assist the transfer of charge from the oxide ion to the electrons in the electrode on the fuel side. This oxygen-rich species is provided by controlling the fuel gas composition.

Future development work will be done by a team consisting of Argonne National Laboratory, Allied Signal Aerospace/AiResearch, and Combustion Engineering, Inc. The focus of this development effort will be to minimize interactions among the different materials, improve the fuel cell performance, and scale up the MSOFC in terms of both size and power level.

2. Advanced Materials for Solid Oxide Fuel Cells

This new initiative is being jointly funded by the DOE Morgantown Energy Technology Center, EPRI, and the Gas Research Institute. The objective is to develop materials which permit the operation of a ceramic, solid-state fuel cell at temperatures of 500-800 °C instead of the 1000 °C now used. Lowering the operating temperature would increase the

thermodynamic efficiency of the cell and lower thermal stresses and interdiffusion of the cell components. The present focus is on developing new candidate electrolyte materials. Once suitable electrolyte materials have been identified, compatible electrode and interconnect materials will be developed.

Fig. I-5.

Effect of H₂O Partial Pressure on Interfacial Resistance at Anode/Electrolyte Interface

Fig. I-6.

Effect of CO/CO₂ Ratio on Interfacial Resistance at Anode/Electrolyte Interface

The new electrolyte material, an alternative to the currently used doped zirconium, cerium, and bismuth oxides, should be chemically stable to both hydrogen and oxygen and have a conductivity close to the target value of $0.05 \Omega^{-1}\text{cm}^{-1}$. The approach to finding new electrolyte materials was to identify and test materials which were known to have a range of oxygen stoichiometry or catalytic activity or to have crystallographic features which might facilitate oxygen transport. Initially, the search included materials which had perovskite or scheelite structures.

The first structural class of materials investigated was closely related to materials that are already used in fuel cells. Perovskites such as LaMnO_3 and LaCoO_3 have been used as electrode materials in solid-oxide fuel cells. Perovskites such as SrTiO_3 have the oxygen substoichiometry which could make them good candidate electrolyte materials. They can also be doped to increase the number of oxygen vacancies (and, hence, possibly increase ionic conductivity). Since the electrolyte should have minimal electronic conductivity, perovskites based on zirconium were made and tested in a water-saturated hydrogen/oxygen cell. The perovskite of choice, in this case, was SrZrO_3 . At 600°C , the undoped perovskite had a total

conductivity of $7 \times 10^{-7} \Omega^{-1}\text{cm}^{-1}$ and an ionic transference number (t_i , the fraction of the total conductivity due to ionic transport) of 0.77. At 800°C , the conductivity of this material increased to about $2 \times 10^{-4} \Omega^{-1}\text{cm}^{-1}$ and t_i increased to 0.9. Even though these values indicate that SrZrO_3 is an intrinsic oxide ion conductor, these conductivity values are too low for electrolyte use. The SrZrO_3 material was doped with 10 at. % Y^{3+} on the zirconium site. At 600°C , the conductivity of the doped material was $2 \times 10^{-5} \Omega^{-1}\text{cm}^{-1}$ and t_i was 0.77. Clearly, the dopant improved conductivity at 600°C with no sacrifice in t_i . However, at higher temperatures, there was no substantial improvement in conductivity. Attempts to further dope the material with Y^{3+} or other trivalent cations were not successful because single-phase materials could not be obtained.

The next set of investigated materials was based on catalysts that are used in the petrochemical industry and might have mobile oxygen ions. Scheelites such as CaWO_4 are related to materials which crystallize in fluorites (e.g., ZrO_2 , which is currently used in fuel cells) but have alternating layers of distorted WO_4 tetrahedra and layers of calcium ions. The WO_4 tetrahedra also are bound to one another by a long W-O bond. It is along the WO_4 layer that, conceivably, enhanced oxide ion transport may occur. A material with the scheelite structure in the Bi-V-O system was found to have excellent conductivity ($\sim 1 \Omega^{-1}\text{cm}^{-1}$ at 500°C , as reported by Abraham et al.⁹) but went through several phase transitions during heating to the desired operating temperature and cooling. It also had the potential problem of low chemical stability in the fuel cell environment.

Scheelites in the Nd-M-O (M= Mo or W) system were selected for study because they have high phase-transition temperatures and may have the required chemical stability toward hydrogen. The conductivity of several pellets was measured in a water-saturated hydrogen/oxygen cell. These pellets included $\text{Nd}_2(\text{MoO}_4)_3$, 10% Ti-doped (on W site) $\text{Nd}_2(\text{WO}_4)_3$, and 10% Ca-doped $\text{Nd}_2(\text{WO}_4)_3$. The conductivity measurements of the materials indicated that they were primarily electronic conductors. For example, the molybdate had a total conductivity of $2.64 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ and t_i of 0.34 at 480°C . Increasing the temperature to 800°C increased the overall conductivity to about $1 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$ but decreased t_i to 0.04. Satisfactory pellets of the tungstate could not be obtained.

Substituting titanium for the metal site in $\text{Nd}_2(\text{WO}_4)_3$ might increase the ionic transference because vacancies are being introduced. Preliminary studies have indicated that up to 33% of the tungsten can be replaced by titanium in this material with no loss of homogeneity. For a 10% Ti-doped pellet, at 500°C , there was a three-fold improvement in the total conductivity and t_i stayed about the same. However, at 800°C , t_i increased 10-fold but the total conductivity decreased by a factor of 100. The titanium doping had improved t_i , but the sacrifice in total conductivity was too great for use as a fuel cell electrolyte.

The above results indicate that the perovskites have the oxygen substoichiometry needed for fuel cell use. However, the conductivity of these materials still has to be increased by at least two orders of magnitude. For this reason, other perovskites are being evaluated. The

⁹F. Abraham, M. F. Debreuille-Gresse, G. Mairesse, and G. Nowogrocki, *Solid State Ionics* **28-30**, 529 (1988).

scheelites which were studied were primarily electronic conductors. If their overall conductivity could be increased, they could be candidates for interconnect or electrode materials. The search for new electrolyte materials is being expanded to include materials which belong to other structural classes.

3. Molten Carbonate Fuel Cell Research

The present molten carbonate fuel cell consists of a porous nickel anode, a porous nickel oxide cathode, a liquid electrolyte of lithium and potassium carbonates contained by a LiAlO_2 matrix, and appropriate metal separator sheets. The cell operating temperature is 650°C . Our work on this cell is focusing on developing alternative cathode and anode materials and fabrication techniques, as well as cell testing.

a. Cathode Material Studies

Work on cathode materials has focused on examining the effect of dopants on the conductivity of Li_2MnO_3 , which (along with LiFeO_2) is being developed as a replacement for NiO as a cathode material. Conductivity measurements of undoped Li_2MnO_3 made under a range of oxygen partial pressures (0.2 to 1.4 atm) at 650°C showed an inverse relationship between conductivity and oxygen partial pressure. Thus, undoped Li_2MnO_3 behaves as an n-type semiconductor in the cathode environment. The conductivity of Li_2MnO_3 should be enhanced by incorporating a dopant on the appropriate substitutional site. For example, if a simple defect is assumed, cations in the 5+ oxidation state substituted on a manganese site would enhance the n-type behavior and, hence, the conductivity. Moreover, cations in the 2+ state substituted on either a lithium or a manganese site could also result in increased conductivity. Substitution for lithium would result in an improved n-type semiconductor, while substitution for manganese would tend to result in a p-type semiconductor. The results of resistivity (i.e., reciprocal of conductivity) measurements for several doped samples at 650°C in air are summarized in Table I-3. The data show that all dopants caused some decrease in resistivity; in particular, Zn, Al, and Nb dopants decreased the resistivity to the extent thought to be necessary for a fuel cell cathode. Since the defect characteristics cannot be predicted accurately or measured directly, other tests are being used to assess the effect of the dopant incorporation.

To this end, Seebeck measurements were made as a function of oxygen partial pressure and temperature for several doped Li_2MnO_3 samples. The sign of the Seebeck coefficient is indicative of conductor type; a positive coefficient denotes a p-type, and a negative coefficient signifies an n-type semiconductor. Some results are plotted in Fig. I-7 for the temperature range and gas composition typical of a fuel cell cathode. The data indicate that the Seebeck coefficient becomes more negative when Li_2MnO_3 is doped with Nb^{5+} or W^{6+} cations, whereas the coefficient changes very little when it is doped with Al^{3+} or Zn^{2+} . Because this study is ongoing and the effect of dopant concentration has yet to be assessed, we cannot offer a reason for the Al^{3+} and Zn^{2+} dopant results.

Also, thermogravimetric analysis was carried out on undoped and niobium-doped Li_2MnO_3 samples, with the variables being oxygen and carbon dioxide partial pressures at 650°C . Gas compositions with up to 0.5 atm CO_2 and up to 0.5 atm O_2 were used. Neither the

doped nor the undoped compound showed any significant variation in mass with changing cover gas at cell operating temperatures. This is consistent with our measurements which indicated that Li_2MnO_3 conductivity was not a significant function of this range of cover gas composition.

Table I-3. Bulk Resistivity of Doped Li_2MnO_3 at 650°C

Dopant	Mole Fraction M/Mn ^a	Resistivity, $\Omega\text{ cm}$
Undoped		700
Ca	0.025	185
	0.050	500
Zn	0.013	147
	0.025	100
	0.037	160
	0.050	85
	0.080	23
Al	0.05	61
	0.09	600
Nb	0.013	213
	0.025	134
	0.05	96
	0.075	13
W	0.02	480

^aRatio of metal dopant to manganese.

Fig. I-7.

Seebeck Coefficients as Function of Temperature for Doped and Undoped Li_2MnO_3 (gas composition: 0.14 atm O_2 , 0.1 atm CO_2 , balance N_2)

b. Anode Material Studies

In last year's report,¹⁰ we identified several stable materials in the anode environment and gave resistivity data for one of them, LiFeO_2 . In this reporting period, we determined the resistivity of another anode-stable compound, MnO . The stoichiometry of MnO when synthesized in anode conditions has not been studied directly, but there is indirect evidence that the conductivity is at least, in part, due to lithium doping.

The anode sample is prepared in such a way that it is thermodynamically stable in the anode environment. It is reacted in alkali metal carbonates with the cover gas composition and temperature that are typical of the fuel cell and then quenched after the reaction. When prepared in this manner, the MnO sample is black instead of the expected green and has a resistivity of about $20 \, \Omega \, \text{cm}$ at 650°C , which is within the range that might be applicable for cell use. These properties could be the result of an oxygen deficiency in the sample, but associated fabrication work has shown that, when sample preparation is done in the absence of lithium, the final product is green. Thus, while the resistivity of the green form has not been determined, the color change from green to black is a strong indication of lithium incorporation, in a manner similar to that observed previously for NiO in the cathode environment.¹¹

c. Electrode Fabrication Work

In an earlier report, we discussed a new fabrication technique that yields the desired complex microstructure for the cathode.¹² The technique involves the fabrication of very small ceramic fibers by a spray process. In 1989, we adapted this technique for use with LiFeO_2 and MnO anodes. This anode work was directed at the problem of accomplishing binder burnoff and sintering of the fibrous ceramics in a way that will maintain the anode stoichiometry. While the previously reported procedures for cathode fabrication can be used as a basis for the anode fabrication, they must be tailored to the specific material being used. In all cases, fibrous agglomerates serve as the basic building block for the fabrication process.

When making an LiFeO_2 anode by our new technique, we can take advantage of the fact that the same crystalline structure (i.e., disordered cubic) is stable in both the anode and cathode environment. Furthermore, the lattice constant change is not excessive from the standpoint of structural destruction when the compound is transformed from the stable form in the cathode ($4.158 \, \text{\AA}$) to that of the anode ($4.200 \, \text{\AA}$). Binder burnoff and sintering are more easily accomplished in an oxidizing environment than in the reducing anode environment; thus, the best fabrication method for the LiFeO_2 anode involves burnoff and sintering in air, with subsequent equilibration of the structure in the anode environment. We have found that this process results in a sound structure with the required large pores for anode use.

¹⁰M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, p. 36 (1989).

¹¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, pp. 37-40 (1989).

¹²M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1987*, Argonne National Laboratory Report ANL-88-19, p. 35 (1988).

Fabrication of the MnO anode involves a similar but modified approach. With this approach, Mn_2O_3 is fabricated into fibers, which are sintered in air at 900°C , chopped, tape cast into a thin body, and sintered into an electrode. At the sintering conditions for the electrode, air at 1200°C , Mn_3O_4 is the stable oxide of manganese. The last step in anode fabrication is the equilibration of the Mn_3O_4 porous plaque in anode conditions, resulting in a stable MnO electrode. This is done by heat treating the plaque at 700°C in anode gas, typically 80% H_2 -20% CO_2 , humidified at 60°C . The lithiation of the MnO may be done during this last step or after cell assembly. The effect of lithiation conditions is now being studied.

The conversion of the Mn_3O_4 structure to MnO in anode conditions can be done without loss of structural integrity. Moreover, it is accompanied by a potentially useful structural change. Figures I-8 and I-9 show cumulative pore volume and differential surface area for the MnO structure, respectively. These figures show that, while the converted structure retains its integrity, it has a much higher surface area, a significant amount of which is contained

Fig. I-8.

Pore Volume of MnO Structure Prepared in Air and Heat Treated in Anode Gas

Fig. I-9.

Surface Area of MnO Structure Prepared in Air and Heat Treated in Anode Gas

in very small pores ($<0.1 \mu\text{m}$). Because of the reaction kinetics at the fuel cell anode, increased surface area is probably not necessary. However, as will be discussed in Sec. I.E.3.d, high surface area is very important for cathode operation. Thus, this technique might be useful for preparing high-surface-area Li_2MnO_3 cathodes.

d. Cell Testing

Cell testing has been done for a variety of cathode materials and for an undoped LiFeO_2 anode. The results to date for the cathode tests are not consistent with what had been generally thought to be the cathode material requirements; that is, they indicate that the surface area is of greater importance than material conductivity over a fairly wide range of conductivity. Comparison of Figs. I-10 and I-11 shows that the performance of these cathodes

Fig. I-10.

Typical Performance of Cells with Selected Cathode Materials (numbers in parentheses next to cathode material identification are resistivities at 650°C)

Fig. I-11.

Surface Area Distribution for Cathodes Reported in Fig. I-10

correlates well with surface area distribution (i.e., performance is best with significant surface area in the small pore size range), but not with resistivity. The LiCoO_2 cathode performed comparably to a state-of-the-art NiO cathode fabricated by Gould Inc., but it also suffered from the same problem as NiO; namely, the cobalt dissolved in the carbonate melt and reprecipitated as cobalt metal in the electrolyte structure.

For the Li_2FeO_2 anode, the test results indicated that the performance at low current densities (less than about 50 mA/cm^2) is near that for the state-of-the-art nickel anode, but that the performance decays with time at higher current densities. Furthermore, the anode test indicated that the solubility of iron in the anode conditions is higher than that in the cathode conditions. This is a very promising result for the use of LiFeO_2 as a cathode, but not necessarily for its use as an anode.

Several electrodes were also run in a diagnostic cathode half-cell. The polarization data from these tests give linear Tafel plots; Fig. I-12 shows Tafel plots as a function of oxygen partial pressure for an undoped LiFeO_2 cathode half-cell. Curves which are linear in the Tafel region (i.e., at high overpotential) indicate that the rate-limiting step is electron transfer. In comparison, NiO cathodes produce nonlinear Tafel plots because the reaction rates are diffusion controlled. Thus, increasing the active surface area should make the LiFeO_2 cathodes perform kinetically more like NiO and thereby improve their in-cell performance.

Fig. I-12. Performance Curves from Half-Cell Tests with Undoped LiFeO_2 Cathode at Different Oxygen Partial Pressures

II. FOSSIL FUEL RESEARCH

The fossil fuel research at CMT includes several projects in the area of fluidized-bed combustion (FBC) technology, heat and seed recovery studies for coal-fired magnetohydrodynamics (MHD), and research on multiphase flow in fluidized-bed systems.

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. The fluidized-bed combustion projects at CMT include (1) the measurement and control of alkali vapor in pressurized fluidized-bed combustor (PFBC) off-gas, (2) testing and evaluation of Illinois char as a fuel for a PFBC system, (3) materials testing for an atmospheric fluidized-bed cogeneration air heater, (4) investigation of metal wastage on FBC heat exchanger surfaces, and (5) studies of chaotic behavior in fluidized beds.

1. Measurement and Control of Alkali from PFBC Off-Gas

One of the potential problems of the pressurized fluidized-bed combustion/gas-turbine combined-cycle system (PFBC/GTCCS) for power generation is the presence of vapor-phase alkalis, such as chlorides and sulfates of sodium and potassium, in the PFBC off-gas that could cause corrosion of gas turbine hardware. The objective of this effort is to develop a fixed, granular-bed sorber that will remove these alkali corrodents from the off-gas. An activated-bauxite alkali sorber is being operated with a laboratory-scale PFBC facility at CMT to (1) measure the alkali vapor concentration in the PFBC off-gas and (2) demonstrate sorber effectiveness for the control of alkali vapors from actual PFBC off-gas.

Earlier test results with the on-line alkali analyzer developed by Ames Laboratory had shown that its stainless steel sampling line captured alkali vapors and distorted the accuracy of the alkali-vapor measurements.¹ As a result, we developed an analytical alkali sorber bed technique for reliable quantitation of vapor-phase alkali in the PFBC off-gas on a time-averaged basis. This technique, which does not require use of a sampling line, involves post-test analysis of sections from an activated-bauxite sorber bed with an atomic absorption spectrometer. With this technique, alkali vapors in the PFBC off-gas are captured by the sorbent through physical adsorption, the adsorbed alkalis are recovered by a simple water leaching, and the resulting solution is analyzed for alkalis. The water leaching regenerates the activated bauxite for continued use.

Because of the excellent results obtained with the analytical alkali sorber bed technique, we are striving to develop a regenerable activated-bauxite sorber alkali monitor (RABSAM) to be employed as an alternative to the on-line alkali analyzer for field application.

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

The RABSAM will use commercially available activated bauxite, which contains some clay impurities that can react with alkali vapors in the PFBC off-gas; therefore, our 1989 effort was focused on developing a technique for removing or deactivating these clay impurities.

The deactivation of these clay impurities was achieved by a NaCl-solution impregnation technique. With this technique, the fresh activated bauxite is impregnated with NaCl solution, and the NaCl-impregnated activated bauxite is then heat-treated at a controlled temperature (1000 K), followed by water leaching, acid leaching, and Soxhlet extraction with deionized water to remove water-soluble sodium from the regenerable activated bauxite. With a 5 M NaCl solution, the complete deactivation of clay impurities was achieved within 5 h. This technique also effectively opened the structure of the activated bauxite and created fine pores, thereby resulting in a ~20% increase in the total porosity and an increase in specific surface area from 87 m²/g to 121 m²/g. High surface area is essential for the NaCl-vapor adsorption process.

Experimental work will be continued to optimize this NaCl-solution impregnation technique. The regenerable activated bauxite will also be tested for its capability for alkali-vapor sorption and water-leaching regeneration.

2. Testing and Evaluation of Illinois Char

To promote the utilization of Illinois high-sulfur coals, the Illinois Center for Research on Sulfur in Coal (CRSC) is sponsoring the development of a coal pyrolysis process. This process, which aims to produce valuable liquid fuels and a devolatilized solid char by-product, will be economically viable only if the char can be effectively utilized. The objective of this effort was to evaluate the char as fuel for a PFBC/GTCCS for power generation. To this end, a high-sodium (0.13 wt %) and high-chlorine (0.34 wt %) coal (Illinois No. 6 seam) and its derived char were combusted in our laboratory-scale PFBC/alkali sorber facility at a bed temperature of 1173-1223 K and system pressure of 0.9 MPa (9.2 atm) absolute. We then determined the combustion characteristics and alkali-vapor emission levels for the coal and char. The char, which contains 14.0 wt % volatile matter on a moisture-free basis, was produced at 890 K in an atmospheric bubbling fluidized-bed combustor with a sand bed.

The pyrolysis of coal resulted in 73% and 94% reductions in the S and Cl contents, respectively, in the char; however, as expected because of the low temperature for the pyrolysis process, the char had significantly higher Na and K contents than its parent coal. Combustion efficiency of the char in PFBC varied from 81 to 87.9%, which is somewhat lower than the 97.8% achieved in coal combustion. The char combustion met the required 70% sulfur retention of the New Source Performance Standards (NSPS) with a Ca/S mole ratio of 0.8-0.9, whereas the coal combustion required a Ca/S ratio of 1.37. The nitrous oxide gas concentration for both char and coal combustion was 50-100 ppm (by volume), which is significantly lower than the NSPS requirement. The HCl emission was measured to be 13 and about 200 ppm (by weight) in the flue gas for char and coal combustion, respectively. For both char and coal combustion, the alkali-vapor concentration in the PFBC off-gas was measured to be more than five times greater than the currently suggested alkali specification limit of 0.024 ppm for an industrial oil-fired gas

turbine. This finding suggests that a way of controlling those vapors may be needed for the PFBC application.

Results of this work showed that the char can be combusted in a PFBC and has the potential for use as a fuel in a PFBC/GTCCS; however, further work is needed to better define PFBC operating conditions for achieving sustained stable in-bed combustion and improved combustion efficiency of char particles.

As an extension of this work, two more Illinois coals will be tested to establish the alkali-vapor data base that is needed to allow an appropriate evaluation of the alkali-vapor corrosivity of the PFBC off-gas generated from burning Illinois high-chlorine, high-sulfur coals.

3. Atmospheric Fluidized-Bed Cogeneration Air Heater Experiment

Argonne is managing the Atmospheric Fluidized-Bed Cogeneration Air Heater Experiment for DOE. The objective of this project is to assess materials and process performance of in-bed air heaters for cogeneration of electricity and hot air in an atmospheric fluidized-bed combustor (AFBC). The ANL divisions involved in this effort are CMT and Materials and Components Technology.

Rockwell International was subcontracted for the required modification, installation, and experimental testing of heat-exchanger tube bundles in the DOE-owned AFBC unit (1.8-m by 1.8-m square cross section) located at a Rockwell site in El Segundo, CA. Test articles were supplied by ANL and by Westinghouse Corp. and three boiler vendors. The duration of the test was about 2000 h. About 1700 h of testing was completed in 1988, the remainder in 1989. The need for repairs to the main compressor supplying cooling air to the fluidized bed delayed the 1989 test schedule by about six months. Argonne and the Westinghouse team are performing data analysis and an assessment of the heat exchanger performance, which will be completed in 1990.

The test articles are intended to provide material wastage information that will enable projections of service life in an AFBC environment. Several types of articles were tested: platen specimens assembled into in-bed tube bundles, cylindrical specimens inserted around internally cooled probes, specimens of various geometries (U-tubes and tab coupons) attached to uncooled probes, and tube clamps made from a candidate alloy. The analysis consists of metallographic examination of specimens and confirmation of the conditions under which they were exposed by study of the data records from the experimental testing. Materials examination and data analyses are underway at ANL, and tube platens were shipped to the boiler vendors in early December 1989 for analysis.

4. 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 (CRSC), Tennessee Valley Authority (TVA), ASEA Babcock, Foster Wheeler Development Corp., and Combustion Engineering, Inc. The ANL divisions involved in this effort are CMT and the Energy Systems Division. The overall objective is to develop guidelines, based on model predictions and experimental data, for the design and operation of FBCs with minimal metal loss.

To develop the necessary understanding of the processes causing erosion in fluidized beds, hydrodynamic and erosion experiments are being analyzed by means of computer models of both the fluidized-bed hydrodynamics and the in-bed erosion process. This close coupling between experiments and mechanistic computer modeling is necessary for the proper interpretation of experiments and validation of the models.

Activities underway include (1) experiments in an erosion test facility to determine the effects of particle size and particle velocity at the limits of detectable erosion, (2) fluidized-bed experiments at ambient conditions to determine solids motions and erosion of immersed tubes, and (3) analysis of these experiments using mechanistic computer models of the fluidized-bed hydrodynamic and erosion processes.

As reported previously,² we have developed computer models incorporating hydrodynamics of the solids and bubble motion and the erosion of tubes resulting from the impaction and abrasion of particles. The hydrodynamics model is capable of two-dimensional, time-dependent solutions of mass, energy, and momentum conservation equations for multiphase nonequilibrium systems.

In 1989 work, this model was refined and partly validated against experimental data. This validation of the hydrodynamic model was accomplished by comparing predictions with experimental data obtained in so-called two-dimensional (thin in the front-to-back direction) fluidized beds containing a single centrally located rectangular obstacle. Time-averaged porosity distribution and porosity fluctuation data were measured by means of a gamma-ray densitometer with a Cs-137 source and a NaI scintillation counter mounted on a movable platform.³ This arrangement allowed measurements to be taken at various locations in the fluidized bed. The computed and experimental time-averaged porosities are shown in Figs. II-1 and II-2, respectively. Overall, the computed and experimental porosities are in reasonable agreement. The frequency and amplitude of the porosity fluctuations at various locations in the fluidized bed are shown in Table II-1. The predicted amplitude variations are in good agreement with experimental data for locations 1-5, which are regions near the inlet air jet and around the side of the obstacle. The agreement is poorer for locations above the obstacle (6-9). The predicted frequencies are in reasonable agreement with experimental values, except just underneath the obstacle (location 2) and above the obstacle (location 7).

²M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, p. 49 (1989).

³J. X. Bouillard, R. W. Lyczkowski, and D. Gidaspow, *AIChE J.* **35**, 908-922 (June 1989).

Fig. II-1. Computed Time-Averaged Porosity (ϵ) Distribution in Fluidized Bed with Centrally Located Rectangular Obstacle

Fig. II-2.

Experimental Time-Averaged Porosity Distribution in Fluidized Bed with Centrally Located Rectangular Obstacle

Table II-1. Predicted and Experimental Porosity Amplitudes and Frequencies (for the first two seconds) in Fluidized Bed with Centrally Located Rectangular Obstacle

Location	Amplitude of Porosity Fluct.		Frequency of Porosity Fluct., Hz	
	Predicted	Expt.	Predicted	Expt.
1	0.34	0.38 ± 0.05	8.4	8.2
2	0.49	0.49 ± 0.05	9.14	3.75
3	0.26	0.30 ± 0.05	0.95	0.75
4	0.55	0.62 ± 0.05	2.7	3.0
5	0.51	0.64 ± 0.05	5.3	5.2
6	0.42	0.62 ± 0.05	1.3	2.0
7	0.0	0.24 ± 0.05	3.6	1.8
8	0.13	0.64 ± 0.05	1.9	1.8
9	0.29	0.65 ± 0.05	1.7	1.8

In addition to the porosity comparison, the solids velocity vector fields measured at the University of Illinois with a radioactive tracer particle in a fluidized bed were compared with calculated values. The prediction of a vortex pattern, a nearly 0° angle of incidence at the side of the rectangular obstacle, and deflection around the lower corners was experimentally confirmed. However, the predicted solids flow above the obstacle was incorrect. This error may have been caused by the assumption of symmetry about the center line in the simulation.

A new activity in FY 1990 is an effort by Babcock & Wilcox (B&W) under ASEA Babcock sponsorship to develop a three-dimensional fluidized-bed hydrodynamics model by building upon the work at ANL.

We have also developed erosion models which relate solids motion to metal wastage. The models account for particle characteristics and materials properties and for the relative contributions of impaction and abrasion erosion. The hydrodynamic calculations provide the solids energy and direction of motion used as the starting point in the erosion calculation.

A workshop was held at ANL in October 1989 to demonstrate the hydrodynamic and erosion computer models and to provide hands-on experience in using these models for most of the project participants. Each participant was provided a user's manual and copies of the computer codes for the models, which were subsequently installed on the participants' computer systems. Feedback from the participants was very positive.

As part of the experimental work, Combustion Engineering has collected data on erosion rates at particle sizes and particle velocities encountered in fluidized-bed combustors. The Ash Erosion Test Facility at Combustion Engineering was used to obtain these data. This information is being employed to develop the appropriate materials properties relationships for inclusion in the erosion models.

Other experiments provided hydrodynamic and erosion data from several fluidized beds. Physical hydrodynamics experiments were conducted at the Illinois Institute of Technology and at the University of Illinois (Urbana-Champaign) to provide information on solids and bubble motion for validating the computer models. Experiments in the variable-dimension, large-scale test facility at Foster Wheeler are providing information on the significance of data from experiments in smaller scale fluidized beds. In addition, erosion of tubes in a small array is being measured at Foster Wheeler for direct comparison with calculated erosion rates, and further information concerning erosion and corrosion is being provided by the Tube Metal Wastage Program at TVA in support of its 160-MW AFBC Demonstration Project.

In other work during 1989, we demonstrated the feasibility of continuously monitoring erosion in pilot-plant and full-scale FBCs. A monitor consisting of a piezoelectric transducer coupled to the inner surface of a cylindrical probe was successfully tested up to a temperature of 773 K. A method of brazing the transducer to the probe was also developed. Information on the thickness of the probe is continuously relayed through coaxial signal wires to an electronic signal processing unit. With such an erosion monitor, it should be possible for the operator to detect unusually erosive coal and/or operating conditions and take preventive measures before damage becomes severe.

Effort at ANL in FY 1990 and 1991 will involve validating the computer models with the experimental data, interacting with B&W to develop a three-dimensional hydrodynamic model, developing mechanical-wear guidelines based on model predictions and experimental data, and completing software documentation and user guides for the computer models.

5. Investigation of Chaotic Behavior of Fluidized Beds

Measurements of pressure, voidage, and gas and solids velocities made in fluidized beds usually show rapid fluctuations. Figure II-3 is a plot of typical time series data obtained for the pressure fluctuation of a fluidized bed.⁴ The fact that fluidization processes can be described by the nonlinear equations of multiphase flows prompted the following question: do these fluidization pressure data exhibit strictly stochastic features, or do they exhibit characteristics of deterministic chaos as well? To address this question, we have employed a combination of nonlinear dynamical techniques on a relatively large data set for fluidized-bed pressure fluctuations.

The calculational approach that we have chosen is the Grassberger-Procaccia correlation integral method.⁵ Since we are analyzing actual experimental data, noise inevitably arises from a variety of sources. Therefore, we have utilized a noise reduction technique called singular spectrum decomposition, which is a well-known method in signal processing.⁶ We

⁴D. Dent, Commonwealth Scientific and Industrial Research Organizations, Australia, private communication (1989).

⁵P. Grassberger and I. Procaccia, *Physica D* **9**, 189 (1983).

⁶D. S. Broomhead and G. P. King, *Physica D* **20**, 217 (1986).

have integrated this composite approach⁷ with mutual information analysis⁸ and applied them to the experimental time series data for fluidized-bed pressure fluctuations.⁴

The pressure data were obtained at a sampling rate of 500 digitizations per second with an analog-to-digital (A/D) converter. The total data set was digitized in an hour of continuous run. The present analysis used several subsets of the data of length between 15,000 and 50,000 points.

Fig. II-3.

Plot of Pressure Fluctuation Data (in arbitrary units) as Function of Time. Data were obtained from Dent.³

The correlation integral $C(L)$, a widely used measure of chaotic behavior, is defined as:

$$C(L) = \lim_{N \rightarrow \infty} \frac{1}{N^2} \{ \text{numbers of pairs of points on the attractor whose distance is } < L \}$$

where N is the number of embedding-dimension vectors constructed out of the scalar time series. For some range of L called the scaling region, $C(L)$ scales as L^D , where D is the correlation dimension of the "attractor" (a property of systems that exhibit deterministic chaos).⁵ A

⁷A. M. Albano, J. Muench, C. Schwartz, A. I. Mees and P. E. Rapp, Phys. Rev. A. **38**, 3017 (1988).

⁸A. M. Frazer and H. L. Swinney, Phys. Rev. A **33**, 1135 (1986).

saturation of D as the embedding dimension d increases is an indication that the experimental signal has a nonrandom component.⁵

The correlation integral was calculated and the correlation dimension D extracted from a local slope analysis. The resulting D as a function of d is displayed in Fig. II-4. Up to $d = 10$ there is no sign of saturation (i.e., D does not reach a maximum value and remain constant with increasing d). However, the values of D that have been obtained are significantly below those from a truly stochastic process, such as arising from a "good" random number generator. The present results indicate the presence of a nonrandom component in the process underlying the time series data. Nevertheless, the signal-to-noise ratio and the rapidly shrinking scaling region with increasing d rule out an unambiguous determination of the saturation regime and, hence, an evaluation of the dimension of the corresponding attractor. If an attractor exists for the present data, it does not have a low value for the correlation dimension (i.e., in the range of 2-3).

Fig. II-4.

Correlation Dimension as Function of Embedding Dimension (empty squares, pressure data; filled squares, random numbers)

There are several critical issues arising from the application of nonlinear dynamical techniques to the analysis of systems of "real world" interest. For example, a small data set size and the presence of noise would invalidate embedding of data to arbitrarily high dimensions. This, in turn, would severely limit the possible detection of moderate-to-high dimensional attractors. These factors provide a serious challenge to the effectiveness of applying the available data analysis techniques to chaotic time series data from fluidized beds. Nevertheless, one can derive useful information such as the presence of nonrandom processes and the lower bound on the relevant dimensions of the possible attractor, as the present analysis showed.

Additional work is being done to analyze a set of fluctuating O_2 partial pressure data from an operating fluidized-bed combustor to further investigate the possible chaotic behavior of fluidized beds.

B. *Magnetohydrodynamic Heat and Seed Recovery Studies*

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 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 0.1 MPa (1 atm) and approximately 2300 K and enters a bottoming cycle that is similar in function to the steam bottoming cycle of a conventional coal-fired 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 nitrous oxide emissions to acceptable levels, and inject secondary air to complete combustion of the fuel. The Chemical Technology Division 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.

1. Materials Studies

Combustion gases containing sulfur and alkalis have been a concern with regard to the corrosion of heat exchanger tube materials in conventional coal boilers. Such corrosion is also a problem for MHD combustion gases, especially because of their higher alkali content. Laboratory autoclave tests are in progress to study the corrosion of candidate superheater and air-heater alloys exposed to simulated MHD conditions of gas temperature and composition, deposit chemistry, and metal temperatures.

During 1988, we analyzed candidate air-heater alloys exposed to MHD conditions for up to 2000 h. Ferritic alloys (T22, 5Cr-0.5Mo, and 9Cr-1Mo) and 304H were tested at a metal temperature of 870 K and a gas temperature of 1090 K. Austenitic alloys (304H, 316, 310, 321, and 800H) were tested at a metal temperature of 1035 K and a gas temperature of 1255 K. Test results were summarized in last year's report.⁹

During 1989, we analyzed candidate steam superheater (SSH) alloys exposed to MHD conditions for approximately 2000 h. The austenitic SSH alloys (304H, 316, 310, 321, and 800H) were coated with tube deposits (~80 wt % K_2SO_4) from the U.S. DOE MHD

⁹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, pp. 50-51 (1989).

bottoming-cycle pilot plant (Tullahoma, TN) and tested in a laboratory autoclave furnace at a metal temperature of 840 K and a gas temperature of 1480 K.

All the austenitic alloys developed thin (Cr, Fe) oxide scales; however, energy dispersive X-ray analysis revealed the presence of some sulfur at the scale/substrate interface region. Since the metal temperature was only 840 K, the observed sulfur penetration was small when compared with that reported previously for the same alloys when tested at air-heater metal temperature conditions of 1035 K.⁹

Figure II-5 is a plot of the metal recession data obtained in the SSH materials tests. Also plotted in this figure are test results for ferritic and austenitic alloys under conditions expected for an intermediate-temperature air heater (ITAH) at the maximum service temperature region and at the transition region from a high-grade austenitic to a lower-grade ferritic alloy. The arrow on the right vertical axis in Fig. II-5 indicates the 2000-h metal recession measurements that correspond to an acceptable corrosion rate of 0.5 mm/yr, which was derived by assuming linear corrosion kinetics. The austenitic alloys exposed under SSH test conditions showed negligible corrosion (well below the 0.5 mm/yr limit), and they should perform adequately in this type of service. The results of the earlier ITAH tests were less encouraging. Although type 310 stainless steel appears adequate for service at ITAH conditions, the low code-allowable stress values for this alloy at temperatures of 1035 K would probably limit its use in commercial systems at these conditions to that of a cladding or a coextruded material with a stronger substrate. The ferritic alloys were also found to be unacceptable for service at the ITAH transition region conditions. This means that their use will have to be restricted to lower service temperatures, and that more expensive austenitic steels, such as 304H, will have to be used at these conditions.

Fig. II-5. Metal Recession Data for Ferritic and Austenitic Alloys Exposed to MHD Conditions for 2000 h. (SSH conditions: metal T, 840 K; gas T, 1480 K. ITAH conditions: metal T, 1035 K; gas T, 1255 K. ITAH transition conditions: metal T, 870 K; gas T, 1090 K.)

Plans are being made to test additional alloys at the ITAH conditions. These tests will be completed in FY 1990.

2. Nitrous Oxide Kinetics

In an MHD plant, nitrous oxide generated at the high combustion temperatures in the topping cycle will decompose in the radiant boiler of the steam bottoming cycle as the gas cools under reducing conditions from ~2300 K to ~1400 K. Kinetic codes developed for design of the radiant boiler^{10,11} have been partially validated with experimental data obtained from the large DOE MHD bottoming-cycle pilot plant in Tullahoma, TN. During 1989, we initiated detailed design of a small-scale one-dimensional flow reactor for the investigation of NO_x decomposition kinetics under radiant boiler temperature conditions. The design, fabrication, and assembly of the test equipment are expected to be completed in 1990. Experimental data from the flow reactor will be used to provide further validation of the available NO_x decomposition kinetics codes.

C. *Multiphase Flow Reactor*

A collaborative effort was initiated in 1989 with Ohio State University to study the interfacial phenomena and dynamics of bubble wakes in three-phase (gas-liquid-solid) fluidized beds. The overall objectives are to study the local hydrodynamic behavior of gas bubbles and their wakes in gas-liquid-solid flow systems and to determine how such behavior affects the scale-up criteria for optimum design of three-phase flow systems.

Effort has been initiated to design and fabricate a pilot-scale (60-cm dia) test facility at ANL. We will determine bubble properties; mixing; and gas, liquid, and solid holdups in the pilot-scale facility. Then we will compare the experimental results with bench-scale data obtained at Ohio State University, as well as calculated results from mechanistic models that have been developed to quantitatively describe flow in a three-phase medium. From this, scale-up criteria will be developed for larger systems. Completion of the facility and the beginning of experimentation are scheduled for 1990.

¹⁰A. J. Sistino, *Analytical Studies of NO_x Decomposition in the Radiant Boiler of an Open-Cycle MHD Power Plant*, Argonne National Laboratory Report ANL/MHD-79-7 (1979).

¹¹L. W. Crawford et al., "On Application of MHD Pollutant Content Technology to Control of NO_x and SO_x," ASME Joint Power Generating Conf., paper no. 84-JPGC-APC-8, Toronto, Canada, September 30 - October 4, 1984.

III. MUNICIPAL AND HAZARDOUS WASTE TECHNOLOGIES

The CMT effort on municipal and hazardous waste technologies involves research into the thermochemical conversion of municipal solid waste (MSW) and the development of methods for treating hazardous waste.

A. Energy from Municipal Waste

During this past year, our effort in this program was concentrated on developing a computer model to simulate the MSW combustion process and the formation of products not only during combustion but also during cooling of the combustion products in the heat recovery and gas cleanup system. This model will be used to establish the relationship between the feed quality and operating conditions to the output characteristics (such as the flame temperature, the bed profiles, and the composition of the gases emerging out of the bed and the flame zone).

The model has been developed for the MSW combustor shown by the schematic in Fig. III-1. The feed enters at the left end and is carried across a grate, where it undergoes pyrolysis and produces fuel gases, char, and ash. The char and ash are discharged into a quench tank at the right. (Future versions of the model will consider the combustion of char remaining on the grate.) Primary air, supplied below the grate, carries the fuel gases upwards into the flame zone where they burn in contact with the secondary air. The flames provide the heat required for the drying, heating, and volatilization reactions taking place within the bed. Part of the heat from the flames is recovered by water walls that line the flame zone. The flue gases leave the combustor at the top and are taken for further heat recovery and cleanup.

Fig. III-1. Schematic of Municipal Solid Waste Combustor (H_{in} = initial bed height, L = bed length, B = bed width)

In our two-dimensional model, we assumed that MSW is composed of pseudo-components such as cellulose, plastics, etc., which pyrolyze through numerous pathways to yield fuel gases, ash, and char according to the reaction:

In this reaction, the first reaction pathway produces $[\text{Gas}]_1$ (e.g., hydrogen), char, and ash. Similarly, the other pathways produce different gases in addition to char and ash. The model incorporates the pyrolysis kinetics of the solids and simulates the heat and mass transfer within the MSW bed. It is assumed that the bed is well mixed in the vertical direction because of the tumbling action caused by movement of the grate.

The model equations were solved to generate the temperature and mass flow profiles along the length of the bed, as illustrated in Fig. III-2. Three distinct regions are evident from the profile. In the initial heatup zone, there is no change in the mass flow rates as the solids are heated toward reaction temperature. In the next zone, the reaction zone, the reactant cellulose begins to pyrolyze, producing char and volatiles. Finally, in the burnout zone, no more reactant is left and, therefore, no further change in the mass flow rates occurs. The solids temperature rises toward its steady-state temperature, which is determined by heat input from the flames and cooling due to primary air. The results also indicated the length of grate necessary for the heating (2-4 m) and volatilization (0.5-2 m) of the solids and the decrease in equilibrium flame temperature (5-10°C) due to the sensible heat lost with the exiting solids.

The results also revealed that there is a well-defined "feasible operating range" of variation in the solids feed rate for a given air flow rate. This feasible range is sharply bounded by inadequate fuel gas generation at one end and incomplete volatilization of the solids at the other end. Similarly, for a given solids throughput, a feasible range of air flow rates was identified and is shown by the curved surface in Fig. III-3. The feasible range is sharply bounded by either lack of oxygen to support combustion, too slow a bed heatup due to excessive primary air, or too much excess air. Outside these feasible operating ranges the combustion cannot sustain itself.

Parametric studies showed that the air flow rate is the most important operating variable because it affects both the flame and bed temperatures. These studies also showed that the equilibrium flame temperature is sensitive to the total air fed to the combustor system but not to its distribution between primary and secondary air. The distribution, however, does affect the bed temperature profile and, therefore, the reaction rates. Bed height was found to have negligible effect on the bed and flame temperatures.

Fig. III-2. Typical Temperature and Mass Flow Profile along Bed Length

Fig. III-3. Flame Temperature as Function of Primary and Total Air (as percent of stoichiometric air)

Although the present version of the model can provide a better understanding of the physical and chemical processes taking place in MSW mass burning, we have identified a

number of areas for additional work which can lead to better predictive capability. These include the incorporation of pyrolysis kinetic data for other components such as hemicellulose, plastics, etc., and combustion of the char within the bed; consideration of the air flow dynamics inside the bed; and, for a given flame zone configuration, kinetic-based calculations for the flame temperature and flue gas composition distribution.

B. *Hazardous Waste Treatment*

Efforts are underway to develop methods for (1) treatment/disposal of reactive metals, (2) microwave-assisted detoxification of hazardous waste containing halocarbons, and (3) red water treatment.

1. Treatment/Disposal of Reactive Metals

The objective of this effort is to design and analyze a process for the conversion of waste sodium, including sodium contaminated with small amounts of radionuclides, to a glass form and to provide technical assistance in the commercial demonstration of the process on a pilot scale of 50 to 100 kg/h. In earlier work, a one-step integrated process was developed for the conversion of waste sodium to a glass form for ultimate disposal.¹ At the heart of the process is a low-g and low-pressure drop cyclonic reactor designed to withstand high operating temperatures. The solid reactants, such as silica and lime, are introduced into the reactor pneumatically. Liquid sodium is injected into the reactor with nitrogen as an aspirator and atomizer. The oxidation of the sodium and the formation of the glass both occur primarily at the walls of the cyclonic reactor, and the product glass is withdrawn from the reactor bottom.

Our earlier experimental work² had identified three different types of glasses as suitable waste forms for use with different kinds of sodium:

1. For sodium containing no radioactive contaminants, simple soda-silica glasses are a suitable waste form.
2. For sodium containing short-lived radionuclides, a glass composition similar to 30% Na₂O-10% CaO-3% Al₂O₃-57% SiO₂ or 30% Na₂O-10% B₂O₃-3% Al₂O₃-57% SiO₂ would be adequate to make the sodium inert and to isolate the radioactive contaminants from the environment for a prolonged period.
3. A low-sodium glass such as 11% Na₂O-1% CaO-2% Al₂O₃-9% B₂O₃-77% SiO₂ would provide environmental isolation for long-lived radioactive species.

¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 77 (1987).

²M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, pp. 62-63 (1989).

Even though the minimum reaction temperature for the waste sodium was identified as $\sim 300^\circ\text{C}$, a reactor temperature of 1000°C or higher would be needed for the product glass to be workable. Thermochemical calculations show that if sodium and silica are reacted in the ratio of one mole of silica per mole of sodium with four times the stoichiometric amount of air required for this reaction, the adiabatic reaction temperature would be $\sim 1175^\circ\text{C}$. With additional silica or other oxides in the reactant mixture, the adiabatic reaction temperature would decrease. If any of the other cations are introduced as carbonates rather than oxides, the additional energy required to decompose the carbonates would also lower the adiabatic reaction temperature. Thus, the combined sodium oxidation and glass-making process may or may not be self-sufficient in energy requirements, depending on the choice of glass composition, the reaction temperature, excess air used, and the chemical form of the glass-making ingredients chosen.

Process energy requirements to convert waste sodium to the different types of glasses were determined for a range of processing temperatures. The results of these calculations are shown in Fig. III-4. For these calculations, we assumed that sodium is processed at a rate of 50 kg/h with four times the stoichiometric air required for the oxidation of sodium, and that no heat is recovered. Figure III-4 shows that the process energy requirements increase rapidly as the processing temperature increases. In addition, the most refractory of the glass compositions considered (curve f) requires an external energy input an order of magnitude greater than that for the soda-silica, soda-silica-boron, or soda-silica-lime glasses (curves a, b, and c, respectively).

Fig. III-4.

Process Energy Requirements for Selected Glasses:

- (a) $\text{Na}_2\text{Si}_2\text{O}_5$
- (b) $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 0.33\text{B}_2\text{O}_3 \cdot 0.1\text{Al}_2\text{O}_3$
- (c) $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 0.33\text{CaO} \cdot 0.1\text{Al}_2\text{O}_3$
- (d) $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 0.5\text{B}_2\text{O}_3 \cdot 0.15\text{Al}_2\text{O}_3 \cdot 1.35\text{SiO}_2$
- (e) $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 0.33\text{CaO} \cdot 0.15\text{Al}_2\text{O}_3 \cdot 1.35\text{SiO}_2$
- (f) $\text{Na}_2\text{Si}_2\text{O}_5 \cdot 0.09\text{CaO} \cdot 0.18\text{Al}_2\text{O}_3 \cdot 0.82\text{B}_2\text{O}_3 \cdot 5\text{SiO}_2$

Thus, without heat recovery, external energy must be provided to the process. This external energy may be provided as electrical resistive heat for cases of low energy requirements. Means for adding this external energy could include preheating of the ingredients, preheating of the air, or introducing fuel directly into the reactor.

Future work will be directed toward a pilot-plant demonstration of the process with nonradioactive sodium. This will include conceptual design of the reactor, feed systems, and product removal equipment.

2. Microwave-Assisted Detoxification

More than 10% of the hazardous waste streams at DOE Defense Programs sites contains halocarbons. Microwave-assisted detoxification appears to offer economic advantages over other methods of treatment/disposal of these waste streams. The purpose of this research is to investigate the technical feasibility of a microwave-assisted chemical process for detoxification of these hazardous organic wastes.

In previous work,³ a 600-W, 2.45-GHz microwave furnace was used to test the microwave-assisted oxidative degradation of trichloroethylene (TCE) adsorbed on catalyst-loaded active carbon. The results of these studies established that TCE adsorbed on an active carbon bed (loaded with Cu and Cr catalysts) when heated with microwave radiation to moderate temperatures ($<400^{\circ}\text{C}$) in the presence of moist air can be readily detoxified (i.e., converted into less-noxious or removable products such as HCl, CO, and CO_2). Conversion of greater than 80% TCE to degradation products was observed in single-pass experiments. Furthermore, the used carbon bed was regenerated by microwave heating when a moist- N_2 or moist-air stream was passed through the bed. In separate experiments,³ conversion of trichloroethane as high as 98% in a single pass was observed at temperatures $<500^{\circ}\text{C}$, with no oxygenated products of incomplete combustion.

During the last year, we completed assembly of a microwave-induced plasma system. Generation of reactive species in a plasma offers the prospect of achieving microwave-assisted detoxification at an acceptable cost. The plasma is maintained in a single-mode-resonance silica reactor (6 x 11 x 23 cm) with tuning by a "short." A 6 kW, 2.45 GHz microwave generator serves as the microwave source. In preliminary experiments to investigate conditions required to initiate and sustain a plasma, we operated the reactor with an alumina bed on a frit, with frit alone, and without either frit or alumina bed. It had been thought that the bed material would provide sufficient surface area to produce plasma-generating reactions. The frit provided support to the bed material and/or improved gas flow distribution.

At a pressure slightly above atmospheric, the reactor was operated with a flowing gas bearing vaporized chlorohydrocarbon. The flow rate of the oxygen/argon carrier gas was measured by a wet test meter and also monitored by a Matheson gas flow meter during 11 experimental runs. Just before striking the plasma, the vapor of the chlorohydrocarbon ($\text{C}_2\text{H}_3\text{Cl}_3$ or C_2HCl_3) was absorbed in coconut shell activated carbon kept in an ice bath for a period of 30 min so that the mass flow rate of the chlorohydrocarbon could be obtained. During this step a

³M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1987*, Argonne National Laboratory Report ANL-88-19, pp. 78-79 (1988).

sample of gas containing the vapor (before it flowed to the active carbon bed) was also collected, and the composition of incoming gas was determined from this sample.

After a stable plasma was established at atmospheric pressure with the chlorohydrocarbon-bearing vapor flowing, 10 min was allowed before an exit gas sample was collected. The exit gas also was scrubbed with 1 N NaOH solution before the gas was released to the laboratory vent. Gas composition was determined from the exit gas sample and the scrubber solution for a specific time period of gas flow (after stable operations were obtained). This scrubber solution was kept separate from a second scrubber solution, from which the cumulative chloride content was determined.

Typical exit gas analyses for the 11 experimental runs (five with $C_2H_3Cl_3$ and six with C_2HCl_3 as feed material) showed that a significant fraction of the residual chlorohydrocarbon in $C_2H_3Cl_3$ combustion was C_2HCl_3 . It appears that the C_2HCl_3 is the more stable of the two.

The conversion of chlorohydrocarbons (CHC) was determined from the equation:

$$\text{Conversion of CHC} = \frac{[CHC]_{in} - [CHC]_{res}}{[CHC]_{in}} \times 100$$

where $[CHC]_{in}$ is the input CHC concentration, and $[CHC]_{res}$ is the residual CHC concentration. For determination of $[CHC]_{res}$, we used an average of two exit gas analyses.

The experimental results showed that conversion in a single pass for both chlorohydrocarbon compounds was about the same (95.9-98.3%), the conversion of C_2HCl_3 being slightly lower, and that the reactor configuration did not significantly change the chlorohydrocarbon conversion. However, operation was smoothest using the reactor containing the frit without the alumina bed. The chlorine balance (i.e., total chlorine in absorber solution for 30 min divided by total chlorine in the input stream for 30 min times 100) indicated that all chlorine from $C_2H_3Cl_3$ appears as HCl, whereas for C_2HCl_3 only about 30 to 40% of the chlorine can be accounted for as HCl. It appears that the feed composition is such that sufficient internal hydrogen may not be available for all chlorine to be eliminated as HCl.

Experimental work in 1990 will continue to examine the use of a microwave-induced plasma for destruction of halocarbons.

3. Development of a Separation Process for Red Water Treatment

The final step in the production of TNT (2, 4, 6-trinitrotoluene) involves its purification by selective conversion of the unsymmetrical isomers into water-soluble sulfonates by reaction of the crude TNT with an aqueous sodium sulfite (sellite) solution. This treatment generates an intense, red-colored waste stream commonly referred to as "red water," which has

been listed as a hazardous waste by the EPA. Its composition is primarily sodium salts of aqueous-soluble organic sulfonates and of sulfate, sulfite, nitrate, and nitrite. Trinitrotoluene is no longer produced in the United States due, in large part, to the lack of an economical and environmentally acceptable waste disposal process for the red water.

A new process for treating red water is being developed at ANL. This process couples the separation of the organic and inorganic constituents of red water with treatment of the organics by biodegradation. The level of separation will be sufficient to qualify the inorganic residue as a nonhazardous by-product. To minimize sludge formation in the biotreatment step, all inorganic constituents are removed from the organic feed stream, and the sodium salts of organic red water compounds are converted to their respective acidic forms.

Initial efforts in CMT have focused on identifying viable processes for carrying out the organic/inorganic separation. The three technologies chosen as candidate processes for laboratory investigation are (1) foam fractionation, (2) flocculation, and (3) aqueous biphasic solvent extraction. These processes are summarized below.

a. Foam Fractionation

Foam fractionation is one of several adsorptive bubble techniques for selectively separating solutes from a solution or particulates from a suspension. These separation processes take advantage of the tendency of either hydrophobic or surface active substances to preferentially concentrate at the air/water interface. In foam fractionation, rising gas bubbles are used to carry the substance to the liquid surface where a collectable foam is produced. With pH adjustment to acidic conditions, red water produces a stable foam. The organic constituents of red water can be concentrated in such a foam, and under the limited set of conditions tested thus far, concentration factors in the range of 10-30% have been realized in a single stage. Unfortunately, removal of the organic components makes it progressively more difficult to obtain a stable foam. This makes it very difficult to achieve a high degree of separation and still maintain high throughput operation. For this reason, foam fractionation is the least attractive process of the three that were investigated.

b. Flocculation

The second separation approach that was studied involved the treatment of red water with organic flocculants to effect an organic/inorganic separation by either complexation-flocculation or complexation-ultrafiltration processes.

Initial experiments have shown that polymeric flocculants can be used to selectively precipitate the organic constituents from red water. High molecular weight ($\geq 10^6$ daltons) flocculants having quaternary ammonium functional groups are very effective in this regard. With red water samples diluted 1:50 with distilled water, a cationic flocculant (Magnafloc 1596C-SP) at a concentration of 250 ppm produced an easily filtered precipitate, which resulted in a 50% reduction in organic concentration. Combining the use of a flocculant with ultrafiltration achieved an 80% organic removal. These results suggest that flocculation in

conjunction with ultrafiltration could be very effective as a polishing step for producing an inorganic stream that will not be included in the EPA hazardous waste list.

c. Biphasic Solvent Extraction

Aqueous biphasic solvent extraction is thought to be the technology with the greatest promise for successfully separating the organic and inorganic constituents of red water. Biphasic separation involves solute partitioning between two immiscible aqueous phases--a polymer-rich solution and an inorganic-salt solution. Biphasic formation may also be achieved with immiscible, water-soluble polymers (e.g., polyethylene glycol and Dextran). With regard to wastewater treatment, aqueous biphasic systems have similarities with conventional solvent extraction but do not utilize an organic solvent, which itself may become a source of pollution. In addition, the water-soluble polymers used in biphasic formation are inexpensive, nontoxic, and biodegradable.

Research to date on aqueous biphasic solvent extraction has concentrated on the polyethylene glycol (PEG)/ Na_2SO_4 system. At room temperature, a concentration of approximately 7.5% PEG and 6% Na_2SO_4 (by weight) forms an aqueous two-phase system. As the phase diagram in Fig. III-5 indicates, increasing temperature from 25 to 80 °C promotes biphasic formation at significantly lower salt and PEG concentrations. Recovery of waste heat from the sellite purification process would permit biphasic formation at a much reduced PEG concentration.

Fig. III-5.

Binodial Curves for the Polyethylene Glycol/Sulfate System. (System compositions above the binodial are biphasic.)

Red water introduced into such a system concentrates the organic constituents in the PEG phase with a distribution ratio of about 10 for a single stage. Through successive batch contacts of undiluted red water with 7.5% PEG, a 1000-fold reduction in organic concentration was achieved by the fourth stage. Literature data indicate that the distribution

ratios of the inorganic salts should be between 0.75 and 1.0.⁴ With these distribution ratios, an extremely effective countercurrent solvent extraction process could be designed.

During the next year, a bench-scale demonstration of a continuous, countercurrent aqueous biphasic system for solvent extraction will be set up. Experience with the bench-scale demonstration will become the basis for producing a conceptual design and cost estimate for a full-scale plant, integrating both the organic/inorganic separation and the biotreatment of a salt-free, red water stream. This would be followed by further studies at an appropriate field site before moving to full-scale design and implementation at an army installation.

⁴T. I. Zvarova et al., *Mikrochemica Acta* (Wien) **3**, 449 (1984).

IV. NUCLEAR TECHNOLOGY

This CMT effort involves (1) investigating processes for the extraction, separation, and recovery of transuranic elements in nuclear waste streams, (2) developing a process for producing ^{99}Mo from low-enriched uranium targets, (3) examining waste-package performance in potential high-level waste repositories located in tuff and basalt, and (4) developing a reprocessing method for the core fuel and blanket material of a sodium-cooled fast reactor.

A. *Separation Science and Technology*

The Division's work in separation science and technology consists of four projects. The first is 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 the design of flowsheets for specific waste streams and estimation of 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 is the development of the ANL-designed centrifugal contactor for nuclear waste processing. The greatest part of this effort has been done in support of the first project, where centrifugal contactors have been developed for specific TRUEX applications. A new effort this year, in support of Integral Fast Reactor waste treatment processes (Sec. IV.C.3), is the development of a pyrocontactor for use at 500°C with molten salt and molten metal. The third project 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. The fourth project, which is discussed in Sec. III.B.3, is the development of a separation process for the treatment and safe disposal of red water, a hazardous waste generated during the manufacture of TNT.

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, 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 defense TRU-containing waste and high-level waste (HLW), where such processing offers financial and operational advantage to the DOE community.

a. The Generic TRUEX Model

The largest effort associated with the TRUEX Technology-Base Development Program has been the development of the Generic TRUEX Model (GTM). This model is used to generate TRUEX solvent extraction flowsheets based on user-specified input. The model can be run on a personal computer (either a Macintosh or an IBM compatible) and is useful for flowsheet development directed to establishing a TRUEX process for specific waste streams; for assessing the costs and space requirements for installing the process; and for improving, monitoring, and controlling on-line TRUEX processes. The first-generation GTM was made available in 1989. The first version released was for the Macintosh computer; later that year, the IBM-PC compatible version was released. The first-generation GTM has the capability to calculate distribution ratios for the important components of acidic nitrate-based TRU-containing waste and high-level waste streams in TRUEX-process flowsheets for either the TRUEX-TCE or the TRUEX-NPH solvent. All calculations are based on an operating temperature of 25 °C. The GTM also calculates the concentration profile of feed components in flowsheets that are designed by the user and generated by the model. Results are displayed in tabular and graphical form. The space and cost requirements for installing a solvent extraction process that uses an Argonne-design centrifugal contactor in a canyon, shielded cell, or glove box are estimated by the model. All these calculations are performed in a way that allows persons with limited computer knowledge to use the model. Help commands are available during the input of information to explain the necessary form of the input. The GTM continues to be refined, and the second-generation GTM will be released in the spring of 1990. This new version will be faster and more sophisticated than the first versions, allowing for solvent loading, aqueous-phase complexation in every stage, and the modeling of the TRUEX process in pulsed columns and mixer settlers as well as centrifugal contactors.

To model pulsed columns using the SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction) worksheet in the GTM, the worksheet was changed so that it can handle any amount of other-phase carryover in a centrifugal contactor (aqueous phase into organic phase and vice versa) and, therefore, any amount of backmixing in a pulsed column. Then, using data in the open literature with a new model for pulsed columns based only on backmixing (i.e., bulk mass transfer), we were able to model both the extraction and stripping sections in a sieve plate column with a single stage height and a single value for the amount of backmixing. The success of this effort indicates that a single SASSE worksheet can be used to model the extraction behavior of all chemical components in a pulsed column, an option that is not available for other pulsed-column models, that is, the HETS (height of an equivalent theoretical stage) or HTU (height of a transfer unit) methods.¹ Initial testing of the new pulsed-column model showed that it is sensitive to the distribution coefficients of each species, the continuous phase, and the effluent concentration, and that it generates more accurate results than either the HETS or HTU methods. For example, for a particular pulsed column run at one set of conditions, the stage height for extraction and stripping was estimated to be 0.73-1.50 m with HETS, 0.50-0.79 m with HTU, and 0.59-0.75 m with our model.

¹R. E. Treybal, *Liquid Extraction*, 2nd ed., McGraw-Hill, New York (1963).

Future goals of this effort are to design an expert system for monitoring and controlling on-line TRUEX processes. In this regard, a major task in 1990 is to establish a guide for this purpose. This guide will discuss all aspects of monitoring and controlling TRUEX processes, e.g., means of monitoring the process, locations of equipment for process monitoring, means to detect process upsets, the time frame of finding that a process upset has occurred, means to correct the process perturbation, and the response time of this action. This guide will be vital to plant processing personnel and to building an expert system for monitoring and controlling a TRUEX process.

b. TRUEX Data-Base Generation

In this effort, we are collecting data to be used in the model for the TRUEX process for defense HLW and other nitrate-based TRU-containing waste. The data base, generated over the past three years from the literature and our own laboratory measurements, contains the extraction behavior for all important feed components over a range of possible waste stream compositions. As a result of this work, it now includes the extraction behavior of important feed components as functions of solvent composition and temperature. Because of the growing concern over the use of chlorinated solvents, work in 1989 has been directed almost exclusively to the TRUEX-NPH solvent. Data have been collected for actinides [Am(III), Cm(III), Np(IV), Np(V), Pu(IV), Th(IV), and UO_2^{2+}]; rare earth fission products (La, Ce, Pr, Nd, Sm, Eu, and Gd); other fission products (Y, Zr, Mo, Tc, Ru, Rh, and Pd); and important inert elements and species (Fe, Al, Mn, Ni, NO_3^- , and $\text{C}_2\text{O}_4^{2-}$). Figures IV-1 and -2 are representative of the data collected.

Fig. IV-1.

Effect of CMPO and TBP Concentrations on Americium Extraction from HNO_3 Containing 3.2 M Nitrate at 25°C

Figure IV-1 illustrates the dependence of the americium distribution ratio ($D_{\text{Am}} = [\text{Am}]_{\text{org}} / [\text{Am}]_{\text{aq}}$) on the solvent composition as the HNO_3 concentration of the aqueous phase increases from 0.02 to 1 M, with the ionic strength maintained at 3.2 M by varying the concentration of NaNO_3 . Increases in the CMPO concentration from 0.1 to 0.4 M increase the extraction of americium as a result of the simplified equilibrium:

where the bar represents an organic-phase species. Increases in the TBP concentration (see data for 0.2 M CMPO in Fig. IV-1) decrease the extraction of americium but to a small extent. Because TBP is a poor extractant for americium, it acts more or less indirectly in effecting the extraction of americium by forming, for example, a $\overline{\text{TBP} \cdot \text{CMPO}}$ complex in the organic phase. The overall decrease in the americium distribution ratio with increasing HNO_3 concentration results from increasing the organic-phase concentration of HNO_3 , which decreases the concentration of CMPO by increasing the concentration of the less powerful extractants $\overline{\text{CMPO} \cdot \text{HNO}_3}$ and $\overline{\text{CMPO} \cdot 2\text{HNO}_3}$.

The effects of temperature on the extraction of curium and oxalic acid are shown in Fig. IV-2. For curium, the typical effect of temperature on metal extraction is observed, i.e., an increase in the temperature from 25 to 50°C decreases the extraction of curium. For oxalic acid, an increase in the temperature from 25 to 40°C had no effect on its extraction. (The 40°C data were measured by H. Diamond, ANL's Chemistry Division.) The absence of a temperature effect on acid extraction has also been observed for HNO_3 .

Fig. IV-2. Extraction of Curium (a) and Oxalic Acid (b) from HNO_3 by TRUEX-NPH at Two Temperatures

c. Development of Computerized Data Base

The success of the GTM is dependent on underlying data that are sound, correct, and defensible. Further, the source of data must be easily traceable and auditable. Over the past several years, we have collected the data necessary to model the TRUEX process for high-level defense waste and other nitrate-based TRU-containing waste (Sec. IV.A.1.b). We have developed a computerized data base that contains the collected data and facilitates modeling, identifying further data needs, and auditing (determining source of data and data quality).

The design of the data base structure is essentially complete. The data base uses a Macintosh personal computer in conjunction with the computer program Fourth Dimension supplied by Acius, Inc. (Cupertino, CA). Fourth Dimension has hierarchical characteristics with powerful custom-design features to suit individual needs. Distribution coefficients of pertinent nuclides and major process chemicals have been incorporated into this data base.

Future work includes the entry of distribution coefficients that continue to be measured in our laboratory as well as those obtained from the literature; this effort will be followed by entry of activity coefficients of nuclides.

d. Laboratory Verification Studies

Laboratory verification tests of the TRUEX process were continued this year to investigate the extraction of actinides and other components from acidic waste solutions using centrifugal contactors. Objectives of these experiments were to (1) develop a better understanding of the chemistry of the TRUEX process, (2) test and verify process modifications, and (3) verify the species extraction behavior predictions and flowsheet calculations with the Generic TRUEX Model. Two pilot plants, each consisting of a sixteen-stage 4-cm centrifugal contactor, are available for completing these tests. One pilot plant is used for nonradioactive experiments, while the second unit is located in a glove box and is used for radioactive tracer experiments. Approximately 100 samples are collected during each verification test. Analyses of the nonradioactive samples include metals analysis by inductively coupled plasma/atomic emission spectrometry (ICP/AES), acid analysis by pH titration, and ion specific electrode analysis for F^- . Gamma-emitting isotopes are counted by intrinsic germanium and Na/I detectors, while alpha-emitting isotopes are counted by a liquid scintillation counter.

Six verification tests were completed this year: four tests with the TRUEX-TCE solvent and two with the TRUEX-NPH solvent. The flowsheet shown in Fig. IV-3 is typical of all of the completed verification tests. Variations between tests included changes in the extraction-section feed composition, the feed-stream flow rates, and/or the TRUEX-solvent composition.

Three of the six verification tests were done with nonradioactive feed solutions. Two of these were completed with the TRUEX-NPH solvent at an elevated temperature of 50°C, and the other used TRUEX-TCE solvent at ambient temperature. In the nonradioactive tests, nitric acid was the most important component studied. A typical nitric acid concentration profile from one of these tests (TRUEX-TCE at ambient temperature and a synthetic HLW stream) is shown in Fig. IV-4. In this figure, the experimental nitric acid concentrations for both the aqueous and organic phases are plotted along with predictions obtained from an upgraded version of the GTM. The nitric acid concentration in the aqueous-phase samples was measured by standard aqueous titration methods, and the nitric acid concentration in the organic phase was measured by directly titrating an organic sample with tetrabutylammonium hydroxide. As shown in Fig. IV-4, there is good agreement between the experimental data and the GTM predictions. These data and their fit by the model are typical of the nitric acid data collected in the other verification tests.

Fig. IV-3. Typical Flowsheet for a Verification Run with Radioactive Tracer

Three verification tests were done with radioactive isotopes added to the extraction-section feed solution (DF). All three tests were completed with the TRUEX-TCE solvent at ambient temperature. Adding radioactive isotopes allowed us to collect accurate concentration data throughout the stages of the centrifugal contactor. Using radioactive tracers is more accurate than ICP/AES analysis, and, in general, lower concentrations can be measured. A typical concentration profile is shown in Fig. IV-5 for the radioactive isotope gadolinium-153. In this figure, the gadolinium concentrations in each stage are shown along with the predictions obtained with an upgraded version of the GTM. The GTM predictions are fairly good for the extraction, scrub, and first strip sections (stages 1-9), but not for the second strip section (stages 10-13). The other isotopes measured (including Am and Ce) showed this same trend. One possible reason for this discrepancy is that the organic-to-aqueous (O/A) flow ratios in the various sections might not have been what we expected, since small differences in a solution flow rate can have a large effect on the concentration profile. Data from this series of tests are still being analyzed.

Fig. IV-4. Typical Acid Profile from Verification Test with Nonradioactive Feed Solution

Fig. IV-5. Gadolinium Concentration Profile from Verification Test with Radioactive Isotopes Added to Feed

Verification tests will continue in 1990. We will investigate the extraction of rare earth fission products, actinides, nitric acid, hydrofluoric acid, oxalic acid, iron, and other metals from simulated acidic waste solutions. In addition, the operability of various solvent cleanup flowsheets will be investigated.

e. TRUEX-NPH Solvent Degradation

During operations to extract TRU elements from aqueous HLW, TRUEX-NPH solvent will undergo radiolysis and hydrolysis. These reactions decrease the concentration of CMPO and, thus, decrease the extraction ability of the TRUEX-NPH solvent. Moreover, if acidic degradation products are not removed, their strong extraction properties at low aqueous-phase acidities prevent the stripping of Am and Pu carried in the solvent that is to be recycled. During 1987-1988, we completed experimental studies of hydrolysis and radiolysis of TRUEX-NPH solvent² but did not completely evaluate the data. A recent effort has involved retrieval, organization, and interpretation of the data.

In the earlier experiments, hydrolyzed solvent samples were prepared by continually mixing the solvent with aqueous solutions of several different compositions at 50, 70, and 95 °C for times up to 800 h. The set of solutions included 0.25, 2.5, and 6.0 M HNO₃, as well as two solutions simulating a waste stream (Current Acid Waste) containing a mixture of metal ions and nitric acid concentrations of 1.6 and 2.6 M. Radiolyzed solvent was prepared by exposing solvent samples to gamma radiation while in contact with aqueous solutions of the same composition but at a constant temperature of 50 °C. Subsequent measurements of distribution ratios for americium between degraded solvent and aqueous HNO₃ were used as an analytical tool for determining solvent damage. In the measurements of D_{Am} between degraded solvent and nitric acid, three different acid concentrations were used: 0.01, 0.05, and 2.0 M. At the highest acid concentration, D_{Am} is assumed proportional to the concentration of CMPO to the third power. Therefore, distribution ratios at 2.0 M HNO₃ were used for following the loss in CMPO concentration as a function of treatment.

(1) Radiolysis

The D_{Am} values obtained with 2.0 M acid were used to calculate the molecules of CMPO destroyed per 100 eV absorbed dose (G values). Since the G values showed no regular dependence on the composition of the aqueous solutions in contact with the solvent during irradiation, the data were combined to yield an average G value. The decrease of CMPO concentration with time can be expressed by the equation:

$$-\frac{C}{C_0} = \frac{MG(Pt)}{C_0} - 1 \quad (2)$$

²M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, pp. 71-74 (1989).

- where
- C = concentration of CMPO remaining, mol/L
 - C_o = initial concentration of CMPO, mol/L
 - G = molecules CMPO destroyed/100 eV absorbed
 - M = a product of dimensional equivalents, 3.73×10^{-4} (100 eV) $W^{-1} h^{-1} \text{ mol molecule}^{-1}$
 - P = power density of feed solution, W/L
 - t = time of irradiation, h

Substituting the relation of D_{Am} to CMPO concentration into Eq. 2 gives

$$-\left(\frac{D_{Am}}{D_{Am_0}}\right)^{1/3} \frac{C_o}{M} = G(Pt) - \frac{C_o}{M} \quad (3)$$

The G value is the slope of the graph of the term on the left-hand side of Eq. 3 vs. Pt, as shown in Fig. IV-6. The G value thus derived is 0.66 molecule CMPO destroyed per 100 eV absorbed.

Fig. IV-6. Dependence of a Function of D_{Am} (left-hand side of Eq. 3) on Dose (power density multiplied by irradiation time)

(2) Hydrolysis

The loss of CMPO concentration by hydrolysis, as indicated by D_{Am} measurements, can be correlated with a rate law that is pseudo first order with respect to CMPO

concentration and proportional to the hydrogen ion activity of the aqueous phase at 25 °C. In Fig. IV-7, the rate constants for hydrolysis of CMPO obtained at 50, 70, and 95 °C are correlated by the Arrhenius equation, $k = Ae^{-E/RT}$. The slope and intercept from this plot yield values of $A = 2.47 \times 10^{14} \text{ L mol}^{-1} \text{ h}^{-1}$ and $E = 27.3 \times 10^3 \text{ cal mol}^{-1}$. By using these constants and the hydrogen ion activity at 25 °C, the loss of CMPO by hydrolysis can be calculated at any temperature.

Fig. IV-7. Correlation of the Rate Constant for Hydrolysis of CMPO with Temperature

The expressions for radiolysis and hydrolysis rates of the solvent have been combined into algorithms expressing the destruction of CMPO expected to occur in TRUEX processing and will be included in the second-generation GTM.

2. Centrifugal Contactor Development

The basic design of the Argonne centrifugal contactor has been modified to adapt it for specific solvent extraction processes. A key feature in these design efforts is the use of computational models for (1) the flow of the organic and aqueous phases through the contactor and (2) the vibrational parameters of the spinning motor/rotor combination in the contactor. The flow model was developed at CMT several years ago. The vibrational model (called BEAM IV), which was developed at Virginia Polytechnic Institute and State University, was recently simplified to better support our development efforts. Other contactor-related efforts in 1989 included (1) additional work to support the development of the GTM, (2) consultation with the Westinghouse Hanford Co. on improving its plant-scale contactor, (3) building, testing, and starting up a pilot-scale contactor at Y-12, and (4) developing and testing the key features needed for a contactor to be used in pyrochemical processing.

In support of TRUEX technology-base development (Sec. IV.A.1), we have completed the testing of a new 16-stage 2-cm contactor (minicontactor) and simplified the model for analyzing vibrations in the rotating motor/rotor system of the contactor. Since the new 2-cm contactor requires only 1 L of feed solution instead of the 10 L needed for the 4-cm contactor, it is very useful in those cases where more feed may be difficult and expensive to prepare, or cannot be accommodated in the test facility, or is simply unavailable. The 2-cm unit, designed and built in 1988, was tested in 1989 and is now fully operational. The flow tests showed good contactor operation with both the TRUEX-NPH and TRUEX-TCE solvents at total throughputs up to 40 mL/min for O/A flow ratios from 0.2 to 5 and should, therefore, hold for all O/A flow ratios. Remote-handling features were included so that this minicontactor can be used in either a glove box or shielded-cell facility.

To make the BEAM IV vibrational model easier to use and more accessible, we transferred it into an Excel worksheet called "Beam." While the model is simpler to use, it still employs the transfer matrix method on which the BEAM IV model is based. Data needed for this Beam worksheet were obtained from experimental testing of motors and motor/rotor systems using the Zonic Real Time Spectrum Analyzer. A schematic of the 11 sections of the motor/rotor system used in the Beam worksheet is given in Fig. IV-8. Each section consists of elastic properties and dynamic components that are easy to model with a simple transfer matrix. Matrices for the 11 sections are combined into one overall matrix that models the motor/rotor system. With the use of a macro program written especially for the Beam worksheet, one can do (in less than a minute) the required convergence calculations needed to determine the first critical speed of the motor/rotor system. Thus, with this new model, one can easily determine how a change in the rotor design will affect the critical speed of the motor/rotor system. The new model will be used to modify existing units and design new contactors.

Fig. IV-8. Schematic of Motor/Rotor System Used for Analysis of Contactor Vibrations

Contactor work was done in conjunction with two other DOE sites: Westinghouse Hanford and the Y-12 plant at Oak Ridge, Tennessee. At Westinghouse Hanford, we consulted on the final design of a 10-cm centrifugal contactor for plant processing of Plutonium Finishing Plant wastes using TRUEX to remove the transuranic elements. This involved determining ways to reduce contactor power with increasing rotor speed. We also consulted on the selection of an

appropriate Argonne centrifugal contactor for use in a remote pilot plant at Westinghouse Hanford. For the Y-12 plant, we designed, built, tested, and started up a 16-stage 4-cm centrifugal contactor for a pilot plant facility. The Y-12 contactor is designed for hands-on operation with many solvents over a wide range of O/A flow ratios (essentially 0 to ∞). Because of the flexibility of this unit, it can be used to evaluate a wide variety of flowsheets proposed for uranium scrap recovery.

To operate the Argonne centrifugal contactor at high temperatures (500 to 800°C) with liquid metals and molten salts, a completely new contactor is being developed. We analyzed and tested the key concepts of this pyrochemical contactor or, simply, pyrocontactor, and concluded that such a unit is feasible. The design issues considered include (1) the materials of construction, (2) motor isolation from the high process temperatures, (3) dispersion of the more dense phase in the less dense phase within the mixing zone, (4) separation of the more dense phase from the less dense phase in the centrifugal separating zone, and (5) vibrations in the motor/rotor system. Pyrocontactor feasibility was verified through a series of modeling efforts and experimental tests of the key design concepts. The main difference between current contactors and the pyrocontactor is in the mixing zone, where rotor vanes and housing baffles will be required. In 1990, a prototype that operates at 500°C will be built for pyrochemically treating wastes from the processing of the Integral Fast Reactor fuel.

3. Separation and Purification of ^{99}Mo

Currently much of the world's supply of $^{99\text{m}}\text{Tc}$ for medical purposes is produced from ^{99}Mo derived from the fissioning of high-enriched uranium (HEU, 93% ^{235}U). The purpose of this study is to assess the feasibility of substituting low-enriched uranium (LEU, <20% ^{235}U) for HEU in targets for production of fission-product ^{99}Mo . Switching from HEU to LEU while maintaining ^{99}Mo yields and target geometries requires a denser fuel. Uranium silicide dispersed in aluminum ($\text{U}_3\text{Si}_2\text{-Al}$) with a uranium density of 4.8 g/cm³ is the ^{99}Mo target fuel of choice, especially with its approval by the Nuclear Regulatory Commission for use as a reactor fuel.³

The current process for basic dissolution involves dissolving the entire target of $\text{U}_3\text{Si}_2\text{-Al}$ fuel in NaOH/ NO_3 solution.⁴ During the dissolution, uranium and various fission products precipitate as hydrated hydroxide salts. This mixture is diluted and filtered, and the solution is acidified for purification of the molybdenum on an alumina column. Because the dissolution of U_3Si_2 is extremely slow with NaOH/ NO_3 solution alone, the current process was modified into two steps. The first step dissolves the Al6061 cladding and the aluminum fuel matrix in a 3 M NaOH solution, leaving behind the U_3Si_2 particles. The high density of the U_3Si_2 (12 g/cm³) allows the basic aluminum-containing solution and the precipitated hydroxide/salt components of the aluminum alloy cladding to be decanted easily from the silicide particles. The U_3Si_2 can then be dissolved separately in NaOH/ H_2O_2 . Uranium stays in solution

³U.S. Nuclear Regulatory Commission, *Safety Evaluation Report Related to the Evaluation of Low-enriched Uranium Silicide-Aluminum Dispersion Fuel for Use in Non-power Reactors*, NUREG-1313 (July 1988).

⁴J. Salacz, "Reprocessing of Irradiated Uranium 235 for the Production of Mo-99, I-131, Xe-133 Radioisotopes," *Revue IRE Tijdschrift*, Vol. 9, No. 3 (1985).

as a peroxo complex until the peroxide is destroyed. Once the uranium has precipitated, the process is the same as that currently in use.

a. Experimental Results--Processing of Uranium Silicide Fuels

This two-step process would be clearly advantageous if (1) the concentrated aluminum solution from the first step is handled separately, (2) the solution resulting from dissolving the uranium silicide contains all the fission products, and (3) only the silicide solution needs to be treated for recovery of iodine and molybdenum. Results of 1988 work, however, indicated that loss of ^{99}Mo from the fuel particles into the aluminum matrix due to fission recoil is substantial, and that the two-step dissolution must be modified to recover the molybdenum lost to the decladding solution.⁵ The measured 19% experimental loss of ^{99}Mo was nearly the same as the calculated loss of 20%, assuming a U_3Si_2 particle size distribution of 0 to 150 μm . To verify this effect, three compacts were irradiated in the ANL JANUS reactor. Each compact was prepared with sieved U_3Si_2 particles and aluminum powder; the size distribution of U_3Si_2 in each compact is given in Table IV-1. After irradiation, each compact was digested separately in 3 M NaOH. The resultant solutions (including washes of the silicide particles containing small amounts of black precipitate) were counted for gamma activities. They were subsequently filtered through Whatman 41 paper and recounted. The U_3Si_2 particles were dissolved in 1.5 M NaOH/15% H_2O_2 and also gamma counted.

Table IV-1. Calculated and Experimental Loss of ^{99}Mo , ^{131}I , and ^{239}Np to Sodium Hydroxide Dissolving Solution

U_3Si_2 Particle Size Range, ^a μm	Calc. Loss (%) Recoil to Al Matrix ^b			Exp. Loss (%) to Filtered Al Fraction ^c		
	^{99}Mo	^{131}I	^{239}Np	^{99}Mo	^{131}I	^{239}Np
125-150 (138)	8.8	7.2	0	10.4	6.7	0.7
73-88 (81)	15.0	12.2	0	18.2	12.7	1.7
40-45 (43)	28.3	23.0	0	30.1	19.8	2.2

^aSphere diameters for which the losses were calculated are in parentheses.

^bAssumes a fission fragment range of 8.1 μm for ^{99}Mo and 6.6 μm for ^{131}I .

^cThe concentrations of ^{99}Mo and ^{131}I were the same before and after filtering.
The loss of ^{239}Np to the unfiltered solution was 4% for all three fractions.

Table IV-1 gives the calculated and experimental loss of ^{99}Mo , ^{131}I , and ^{239}Np to the dissolving solution. Calculations of ^{99}Mo loss from the U_3Si_2 particles into the aluminum matrix are based on the following equation:

⁵M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, p. 75 (1989).

$$f = 0.5 (3\lambda/D - \lambda^3/D^3) \quad (4)$$

where f = fraction of fission products
 D = diameter of the particle (sphere)
 λ = fission fragment range (based on data from Frank⁶ and Northcliffe and Schilling⁷)

As shown in the table, the calculated losses for ⁹⁹Mo and ¹³¹I are in good agreement with the experimental values and confirmed the substantial ⁹⁹Mo loss. Certainly, ⁹⁹Mo loss strongly depends on the U₃Si₂ particle size.

The behavior of ²³⁹Np in these samples should be indicative of that of uranium and other species that are not fission products. Because ²³⁹Np is not formed by fission, it does not have the recoil energy necessary to release it from the fuel particles and can be used as a marker for the behavior of other materials. The loss of neptunium to all three dissolver solutions was 4%. Filtering the solutions through a rather coarse filter paper (designed to retain 20-25 μ m particles) removed the larger fines. The amount of true fines left in the solution after filtration appeared to be inversely proportional to the average particle size of the sieved fractions.

Another way to interpret the ²³⁹Np results is that some dissolution of the fuel particles is occurring during dissolution of the aluminum. To explore this possibility, experiments were run to (1) verify results of earlier experiments indicating low solubility for the U₃Si₂ in hot sodium hydroxide solutions, (2) measure the effect on dissolution rate of the U₃Si₂ particle size, and (3) measure the effect on dissolution rate of the sodium hydroxide concentration. In these experiments, 0.5 g uranium silicide samples with particle diameters in the ranges 40-45 μ m, 73-88 μ m, and 125-150 μ m were heated at 70°C with 30 mL of a basic solution. The base was either 3 M or 6 M sodium hydroxide; some solutions also contained 0.2 M sodium carbonate. (Sodium carbonate increases the solubility of U⁶⁺ in the NaOH solution.) Results of this study are that

- (1) the rate of U₃Si₂ dissolution was very low, and dissolution of the fuel by the basic solution used to dissolve the cladding material will be only a few tenths of a percent at most;
- (2) increasing the concentration of sodium hydroxide from 3 M to 6 M increased the extent of fuel dissolution, but, even with 6 M sodium hydroxide, dissolution of the fuel was minimal; and
- (3) the effect of particle size on the rate of uranium silicide dissolution was imperceptible within experimental uncertainties.

⁶P. W. Frank, *Recoil Range of Fission Fragments*, Bettis Technical Review, Reactor Technology for April 1964, Bettis Atomic Power Laboratory USAEC Report WAPD-BT-30, pp. 47-52 (April 1964).

⁷L. C. Northcliffe and R. F. Schilling, in *Nuclear Data Tables*, "Range and Stopping Power Tables for Heavy Ions," Vol. 7, No. 3-4, Academic Press, New York, p. 233 (January 1970).

Because of the ^{99}Mo loss from the targets during dissolution of the aluminum cladding and matrix, we looked at adding 30% hydrogen peroxide directly to the basic solution to dissolve the fuel. This addition was made after all the aluminum in the target had been dissolved. The presence of the precipitated hydroxides from the aluminum-alloy cladding acted to catalyze the autodestruction of the hydrogen peroxide. This formed large quantities of gas (presumably O_2), with no peroxide reaching the bottom of the beaker to dissolve the U_3Si_2 . This result led to the conclusion that a one-step process for dissolving the complete target with hydrogen peroxide is not feasible; the precipitate must be removed before uranium silicide can be dissolved.

b. Conceptual Design of a Dissolver for Uranium Silicide Fuel

Based on the experimental results in Sec. IV.A.3.a, we developed the conceptual dissolver system shown in Fig. IV-9.

Fig. IV-9. Schematic of U_3Si_2 -Target Dissolver System

With this arrangement, the irradiated target(s) is charged into the dissolver through its removable lid. A solution of $\sim 3 \text{ M}$ sodium hydroxide (perhaps with NaNO_3 to limit H_2 production) is then added to the dissolver through a port in the dissolver's side. (The

dissolver can be cooled or heated as needed by a thermostated jacket surrounding it.) A gas sparge at the bottom of the reactor may be used to purge gaseous fission products and mix the contents. The cladding and the aluminum powder in the fuel meat dissolve, leaving a flocculent precipitate and the dense uranium silicide particles. At the completion of this step, the basic aluminum solution and the flocculent are pumped from the dissolver, and the dense fuel particles are left behind. This slurry is pumped through a filter (or a continuous centrifuge) as the solution is stored in a collection tank. Part of the solution is returned to the dissolver to act as a wash for removing the rest of the precipitates from the silicide particles. After this washing operation is completed, a fraction of the basic aluminum solution is returned to the dissolver, and a 30% H_2O_2 solution is administered dropwise to the dissolver as the uranium silicide is dissolved. After dissolution of the U_2Si_2 , the dissolver is heated to destroy the excess peroxide and, thus, to precipitate UO_3 . The solution is then removed from the dissolver through the gas sparge outlet, while the UO_3 and base-precipitated fission products are separated by filtration. The basic aluminum solution is passed into the dissolver and through the filtered UO_3 before being combined with the earlier effluent. The solution and the uranium precipitate are then treated in the same manner as is currently done for uranium aluminide targets.

B. *High-Level Waste/Repository Interactions*

The safety assessment of nuclear waste disposed in a geologic repository is a unique environmental problem in that it requires a solution that will remain technically valid over many thousands of years. An extensive modeling and experimental program is underway to evaluate the long-term behavior of both emplaced materials and the host environment under disposal conditions. Programs are in progress in CMT to evaluate the performance of both waste glass and spent fuel under water-saturated conditions and the water-unsaturated conditions anticipated in the proposed high-level waste (HLW) repository site at Yucca Mountain, Nevada. Experiments in these programs simulate or accelerate the reaction process so that reaction mechanisms and long-term radionuclide release properties can be assessed. Additionally, we are evaluating experimental strategies that may be used to validate predictive models of the integrated repository system. Experiments are also in progress to measure the effects of radiation on the environment at both the Yucca Mountain site and the salt caverns at the Waste Isolation Pilot Plant (WIPP). All of these studies provide information that will be useful in demonstrating the suitability of these repositories for final storage of nuclear wastes.

1. Yucca Mountain Project

The proposed site for the first repository for storage of high-level nuclear waste in the United States is in the tuff beds of Yucca Mountain, Nevada. The site is unique among those being characterized internationally because it lies several hundred meters above the water table in a hydrologically unsaturated zone. To characterize the long-term behavior of waste in the repository, CMT is investigating the reaction of glass and irradiated reactor fuel under anticipated repository conditions and evaluating the effect of radiation on the near-field environment and on the corrosion of proposed container materials under the auspices of the Yucca Mountain Project (YMP). The CMT testing programs have developed new experimental techniques for simulating and monitoring materials interactions in systems with small amounts of water and have focused on obtaining data that will be used directly in licensing the proposed site.

a. Glass Studies

Simulated waste glasses and naturally occurring glasses are being studied by long-term unsaturated, vapor hydration, vapor hydration/leach, and static leach tests at temperatures up to 240 °C.

(1) Unsaturated Testing

Because the proposed nuclear waste repository lies in the hydrologically unsaturated vadose zone, it is anticipated that only very small amounts of liquid water will be available to interact with the waste glass and the stainless steel waste package components throughout the service life of the repository. The YMP Unsaturated Test was designed to study glass/steel/fluid interactions under these conditions. In this test, groundwater from the Yucca Mountain site is dripped onto a model waste package composed of a cylinder of waste glass sandwiched between two perforated stainless steel disks at 90 °C. The nature and degree of reaction are assessed from solution analysis and inspection of the waste package surface by various analytical techniques, including scanning electron microscopy (SEM) with an energy dispersive X-ray fluorescence spectrometer (EDS), secondary ion mass spectrometry (SIMS), and X-ray diffraction (XRD).

Because the precise conditions in the repository over long times are not known, it is important to understand the effects that different parameters have on the glass reaction rate and subsequent release of radionuclides from the glass. A series of parametric experiments has been ongoing for over four years to investigate the influence of various parameters on glass reaction. All the experiments are performed at 90 °C with a simulated waste glass (SRL 165) and groundwater (J-13) preequilibrated with tuff at 90 °C. Experimental conditions for the standard test and five variations are summarized in Table IV-2.

Table IV-2. Experimental Conditions Used in Parametric Unsaturated Test Series

Experiment No.	Experimental Parameters
Standard Test	Glass surface area of 13.5 cm ² , drop volume of 0.075 mL, drop interval every 3.5 days, glass in contact with sensitized 304L stainless steel.
PII	Exclusion of metal contact with glass, standard conditions.
PIII	Cast glass area reduced 65%, standard conditions.
PIV	Cast glass area reduced 65%, drip volume reduced 50%.
PV	Drop interval rate increased from 3.5 to 14 days.
PVIII	Varying degrees of metal sensitization, standard conditions.

In addition to a silicon-rich surface layer, calcite, gypsum, and several sodium-rich phases were identified on the reacted glass surfaces. Exfoliation of the surface layer occurred to varying degrees and had an important role in the observed extent of glass reaction and element release. In this process, the layer cracks and falls away to expose patches of fresh glass surfaces, which are then available for further reaction with the fluid.

The lithium concentration in the solution provided a good monitor of glass reaction, since the glass is the dominant source of lithium and little or no lithium is accommodated in any of the secondary phases that form. The normalized mass loss of lithium after various reaction times is presented in Fig. IV-10. As shown in this figure, the release trend of uranium generally mimics that of lithium. Lithium release was similar for all experimental variations except PIV, where exfoliation of the surface layer was the most extensive. Release in experiment PIV was 10 to 20 times greater than that of the standard test.

Fig. IV-10. Normalized Release of Lithium and Uranium in the Parametric Unsaturated Tests Using SRL 165 Glass at 90 °C

(2) Vapor Hydration Experiments

Prior to contact by liquid water, high-level nuclear waste glass will be contacted by water vapor. The temperature of the glass surface and the anticipated free air exchange in the repository will control the relative humidity (RH) near the glass surface. The RH controls the amount of water condensed on the glass available for further reaction. We have collected water sorption isotherms on SRL 165 and WVCN 44 waste glasses at room temperature. These isotherms showed little sorption at relative humidities below about 95% but greater sorption at higher humidities. In a vapor environment, hydration will occur between the glass and this small amount of sorbed water. The results of our hydration experiments in a vapor environment suggest that ion exchange releases alkali into the sorbed film which decreases the

vapor pressure of the film and increases the amount sorbed. Therefore, significant volumes of water may condense on and subsequently react with the glass, even at low relative humidities. As the glass reacts, released species quickly approach their solubility limits in the small solution volume, and precipitates form in the solution. Our hydration experiments have shown these precipitates to affect the glass reaction rate.

The hydration experiments were performed with SRL 165 and WVCN 44 glasses at temperatures between about 50 °C and 240 °C and RH between about 50% and 100%. The degree of reaction was greatest at 100% RH and at high temperatures. Analysis of the reacted glass showed that a reacted layer had formed as the surface region became depleted in alkali metal and alkaline earth elements. The thickness of the reacted layer is used as a measure of the extent of glass reaction. The species released from the glass may become incorporated into a potpourri of mineral phases that form on the outer surface or sometimes within the reacted layer.

The precipitates formed were characterized with respect to morphology and composition by using an SEM with EDS and a backscattered electron detector. Sufficiently large or abundant precipitates were removed from the sample and structurally analyzed by XRD. Most experiments performed to date have involved reactions at high temperatures in saturated steam because the extent of reaction is high and precipitates can be generated for identification within a few days.

These experiments showed that the extent of reaction is low for the first few days, with no measurable reaction layers or precipitates forming. During this phase, ion exchange is the predominant reaction. Samples showed only NaCl precipitates or residue that formed as the samples were allowed to dry. After several days of reaction, measurable reaction layers were produced and various minerals precipitated. Alucime or similar zeolites were usually the first to form. Next, various calcium silicates and uranium silicate formed. It is postulated that the formation of secondary mineral phases reduces the solution concentrations of controlling species and allows the glass reaction to occur at a high rate. These hydration experiments also showed that small amounts of water may result in greater extents of reaction than the large volumes in static leach tests because the formation of stable mineral phases maintains low solution concentrations, which allow the reaction to proceed at a higher rate. Greater solution volumes require more glass to react and thus longer reaction times to reach saturation and form precipitate.

These experiments are extremely useful in projecting performance of a given glass because they generate the mineral phases that control the reaction rate. The minerals formed may be compared to those predicted by the EQ3 data base.⁸ In many cases, the minerals experimentally formed are not included in the data base. Also, the solubilities of the minerals in the data base may differ from those of the experimentally generated phases, because of compositional differences, and determining the solubilities of the minerals actually formed may

⁸T. J. Wolery, *Calculation of Chemical Equilibrium between Aqueous Solution and Minerals: The EQ3/6 Software Package*, Lawrence Livermore National Laboratory Report UCRL-52658 (1979).

be necessary. This experimental procedure may be used to generate minerals for such solubility studies.

(3) Vapor Hydration/Leach Experiments

The extent of vapor hydration or aging of the glass during the pre-liquid contact period is a function of the glass composition, the relative humidity, reaction time, and the temperature. The importance of glass aging is that the altered glass may react differently when contacted by liquid water than fresh glass. The observation that (1) the reaction rate is more rapid for aged glass or (2) the release of radionuclides to solution is not solubility limited must be taken into account when developing models of repository performance.

To investigate whether the leaching of glass in liquid water is affected by hydration aging, two different glass compositions, both doped with the transuranic elements Np, Pu, and Am, were reacted in water vapor at 200° C. The glasses were representative of those that will be produced by the Defense Waste Processing Facility at the Westinghouse Savannah River Co. (WSRC) and by the West Valley Demonstration Plant (WVDP) in New York. As a result of hydration aging, the outer surfaces of the glasses were transformed into a hydrous layer on which several different mineral phases were identified. The thickness of the hydrous layer ranged between 1 and 70 μm , depending on the reaction times, and the mineral phases consisted primarily of zeolites and calcium silicates.

One specimen of each glass was utilized for the identification of the mineral phases. These phases were carefully removed from the surface and examined by SEM/EDS and XRD to determine their identity. The phases were also examined for radionuclide content. This measurement is important because transuranic elements incorporated into stable minerals are not released into the groundwater. Individual minerals were removed from the surface, cleaned to remove remnants of the hydrous layer, and analyzed by either acid dissolution and alpha spectroscopy or by alpha track counting. The dissolution indicated that the transuranic elements were preferentially incorporated into the minerals, and the alpha track counting indicated that these elements were uniformly distributed throughout the mineral and not simply sorbed on the mineral surface.

The remaining hydration-aged samples were leached in water for 28 days at 90° C. Specimens of unreacted glass were also leached for comparison. Typical results of the leaching experiments are shown in Table IV-3. The test results indicated that the aged glasses react significantly faster than the fresh glass, as measured by the weight loss and normalized release of the glass elements B, Li, and Na. However, the most striking result is the releases of Am and Pu. In tests using fresh glass these elements are found sparingly in solution and are usually precipitated back onto the glass surface or sorbed to the walls of the metal leaching vessel. For aged glass, however, nearly all of the Am and Pu released from the glass was found in the test solution. When the test solutions were passed through 18 Å filters, the transuranic content was reduced, indicating that the elements were suspended in solution as colloidal material. This is an important point because colloidal material may have different groundwater transport properties than dissolved material.

(4) Static Leach Experiments

The glass surface area/leachant volume (SA/V) ratio is a critical parameter in static leach experiments because it determines the rate at which the solution becomes saturated or approaches steady state with respect to dissolved glass components and the eventual formation of secondary phases. High SA/V ratios are often used to accelerate the attainment of solution saturation, and the factor $SA/V \cdot t$ (t = time) is used to compare results attained at different SA/V ratios. For example, a test run for 10 days at a SA/V ratio of 10 m^{-1} (MCC-1 type test⁹) would be predicted to have the same final leachant composition as an equivalent test run for 2 days at an SA/V ratio of 50 m^{-1} . The allure of using such a simple factor to "accelerate" glass reaction based on solution concentration is strong. However, conditions expected in an unsaturated environment complicate this application of SA/V ratio. Important factors to be evaluated with respect to SA/V ratio include those which affect the solution composition independent of simple dissolution of the glass network. One such factor is the presence of silicon in the leachant.

Table IV-3. Normalized Release of Glass Components during Hydration/Leach Tests

Element	Normalized Release, g/m^2			
	WSRC Glass		WVDP Glass	
	Fresh	Hydrated	Fresh	Hydrated
B, Li, Na	1.5	30	10	25
Am, Pu	0.1	2	0.001	0.2
Np, U	0.6	15	2	10

Experiments are in progress to investigate the use of SA/V scaling in various leachants relevant to the tuff repository. Monolithic samples of a synthetic nuclear waste glass (SRL 131) were leached at 90°C in deionized water, a 60 ppm Si solution, and a 120 ppm Si solution. Tests were performed for up to 100 days at SA/V ratios of 10, 50, and 100 m^{-1} . Final elemental solution concentrations have been obtained, and sample characterization is in progress.

The overall extent of reaction for the same time periods was found to decrease with both an increase in SA/V ratio and an increase in the leachant silicon

⁹D. M. Strachan, B. O. Barnes, and R. P. Turcotte, "Standard Leach Tests for Nuclear Waste Materials," in *Scientific Basis for Nuclear Waste Management*, Vol. 3, ed., T. G. Moore, Plenum Press, New York, pp. 347-354 (1988).

concentration. This supports the hypothesis that the release rates are solubility limited rather than limited by the layer thickness or the existence of a protective layer. Any diffusion limitations due to the reacted layer will be more pronounced in experiments at lower SA/V ratios, which generate thicker layers. If the release of one element is affected more by the layer than others, the possibility exists that equilibria with secondary phases will be affected, thereby influencing the solution concentration as well.

Slightly higher solution pH values and concentrations of Si (prior to reaching saturation), Li, B, and Na were observed in tests done at 100 m^{-1} than in those done at 50 m^{-1} at equivalent SA/V t. These differences were seen to increase with larger SA/V t in all leachant solutions. Larger surface areas release more alkali and result in higher pH values. The higher pH values promote glass dissolution, which may result in nonuniform acceleration of elemental release and different solution concentrations. These effects could lead to different controlling equilibria (i.e., formation of different alteration products) in experiments performed at different SA/V ratios. For example, preliminary analysis of the reacted samples determined that birnessite ($\text{Mn}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) forms as a precipitate on samples reacted in deionized water with an SA/V ratio of 10 m^{-1} but not on samples reacted for equivalent values of SA/V t with an SA/V ratio of 50 or 100 m^{-1} . The use of SA/V t scaling is deemed inappropriate under these conditions.

(5) Natural Analogue Experiments

Naturally occurring glasses are useful in validating both predictive computer codes for long-term waste performance and laboratory experiments used to accelerate glass reactions. If an experimental method can successfully reproduce the reaction progress of a natural glass over geologic times, then that method may be expected to predictably accelerate the reaction of similar synthetic waste glasses.

We are currently investigating the experimental alteration of basalt glass and obsidian in water vapor in support of similar experiments with synthetic waste glasses. These glasses have compositions similar to the glasses to be used for waste isolation and are thus useful analogues.

We have reproducibly altered basalt glass at 200°C for up to 150 days in saturated steam. The thickness of the alteration layer grew as a linear function of time. Analyses with SEM/EDS are being performed to characterize the alteration layer. Additional experiments at 175°C are in progress.

Obsidian glasses were hydrated at 175 and 160°C and at 60, 90, and 100% RH. Hydration rates were found to be about 30% lower for obsidian reacted at 60% RH than at 100% RH. A similar effect of RH was observed for naturally altered obsidian. We next obtained sorption isotherms for water on natural obsidian at 20, 30, and 50°C . The data indicated that the amount of water sorbed increased with the RH at all temperatures. We interpreted the higher hydration rate at higher RH to be related to the chemical potential of water sorbed onto the glass surface. As the relative humidity decreases, the driving force for water to diffuse into the glass is reduced, and the penetration depth is reduced.

b. Spent Fuel Studies

In addition to glass studies, experiments designed to determine radionuclide release rates by exposing spent fuel to repository-relevant groundwater are being performed in CMT.

(1) Isotope Exchange

We performed a scoping experiment to determine the release rates from an unirradiated UO_2 powder specimen in J-13 well water under saturated conditions. For this experiment, a method was developed for utilizing the mass spectrometric isotope dissolution (MSID) technique to determine whether the dissolution rate of the UO_2 matrix is in accordance with an existing kinetic model.¹⁰ The use of a powder specimen was intended to accelerate the dissolution process. The specimen was an intimate mixture of two UO_2 powders, one depleted and the other enriched in ^{235}U , giving an overall enrichment of 14.3 wt % ^{235}U .

The experiment was conducted at room temperature in two cycles. In cycle 1, the UO_2 powder was placed in a basket, which was then submerged in J-13 water and sealed within a stainless steel vessel. Small samples of the leach solution were withdrawn at pre-determined intervals for analysis and promptly replaced with fresh J-13 water. Cycle 1 was intended to stabilize the uranium release rate for 160 days. In cycle 2, the leach solution was replaced with J-13 water that was spiked with a natural uranium salt. The isotopic imbalance created by the spike caused exchange reactions, which were monitored by MSID analyses. The isotopic distribution in the depleted, enriched, and mixed powders is shown in Fig. IV-11. It is clear that the enriched powder portion had a significantly higher dissolution rate than the depleted powder portion, owing to some undisclosed difference between the powders. The presence of this inhomogeneity has precluded use of the kinetic model calculations but allowed us to utilize the MSID data in recognizing and quantifying such conditions in solid specimens.

In addition to demonstrating the utility of the MSID method in unraveling solid-phase inhomogeneity problems, the experiment yielded information of interest to forthcoming HLW leach tests. For example, the effectiveness of filters commonly used in leachate sampling operations was clarified. In addition, we concluded that (1) during cycle 1, the uranium concentration in the leachate goes through a maximum before reaching a plateau, (2) replenishments with J-13 water of the sample volumes taken for analysis require dilution corrections, (3) the high rate of isotopic exchange reactions at the beginning of cycle 2 requires increased sampling frequency, (4) addition of a uranyl hexantrate spike to J-13 water has essentially no effect on the pH and ionic concentrations, except for an expected increase in NO_3^- concentration, and (5) the scoping experiment produced high-precision MSID data that would have been suitable for UO_2 matrix dissolution measurements if the specimen were homogeneous.

¹⁰C. J. Bruton and H. F. Shaw, Mat. Res. Soc. Proc. **112**, 485 (1988).

Fig. IV-11.

Distribution of ^{235}U and ^{238}U in the Depleted, Enriched, and Mixed Portions of the Dissolved Uranium for Cycles 1 and 2

(2) Unsaturated Testing

A set of parametric experiments, wherein nonirradiated UO_2 encased in Zircaloy cladding is contacted by dripping tuff-equilibrated J-13 water (EJ-13) at 90°C , has been in progress for over 4-1/2 years. These experiments simulate conditions expected to exist in an unsaturated repository and have been designed to (1) identify secondary phases that form during UO_2 alteration, (2) identify parameters that affect UO_2 dissolution, and (3) gain experience before applying such a test method to actual spent fuel.

Experimental results have identified a pulsed uranium release that occurs during the first 25 to 95 weeks of testing. This pulsed release occurred concurrently with the formation of the mineral schoepite ($\text{UO}_3 \cdot n\text{H}_2\text{O}$) on the UO_2 surfaces. Uranium release rates into solution decreased substantially after ~95 weeks, during a period when several alkali/alkaline earth uranyl and uranyl silicate phases were observed to have formed on the top UO_2 surfaces. These later phases apparently have incorporated cations from the EJ-13 water and exhibit lower uranium solubilities than those of the schoepite formed earlier. Restricted water flow on the top UO_2 surfaces, as indicated by the clustering of secondary phases on the top surface and little evidence of reaction on the bottom surface, appears to dominate the uranium release. By contrast, experiments showing the largest uranium release had evidence of

unrestricted water flow, including the formation of schoepite on the top and bottom surfaces. Thus, it appears that water flow patterns across the test sample surface may be more important in controlling the uranium release than the water drip rate or available UO_2 surface area.

The unsaturated experiments are being continued to observe whether additional phases form as the reaction progresses. Additionally, a second set of experiments has been initiated, wherein the original Teflon support stand for the UO_2 sample has been replaced by a stainless steel plate. This second set of experiments is being conducted to assess the possible interaction of dissolved Teflon with uranium mobility and secondary phase formation.

c. Radiation Studies

The objective of this CMT effort is to evaluate the effect of ionizing radiation on the performance of the waste package in the proposed Yucca Mountain HLW site. The placement of high-level waste containers in the underground facility will perturb the pre-emplacement environment by raising the ambient temperature and exposing the environment to gamma radiation levels that initially may be above 0.1 Mrad/h. Determining the effects of both of these perturbations on the gaseous/aqueous environment of the waste package is important to characterizing the performance of the HLW package during the containment period. In 1989, we investigated NO_x yield, ammonia formation, and corrosion-product formation in an irradiated environment.

The NO_x yield studies completed an experimental effort that was initiated in FY 1988.¹¹ Our recent experiments established the yields of NO_x , ammonia, and nitrous oxide as a function of absorbed dose (up to 300 Mrad) at 150, 180, and 200 °C. As in our earlier experiments at lower temperatures (30-120 °C), these experiments were conducted in 304L stainless steel vessels with gamma radiation in the dose-rate range of 0.1-0.4 Mrad/h. Both dry air and air saturated with water vapor at room temperature were used as the starting gas composition.

The experimental trends established at lower temperatures were also observed in the higher-temperature experiments completed in 1989. Nitrous oxide yield increased slightly with increasing temperature and was not affected by the presence of water vapor. Net NO_x formation, as gaseous NO_2 or HNO_3 adsorbed onto the vessel walls, was also similarly affected by changes in the temperature. The small amount of water vapor present in these experiments, $<<1\%$ RH at the temperature of the experiment, was sufficient to convert most of the NO_2 generated into NO_x (presumably HNO_3) adsorbed onto the vessel surface. In all experiments little or no ammonia formation was noted.

Ammonia formation is an important technical concern since some copper-based materials under consideration as container materials are susceptible to ammonia cracking. Two sets of experiments were performed to investigate the possibility that ammonia might form.

¹¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, p. 95 (1989).

In the first, results published by Sato and Steinberg¹² were reexamined experimentally. These researchers had observed ammonia formation in bubbled-air systems irradiated at an absorbed dose up to 22 Mrad (0.2 Mrad/h) and room temperature. This finding conflicted with other results reported in the literature. We were, however, able to qualitatively reproduce their results, confirming that ammonia can be generated in air-saturated systems. In the second set of experiments, we determined ammonia/NO_x yields in an irradiated environment (0.14-0.36 Mrad/h) with depleted levels of oxygen at temperatures of 28-152 °C. The two initial gas conditions investigated were (1) 0.1% oxygen in nitrogen saturated with water vapor at room temperature and (2) 0.1% oxygen, 20% hydrogen in nitrogen. Under both conditions ammonia was the primary fixation product, even though oxygen was still present in the irradiated system.

As a result of the ammonia formation experiments, we concluded that (1) the presence of oxygen is not sufficient to inhibit the formation of ammonia in irradiated air-like systems, and (2) the presence of hydrogen (at least initially) is not required to generate ammonia. Based on these results, ammonia formation cannot be easily discounted under YMP-relevant conditions. This was contradictory to what was expected and has fostered a more detailed experimental effort to determine the relative importance of oxygen/water and oxygen/hydrogen ratios in the underlying radiation chemistry.

The objective of the corrosion studies was to establish the relationship between the corrosion products observed on selected candidate materials and the irradiation environment. This work was performed to (1) provide preliminary input to planned atmospheric corrosion experiments and (2) resolve some of the existing discrepancies in the literature relative to corrosion product formation. Four candidate container materials were evaluated in an irradiated (0.26 Mrad/h) moist-air environment at 120 °C: Incoloy 825, oxygen-free copper (CDA-102), 7% aluminum bronze (CDA-613), and 70/30 copper nickel (CDA-715).

Relative rates of corrosion observed (uniform corrosion was assumed) were Cu > Cu-Ni > Al-bronze >> Incoloy 825. Two important additional findings resulted from the completed experiments. The first was that, under "intermediate" moisture conditions (3-15% RH), some localized corrosion (pitting) occurred in the copper-based materials. This result was not expected and has increased the concern about material performance in irradiated moist-air systems. The second finding was that a very clear correlation existed between relative humidity and the corrosion products formed. This correlation was an important key in explaining the discrepancies in the literature and resulted in a clearer understanding of the behavior of the various materials in the expected repository environment. Future work will involve collecting quantitative measurements of corrosion rates under repository-relevant conditions.

2. Defense Programs

The Defense Waste Processing Facility at WSRC is scheduled to begin production of radioactive glass early in the 1990s. Prior to startup, the glass producers must demonstrate

¹²S. Sato and M. Steinberg, *Radiation Chemical Nitrogen Fixation in Air-Water Systems*, Brookhaven National Laboratory Report BNL-13692 (1969).

that they can produce a consistent product, and DOE must indicate how the glass will perform in the storage environment. To assist with the second requirement, CMT is undertaking two tasks: (1) critical review of parameters that affect glass reaction in an unsaturated environment and (2) long-term testing of fully radioactive glasses made from actual waste taken from the WSRC.

a. Critical Review

The predicted repository environment at Yucca Mountain has been described by the YMP as hydrologically unsaturated with possible air exchange with the neighboring biosphere. We have identified several environmental conditions which may affect the durability of waste emplaced in such an environment over repository-relevant time periods and have reviewed the existing literature to evaluate the state of knowledge regarding the influence of these conditions on the glass reaction. Commonly used experimental methods were also critically analyzed to determine if the data produced will be useful in characterizing the waste stability in the YMP repository.

Although large amounts of liquid water are not expected to contact the waste during the repository lifetime, water vapor or small volumes of transient water may contact the waste at any time after emplacement. We have identified the amount of water contacting the glass waste to be a primary parameter affecting the waste durability. Other primary parameters identified are the waste temperature, radiation fields, the glass composition, and secondary or alteration phases that form during glass hydration.

Several conclusions were drawn from our critical review of published results relevant to the influence of these environmental parameters on the glass reaction:

1. A number of empirical models have been proposed to correlate glass composition to the release rate of an element (usually silicon) in a standard leach test. With some ad hoc adjustments, these models can usually predict reaction trends of various glass compositions.
2. Alpha and beta decay may destabilize solid matrices and so reduce durability. Gamma fields produce nitric acid in moist air, which will acidify any liquid water that may accumulate.
3. The glass reaction rate increases with temperature. The stability of secondary phases may be sensitive to temperature.
4. The glass SA/V ratio is an important parameter in leaching tests. A high SA/V ratio is often used to accelerate the approach to leachate saturation, although the glass reaction rate is not itself increased. Difficulties may arise due to complicated pH effects.
5. The glass reaction increases with the relative humidity. The reaction occurs in a thin film of condensed water and results in a very high SA/V ratio.

Precipitates may form after only a few days at elevated temperatures due to saturation of the solution after very little glass has reacted.

6. Precipitates or reacted layers may impede the ingress of water and so quench the reaction.

The major conclusion of this study is that, while useful data exist for describing glass behavior in water-saturated systems, few experiments besides those performed in CMT give insight into the reaction in water vapor.

b. Long-Term Leach Tests

Long-term leach tests of glass will be performed using fully radioactive glass produced by mixing glass frit with sludge taken from Savannah River HLW storage tanks. To prepare for these tests, hot cells at CMT were adapted for glass preparation and testing. Additionally, methods to analyze the reacted glass structure were developed.

The long-term performance of a nuclear waste repository is determined by the stability of the waste form and the mobility of radionuclides contained in the glass. The technique of analytical electron microscopy (AEM) provided the first comprehensive identification of the secondary mineral phases formed during simulated terrestrial weathering of nuclear waste glasses. This technique combines transmission electron microscopy and supporting spectroscopic methods. Data from AEM analysis allow one to obtain a complete description of the reacted glass, from the outermost surface in direct contact with the leachant solution to the reacting front that migrates into the bulk glass.

We have performed SEM and AEM analyses of SRL 131 glass that had been reacted for 546 days at 90° in deionized water. Figure IV-12 shows that six distinct layers

Fig. IV-12.

Glass Mixed with Radionuclides and Exposed to Weathering Conditions. Six layers of minerals formed, as shown by numerals 1-6.

form on the glass. For example, manganese and iron oxyhydroxide phases and saponite are precipitated onto the residual glass surface from the leachant solution. In addition, smectites (layers 2 and 3), serpentine (layers 2 and 3), and manganese and uranium-titanium oxyhydroxide phases (layer 1) formed *in situ* within the glass residual layers, as shown in Fig. IV-13. Such detailed analysis of the reacted surface region is very helpful in understanding the glass reaction process.

Fig. IV-13. High-Resolution Imaging of the First Three Layers of the Glass in Fig. IV-12. Inset: a close-up of the second layer's structure

3. Repository Technology Program

a. Development of Model Validation Strategy

The objective of this effort for the Repository Technology Program (RTP) is to develop a strategy for validating performance-assessment modeling codes for near-field waste package/groundwater interactions over a range of conditions applicable to the proposed Yucca Mountain repository site. One validation approach is to conduct experimentation based on a laboratory analogue or integrated test methodology, followed by comparison of the experimental results with those predicted by model calculations. Such an approach appears straightforward, but since experimentation is used for both model development and model validation, a clear distinction between the experiments must be maintained such that input used for generating models is not the same input that is used for validating models.

The basis for near-field performance assessment depends on the coupling of sub-models that describe three events: ingress of groundwater, reaction of groundwater with the waste package, and transport of radionuclides through the near-field environment. The experimental strategy revolves around (1) identifying those independent variables that affect each

of the three events, (2) identifying the dependent variables that describe the data needs to assess the repository performance, (3) simplifying the overall approach through the use of bounding assumptions, and (4) establishing whether the dependent and independent variables can be measured and/or controlled during experimentation.

Although sub-models for each of the three events are still undergoing development, the dependent and independent variables for each can be identified along with the processes involved (see Table IV-4). The effect of all the independent variables on the resultant processes is not known, and a final description is not available concerning either the materials that will comprise the repository (i.e., waste package materials and host rock) or the environment of the waste package and near field. However, enough information is available to allow the validation strategy development to proceed.

Table IV-4. Independent and Dependent Variables Affecting Near-Field Performance

Events	Interactions	Independent Variables	Processes Involved	Dependent Variable
Groundwater Ingress	Rock/Water/Air/ Other Materials	Temperature, time, radiation, rock composition, initial water composition, degree of saturation, other materials	Devitrification, hydration, chemical reaction	Solution composition contacting waste
Waste Package Reaction	Humid Air/Metal/ Waste Form/Liquid Water/ Other Materials	Solution composition in, temperature, time, radiation, relative humidity, metal composition and treatment, waste form composition, surface area, volume of water, localized redox environment, nature of reacted layers, glass devitrification, surface roughness, pH, gas composition, water flow, glass stress	Metal corrosion, hydration, dissolution, ion exchange	Solution composition after reaction with waste
Radionuclide Transport	Rock/Water/Air/ Radionuclides	Solution composition in, K_d , D_{app} , Pr , γ , b , v_x , hydrodynamic dispersion coefficients, degree of saturation, speciation of radionuclides ^a	Dissolution, complexation, ion exchange, sorption, precipitation	Solution composition beyond near field

^aSymbols are defined as follows:

- v_x = average linear velocity of groundwater flow
- D_{app} = diffusion coefficient for each radionuclide
- K_d = distribution coefficient for each radionuclide
- Pr = density of rock
- b = fracture half width
- γ = radionuclide decay constant

The next step is simplification of the experimental strategy by restricting or eliminating independent variables for each of the three events. The types of simplifications that are appropriate for initial model validation experiments are as follows:

1. Control the volume of water available for waste form reaction by experimentally establishing either saturated conditions (the waste package inundated with liquid water) or unsaturated conditions (no direct liquid flow pathway from the waste package to the rock).
 2. Fix the composition of the solution contacting the waste package. For example, use J-13 water or J-13 water equilibrated with tuff at the test temperature.
 3. Maintain the test at a fixed temperature, excluding localized waste-form heating.
 4. Eliminate the container material and associated corrosion products.
 5. Induce or accelerate fracture or matrix flow for radionuclide transport by the spatial arrangement of the test components.
 6. Use waste forms (glass or spent fuel) that have the poorest performance with respect to radionuclide release.
 7. Use waste forms that have not been subjected to aging.
 8. Measure only the quantitative release of radionuclides in solution (as opposed to determining the chemical species in solution).
 9. Provide as input to the radionuclide transport only the total radionuclide content of the solution (no speciation or fractionation between colloidal and soluble species).
 10. Assume that the experimental parameters required to model radionuclide transport are constant with respect to samples of tuff taken from localized areas of the repository horizon. This allows one tuff core to be used in validation testing, while another tuff core is used to measure the independent variables. An alternative simplification would be to assume that crushed tuff could be used in place of tuff core in both modeling and experimentation.
- b. Development of Radiation Modeling and Testing Strategy

In a collaborative effort between ANL and Lawrence Livermore National Laboratory, a modeling and testing strategy was developed to establish the effect of ionizing radiation on the expected waste package environment at the proposed Yucca Mountain HLW repository site. This work is an important step in planning and focusing the future work so that needed data are available at the time of license application.

We determined that the radiolytic alteration of the waste package environment depends on several factors. During the containment period, the gas composition depends on

(1) the initial gas phase present, (2) the gamma radiation level, (3) material-specific surface interactions, and (4) gas exchange/transport throughout the repository horizon. In the event of container failure, additional considerations are (1) surface dose rate due to alpha and beta particles, (2) the composition of the aqueous medium, and (3) the effect of radiolysis on the aqueous speciation of radionuclides. The current data base and modeling methodology were found to be inadequate to predict radiolytic alteration of the waste package environment.

In 1989, we developed a testing methodology to generate the data needed to model the effect of ionizing radiation on the waste package environment. The objective was to support the testing strategy by (1) developing an experimental methodology to determine the yield of important radiolytic products and (2) performing scoping experiments according to that methodology. Important radiolytic products identified were nitrogenous compounds (NO_x and ammonia), organic acids, and ozone. The extent that they are formed needs to be determined as a function of irradiation conditions relevant to the proposed Yucca Mountain repository. The yield data generated will be used as input to help predict, by modeling, radiolytically induced changes in the waste package environment.

With the exception of ammonia formation, the experimental methodology recommended was to perform long-term batch studies over the range of conditions expected and in the presence of the components of the waste package. Ammonia production needs to be separately evaluated on a more detailed mechanistic level, since its possible formation has a significant effect on the selection of copper-based container materials.

We completed scoping experiments to address two repository-relevant concerns that are not well understood: (1) the effect of high water vapor content on nitrogen fixation and (2) the effect of material interactions on the observed yields. These experiments were conducted with Pyrex vessels that were kept dark to prevent photolysis. Experiments were performed with waste package components at 30 and 90°C, 0-100% RH, and a fixed partial pressure of air (~88 kPa at experiment temperature). Dose rates were 0.1 to 0.3 Mrad/h with total absorbed doses up to 80 Mrad. Product formation was monitored by a combination of gas chromatography and ion-selective electrode analysis.

Increasing the surface area of waste package components (tuff rock, candidate container materials) always resulted in a net decrease in the gaseous concentration of the radiolytic products. This effect was preliminarily attributed to a combination of increased sorption of the radiolytic products formed and the surface catalysis of the decomposition of key intermediates (such as nitrogen dioxide). High water vapor content affected nitrogen fixation yields in two ways. First, the relative amount of the nitrogen oxides formed was a function of the water vapor content. Nitrous oxide yield decreased as the relative humidity increased, and the NO_x yield appeared to initially increase, pass through a maximum at 40-50% RH, and subsequently decrease. The range in yields observed was $G(\text{NO}_x) = 0.4$ to 2.5 molecules/100 eV absorbed dose. The second effect noted was that increased moisture content resulted in increased ammonia production. As was observed in work performed for the YMP (Sec. IV.B.1.c), ammonia formed in an oxygen-containing irradiated system.

c. Application of Laser Photoacoustic Spectroscopy to Actinide Speciation

The experimental technique of laser photoacoustic spectroscopy (LPAS) was further developed in work that was funded by the RTP. The objective of this task was to demonstrate that LPAS could be used quantitatively to obtain data needed to model and evaluate the performance of the waste package. The specific application of this high-sensitivity laser system is to determine needed radionuclide solution data at concentrations that are near those expected in the repository. It is important to work at low concentrations because many interactions that are concentration dependent lead to speciation.

The LPAS technique has been used to qualitatively establish the presence of species at very low concentrations. Our contribution to the development of this technique was to (1) improve the sensitivity relative to other published values by a factor of almost ten and (2) modify the system to perform at temperatures above ambient. This latter modification is needed in determining important solution data.

Laser photoacoustic spectroscopy as an analytical technique has not, prior to this work, been used quantitatively because of experimental difficulties in system-to-system reproducibility. Overcoming this problem was a necessary step to showing that this technique will yield the needed solution data. The sensitivity of our LPAS system is 3×10^{-7} absorbance units per centimeter in the blue-green region of the spectrum.

The specific system chosen for LPAS study was the hydrolysis of Pu(VI), i.e., the reaction of Pu(VI), as PuO_2^{2+} , with water as the pH is increased in an aqueous system. The two hydrolysis reactions that appear to be most important in this system are usually represented by the following:

The hydrolysis of Pu(VI) was selected for the following reasons: (1) it is a repository-relevant species (PuO_2^{2+} is expected to be an important species in the unexpected condition of site saturation in the YMP site); (2) relatively large spectral changes have been noted due to hydrolysis, (3) the hydrolysis constants associated with reactions 5 and 6 have not been well established, and (4) hydrolysis is expected to be an important process in determining the speciation under anticipated repository conditions.

Since the objective of this work was to make quantitative measurements of the first hydrolysis constant, the work was performed in sodium perchlorate medium. This has historically been the medium of choice for hydrolysis studies since the ionic strength of the medium must be established, and perchlorate is a noncomplexing ion. Performing work in this medium helped establish an unambiguous characterization of the spectrum of the various species.

This information can then be used in experiments performed with repository-relevant groundwaters, such as J-13, to establish the speciation of plutonyl species present.

The use of LPAS for making quantitative measurements with the PuO_2^{2+} hydrolytic system was clearly demonstrated in this report period. The Pu(VI) absorption bands in the 600-700 nm region were characterized at pH = 1 to 7 and room temperature. The ability to examine a very low Pu(VI) concentration ($2.6 \times 10^{-4} \text{ M}$), made possible by the use of LPAS, was important in identifying the absorption bands observed with the predicted hydrolysis products of PuO_2^{2+} . The first hydrolysis constant was estimated to be 5.24, which is in general agreement with data in the literature.¹³ The quantitative data obtained showed that the extent of hydrolysis was underpredicted when less direct means of establishing speciation (e.g., potentiometric titrations) were employed. An absorption band associated with polynuclear species of plutonyl was identified, and some polymeric character of this species was observed. In future work, we will further characterize, both quantitatively and qualitatively, the PuO_2^{2+} hydrolytic system.

4. Waste Isolation Pilot Plant (WIPP) Project

The WIPP site is located in the Salado bedded salt formation in southeastern New Mexico in the northern portion of the Delaware Basin. This site is being characterized for use as a permanent disposal site for TRU waste and is scheduled to open within the next few years. The objective of our work is to investigate the effect of ionizing radiation on the potential for gas generation in the WIPP site. Two specific technical concerns are (1) the radiolytic alteration of noncellulosic plastics by alpha particle interaction to plastics that are biodegradable and (2) gas generation due to alpha particle interaction with the WIPP brine, if site inundation were to occur. This work is being coordinated at ANL through Sandia National Laboratories.

For the first technical concern, selected plastic materials are being irradiated with alpha particles in environments identified as relevant to the WIPP Project. The objective is to determine the extent that nonbiodegradable plastics present in the WIPP waste canister will be radiolytically converted to biodegradable material. All the work is being performed in conjunction with Dr. Dunja Grbic-Galic at Stanford University, who will be performing the bioassay of the irradiated materials.

The anticipated environment following emplacement of the waste drums depends on the contribution of several processes that are not yet fully understood. Conditions identified as appropriate for experimental work include: temperature, $\sim 30^\circ \text{C}$; pressure, 1-150 atm; relative humidity, 70%; and atmosphere of carbon dioxide, hydrogen, hydrogen sulfide, methane, nitrogen, and water vapor. These conditions were chosen on the basis of several expectations concerning the repository environment. Actual temperatures in the repository are only expected to increase slightly from the ambient temperature of 27°C . Gas generation, following repository closure, is expected to cause a pressure buildup. A gas phase that is evolving from air to hydrogen/carbon dioxide/nitrogen saturated with water vapor is expected to predominate throughout most of the repository history. The expected relative humidity is 70%, corresponding

¹³C. F. Baes and R. E. Mesmer, *The Hydrolysis of Cations*, John Wiley and Sons, New York (1976).

to the vapor pressure of brine-saturated water. Although direct contact between brine solution and the waste drums may never occur, this case is being considered as a limiting condition.

The work is divided into three phases: (1) developmental experiments, (2) three-month scoping experiments, and (3) long-term WIPP-specific experiments. The third phase will be based on the results of the first two and will not be fully defined until these are completed. Results will be presented in future reports in this series. The second technical concern, gas generation caused by alpha particle interaction with the WIPP brine, will also be investigated in the near future.

C. *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 processed 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 re-enriching the core alloy with plutonium bred in the blanket. To accomplish this, major efforts are directed toward flowsheet development for the process, experiments on process chemistry, engineering-scale demonstration of the electrorefining process, and studies of IFR waste treatment and management.

1. Process Flowsheet and Chemistry Studies

The IFR pyrochemical process for recovery of pure uranium (for blanket element fabrication) and a U-Pu mixture (for driver elements) is based on the ability of a solid cathode to remove only pure uranium, even in the presence of much more PuCl_3 than UCl_3 in the molten chloride electrolyte salt. The reference flowsheet was presented in a previous report.¹⁴ The reference electrorefining apparatus for processing the IFR fuel and blanket material is illustrated in Fig. IV-14. Spent fuel pins are chopped and put in a basket for dissolution in the electrorefiner (ER) at 773 K (500 °C). Cadmium dichloride (CdCl_2) is then added to oxidize alkali, alkaline earth, and most rare earth metals to their chlorides, which become a part of the molten chloride electrolyte. Essentially pure uranium is electrotransported to the solid cathode; a mixed U-Pu product is electrotransported to a liquid cadmium cathode (not shown in Fig. IV-14). These cathodes are removed from the ER cell and retorted to vaporize the cadmium and any occluded salt and to consolidate the product by melting. Noble metals, which do not electrotransport, fall

¹⁴M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1986*, Argonne National Laboratory Report ANL-87-19, p. 98 (1987).

into the cadmium pool; they eventually are removed by mechanical means and by distillation of the pool. The salt is freed of lanthanides and actinides by reduction and returned to the process; the small amount of excess salt can be classified as a nonTRU waste. After hundreds of batches of fuel have been processed, sodium buildup will require that the entire salt batch be discarded. This salt, which contains fission-product Cs, Sr, and I, may be incorporated into concrete to produce a disposable (nonTRU) waste form. The rare earths from the reduction and the noble metal fission products are consolidated into copper to provide a permanent disposable waste form.

The chemistry of the pyroprocess is based on the relative ease of oxidation of the elements that make up the metal fuel. This was determined from the free energies of formation of chlorides of these elements (CsCl , CeCl_3 , UCl_3 , etc.). Our calculations indicated that alkali and alkaline earth metals are readily oxidized into the salt, and less easily oxidized (noble) elements remain as metals. The amount of oxidant can be adjusted so that the actinides and rare earths are found both as metals and in the salt, although actinides will mostly be found as metal and rare earths will mostly be chlorides. Thus, oxidation effects most of the separation of actinides from fission products.

Fig. IV-14. Schematic Representation of Electrefiner Operation with Anodic Dissolution of Fuel and Electrotransport to a Solid Cathode. (The abbreviation N.M. FPs represents noble metal fission products.)

Separate collection of the uranium product and the mixed actinide product is possible because uranium is slightly less easily oxidized than the other actinides, and because the oxidation state is such that the salt contains a mixture of actinides. When electrotransport is used simultaneously to oxidize the metals to their chlorides at an anode and to reduce an equivalent amount of chloride to metal at a solid metal cathode, uranium is preferentially deposited and the other actinides are preferentially oxidized. The product is essentially pure uranium, contaminated with the salt.

When the cathode is a crucible containing liquid cadmium, plutonium, the minor actinides, and the rare earths are all stabilized as metals by interaction with the cadmium. Uranium is not. The cadmium electrode product is thus a mixture of actinides with small amounts of rare earths. The composition of the mixture is determined partially by the composition of the anode metal, but mostly by the composition of the salt. Our procedure is to control the salt and anode compositions by removal of selected amounts of uranium with solid cathodes so that the cadmium cathode has the desired composition. We have been successful in producing the predicted salt and cathode compositions from uranium-plutonium-rare earth mixtures. Also, analysis of existing experimental transport data has shown that americium follows the plutonium in the electrotransport process.

After some number of batches of fuel have been processed (perhaps a dozen, depending on the age of the fuel and its activity), it will be necessary to remove noble metal fission products from the cadmium by mechanical removal of solids or by removal and distillation of the cadmium pool. Removal of the rare earths from the salt by reduction with Cd-Li alloy will purify the salt sufficiently to allow recycle (Sec. IV.C.4). Cesium and strontium are the only radioactive species remaining in the recycled salt. Both the noble metals and the rare earths will be in a metallic form and can easily be incorporated in a copper matrix, a waste form that is expected to be satisfactory for disposal.

Both the individual operations that make up the pyrochemical process and their arrangement into a complete process have been developed with the aid of Pyro, an ANL computer code that predicts the distribution of the elements in the electrorefiner. The predictions of this code have been tested by analyzing the salt and metal phases for uranium, plutonium, and rare earths in a series of electrotransport experiments. The results showed that the predicted product compositions agree with experimental results within the accuracy of the chemical analysis ($\pm 0.5\%$).

Another important issue for both product collection and rare-earth removal is the relative partition of plutonium and the rare earths between cadmium and salt. We have used available data to predict the separation of plutonium and neodymium, assuming that the other rare earths behave like neodymium. This assumption was supported by scoping experiments (competitive partition of rare earths) conducted under simulated electrorefiner operating conditions; partition coefficients for five of the seven most abundant rare earth elements were identical within experimental error. Under reducing conditions, however, europium and samarium strongly favored the salt phase relative to the other rare earths because of their very stable 2+ oxidation state. More precise rare-earth characterizations are underway; in the case of europium, they have shown that cadmium chloride is not a sufficiently strong oxidizing agent to produce the 3+ oxidation state. Nonetheless, all rare earths can be removed from the salt with alkali-cadmium alloys. Studies to quantify the distribution of rare earths between the salt and liquid cadmium will continue.

2. Process Development Studies

The electrorefining process under development uses solid and liquid cathodes; the solid cathode collects uranium, and the liquid cadmium cathode collects U-Pu. The solid cathode

product contains about 10-15 wt % electrolyte with a small amount of cadmium, whereas the liquid cadmium cathode product contains a significant quantity of cadmium as well as uranium, plutonium, and electrolyte. Purification and consolidation of the cathode products are accomplished by distilling off the cadmium and salt and then heating the remaining above the melting point of uranium. Earlier, this process was demonstrated for the dendritic uranium deposits.¹⁵ Experiments conducted to demonstrate purification and consolidation of liquid cadmium cathode products are described below. A major question to be answered was whether or not the PuCd_6 intermetallic compound could be decomposed by retorting.

The starting compositions for these experiments were selected to simulate the expected product in the recovery of uranium and plutonium in a liquid cadmium cathode. The starting materials were slowly heated in a BeO crucible under a partial vacuum (5-10 mm Hg) to about 700°C. The material was cooled and sampled to obtain an intermediate composition, which is shown in Table IV-5 along with the starting composition.

Table IV-5. Starting, Intermediate, and Final Compositions for Product Purification and Consolidation

	Starting Composition, g (wt %)	Intermediate Composition, ^{a,b} g (wt %)	Final Composition, g
Run 1	100.42 U-Zr (21.75) 28.92 Pu (6.26) 332.40 Cd (71.99)	100.42 U-Zr (52.60) 28.92 Pu (15.15) 61.56 Cd (32.25)	129.33 U-Pu-Zr ^c
Run 2	128.21 U (26.08) 28.07 Pu (5.71) 335.19 Cd (68.21)	128.21 U (75.28) 28.07 Pu (16.48) 14.03 Cd (8.24)	156.28 U-Pu ^d

^aX-ray diffraction analysis identified intermediate phases to be α -U and PuCd_6 .

^bMaximum heating temperature was 668°C for Run 1 and 702°C for Run 2.

^cProduct contained <150 ppm Cd and Be.

^dProduct contained 54 ppm Cd and 287 ppm Be.

X-ray diffraction analysis identified α -uranium and PuCd_6 as the intermediate phases. The distillation and consolidation were completed by heating the intermediate material to about 1300°C (above the melting point of uranium). The composition of the final product is given in Table IV-5. In the first experiment, the U-Pu-Zr product contained less than 150 ppm of cadmium and beryllium (the latter is from the BeO crucible). The U-Pu product from the second experiment contained 54 ppm cadmium and 287 ppm beryllium. These experiments

¹⁵M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1987*, Argonne National Laboratory Report ANL-88-19, p. 97 (1988).

demonstrated that a purified and consolidated U-Pu product can be obtained from the electrolyzer product (U-Pu-Cd-salt), and that essentially no uranium or plutonium is lost in the process. Future efforts will concentrate on purifying and consolidating larger quantities of uranium deposits from an engineering-scale electrolyzer.

3. Engineering-Scale Process Development

The key steps in the pyrochemical processing of spent fuel are dissolution and product recovery by using either solid or liquid cathodes or direct chemical reduction. Progress made in developing each step is discussed below.

a. Dissolution of Spent Fuel

Earlier laboratory-scale tests¹⁶ with individual clad fuel segments showed that anodic dissolution of clad metal fuel in the electrolyte is the preferred method for fuel dissolution; it is more rapid than direct dissolution in a liquid cadmium anode. The voltage used is sufficient to oxidize the heavy metal pin but leave the cladding shell intact. In this report period, anodic dissolution was demonstrated at the plant scale (~10 kg batch size) by filling perforated prismatic baskets hanging from a common anode shaft with clad fuel and rotating them in molten electrolyte.

In the fuel dissolution step, uranium and plutonium metals are oxidized at the anode (fuel segments in the anode baskets), and uranium and plutonium chlorides are simultaneously reduced at the cathode. (The Cl⁻ balance is maintained.) The oxidation-reduction reactions for uranium, the bulk of the fuel, are as follows:

Anode

Cathode

For the anode processes, reaction 7 is the normal oxidation of the fuel. Reaction 8 is a parasitic reaction which oxidizes U³⁺ to U⁴⁺. This reaction occurs at the metal basket surfaces and on the

¹⁶M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1987*, Argonne National Laboratory Report ANL-88-19, p. 94 (1988).

metal surface of the cladding hulls. (A corresponding reaction of U^{4+} to U^{3+} , reaction 11, occurs at the cathode.) This reaction results in no fuel dissolution unless the U^{4+} ion is brought into contact with the fuel matrix in the anode. After this contact is made, anode reaction 9 occurs with resultant fuel dissolution. This was an important consideration in designing the anode baskets. With four prismatic baskets arranged on an anode shaft in the shape of a plus (+), each basket is following in the wake of another basket when the anode shaft is rotated, and the U^{4+} rich salt is continuously contacted with fuel as the salt flows through the openings in the baskets. With this arrangement, current efficiencies of greater than 50% and anodic dissolution rates of 0.5 kg uranium per hour have been achieved. Anodic dissolution of 10 kg batches is now a routine operation.

b. Electrotransport to Solid Cathode

In the IFR process, uranium is electrotransported from the cadmium pool (anode) and deposited on a solid cathode, either single mandrel or multiple pins. The pool of cadmium serves as a cathode during the anodic dissolution step. Product collection on the cathode has also been done concurrently with anodic dissolution. This later mode of operation cuts overall processing time, since the dissolution and collection processes are occurring at the same time.

With a single cylindrical iron mandrel (4.4-cm dia and 30-cm long) as cathode, the dendritic deposit of heavy metal had to be physically removed from the mandrel in a product recovery step. With multipin cathodes, the uranium rods were melt consolidated along with the dendrite deposit, and physical removal from the base cathode material was not required. Uranium deposits obtained by us on a multipin cathode are shown in Fig. IV-15. The cathode shaft is rotated during electrotransport (deposit), and scrapers limit the overall diameter (20 cm) and length (33 cm) of the deposit. Individual dendrites which grow beyond these limits are broken off by the scrapers, fall into the cadmium pool, and are recycled. Experimental variables included rod arrangement patterns in the cathode and stirring conditions. The weight of uranium deposited in three multipin cathode tests was 7.4-9.7 kg, with a collection rate of 0.20-0.24 kg/h.

c. Electrotransport to Liquid Cadmium Cathode

Plutonium or plutonium/uranium is collected in a cadmium pool contained in a ceramic crucible suspended in the electrolyte phase. To keep deposit size reasonable, it is necessary to collect an amount of plutonium in the cadmium pool in excess of the solubility of plutonium in cadmium (3.62 wt % at 500°C). When plutonium exceeds its solubility in liquid cadmium or liquid Cd-U, it precipitates as $PuCd_6$, an intermetallic compound. In laboratory-scale work (0.2 kg plutonium), we produced liquid cadmium cathodes which contained about 15 vol % solid (as $PuCd_6$). For an engineering-scale electrorefiner, a 10 kg batch of fuel will contain about 2.0-2.5 kg plutonium. A cathode pool containing about 30 kg of cadmium, along with a 5 L ceramic crucible, is required for this plutonium collection.

In this report period, we electrodeposited kilogram quantities of uranium metal into a liquid cadmium cathode in a 3-L beryllia crucible that had been suspended in the electrolyte phase at 500°C. Figure IV-16 shows a cross section of one of the Cd-U ingots. Since

Fig. IV-15.

Photograph of Uranium Deposit on
Multipin Cathode

Fig. IV-16.

Photograph of Sectioned Product from
Liquid Cadmium Cathode Test

the glove box in which this engineering development work was carried out is not a plutonium facility, uranium was used as a stand-in for plutonium. Uranium does not form an intermetallic compound with cadmium when the uranium solubility is exceeded at operating temperature (500°C); thus, a higher U/Cd ratio is required to form the same volume percentage solids in the cadmium as for the case of Pu/Cd. For the three runs, the amount of uranium solids in the cadmium ingot was 10-14 vol % (2.8-4.4 kg), which met our experimental goal.

When the product ingots were removed from the crucible, they were coated with electrolyte, which did not separate easily from the cadmium. The amount of electrolyte varied from 1.5 to 5 wt % of the product ingot. The highest uranium deposition rate attained in the three cadmium cathode deposition runs was 0.054 kg/h. The low deposition rate of uranium obtained in these experiments (0.03-0.054 kg/h) is significantly below the desired rate (~0.4 kg/h). Future efforts will investigate design and process changes to improve the achieved deposition rate.

d. Direct Chemical Reduction

Plutonium/uranium may also be deposited into a cadmium pool by chemical reduction. Use of a lithium reductant reduces PuCl_3 and UCl_3 out of the electrolyte and deposits the metal in the cadmium pool. Development work on this alternative has started and is in a preliminary stage. The reaction for the reduction is extremely fast, but reduction can take place in the electrolyte phase (lithium metal is slightly soluble in the electrolyte) away from the cadmium-electrolyte interface. Cathode designs and operating procedures are being developed to confine the reaction space and to cause the reduced heavy metal to consolidate into the cadmium pool.

In two runs (CRU-1 and -2) agitation was provided at the salt-metal interface by an impeller within the BeO reaction crucible. In two other runs (CRU-3 and -4), agitation was not used, and the reaction crucible was made of alumina. Best results were obtained in one of the runs without agitation (CRU-3). For this run, all of the uranium equivalent to the amount of reductant used (1.7 kg) was found in the metallic phase of the product (composition: 21.3 wt % U, 67.9 wt % Cd, 10.8 wt % salt), which was contained within the alumina crucible. In the runs with agitation, much of the uranium was found in material which overflowed the crucible or which was bonded to the impeller.

4. Waste Treatment Processes

Methods are being developed to convert solid wastes generated by processing IFR fuel into disposable forms. The principal solid radioactive wastes from the IFR process are cladding hulls, salt from the electrorefiner, and cadmium from the electrorefiner. The salt contains the alkali metals, alkaline earths, rare earths, and halides; and the cadmium contains the noble metal fission products. The salt also contains from 0.5 to 1% of the actinides fed to the electrorefiner. The actinide contents of the waste metal and the cladding hulls are expected to be very low.

a. Waste Flowsheet

In the reference flowsheet that we developed for IFR waste treatment, the salt from the electrolyzer is first contacted with a Cd-U alloy to extract nearly all of the transuranic elements from the salt while most of the rare earths are retained in the salt. The product metal solution is retorted to remove cadmium, and the TRU-rich residue is sent to the electrolyzer. The salt, which now contains only trace amounts of TRU elements, is contacted with a Cd-Li alloy to strip away uranium, residual TRU, and rare earths. The stripped salt, which is expected to be nonTRU, is immobilized and packaged for disposal.

The waste cadmium from the electrolyzer and the cadmium solution from salt stripping are combined and retorted to remove excess cadmium, which is returned to the process. The residue containing the noble metal and rare earth fission products is combined with the cladding hulls and dispersed in a corrosion-resistant metal matrix for disposal. Most of the actinide losses from the process (about 1% of the uranium in the fuel processed and less than 0.1% of the transuranic elements) will be contained in this metallic waste form.

b. Salt Treatment

Work to develop waste processing methods has been directed primarily at separating TRU elements from rare earths in the salt wastes, stripping actinides and rare earths from salt, and immobilizing the treated salt. The recovery and stripping steps are based on the distribution of rare earths and actinides between a chloride salt and weakly reducing cadmium alloys. The equilibrium distribution between the salt and metal phases of any two elements that form trivalent chlorides is determined by reactions such as:

As a result, if the LiCl content of the salt is constant, the distribution coefficients (mole fraction in salt/atom fraction in metal) of actinides and rare earths are approximately inversely proportional to the lithium content of the cadmium phase to the third power. Distribution coefficients for several actinides and rare earths are shown in Fig. IV-17 as a function of lithium metal concentration in cadmium. Distribution coefficients were determined from chemical analyses of filtered salt and metal samples from electrolyzing experiments for coefficients from about 0.01 up to 50, where analytical results were reliable; values shown outside that range are extrapolations. Because measurements of lithium concentrations in cadmium were accurate only above about 0.04 mol %, the relationships between the distribution coefficients and lower lithium concentrations were established from the emf determined by an Ag|AgCl reference electrode.

The slope of the lines in Fig. IV-17 is slightly greater than the predicted -3.0 because the activity coefficient of lithium in cadmium depends on lithium concentration, varying from 1.6×10^{-3} at a lithium concentration of 0.013 mol % to 3.7×10^{-3} at 6.1 mol %. The

curvature of the americium line was attributed to the formation of AmCl_2 in more reducing systems. Neptunium distribution coefficients were not measured but were estimated to be less than the uranium coefficients.

Fig. IV-17. Distribution Coefficients of Actinides and Rare Earths between Chlorides Salts and Cd-Li Alloys at 500°C (salts: LiCl -42 mol % KCl or LiCl -29% CaCl_2 -18% BaCl_2)

The data indicate that the actinide and rare earth contents of the chloride salt can be made extremely low by contacting the salt with a cadmium alloy containing only about 1.5 mol % lithium (0.1 wt %). This has been demonstrated in laboratory experiments in which the actinide and rare earth contents of a salt were reduced from the 0.1 to 1.0 wt % range to the parts per million range in a single contact with a Cd-0.1 wt % Li alloy. The residual actinide content ($\text{U} \sim 10$ ppm, $\text{Pu} \sim 1$ ppm) was attributed to small particles of insoluble oxides. The removal of a large fraction of such insoluble compounds by passing the salt through stainless steel filters was also demonstrated by producing a salt with total alpha activity of <10 nCi/g. The overall TRU decontamination of this stripping-filtering procedure was about 1×10^5 .

Because of the large differences between the distribution coefficients of actinides and rare earths, as shown by the data in Fig. IV-17, TRU elements can be separated from rare earths by a multistage extraction process that employs Cd-U alloys as the extractant. When a salt containing uranium, transuranics, and rare earths is contacted with a Cd-U metal solution, uranium in the metal phase will exchange with the transuranics and rare earths in the salt to establish metal phase concentrations as required by the relationships among the distribution coefficients. The fraction of transuranic elements extracted from the salt will be greater than the fraction of rare earths extracted. Calculations have shown that more than 99.9%

of the americium and less than 20% of the neodymium would be extracted from a waste electrorefiner salt in five to six equilibrium stages of countercurrent contact with a metal/salt weight ratio of 3-5. Work is underway to develop suitable centrifugal contactors for this extraction process (see Sec. IV.A.2).

c. Salt Immobilization

Because the stripped waste salt will contain nearly all of the fission product Cs, Sr, and I, the salt must be immobilized and encapsulated to meet the federal regulations for disposal of high-level radioactive wastes.

Dispersal of the salt in a portland cement-base mortar was investigated as a means of immobilizing the waste salt. A mortar made from 25% Type I portland cement, 25% Class F fly ash, and 50% blast furnace slag with a water/solids ratio of about 0.4 was found to be strong and to have a high resistance to leaching when the mortar had up to 10 wt % LiCl-KCl. Grouts containing up to 15 wt % salt were sufficiently fluid that they could be mixed and pumped into waste canisters, and set times were longer than 8 h, which would allow ample time for mixing and casting into canisters. Held at room temperature, the mortar strength reached 20 MPa in 7 days and exceeded 40 MPa after 56 days. Waste forms that were cured at temperatures up to 125 °C, simulating fission product heating, had higher early strengths, but their long-term strengths were lower by 10 to 20%.

In addition, the leach rate of salt from this mortar was quite low; from measurements on small specimens, we estimated that only 20 to 25% of the chloride salt would be leached from a salt-mortar waste form the size of a 55-gal drum if it were immersed in flowing water for 100 y. Without blast furnace slag in the mortar, the leach rates would be two to three times higher.

The strength and leach resistance of salt-mortar waste forms appeared to be adequate for a high-level waste form, but the water in the mortar was decomposed by beta-gamma radiation. A mortar containing 7 wt % of waste salt would receive an initial dose rate of about 0.05 Mrad/h from Sr-90 and Cs-137 and a total dose of about 5×10^4 Mrad. Irradiation of mortars that contained blast furnace slag yielded only hydrogen, an undesirable product. The rate of hydrogen production was constant and steady-state radiolytic pressures were not attained up to a total dose of 500 Mrad. Hydrogen yields depended on salt content; at 25 °C, the hydrogen yield was 0.14 molecules/100 eV for a mortar containing 3 wt % salt and 0.22 molecules/100 eV for a mortar with 10 wt % salt. Hydrogen yields decreased with increasing temperatures; for a mortar containing 10 wt % salt, hydrogen yields were 40% lower at 75 °C than at 25 °C, and 90% lower at 120 °C.

Small amounts of oxygen-rich electron scavengers, such as NO_3^- and IO_4^- , were added to the mortar-slag-salt mixture in an attempt to decrease the hydrogen yields. As illustrated in Fig. IV-18, the addition of 1 wt % NaNO_3 to a salt-mortar specimen decreased the radiolytic pressurization and thereby reduced the amount of hydrogen produced. The radiolysis products were changed from only hydrogen to hydrogen, nitrogen, and N_2O . The addition of 1 wt % NaIO_4 also decreased the pressurization but did not change the radiolysis products.

Further studies are underway to identify other electron scavengers that will lower hydrogen yields but will not decompose to other gaseous products.

Fig. IV-18.

Radiolytic Pressurization as Function of Time for Salt-Mortar Specimens at 25 °C (B-10: mortar with slag and 10 wt % salt; dose rate, 0.35 Mrad/h. B-10+NaNO₃: mortar with slag, 10 wt % salt, and 1 wt % NaNO₃; dose rate, 0.31 Mrad/h)

Although it may be possible to solve the radiolysis problem by adding electron scavengers or venting waste containers, other salt waste forms are being investigated, especially those that contain no water. The simplest approach is encapsulation of the salt in highly corrosion-resistant, thick-walled metal containers or porous metal matrices. Studies are being conducted to determine the effects of ionizing radiation on solid IFR waste salt during interim storage and long-term disposal. Solid salt consisting of 57.2 mol % LiCl, 40.6 mol % KCl, 1.2 mol % NaCl₂, 0.7 mol % CaCl₂, and 0.3 mol % BaCl₂ was irradiated for periods ranging from 1 to 3 months at dose rates between 0.4 and 0.6 Mrad/h and at 25 and 120 °C. The irradiated salt was analyzed iodometrically for chlorine content. The amount of chlorine formed within the solid salt increased approximately linearly with time at a given temperature, and the rate at 120 °C was about twice that at 25 °C. These preliminary experiments indicated that the potential exists for the generation of significant quantities of chlorine and alkali metal within the solid salt.

d. Planned Waste Studies

In the near term, development of waste processes will continue to emphasize methods for treating and immobilizing salt wastes. The work on salt-mortar waste forms will be completed with the measurement of cesium and strontium leach rates and determination of additives that reduce the production of radiolytic hydrogen. Future experiments related to the storage and disposal of solid salt will be conducted to identify and evaluate container materials which are radiation and corrosion resistant with respect to chlorine, alkali metals, and chloride ion. Long-term experiments are also being planned to determine if chlorine generation reaches a steady state.

Immobilization of salt in water-free ceramic matrices will also be explored. In this approach, the salt would be absorbed into a porous ceramic, sealed in a metal container, and then hot-isostatically pressed to at least partially seal the ceramic pores. The possibility of incorporating a zeolite in the ceramic to preferentially adsorb cesium and/or strontium ions will also be explored.

D. *Plutonium Residue Recovery*

The objective of this program is development of an effective pyrochemical process for the recovery of plutonium from intractable residues. Lawrence Livermore National Laboratory (LLNL) is working jointly with ANL to (1) devise a single economical pyrochemical process capable of recovering plutonium from all the types of scrap and residue now being generated or in storage from previous DOE weapons production operations; (2) remove and concentrate other TRU materials from the wastes so that the bulk of the pyrochemical process effluents can be classified as nonTRU wastes; and (3) provide a basis for the upgrading of recycle weapons materials.

Savannah River Laboratory (SRL) is working with ANL in an adjunct program to use a pyrochemical head-end step to convert intractable residues to a form that can be introduced into existing aqueous processes. The progress in both programs during 1989 is summarized here.

The anticipated processes use liquid metals and molten salts at elevated temperature to effect the necessary separation and chemical conversion. Separations are possible because of the differing stabilities of compounds in the molten salt phase relative to those in the liquid metal phase. Several flowsheets are under consideration but common to all is the reduction of PuO_2 from an oxide residue as an initial step. The current program effort has concentrated on this reduction step because it is common to all flowsheets, and because the other steps of the processes have been or are part of existing production methods (e.g., electrorefining), have been demonstrated during process development work on other processes (e.g., salt and metal extractions), or have sufficiently sound theoretical (i.e., thermodynamic or kinetic) basis to give confidence that they can be blended into successful production processes.

The reduction step requires a feed material, solvent/reductant, and a salt fluxing agent and produces salt and metal effluent streams. Feed material for the developed process can be any of the 22 categories of weapons production residues. Feed material for the current process development effort was selected to be representative of the most difficult to process residues to be used as a process feed. Acid-leached LECO analytical crucibles (ground) from SRL and incinerator ash heels from Rocky Flats (calcined and ground) are considered the most intractable of feed materials. These materials contain a wide spectrum of metals and have plutonium content ranging from <1% to ~20% by weight.

In addition, SRL has asked us to determine whether the plutonium remaining in the slag from bomb reduction of $\text{PuO}_2/\text{PuF}_4$ by calcium can be extracted with pyrochemical procedures. We were also asked to design and fabricate a heated transfer line for transferring molten salts and metals.

Several solvent/reductant systems, including Zn-Mg, Cu-Mg-Ca, Al-Mg, Al, Zn-Ca, and Al-Ca, have been considered for process development. During this period much of our effort was directed toward the use of calcium as a reductant. This stems from a decision by ANL and LLNL to work with a reference flowsheet which employs a Zn-Ca solvent/reductant system. This decision was prompted by the need to recycle materials and reagents and thereby minimize

waste streams. It is anticipated that CaO, the reduction product of the reaction between Ca and PuO_2 , can be electrochemically regenerated from the salt and recycled. Several experiments have been conducted on the electrolytic reduction of the CaO into a liquid zinc cathode. These experiments, though preliminary, demonstrate that the reduction can be accomplished.

Experimental results presented previously¹⁷ indicated that good reduction and recovery of plutonium from intractable residues can be expected by using Zn-Mg, Al-Mg, Al, and Cu-Mg-Ca systems. Additional results obtained using Zn-Ca and Al-Ca reductant systems on incinerator ash heels and bomb reduction slag are presented in Table IV-6. The salt phase used in conjunction with the calcium reductant systems was CaCl_2 -20 mol % CaF_2 . This salt was used because of its low melting point ($\sim 645^\circ\text{C}$) and its ability to dissolve both CaO and PuO_2 .

Problems were encountered in performance of the Zn-Ca experiments, which required use of stirrers and baffles for the reductant/salt/feed in MgO crucibles. Initial attempts to use tantalum stirrers and flow baffles, proven to be useful in the Zn-Mg and Cu-Mg-Ca systems, resulted in rivet failures and collapse of these components. New flow baffles and stirrers of Mo-30 wt% W were built and tested to correct the problem. Post-test analysis of the metal ingots produced by the pyrochemical process indicated that contamination by molybdenum is negligible, and that a small amount of the MgO crucible is being reduced to magnesium.

Based on the plutonium content of the salt phase, the reduction results presented in Table IV-6 appear to be very good, averaging 98.0% after one reduction stage and 99.4% after two reduction stages for the ash heel experiments and 93.6% after one reduction stage for the slag experiments. However, analysis of the metal ingots in at least half of the experiments failed to confirm the good reductions indicated by the salt analysis. The poor material balance obtained in these experiments, which all employed calcium as the reductant, is of concern; we did not find evidence of such a problem in experiments which used magnesium as the reductant.

The metal ingot analyses were performed on pie-shaped portions cut from the ingots and may not be representative of the metal phases formed if the plutonium had precipitated. The possible formation of intractable forms of plutonium in these reductant systems is being examined but identification is difficult because of the low plutonium concentration, $<1.0\%$, in either ingot or salt.

For any of the reduction schemes considered, salt recycle is important to minimize wastes. The usefulness of the salt is limited by its ability to dissolve CaO (~ 17 mol % for the CaCl_2 - CaF_2 salt), and recycling of the salt is dependent on being able to remove this CaO. Electrolytic reduction of the CaO is considered possible, especially with the use of a carbon anode.

¹⁷M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, p. 86 (1989).

Table IV-6. Plutonium Recovery from Nuclear Wastes by Pyrochemical Reduction at 800 °C

Reductant	Pu Reduction, %			
	Ash Heel		Slag	
	Salt ^a	Ingot ^b	Salt ^a	Ingot ^b
Zn-2% Ca	95.2 98.9 ^c	95.0		
Zn-10% Ca ^d	99.5 99.96 ^c	73.7	74.4	74.0
Zn-6% Ca	97.2 99.4 ^c	57.4		
Al-10% Ca ^d	99.9	82.8	99.0	69.8
Zn-3% Ca ^d			99.5	133.5
Zn ^d			99.9	57.0
Al ^d			95.2	95.0

^aBased on δ -spectroscopic analysis of salt phase.

^bBased on inductively coupled plasma analysis of metal ingot.

^cTwo stages of reduction.

^dThe slag contained an additional 2-4% calcium metal.

With the carbon anode, there appears to be a sufficiently large voltage difference between the desired CaO reduction and the undesired reduction of CaCl₂ to achieve a practical separation based on the following reactions with the standard electrode potentials at 727 °C (1000 K):

Also, since the recovered calcium is a required reagent, its recycle into the overall scheme as a Zn-Ca alloy is desirable. Hence, our early experiments have used a liquid zinc cathode to dissolve the calcium produced. Thus far, we have completed four preliminary CaO electrolysis experiments at ~800 °C. In these experiments we started with a CaO-saturated CaCl₂-CaF₂ salt, a carbon anode, and a liquid zinc cathode. At concentrations of 17 mol % CaO in the salt phase and 1 at. % calcium in the zinc phase, the equilibrium decomposition voltage was reduced to

about -1.0 V. Current at ~1.5 A was passed for ~6 h in each experiment, with voltages ranging from 1.8 to 3.2 V. Following the experiment a portion of the zinc phase was submitted for calcium analysis. Based on the amount of calcium obtained and the amount of electrical energy used, current efficiencies of 35-72% were calculated. Analysis of gas samples taken from two of the experiments showed only CO₂ and CO in a ratio of ~5 to 1. Chlorine gas was not found in the gas samples, even though the voltage was allowed to increase to a point where some CaCl₂ might have decomposed. These results, though preliminary, suggest that the electrolytic reduction of CaO is practical.

The ability to transfer salt and/or metal phases at high temperature in any practical pyrochemical scheme is important because it allows the optimization of reagents and the use of multiple stages without the time lost in cooling and reheating reagents or the radiation exposure involved in recovering the frozen contents from the crucible by hand. Because of the experience obtained in the 1960s by CMT on the design, fabrication, and use of heated transfer lines, SRL asked us to design and fabricate a transfer line suitable for use with both salt and metal phases. Because of the high solubility/reactivity of the metal phases, particularly zinc and plutonium, for most readily available construction materials, the choice of the tube metal is limited. Tungsten has the desired inertness but cannot be fabricated into the required forms. A Mo-30% W alloy, which has acceptable inertness and can be machined, with difficulty, is the material which has been chosen for the tube material.

The Mo-30% W alloy is not available in tube form and has to be drilled from rod. The length of tube required, 2-2.5 m, means that special drilling equipment of the type used to drill guns is required. Considerable difficulty was encountered in finding a vendor with suitable equipment and/or interest to undertake the gun drilling of the Mo-30% W rod. Most of the design features of this transfer tube have been finalized, and construction awaits the receipt of the Mo-30% W tube.

Future work on the reduction of PuO₂ contained in residues and slags by Zn-Ca will be directed toward improving the effectiveness of the process and resolving the material balance problem. Also planned are experiments which will produce a solid calcium product rather than a Zn-Ca alloy from the electrolytic decomposition of CaO.

V. APPLIED PHYSICAL CHEMISTRY

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

A. *Fission Product Release from Core-Concrete Melts*

In a severe accident involving loss of coolant in a light water reactor, molten core debris may melt through the reactor vessel and react with the concrete basemat beneath the vessel. The objective of our work is to measure and calculate the vaporization of certain refractory fission products (Sr, Ba, and La) from the molten core-concrete mixtures that would form under these conditions.

The literature contains conflicting results for the fraction of the more refractory fission products that will be released to the environment under these extreme conditions. The Reactor Safety Study^{1,2} gives release fractions (the source term) for the alkaline-earth fission products (Sr and Ba) of 0.02 to 0.06 and for the rare-earth fission products (La, for example) of 0.003 to 0.004. More recent studies^{3,4} propose much larger release fractions for Sr (up to 0.84), Ba (up to 0.60), and La (up to 0.06). As a result of this discrepancy, researchers have explored several alternative methods of calculating release fractions,⁴⁻⁶ which have also yielded conflicting results. Resolution of this controversy is important because even small fractional releases of the refractory fission products can have a significant impact on the consequences of a severe reactor accident.²

1. Experimental Methods

Our experiments were performed using the transpiration method to measure the vapor pressures of Sr, Ba, La, and U, as well as the vaporization of total mass, from simulated core-concrete samples at high temperatures (>2000 K). In these experiments, the transpiration gas was H₂-0.03% H₂O, which has an H₂O-to-H₂ ratio equivalent to an O₂ partial molar free energy of -550 kJ/mol (-130 kcal/mol). The gas flow rate was 200 cm³/min at 25 °C, and the

¹N. C. Rasmussen et al., *Reactor Safety Study*, U.S. Nuclear Regulatory Commission Report NUREG-75/014 (1975).

²R. Wilson et al., *Rev. Mod. Phys.* **57**, S1 (1985).

³*Severe Accident Risks: An Assessment for Five U.S. Nuclear Power Plants*, U.S. Nuclear Regulatory Commission Report NUREG-1150 (1989).

⁴D. A. Powers, J. E. Brockman, and A. W. Shiver, *VANESA: A Mechanistic Model of Radionuclide Release and Aerosol Generation During Core Debris Interactions with Concrete*, U. S. Nuclear Regulatory Commission Report NUREG/CR-4308 (1986).

⁵A. T. D. Butland, M. A. Mignanelli, P. E. Potter, and P. N. Smith, "The Vaporization of Chemical Species and the Production of Aerosols during a Core Debris/Concrete Interaction," in *Proceedings of the Committee on Safety of Nuclear Installations Specialist's Meeting on Core-Debris Concrete Interactions*, Electric Power Research Institute Report EPRI NP-5054-SR, p. 5-33 (1987).

⁶D. Cubbiciotti, *J. Nucl. Mater.* **130**, 3 (1985).

experiments usually lasted for 73 min. The amount of gas was 0.6 mol when the sample was at the desired test temperature (2400 K). The samples consisted of urania (doped with 1 mol % SrO, 0.4 mol % BaO, 1 mol % La₂O₃, and 2 mol % ZrO₂), zirconia, and concrete. The concretes tested in this study were a limestone concrete (7.13 wt % SiO₂), a limestone-sand concrete (28.27 wt % SiO₂), and a siliceous concrete (68.99 wt % SiO₂). The samples were held in molybdenum crucibles (1.7-cm ID x 1.9-cm OD x 3.8-cm height).

Materials vaporized from the samples into the H₂-0.03% H₂O gas stream were condensed in a molybdenum tube (54-cm long x 0.8-cm OD x 0.5-cm ID) whose entrance lay within the crucible a few centimeters above the sample surface. The temperature gradient was such that the condensates were deposited about 10-15 cm beyond the tube entrance. To determine the total mass transpired, the molybdenum condenser tube was weighed before and after each experiment. The condensates were extracted from the molybdenum tube with up to four acid washes. The acids were evaporated to dryness, and the residues were digested in 10-15 mL of hot HCl-H₂O (1:1) or HNO₃-H₂O (1:1). The samples were then diluted to 100 mL, making the solutions 1 M in HCl or HNO₃ for subsequent analysis. The solutions were analyzed by laser fluorescence spectroscopy for uranium and by inductively coupled plasma/atomic emission spectroscopy (ICP/AES) for other metals. To determine phases in the mixtures as well as the distribution of trace elements, the crucibles were cross-sectioned, mounted, polished, and examined by electron probe microanalysis (EPM). Small samples were also taken after cross sectioning and were analyzed by X-ray diffraction (XRD).

2. Calculational Methods

We also performed equilibrium vaporization calculations with the SOLGASMIX computer code,^{7,8} which was modified during our research to allow for more elements (25) and species (250) and to adapt its input and output to our needs. The phase studies using EPM and XRD on cross-sectioned crucibles were important in establishing the thermodynamic data base for our modified SOLGASMIX code. The phase data showed that three condensed phases (a liquid metal, a solid oxide, and a liquid oxide) are required in the SOLGASMIX calculations. In addition, they showed that the liquid and solid zirconates and silicates of Sr, Ba, and La play an important role in the chemistry of these elements in core-concrete mixtures at high temperatures. Thermodynamic data for these compounds were, therefore, included in the data base.

The experimental data and SOLGASMIX calculations were used to estimate the Sr, Ba, La, and U release and the total mass release during the molten core-concrete interaction (MCCI) phase of a severe reactor accident. Although our calculations of release fractions ignore the changes in temperature and composition of the core-concrete mixtures that are expected to occur as a reactor accident progresses, we believe that they are reasonable because the temperature and reducing power of the gas are comparable to the conditions expected in a severe reactor accident.³

⁷G. Eriksson, *Chemica Scripta* 8, 100 (1975).

⁸T. M. Besmann, *SOLGASMIX-PV, A Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems*, Oak Ridge National Laboratory Report ORNL/TM-5775 (1977).

To calculate the release for a hypothetical reactor accident, we divided the amount of each element transported by its initial inventory in the sample and multiplied by 100 to give the percent released to the gas. This percentage was multiplied by the number of moles of gas (CO_2 plus H_2O) that would have evolved from the concrete as it decomposed and was then divided by the number of moles of gas (0.6 mol) used in our experiments. Additionally, the total mass transported was converted to a release fraction as a percent of the initial mass of uncalcined concrete, doped urania, and zirconia.

3. Results and Discussion

The results of the release determined from the experimental and SOLGASMIX values are plotted for the three concrete types in Fig. V-1. The measured release fractions for Sr, Ba, and La are less than 1% for the limestone concrete (7.13 wt % SiO_2), and they are further reduced as the silica content of the concrete is increased (to 28.27 and then 68.99 wt % SiO_2). The uranium release shows little sensitivity to concrete type. This result is reasonable since the urania was a major fraction of the samples and forms no compounds with silica or zirconia. The curves in Fig. V-1 are smooth fits to the SOLGASMIX calculations for the three concrete types. For lanthanum, the calculations deviate from the measurements by the greatest amount (up to a factor of 40). We believe that the data in SOLGASMIX are poorest for lanthanum because the thermodynamic values for lanthanum silicates and lanthanum zirconate were obtained by extrapolating from values calculated for barium silicates and zirconates. The SOLGASMIX calculations are within a factor of four of the measurements for Ba and Sr and within a factor of two of the measurements for U and total mass. We consider this to be good agreement.

Figures V-2 through V-4 show smooth curves through SOLGASMIX calculations for four values (-250, -350, -450, and -550 kJ/mol) of the partial molar free energy of oxygen and for the three concrete types. The experimental data, which are the same as in Fig. V-1, are plotted at the partial molar free energy of oxygen calculated by SOLGASMIX using the oxygen inventory of the sample plus gas. This free energy is close to the minimum for the mass curve in each figure. No other partial molar free energy of oxygen would have resulted in a better fit of SOLGASMIX calculations to the experiments. For example, the partial molar free energy of oxygen in the inlet gas, -550 kJ/mol, leads to very high calculated releases for Ba, Sr, La, and total mass, as indicated in Figs. V-2 to V-4. This value is seen to be a particularly poor representation of the experimental data.

A significant feature of the gas-phase chemistry is the change in partial molar free energy of oxygen from the inlet-gas value (-550 kJ/mol) to the equilibrium value over the sample. The calculated equilibrium value (-400 kJ/mol) is at the center of the horizontal axis in Fig. V-2, further to the left in Fig. V-3 (-376 kJ/mol), and even further to the left in Fig. V-4 (-333 kJ/mol). This shift toward the left is caused by increasing amounts of water vapor in the gas phase over the samples; the calculated values are about 12,000 ppm for the limestone concrete, 21,000 ppm for the limestone-sand concrete, and 57,000 ppm for the siliceous concrete.

Fig. V-1. Release of Sr, Ba, La, U, and Total Mass from Mixtures of Urania, Zirconia, and Three Concretes at 2400 K (limestone concrete, 7.13 wt % SiO_2 ; limestone-sand concrete, 28.27 wt %; siliceous concrete, 68.99 wt % SiO_2)

Fig. V-2. Release of Sr, Ba, La, U, and Total Mass from Mixtures of Urania, Zirconia, and Limestone Concrete at 2400 K

Fig. V-3. Release of Sr, Ba, La, U, and Total Mass from Mixtures of Urania, Zirconia, and Limestone-Sand Concrete at 2400 K

Fig. V-4. Release of Sr, Ba, La, U, and Total Mass from Mixtures of Urania, Zirconia, and Siliceous Concrete at 2400 K

The reaction responsible for increasing amounts of water with increasing amounts of silica in the sample is reduction of the silica by hydrogen to form silicon monoxide. This effect tends to suppress the release of Sr, Ba, and La with increasing silica concentration. The high levels of water vapor calculated by SOLGASMIX to be in equilibrium with the samples were balanced by large amounts of species such as Na(g), Mg(g), SiO(g), and K(g). These species reacted with the water vapor during the condensation process to form oxides and hydroxides so that the exit gas stream contained less than 10 ppm H₂O. Thus, it is appropriate to include in the mass release nearly all the oxygen from the water vapor that is present at 2400 K in equilibrium with the samples.

The SOLGASMIX calculations indicated that the dominant gas-phase species in the limestone-concrete experiment were Sr and SrOH for strontium, Ba and BaO for barium, LaO for lanthanum, and UO₂ and UO₃ for uranium. In the limestone-sand concrete experiment, they were Sr and SrOH for strontium; Ba, BaO, and BaOH for barium; LaO for lanthanum; and UO₂ and UO₃ for uranium. In the siliceous concrete experiment, they were Sr, SrOH, and Sr(OH)₂ for strontium; BaO, BaOH, and Ba(OH)₂ for barium; LaO and La(OH)₂ for lanthanum; and UO₂ and UO₃ for uranium. The hydroxides of Sr, Ba, and La thus increased in concentration as the partial molar free energy of oxygen became more positive.

4. Conclusions

We conclude that the releases of Sr, Ba, La, and U in a severe reactor accident as described here will be less than 1% of their inventory. This is as low as, or lower than, the source-term values in the Reactor Safety Study^{1,2} and disagrees with the much higher values proposed in a more recent study.³ We further conclude that aerosol release will be about 0.5% of the total core-concrete mass.

Our results also indicate that the release of the refractory fission products tends to be suppressed by shifts in the partial molar free energy of oxygen in the gas phase toward more positive values as a result of reactions between the gas phase and the core-concrete mixture and formation of silicates and zirconates of the refractory fission products in the condensed oxide phases.

During the MCCI phase of a severe reactor accident, an oxide phase (concrete, urania, and zirconia) will lie over a metallic phase containing zirconium and stainless steel.⁴ Our work led us to conclude that the gas emanating from this molten core-concrete mixture will have a partial molar free energy of oxygen that is in equilibrium with the overlying oxide phase. The recommended calculational procedure is to assume that the gas (H₂O and CO₂ arising from decomposition of the concrete basemat) is first equilibrated with the metallic phase (reducing most of the H₂O and CO₂ to H₂ and CO) and then with the oxidic phase (partially oxidizing the H₂ and CO to H₂O and CO₂). This approach, which leads to low calculated release fractions for Ba, Sr, and La, has been explored in other recent theoretical work,^{5,6} although the details of the calculations differ in some respects.

Accurate source-term calculations are not yet possible with the existing thermodynamic data base. Needed refinements include measurements of high-temperature

thermodynamic properties for liquid and solid silicates and zirconates of the alkaline earths and rare earths, as well as improved calculational methods for predicting the relative amounts of solid-oxide and liquid-oxide phases. Currently, the calculations predict more solid oxide than is found experimentally; minor changes in the free energy data base may correct this problem. The release of certain radiologically important fission products (particularly Te, Ru, Ce, and Pu) from core-concrete mixtures was not addressed in this study; transpiration studies of these elements are also needed to understand their behavior in a severe reactor accident.

B. *Thermophysical Properties of Metal Fuels*

Measurements and calculational analyses are being performed to provide needed information on the thermodynamic and transport properties of Integral Fast Reactor (IFR) fuels. A summary is given below of our work on (1) fuel-cladding compatibility, (2) the U-Pu-Zr phase diagram, and (3) phase relations in the U-Fe system.

1. Fuel-Cladding Compatibility

An important area in the IFR development is chemical interaction between the U-Pu-Zr alloy fuel and the steel cladding. Because there are low melting eutectics in the U-Fe and Pu-Fe systems, cladding integrity could be compromised by formation of liquid phases during irradiation of fuel. As part of our investigation of fuel-cladding compatibility, we performed differential thermal analysis (DTA) experiments with several mixtures of U-Pu-Zr fuel and stainless steel cladding alloys (HT9, D9, and 316). The compositions for the fuel-cladding mixtures were chosen to yield a nearly constant fuel (U + Zr + Pu) atom fraction of about 0.5 in each mixture, which is the ratio of fuel to cladding in a section of an actual fuel pin. Fuels containing U-10 wt % Zr and U-10 wt % Zr plus 8, 19, or 26 wt % Pu were tested. Each fuel-cladding mixture was heated at 10°C/min to about 1570°C in a yttria crucible, after which several cooling/heating cycles were initiated at various rates.

Overall, similar DTA results were obtained with the various mixtures that we studied. Figure V-5 gives the DTA curves on heating and cooling for a U-10 wt % Zr/HT9 mixture. At about 600-700°C on initial heating, small peaks in the DTA curve (uppermost one in Fig. V-5) corresponding to solid-state transitions in the fuel were seen. Then at about 1200°C, there was a large exothermal peak, which is indicative of a reaction forming more stable products (probably an Fe₂Zr-like phase). On subsequent cooling, the DTA curve indicated primary precipitation in the neighborhood of 1220°C. At about 700°C, there was a marked DTA peak, which we attribute to a freezing transition (i.e., liquid → solid and liquid). The appearance of this peak suggests significant subcooling. Transitions which would be expected at intermediate temperatures were difficult to identify unequivocally from these data. As shown by the bottom curve in Fig. V-5, the peak indicating sample melting was sharp and narrow and suggested formation of a eutectic. As the plutonium content increased, this major peak became wider and smaller. It appears that the temperature range between solidus and liquidus had progressively increased.

Of primary interest to IFR development is the so-called "onset-of-melting" temperature found from heating curves. We found that this temperature fell as the plutonium

content of the fuel increased. Reproducibility of the values with repeated heating and cooling cycles was very good, typically within 2-4 °C. It is difficult to judge the absolute accuracy of these temperatures, however, and we estimate that our onset-of-melting temperatures are probably reliable to about ± 10 -20 °C, with the larger uncertainty being associated with the 19 and 26 wt % Pu fuels.

Fig. V-5.

Differential Thermal Analysis Curves for U-10 wt % Zr/HT9 Mixture (top curve, initial heating; middle curve, initial cooling; bottom curve, subsequent heating)

Scanning electron microscope (SEM) examination of the residues from these tests showed three types of precipitates, and the results qualitatively support the following reaction sequence: primary precipitation of a Fe_2Zr -like phase, followed by secondary precipitation of Fe_2U , followed by formation of a Fe_2U - FeU_6 eutectic. A matrix found in the SEM examination of these samples had a eutectic-like appearance and contained a phase with a very high uranium content, close to FeU_6 . The major peak found in the DTA curves is believed to correspond to a three-phase region of Fe_2U - Fe_2Pu , FeU_6 - FePu_6 , liquid in the phase diagram.

An evaluation of the applicability of these data to IFR development must await further experiments in which the rate of attainment of equilibrium is evaluated. For example, whole-pin heating tests, which will help define this rate, are planned.

2. U-Pu-Zr Phase Diagram

The chief source of information on the important U-Pu-Zr phase diagram is the work of O'Boyle and Dwight.⁹ There are significant uncertainties in their published diagrams,

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

however, and we have undertaken to improve this situation by a combination of phase diagram calculation and experimental measurement. Calculation of a ternary phase diagram requires thermodynamic functions for all phases existing in the three binary subsystems; the ternary phase diagram can be calculated from these functions. We have already completed an analysis of the U-Zr system¹⁰ and have begun a similar analysis of the Pu-U system. A recent assessment of the Pu-U system was published by Peterson and Foltyn¹¹; these authors, however, did not provide thermodynamic data adequate for phase diagram calculations.

In comparing the 500 °C isothermal section of the U-Pu-Zr phase diagram of O'Boyle and Dwight with the Pu-U phase diagram of Peterson and Foltyn, we found that a wide two-phase $\alpha + \zeta$ field in the former was absent in the latter. At about 500 °C that field extends roughly from 14 to 29 at. % Pu. It would be expected, therefore, that a much more extensive three-phase $\delta + \alpha + \zeta$ field would exist in the ternary phase diagram than is indicated by O'Boyle and Dwight. This region is of particular importance to IFR fuel development and represents just one area that should be investigated further.

In assessing the Pu-U system, we expanded our previous work on calculation of the solidus-liquidus in the U-Pu-Zr system.¹² The present evaluation essentially confirmed the earlier findings with only minor modifications. The main conclusion was that the published solidus-liquidus for the Pu-U¹¹ system is not consistent with the accepted enthalpy of fusion of uranium. It is known that, for a melting transition in an alloy (A-B), as the composition approaches a pure component (X_B), the difference between the slopes of the liquidus and solidus curves is determined by just the enthalpy of fusion, ΔH_f° , and the melting point, T_f , of that component. That is,

$$\lim_{X_B \rightarrow 1} \left[\frac{dX_B^\ell}{dT} - \frac{dX_B^s}{dT} \right] = \frac{\Delta H_f^\circ}{RT_f^2} \quad (1)$$

where the superscripts ℓ and s indicate liquidus and solidus, respectively. Our calculated Pu-U diagram shows the correct limiting slopes if we accept the value for the enthalpy of fusion of uranium given by the International Atomic Energy Agency.¹³

The Pu-U system is unusual in that, in addition to the large number of phase transitions in the constituent elements, there are two intermediate phases, η and ζ , which have very broad fields in the phase diagram. We are currently developing an approach for thermodynamic analysis of the unusual features of this system.

¹⁰L. Leibowitz, R. A. Blomquist, and A. D. Pelton, J. Nucl. Mater. **167**, 76 (1989).

¹¹D. E. Peterson and E. M. Foltyn, Bull. Alloy Phase Diagrams **10**, 160 (1989).

¹²L. Leibowitz, E. Veleckis, R. A. Blomquist, and A. D. Pelton, J. Nucl. Mater. **154**, 145 (1988).

¹³F. L. Oetting, M. H. Rand, and R. J. Ackermann, *The Chemical Thermodynamics of Actinide Elements and Compounds*, Part I, *The Actinide Elements*, International Atomic Energy Agency, Vienna (1976).

3. Phase Relations in Fuel-Cladding Systems

Considerable effort has been expended in analysis of fuel-cladding compatibility (Sec. V.B.1). We are also directing our efforts toward gaining a more thorough understanding of the phase relations involved in fuel-cladding systems. Our initial experiments were directed toward the important U-Fe binary system. In the published phase diagram,¹⁴ the liquidus curve over much of the diagram is interpolated; indeed, there are no data whatever in the literature defining that curve. The chief sources of experimental data for the U-Fe diagram are given in the literature.¹⁴⁻¹⁶

Our initial efforts involved DTA studies of a U-Fe mixture containing 50 at. % U in a beryllia crucible. That container material was chosen because it was used with apparent success by Gordon and Kaufmann.¹⁵ We found a very sharp eutectic peak in our DTA curve at the same temperature as had been reported in the literature (725°C),¹⁷ but we observed that the initial liquidus temperature was quite high compared with the estimated liquidus and, more importantly, increased as the sample underwent heating/cooling cycles. After considerable work with this container material, we changed to a yttria DTA crucible (because of its greater stability at high temperatures) and prepared a new alloy sample of the same composition. We found a stable liquidus temperature with cycling but the eutectic peak appeared at 722°C. Although the liquidus peak was very small, the temperature was clearly about 60-70°C higher than the published diagram indicates. In view of these conflicting findings, we are proceeding with an examination of several other U-Fe alloy compositions and with SEM examination of the residues from these tests.

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 (e.g., Li_2O , LiAlO_2 , Li_4SiO_4 , Li_2ZrO_3) as breeder material. We are also conducting several fusion reactor design studies and neutron dosimetry and damage analysis of fusion materials in neutron facilities.

1. Development of Ceramic Tritium Breeder Blanket

Our effort in developing the breeder blanket consists of desorption measurements needed to describe tritium release, computer modeling of tritium release, and experimental determinations of tritium mass transport.

¹⁴T. B. Massalski, *Binary Alloy Phase Diagrams*, American Society for Metals, Metals Park, Ohio (1986).

¹⁵P. Gordon and A. R. Kaufmann, *Trans. AIME* **188**, 182 (1950).

¹⁶J. D. Grogan, *J. Inst. Metals* **77**, 571 (1950).

¹⁷G. G. Michaud, *Can. Metal. Q.* **5**, 355 (1966).

a. Desorption Measurements for the $\text{LiAlO}_2\text{-H}_2\text{-H}_2\text{O(g)}$ System

The objective of this effort is to describe the kinetics of desorption of $\text{H}_2\text{O(g)}$ and $\text{H}_2\text{(g)}$ from ceramic tritium breeders to enable designers and modelers to predict the retention and release of tritium. The behavior of the gaseous species must be determined individually and interactively with each other and with the breeder substrate. We are employing temperature programmed desorption (TPD) to determine the activation energies of desorption of $\text{H}_2\text{O(g)}$ and $\text{H}_2\text{(g)}$ and other kinetic parameters that are needed to describe the release processes of a tritium breeder.

An apparatus for TPD measurements with a stainless steel sample tube was designed and constructed. To allow clear separation of effects in the subsequent analysis, we performed blank experiments to gain information on the behavior of the steel sample tube in the absence of a LiAlO_2 sample when a helium gas containing $\text{H}_2\text{O(g)}$ and H_2 passes through at high temperature. Figure V-6 shows the evolution rate determined for a temperature programmed reaction between the steel sample tube and a gas mixture of He-100 ppm H_2O -500 ppm H_2 . At the moment when this mixture started to flow through the tube (after ~ 2 min), a 200 to 700 °C linear temperature ramp was started. It is evident that with increasing temperature, several processes proceed in a complex way. These processes include consumption of H_2O and dissolution and production of H_2 . For TPD measurements on a sample of breeder material and with a gas containing both H_2O and H_2 , these tube-related processes would be superimposed on processes relating to the sample itself. Substantial complications in the interpretation of the data would arise. The results from the blank experiments are a significant confirmation for what had been suspected previously, namely, that tritium release measurements, either in-reactor or out-of-reactor, must take into account the effect of the system environment on the measured species.

Fig. V-6.

Temperature Programmed Reaction Spectrum of Stainless Steel Sample Tube for a He- H_2O - H_2 Gas Mixture and a Temperature Ramp from 200 to 700 °C

To proceed expeditiously, we concentrated immediate attention on the simplest course: to measure effects with water alone as adsorbate and to minimize or eliminate effects from the steel by stabilizing its surface in an oxidized condition. By treating the sample tube with 200 ppm H_2O in He for a sufficient time at temperatures up to 400°C , we were able to obtain featureless TPD spectra (i.e., no desorption peaks) for temperature ramps of 200 to 600°C . This indicates that one can stabilize the sample tube (in the absence of added H_2) so that it will not introduce spurious TPD peaks under the same conditions.

The TPD spectrum for a LiAlO_2 sample (0.77 g) in a fresh steel tube indicated a reaction between evolved $\text{H}_2\text{O}(\text{g})$ and the unstabilized steel surface. After the sample was dried for two days at 200°C in helium, the TPD data for a 200 to 700°C ramp showed that little H_2O was evolved below 600°C ; no reaction with the steel was evident from the fact that the H_2 curve in the TPD spectrum remained at baseline level. However, on approaching 700°C , the TPD data indicated that substantial H_2O was released and substantial H_2 formed. Our subsequent TPD runs were done in the lower temperature region (200 to 500°C) and with stabilized tube conditions, as evidenced by baseline H_2 traces. The data collected were used for estimating the activation energies for H_2O evolution from LiAlO_2 .

We obtained TPD spectra for LiAlO_2 samples that had been equilibrated with 200 ppm $\text{H}_2\text{O}(\text{g})$ at temperatures of 200, 300, 400, and 500°C . Only a few selected spectra are discussed here. Questions of possible peak overlap remain to be resolved for all spectra.

Figure V-7 shows the TPD spectrum recorded for LiAlO_2 equilibrated with 200 ppm $\text{H}_2\text{O}(\text{g})$ at 200°C , followed by a temperature ramp from 200 to 700°C at a rate of 5.08 deg/min. The peak at 352°C appears reasonably symmetric, though with a somewhat rounded tip that might hide two close peaks that cannot be resolved at the temperature ramp rate used. The desorption activation energy was determined by a method employing the width of the TPD peak at half-peak height.¹⁸ A fairly low value for the desorption activation energy (63 kJ/mol) was calculated, a value that might be associated with a weak chemisorption.

For the 400°C equilibration of LiAlO_2 , if one assumes that the TPD peak represents a single phenomenon, the calculated desorption activation energy is approximately that reported by Kudo (122 kJ/mol) for the decomposition of LiOH [i.e., $\text{H}_2\text{O}(\text{g})$ evolution] from Li_2O breeder material.¹⁹ In Kudo's case, the decomposing LiOH produced a Li_2O surface with scattered OH^- groups so that the fraction of surface covered by OH^- , θ , steadily decreased from 1. In the present work, the initial θ was roughly 0.05, as estimated from earlier adsorption isotherm data.²⁰ It appears reasonable to explore further the hypothesis that, because of this apparent similarity with Li_2O , some sites on LiAlO_2 resemble sites on Li_2O in their H_2O -evolving behavior.

¹⁸J. L. Falconer and J. A. Schwarz, Catal. Rev. Sci. Eng. **25**, 141 (1983).

¹⁹H. Kudo, J. Nucl. Mat. **87**, 185 (1979).

²⁰A. K. Fischer and C. E. Johnson, Fusion Tech. **15**, 1212 (1989).

Fig. V-7.

Temperature Programmed Desorption Spectrum for LiAlO_2 Sample Equilibrated at 200°C with Helium Containing 200 ppm $\text{H}_2\text{O}(\text{g})$ at 1 atm (0.1 MPa). Temperature ramp is 200 to 700°C gas at rate of 5.08 deg/min.

Only one TPD spectrum was recorded for a sample equilibrated at 500°C with 200 ppm H_2O . Though the peak was poorly defined, the peak width analysis suggested a desorption activation energy significantly higher than the ones above. If substantiated, this result would be consistent with our earlier adsorption isotherm measurements, which were interpreted as reflecting two adsorption processes, one with a high activation energy of adsorption.²⁰

Future work will focus on determining the effect of H_2 in the helium gas stream on the desorption rate of $\text{H}_2\text{O}(\text{g})$.

b. Tritium Transport Modeling for Ceramic Breeder Materials

The objective of this effort is to develop a computer model that will predict tritium release from neutron-irradiated lithium ceramics into a gas purge stream. Diffusion of tritium through the grain and desorption from the grain surface have been considered the important processes controlling this tritium release. Recently, our modeling effort has focused on the desorption process, which consists of a surface reaction leading to a surface-bound molecule, followed by desorption of the surface-bound molecule into the gas phase. Reactions which are considered as likely candidates and lead to desorption of tritium from the surface are:

and

Of these, the reactions on the left are first order with respect to tritium, while those on the right are second order with respect to tritium; this difference arises because of the presence of impurity hydrogen in the solid and/or purge gas.

Desorption was determined to be the rate-limiting process in some earlier tritium release experiments. Little is known about the tritium desorption process despite its importance in determining the merits of candidate breeder materials. In most studies, tritium desorption has been treated as occurring from one site with a single desorption activation energy. However, numerous recent experiments suggest that there are several sites for desorption, each with a corresponding activation energy. For example, in the LILA-1 experiment an increase in test temperature during several runs resulted in a small decrease in tritium release from the LiAlO_2 material, followed by an increase to a maximum then a decay to steady state.²¹ Similar tritium release curves were observed for release from Li_2O in the CRITIC experiment.²² This type of tritium release behavior could not be explained using a diffusion-desorption release model with one desorption activation energy, but could be modeled with a desorption activation energy which varies with surface coverage by adsorbed hydrogen.²³

For first-order desorption into a vacuum (or into a rapidly flowing purge stream), the pressure of the desorbing species in the purge stream from one site with desorption activation energy E_a can be calculated as follows²⁴:

$$P = (\nu/C) \exp\{-\nu \beta (E_a/R)I - E_a/RT\} \quad (4)$$

where ν = desorption preexponential term in equation for desorption rate constant
 $[k = \nu \exp(-E_a/RT)]$
 β = heating rate
 E_a = desorption activation energy
 C = initial concentration
 T = temperature
 R = gas constant

²¹M. Briec and E. Roth, "Tritium Extraction Mechanisms from Lithium Aluminates During In-Pile Irradiation Experiments," Proc. of Specialists' Workshop on Modeling Tritium Behavior in Fusion Blanket Ceramics, April 23-24, 1987, Chalk River, Canada, pp. 28-57 (1987).

²²J. M. Miller, R. A. Verrall, D. S. MacDonald, and S. R. Bokwa, "The CRITIC Irradiation of Li_2O -Tritium Release and Measurement," presented at the Third Topical Meeting on Tritium Technology in Fission, Fusion, and Isotopic Applications, May 1-6, 1988, Toronto, Canada.

²³J. P. Kopasz, S. W. Tam, and R. A. Verrall, Fusion Tech. **15**, 1212-1216 (1989).

²⁴A. W. Smith and S. Aranoff, J. Phys. Chem. **62**, 684-686 (1958).

In addition,

$$I = \exp(-\epsilon) [1 - (2!/\epsilon) + (3!/\epsilon^2) - (4!/\epsilon^3) + \dots]/\epsilon^2 \quad (5)$$

where $\epsilon = E_a/RT$. For second-order desorption,²⁴

$$P = \frac{\nu \exp(-E_a/RT)}{C(E_a/R) (1 + \nu \beta I E_a/R)^2} \quad (6)$$

The total release at any time would be the sum of the release over all the active desorption sites. With Eqs. 4-6, one can calculate the tritium release profile as a function of time or temperature given the initial tritium concentration, desorption activation energies, preexponential terms, and the heating rate. Moreover, using the data from constant-rate heating experiments, one can estimate the desorption activation energies from the temperatures at which the maxima in plots of tritium release versus temperature occur. For experiments where the flow rate and heating rate are such that readsorption does not interfere, if the desorption is first order, then an estimate of the activation energy can be obtained from the following²⁵:

$$E_a = RT[\ln(\nu T/\beta) - 3.46] \quad (7)$$

Using an estimate of $\nu = 1 \times 10^8$ and data from Tanifuji et al.,²⁶ we obtained estimates for the activation energies of desorption of tritium from Li_2O . These estimates were then used to calculate the tritium release as a function of temperature from Eq. 4 or 6. Figure V-8 shows the tritium release calculated from our multiple desorption site model and that observed by Tanifuji et al. As can be seen, the agreement between the calculated and observed release is excellent.

It is of interest to compare our estimates of desorption activation energies with some reported in the literature. Our estimates of E_a for desorption of tritium from Li_2O are 140.6, 149.4, 162.8, 178.2, and 186.2 kJ/mol. The first of these estimated activation energies, 140.6 kJ/mol, is expected to be for desorption from a surface with a relatively high surface coverage. This value is in reasonably good agreement with the desorption activation energy reported by Kudo and Okuno (129.7 kJ/mol)²⁷ and Quanci (130.6 kJ/mol).²⁸ The second

²⁵D. A. King, *Surf. Sci.* **47**, 384-402 (1975).

²⁶T. Tanifuji, K. Noda, S. Nasu, and K. Uchida, *J. Nucl. Mater.* **95**, 108-118 (1980).

²⁷H. Kudo and K. Okuno, *J. Nucl. Mater.* **101**, 38-43 (1982).

²⁸J. Quanci, "Tritium Breeding and Release-Rate Kinetics from Neutron-Irradiated Lithium Oxide," PhD Thesis, Dept. of Chemical Engineering, Princeton University (January 1989).

estimated E_a , 149.4 kJ/mol, is expected to correspond to desorption from a slightly more energetic site and is also in good agreement with data reported by Quanci (152.2 kJ/mol).²⁸

Fig. V-8.

Tritium Released from Li_2O as Observed by Tanifuji et al. and Calculated from Multiple Desorption Site Model (Heating Rate = 10 K/min)

A similar estimate for desorption of tritium from Li_4SiO_4 was made by us using a data set from Skokan et al.²⁹ and another data set from Schauer and Schumacher.³⁰ We obtained six activation energies from each data set, ranging from 73.6 to 215.9 kJ/mol for the former and 83.3 to 218.8 kJ/mol for the latter. The agreement between the activation energies calculated from the two data sets was quite good, with a maximum deviation of <10 kJ/mol.

The effect on tritium release of doping Li_4SiO_4 ceramics with either aluminum or phosphorus was studied by Skokan et al.²⁹ Our computer modeling using their data has shown that the effects of doping, based on the most likely defects formed, are as follows: (1) creating a lithium vacancy leads to the availability of a new lower energy tritium desorption process and improves tritium release; (2) creating silicon vacancies decreases the availability of low energy desorption mechanisms and leads to poorer tritium release; and (3) creating lithium interstitials decreases the availability of low energy desorption mechanisms and leads to poorer tritium release.

²⁹A. Skokan, D. Vollath, H. Wedemeyer, E. Gunther, H. Werle, "Preparation, Phase Relationships and First Irradiation Results of Lithium Orthosilicate Doped with Al^{3+} and P^{5+} Ions," presented at 15th Symp. on Fusion Technology, September 1988, Utrecht, the Netherlands.

³⁰V. Schauer and G. Schumacher, "Study of Adsorption and Desorption of Water on Li_4SiO_4 ," to be published in J. Nucl. Mater.

The current estimates of desorption activation energies will be used to calculate the tritium release from in-pile release experiments. Relationships between purge gas chemistry, surface coverage, and desorption activation energies will be derived from laboratory experiments, in-pile experiments, and modeling efforts.

c. Tritium Mass Transport in Ceramic Breeder Materials

Lithium ceramics such as Li_2O are being investigated for use as tritium breeding materials, where the lithium in the breeder material is converted to tritium after reacting with a neutron. The tritium is usually released from the solid as T_2O and HTO . Within the solid breeder, tritium may also be found as LiOT , which may transport lithium (and tritium) to cooler parts of the blanket. This process may cause loss of lithium from the blanket, blocking of flow paths, and increase of the tritium inventory within the blanket. Laboratory studies have established the LiOH(g) pressure for reaction of $\text{Li}_2\text{O(s)}$ with water vapor.³¹ Since the pressure of LiOT and HTO or T_2O above Li_2O is essentially the same as that for reactions involving hydrogen (instead of tritium), we have investigated the transport of LiOH from the blanket material.

For our experimental runs, a fixed-bed system was assembled to obtain high gas velocities and good contact between the gas and the solid breeder at 850°C . In this arrangement, a silver-lined quartz tube was used to hold seven cylindrical Li_2O pellets (8-mm long, 5.3-mm dia) arranged in a close-packed configuration. The quartz tube assembly was placed in a clam shell furnace. Helium flowed through two rotometers, one through a water saturator and the other directly from a high-purity helium tank. The two helium streams were mixed and flowed into the silver-lined quartz tube containing the Li_2O pellets. Needle valves were adjusted to reduce the water partial pressure to 5×10^{-4} atm (~ 50 Pa). Total flow rates as high as $7000 \text{ cm}^3/\text{min}$ (STP) allowed us to reach gas velocities from 50 cm/s to 2600 cm/s at 850°C . The LiOH gas formed by reaction of the water vapor with Li_2O condensed in cooler regions of the silver tube.

After testing, the silver tube was soaked in water to remove the LiOH for chemical analysis. The pressure of LiOH was calculated from the lithium analysis results and the ideal gas law. The gas velocity was calculated from the total volume flow of helium per minute and the total effective areas of the regions between the pellets. For this calculation, effective diameters were computed from

$$d_{\text{eff}} = 4A/P_w \quad (8)$$

where d_{eff} is the effective diameter, A is the geometric area, and P_w is the area perimeter. The effective area is

³¹M. Tetenbaum and C. E. Johnson, J. Nucl. Mater. **120**, 213 (1984).

$$A_{\text{eff}} = \pi d_{\text{eff}}^2/4 \quad (9)$$

The total effective area was determined to be 0.166 cm^2 .

In the case of LiOH gas production from water vapor and lithium oxide, a two-step process is involved. Water vapor diffuses from the flowing helium to the lithium oxide, and then a reaction produces lithium hydroxide gas, which diffuses into the flowing helium. Each of these two steps is diffusion controlled. We assumed that the fractional saturation for the two steps, occurring simultaneously, can be calculated from the product of the fractional saturation of each step.

The fractional saturation of each step may be calculated from Darken,³² who derived formulas for calculating the fractional saturation of slabs, cylinders, and spheres for short times

$$F = 1.128 \sqrt{Dt}/L \quad (10)$$

and for long times

$$F = 1 - 10^{-[(Dt/L^2 + 0.0851)/0.933]} \quad (11)$$

where D is the diffusivity of LiOH or H_2O gas in helium, t is the residence time in seconds, and L is the half-thickness of the gas volume flowing past the lithium oxide. At 850°C the diffusivities calculated with Treybal's equations³³ are 6.22 and $6.98 \text{ cm}^2/\text{s}$ for LiOH and H_2O , respectively. The value of L was determined to be 0.191 cm . For flow velocities of 50 to 2600 cm/s , we calculated that the residence times range from 16 to 0.31 ms . Fractional saturations for LiOH and H_2O were calculated with Eq. 11 for residence times greater than 5 ms and Eq. 10 for times less than 5 ms . These fractional saturations apply to a single-step process. The two-step process is assumed to be the product

$$F_{\text{prod}} = F_{\text{H}_2\text{O}} \cdot F_{\text{LiOH}} \quad (12)$$

³²L. S. Darken and R. W. Gurry, *Physical Chemistry of Metals*, McGraw-Hill, New York, p. 447 (1953).

³³R. E. Treybal, *Mass-Transfer Operations*, 2nd Ed., McGraw-Hill, New York, p. 25 (1968).

The calculated fractional saturation products varied from 1.0 at a gas velocity of 50 cm/s to 0.07 at 2600 cm/s. These fractional saturations compare favorably with the measured LiOH concentration produced from reaction of water vapor with Li_2O during the residence time divided by the LiOH concentration at equilibrium.

Data were taken from Noda's paper³⁴ to calculate the degree of LiOH gas saturation when helium with 500 ppm water is flowed through a cylinder (10-cm long, 2-cm dia) packed with 5-mm dia spheres of Li_2O . Noda's residence times varied between 1.7 and 0.017 s. Our data at low gas velocities (<100 cm/s) produced degrees of saturation in general agreement with Noda for comparable residence times. Since small Li_2O cylinders (8 mm in length) were used in our experiments, we were able to achieve very short residence times with substantial undersaturation at the highest gas velocities. There was reasonable agreement between Noda's measurements and our calculations, both of which indicated that the helium in his experiments was fully saturated with LiOH gas.

This work established conditions for calculating LiOH undersaturation in helium as a function of the dimensions of the Li_2O purge channels and the velocity of the purge gas. This calculation will allow us to model the degree of saturation for various flow rates and channel dimensions with tritium release experiments.

2. Design Studies of Aqueous Lithium Salt Blanket

The International Thermonuclear Experimental Reactor (ITER) is a tokamak reactor which will be used to test components for a prototype fusion power reactor. Its development is a joint project among the European Economic community, Japan, the United States, and the Soviet Union. The development of this reactor is in the preconceptual design phase. To assist in this design effort, we have examined the technical requirements for an aqueous lithium salt blanket (2 M LiOH or LiNO_3) in which tritium fuel is bred. We have quantified the effects of radiolysis, electrolytic decomposition, and corrosion of structural steel and beryllium (neutron multiplier) within the salt solution.

Our earlier work³⁵ showed that gas products from radiolysis can produce a high pressure in the blanket. To minimize radiolysis, a hydrogen cover gas is required, as is a high salt flow rate. In addition, a high capacity recombiner is needed to recombine radiolysis products. Electrolytic decomposition occurs because of ionic fluid flow in the magnetic field. To help minimize the rate of steel corrosion arising from this effect, we earlier determined that the blanket channels must be <1 cm in diameter and the salt flow rate should be <4 m/s.³⁵ In the past year, we examined corrosion of structural steel for the aqueous blanket to determine the species present. In addition, a tritium recovery system was designed. The design is complex for an aqueous blanket because of the presence of radiolysis products, the salt, and large volumes of water.

³⁴K. Noda, "Mass Transfer and Compatibility of Lithium Oxide," presented at ITER Specialist's Meeting on Materials Data Base, August 22-26, 1988, Germany.

³⁵M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, pp. 116-117 (1989).

a. Corrosion of Steel

The thermodynamic code FACT³⁶ was used to determine the corrosion products in an operating 2 M LiOH aqueous blanket at equilibrium. The assumed blanket conditions were temperature of 60°C, pressure of 2 MPa (20 atm), and steel corrosion rate of 50 $\mu\text{m/yr}$. At steady state, iron and chromium would be present at 2×10^{-6} and $<1 \times 10^{-6}$ mol/L, respectively. (Other metals in the steel alloy were ignored for this approximation.) The major radiolysis product included was 0.05 mol hydrogen.

The calculated results from the FACT code indicated that a gas phase, an aqueous phase, and two solids are present at equilibrium. The gas phase contains hydrogen and water. In the aqueous phase, the species present are LiOH (1.02 mol/L), Li^+ and OH^- (0.98 mol/L), H_2 (0.016 mol/L), FeOH^+ (4.9×10^{-11} mol/L), and H^+ (9.2×10^{-14} mol/L). The two solids identified were $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ and Fe_3O_4 , both at 5×10^{-7} mol/L. The magnitude of these two solids indicates the amount of solid formed due to steel corrosion. The presence of these solids would require extensive filtering of the LiOH solution to prevent plugging of blanket channels.

b. Tritium Recovery System

We developed a design for a tritium recovery system that could be used with the aqueous LiOH solution blanket. We included a recombiner and a pressurization/depressurization system to handle radiolysis products. Purification units were included to handle the removal of corrosion products. All of the units required to process the aqueous salt solution and recover the tritium are shown in Fig. V-9. One can follow the flow paths for the salt solution, purified water, and hydrogen in this figure.

Fig. V-9. Flowsheet for Aqueous Salt Solution Blanket System

³⁶G. W. Bole, A. P. Pelton, and W. T. Thompson, *FACT User's Instruction Manual*, McGill University/Ecole Polytechnique, Montreal (1979-1984).

As a point of reference, let us start at the blanket (left-hand side of figure). The salt solution leaves the blanket and is passed to a combination recombiner/depressurizer unit to recombine the radiolysis products and reduce the pressure from 15 atm to 1 atm (1.5 MPa to 0.1 MPa). The salt solution is then passed to a flash evaporator to remove the salt from the water stream from which tritium will be extracted. The liquid phase remaining is a concentrated salt solution, containing radioactive corrosion products. This salt solution is passed through ion exchangers and a filter to remove the corrosion products. The purified solution enters a salt mixer in which nontritiated water is added to dilute the salt solution before it passes to the heat exchanger. After the heat exchanger, the salt solution is again pressurized and reenters the blanket.

The vapor from the flash evaporator is condensed (Condenser No. 1); the water is purified by ion exchange columns which remove ionic species carried from the flash evaporator. The purified water is then passed to a water distillation unit in which the tritium content in the water is increased from 3.7×10^{11} Bq/L to 3.7×10^{13} Bq/L. The concentrated tritiated water is passed to a vapor phase catalytic exchange unit (VPCE) in which the tritium in the water is exchanged with the protium in a hydrogen gas stream. Since this exchange process is not as favorable in this direction, the tritiated hydrogen stream is not as concentrated as was the input tritiated water stream. To remove the tritium from the molecular hydrogen stream, a cryogenic distillation unit is needed. Prior to this unit, the gas is dried to remove entrained water and passed through molecular sieve beds to remove other impurities. The species leaving the cryogenic distillation unit are molecular tritium and molecular hydrogen. The tritium is transferred to the fueling system; the protium is recycled to the VPCE unit. The entrained water is returned to the water distillation unit.

The total throughput for this system was calculated to be 45 g/day tritium, 1.5 kg/day deuterium, and 320 kg/day protium (water distillation factor = 100, cryogenic distillation factor = 1000). The tritium bred in a 880 MW fusion reactor in which the breeding ratio is one would be approximately 150 g/day. Only 30% of this tritium would be collected (45 g/day) because the reactor is expected to be operated for less than 30% of the year. Thus, if the tritiated water concentration is allowed to rise while the reactor is operational (i.e., acting as a storage medium for the unprocessed tritium), and if this processing system is operated >95% of the time, then this system is sized correctly. However, if the processing system is required to collect 150 g/day tritium, then the VPCE unit would have to have three times the protium throughput (970 vs. 320 kg/day) since its efficiency is directly proportional to the protium flow. In addition, the cryogenic unit would have to have three times the refrigerant capacity. No further design studies of the aqueous salt blanket are planned.

3. Design of Breeding Blanket Interface

The Breeding Blanket Interface (BBI) is that system which performs the necessary processing and recycle of the tritium recovered from a fusion reactor blanket. Although considerable attention has been given to studies of tritium breeding and recovery and also to many aspects of tritium processing, very little work had been done on the BBI. Therefore, a study was initiated to define the necessary components of this BBI system and to plan for testing such an integrated system of components in the Tritium Systems Test Assembly (TSTA) at Los

Alamos National Laboratory. This possible upgrade is the subject of an ongoing study, begun in July 1987, involving Los Alamos National Laboratory (LANL), the Japan Atomic Energy Research Institute (JAERI), and Argonne National Laboratory (ANL).

The first phase involved determining the conditions of the product tritium output streams for various blankets. Blankets investigated included the three major blanket types (liquid metal, solid breeder, aqueous salt solution). The conditions determined included temperature, flow rate, chemical composition, and concentrations of impurities and radionuclides. We developed a methodology to systematically evaluate impurity source terms and to follow the transport of impurities and radionuclides through the paths of the system to the blanket output stream. We have performed such analysis for the three blanket types. Results for the liquid metal blanket analysis were reported previously.^{37,38} For the solid breeder blanket, a very detailed study of probable impurity levels was performed, and the data were directly used by the U.S. design team for the ITER to calculate blanket activation and afterheat in the ITER blanket. For the aqueous salt solution blanket, our studies uncovered and/or quantified a number of problems such as radiolysis, electrolysis, and corrosion (see Sec.V.C.2).

We recently completed phase two, preconceptual design of the BBI for two of the blanket types: aqueous salt solution and solid breeder blanket. A summary of the major design features of the two BBI systems is given in Table V-1.

Table V-1. Features of BBI Reference Design for Two Blanket Types

	Blanket Type	
	Aqueous Lithium Salt	Solid Breeder
Breeder material	LiOH (aqueous)	Li ₂ O
Neutron multiplier	Be	Be
Structural material	Stainless Steel (SS)	SS
Coolant	Aqueous Salt Solution	H ₂ O
Tritium enrichment method	Water distillation	none
Tritium enrichment factor	100	---
Tritium recovery method	VPCE ^a	He purge
Tritium carrier	Aqueous Salt Solution	He + H ₂
Tritium concentration in carrier	10 Ci/L (average)	0.1 %
H/T ratio in blanket	2.0 x 10 ⁵ (average)	100
H/T ratio in BBI inlet	2000	100
Tritium capacity	45 g/day	150 g/day
Scale factor for TSTA/BBI	0.010	1.0
Tritium flow rate for TSTA/BBI	0.45 g/day	150 g/day
Protium flow rate for TSTA/BBI	3000 g/day	5000 g/day

^aVPCE = Vapor Phase Catalytic Exchange unit.

³⁷R. G. Clemmer, P. A. Finn, L. R. Greenwood, T. L. Grimm, D. K. Sze, J. R. Bartlit, J. L. Anderson, H. Yoshida, and Y. Naruse, "The Requirements for Processing Tritium Recovered from Liquid Lithium Blankets: the Blanket Interface," Argonne National Laboratory Report ANL/FPP/TM-216 (March 1988).

³⁸R. G. Clemmer, T. L. Grimm, P. A. Finn, D. K. Sze, L. R. Greenwood, J. R. Bartlit, J. L. Anderson, H. Yoshida, and Y. Naruse, "The Blanket Interface to TSTA: the Requirements for Liquid Lithium Blanket Processing," presented at Third Topical Meeting on Tritium Technology in Fission, Fusion, and Isotopic Applications, May 1-6, 1988, Toronto, Canada.

For the reference designs, we prepared a development schedule and estimated costs. Owing to the current budgetary situation, funds are not available to pursue both reference designs. Therefore, current efforts involve studying the available options to identify the best choice at minimum cost. Various methods of reducing the development costs are being evaluated, including the following: (1) concentrate the BBI effort on the solid breeder blanket alone (Li_2O); (2) evaluate various testing scenarios in an effort to minimize the TSTA/BBI budget requirements, yet maintain the stated programmatic goals; (3) evaluate reducing the scope of the testing and/or the possible range of experimental variables; and (4) select (with input from ANL, LANL, and JAERI) the most attractive option and define an experimental program for that option.

4. Dosimetry and Damage Analysis

The goal of this effort is to develop techniques and to measure nuclear properties needed to determine damage from irradiation exposures for fusion materials. In 1989, neutron fluences were measured and radiation damage was calculated for irradiations in the Oak Ridge Research Reactor and High Flux Isotopes Reactor, both at Oak Ridge National Laboratory, and in the Omega West Reactor at Los Alamos National Laboratory. Neutron fluences were determined by a multiple foil activation technique. Radiation damage calculations included determination of atomic displacements, gas production, and other transmutations. These calculations were done with our SPECTER computer code, which has been extended to include more elements and compounds (such as ceramic breeders, insulators, and alloys). Calculations were also completed for the elements yttrium and barium so that damage rates could be determined for the new high-temperature superconductor material $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$.

Our nuclear data measurements have focused on the production of long-lived isotopes in fusion reactor materials. These data are needed for the assessment of waste disposal and reactor maintenance applications. In most cases, there are no previous measurements of the reaction rates. Fusion materials have been irradiated at a variety of facilities, including the Rotating Target Neutron Source II (14 MeV) at Lawrence Livermore National Laboratory, the Fast Neutron Source (14 MeV) at the Japanese Atomic Energy Research Institute, a 10 MeV $\text{H}(\text{T},\text{n})$ source at Los Alamos National Laboratory, and a $\text{Be}(\text{d},\text{n})$ broad spectrum source (0-10 MeV) at Argonne. Following each irradiation, we determine neutron fluences and energy spectra by dosimetry techniques. Various techniques are then used to determine the long-lived activities, including X-ray and gamma spectroscopy and liquid scintillation counting. Radiochemical separations are usually needed to isolate the weak activity of interest, and we must wait one year or longer for interfering activities to decay away. Preliminary results have been obtained for Ag and the rare earth materials Eu, Hf, and Tb. These measurements can be used to adjust the calculated cross sections, providing fusion reactor designers with realistic estimates of activities. Irradiations have also been completed for the important fusion material beryllium, and helium measurements in progress at Rockwell International could resolve a discrepancy between previous integral and differential measurements.

A detailed engineering test plan has been completed for the Dynamic Helium Charging Experiment in the Fast Flux Test Facility at Westinghouse Hanford. The purpose of this experiment is to irradiate vanadium-based alloys with a fusion-like ratio of helium and

atomic displacement damage. Normally, in a fast reactor, helium production is very low compared to a fusion reactor because of the much lower flux of 14 MeV neutrons. Helium can be generated by immersing the vanadium in liquid lithium which is enriched in the isotope ^6Li . The $^6\text{Li}(n,\alpha)t$ reaction will then rapidly make tritium, which readily diffuses into the vanadium. Tritium then decays to ^3He at about 5%/yr. To avoid any delay in the buildup of tritium, we can dope the lithium with a mother alloy of vanadium containing an initial dose of tritium. The tritium will stay in the mother alloy until the reactor facility is started. At temperatures between 400 and 600 °C, the tritium will come out of the mother alloy and rapidly reach equilibrium between the lithium and vanadium samples. Because helium produced by the lithium reaction will evolve into the plenum region of the molybdenum capsules used to contain the samples, stress and tritium leakage calculations have been performed to ensure capsule integrity and safety. By balancing the tritium diffusion, leakage, and production, we can create fusion-like helium production rates in the vanadium samples for periods up to several years in the reactor. The expected performance is illustrated in Fig. V-10. This figure gives calculated results for three variables: the weight distribution of tritium between the lithium and the alloy (k_w), the initial atomic percent of tritium in the lithium (T_o), and the initial atomic enrichment of ^6Li . The staircase pattern reflects the 120-day operating cycle. The condition of $k_w = 0.05$, $T_o = 0.012$ at. %, and natural ^6Li yields a helium generation rate somewhat higher than the desired rate of 5 appm He/DPA (dashed line in Fig. V-10). The other two conditions result in a helium generation rate close to that desired. Our plans for the Dynamic Helium Charging Experiment have passed safety and technical reviews. Work is now in progress to make the vanadium alloys and tritiated mother alloys at Argonne. The molybdenum capsules will be fabricated, filled, and welded at Westinghouse Hanford. We expect to deliver all materials by June 1990 for an irradiation starting December 1990.

Fig. V-10.

Helium Generation vs. Displacement per Atom (DPA) in Vanadium-Based Alloys for the Dynamic Helium Charging Experiment in the Fast Flux Test Facility (FFTF). The dashed line represents the desired rate of 5 appm He/atomic displacement. At a reduced power of 291 MW, FFTF will produce about 30 DPA/yr.

In related work, advanced concepts funding has been received from the Office of Arms Control to work on dosimetric tags and a gamma ray lens. An initial study has been

completed to determine criteria for the selection of tag materials and to characterize the properties of existing tag materials. The most important criteria include radiation sensitivity, *in situ* readability, and resistance to environmental effects and tampering. The idea is to permanently place a thin tag on (or near) missiles capable of carrying fissile materials. If nuclear devices were to be substituted in place of conventional weapons, then the tag would undergo a distinct, irreversible change that could be readily detected on inspection. For example, various plastics and glasses doped with radiochromic dyes and neutron-sensitive materials will discolor in the presence of ionizing radiation. Small color changes could then be detected with various scanning devices. We have also demonstrated a prototype gamma ray lens at gamma energies of 60 and 100 keV. The basic idea is to develop a lens which will collect gamma rays over a large area and focus them onto a small detector. The device can be set up to focus only a preselected gamma energy, and the detector is small ($<100\text{ cm}^3$). Hence, there is an enormous enhancement in the signal-to-background ratio compared to conventional large arrays of detectors. Work is now in progress to demonstrate the concept at higher energies by using a ^{137}Cs source at 662 keV. The lens could then be used to detect fissile material at distances up to 500 m in ground-based applications or up to 1000 km in space.

VI. BASIC CHEMISTRY RESEARCH

Basic chemistry research is being pursued in four different areas: catalytic chemistry associated with molecular energy resources; materials chemistry of superconducting oxides as well as ordered and associated solutions at high temperature; interfacial processes of importance to corrosion science, catalysis, and high-temperature superconductivity; 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 new catalytic chemistry associated with molecular energy resources. Real-time kinetic and spectroscopic techniques at high temperatures and pressures are used to determine the chemistry of small gaseous molecules derived from coal, natural gas, and petroleum. Maximal concentrations of reactive gases are achieved by making use of their complete miscibility with supercritical fluids. Using a high-pressure nuclear magnetic resonance (NMR) probe, we have recently determined the potential energy profile for activation of hydrogen by the commercial OXO catalyst in supercritical carbon dioxide solution. In other research, solution-phase oxide catalyzed hydrogenation and water-gas shift processes that seem to parallel metal oxide surface chemistry are being explored. Also investigated is the organometallic chemistry of extremely robust metallophthalocyanines designed to achieve stereoselective homogeneous hydrogenation and oxidation catalyses at unusually high temperatures.

I. Catalytic Chemistry in Supercritical Media

Because of their complete miscibilities with H_2 , CO, and CO_2 gases, supercritical fluids appear to be nearly ideal media for conducting catalytic reactions that involve these gases. For example, the concentration of H_2 at $25^\circ C$ and a partial pressure of 300 atm in supercritical CO_2 is 12 M, while the hydrogen concentrations under these conditions are only 0.23 M in water¹ and 1.8 M in n-heptane.² In addition, since no liquid/gas interface exists in the supercritical system, stirring to achieve gas dissolution is unnecessary. Although supercritical media for polar reactions may suffer from their low dielectric constants (typically near 1.0), this problem may not be insurmountable, while the aforementioned advantages alone warrant detailed investigation.

Our efforts to explore catalytic reactions in these media were recently initiated with an NMR study of the hydrogenation of cobalt octacarbonyl. This reaction

¹W. F. Linke, *Solubilities*, Vol. 1, American Chemical Society, Washington, DC, p. 1077 (1949).

²F. J. Ungvary, *Organometal. Chem.* **36**, 363-370 (1972).

is key to the commercial production of aldehydes in the OXO process³ and to the cobalt carbonyl catalyzed synthesis of higher alcohols from methanol in the homologation reaction first discovered by Wender et al.⁴ However, our major interest stems from the involvement of reaction 1 in the hydrogenation of carbon monoxide. To achieve optimal concentrations of hydrogen and to explore any potential reactions of CO₂, we chose to investigate the equilibrium in reaction 1 and mechanistic steps leading to it in supercritical CO₂ solution. The observations were achieved by using a high-pressure NMR pressure probe equipped with a toroid detector similar to one described earlier.⁵ Supercritical solutions were prepared by pumping liquid CO₂ into the preheated probe containing H₂, CO, and Co₂(CO)₈ until the partial pressure of CO₂ reached its critical pressure of 73 atm at a probe temperature 1-2 °C above its critical temperature of 31.1 °C.⁶ Cobalt octacarbonyl was found to be highly soluble in CO₂, and concentrations in excess of 0.3 M were easily achieved. A carbon monoxide pressure of 34 atm was sufficient to prevent formation of metallic cobalt from the carbonyls to at least 145 °C. Reaction 1 was followed by means of ⁵⁹Co NMR. Unfortunately, nuclei with large quadrupole moments such as ⁵⁹Co are frequently difficult to observe by high resolution spectrometers owing to their broad resonances, which result from efficient quadrupolar relaxation. However, the low viscosity of the supercritical fluid significantly narrows the line widths by decreasing the relaxation rate.⁷ This effect is illustrated in Fig. VI-1 where the line width of the Co₂(CO)₈ resonance is nearly six times narrower in supercritical CO₂ than in liquid benzene-d₆ (5.1 kHz vs. 30.0 kHz). It should be noted that the base of the resonance in benzene-d₆ effectively occupies the largest spectral window available to the spectrometer. This situation can lead to a variety of instrumental problems in obtaining accurate spectra. Since quadrupolar nuclei occur frequently in organometallic complexes, the line-narrowing effect of supercritical fluids promises to be of great value in high-pressure NMR studies of homogeneous catalyst systems.

Rate and equilibrium data were obtained by integrating the ⁵⁹Co resonances for HCo(CO)₄ and Co₂(CO)₈. A typical spectrum showing both species at 100 °C and a total pressure of 230 atm is shown in Fig. VI-2. The Co₂(CO)₈ peak is at about -2200 ppm, and the HCo(CO)₄ peak is at about -3050 ppm. Since the peaks are widely separated, quadrature phase detection had to be used to allow placement of the transmitter frequency so that we could irradiate equally at each frequency. With this technique, accurate measurements of the carbonyls were achievable, and reproducible equilibrium constants could be obtained whether equilibrium was approached from either the forward or reverse direction of reaction 1.

The equilibrium constant for Co₂(CO)₈ in CO₂ at 100 °C, 0.029, is significantly smaller than that in liquid n-heptane, 0.20,⁸ and may reflect the lower dielectric constant of the supercritical medium. At its critical pressure and temperature, CO₂ has a dielectric constant of approximately 1.1,⁹ while liquid aliphatic hydrocarbons have values near 2.0. The

³P. Pino, F. Piacenti, and M. Bianchi, in *Organic Synthesis via Metal Carbonyls*, eds., I. Wender and P. Pino, Vol. 2, John Wiley and Sons, New York, pp. 43-231 (1977).

⁴I. Wender, R. Levine, and M. J. Orchin, *Am. Chem. Soc.* **71**, 4160 (1949).

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

⁶M. McHugh and V. Krukonis, *Supercritical Fluid Extraction*, Butterworth, Stoneham, MA, p. 4 (1986).

⁷D. M. Lamb, D. G. Vander Velde, and J. Jonas, *J. Magn. Reson.* **73**, 345-348 (1987).

⁸N. H. Alemdroglu, J. M. L. Penninger, and E. Olta, *Monatsh. Chem.* **107**, 1043-1053 (1976).

⁹G. Beggerow, *High-Pressure Properties of Matter*, Springer-Verlag, New York, p. 267 (1980).

hydridocobalt carbonyl product of reaction 1 is more polar than either of the reactants; thus, the equilibrium constant would tend to be larger in the higher dielectric medium.

Fig. VI-1. ^{59}Co NMR Spectra of $\text{Co}_2(\text{CO})_8$ in Liquid Benzene- d_6 and Supercritical CO_2 at 145°C

Fig. VI-2. ^{59}Co NMR Spectrum of Equilibrium Mixture for $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ in Supercritical CO_2

Preliminary results from measurements of the temperature dependence of the equilibrium constants led to enthalpy and entropy values of 5.0 kcal/mol and 7.0 cal/mol·K, respectively. Rate constants for the forward rate of reaction 1 were measured by monitoring the decrease of $[\text{Co}_2(\text{CO})_8]$ with time. Second-order rate constants in accord with the rate law $-d[\text{Co}_2(\text{CO})_8]/dt = k[\text{Co}_2(\text{CO})_8][\text{H}_2]$ were measured at 80 and 100°C, yielding an approximate activation energy of 26 kcal/mol.

In addition to the ^{59}Co measurements just described, ^{13}C and ^1H NMR measurements were used to test for the following equilibria:

The ^{13}C spectrum, Fig. VI-3, measured in the absence of H_2 shows a broad signal near 185 ppm due to coalescence of $\text{Co}_2(\text{CO})_8$ and CO resonances, which occurred at separate frequencies below 145°C. Line-width measurements on the free CO resonance yield an approximate enthalpy of activation for reaction 2 of 24 kcal/mol. In the presence of H_2 , failure to observe a separate ^{13}C resonance for $\text{HCo}(\text{CO})_4$ indicates that reaction 3 is fast, even at low temperatures. Failure to observe broadening of the CO_2 peak near 126 ppm in the presence or absence of H_2 shows that the reactions involving CO_2 , i.e., reactions 4 and 5, are at least not rapid and extensive. In addition, in the absence of dynamic processes, failure to observe the characteristic formate proton signal in the ^1H spectra indicates that the formate product of reaction 5 could only be present at extremely low concentrations. Although methane was added primarily as a source of a narrow line proton signal to shim the magnet and as a gas standard, Fig. VI-3 suggests that the small quintet near -10 ppm, which is due to CH_4 , retains C-H coupling even at 145°C, and thus is not undergoing (at least to the sensitivity of this method) processes of the sort in reaction 6. The proton spectrum in Fig. VI-4 shows separate resonances for H_2 , CH_4 , and $\text{HCo}(\text{CO})_4$ near 4.5, 0.2, and -11.6 ppm, respectively. Reactions 7 and 8 must, therefore, also be too slow (or the equilibrium too insignificant) for observation of dynamic NMR effects on these peaks. The proton resonances of formyls occur at characteristic frequencies near 16 ppm. The formyl product of reaction 7 could not be observed under conditions in which a signal only 1% as large as the $\text{HCo}(\text{CO})_4$ peak would have been distinguishable from the noise. Barring dynamic processes, this would set an upper limit near $2 \times 10^{-4} \text{ M}$ for its concentration.

Fig. VI-3. ^{13}C NMR Spectrum of Equilibrium Mixture for $\text{Co}_2(\text{CO})_8$ in Supercritical CO_2 at 145°C

Fig. VI-4. ^1H NMR Spectrum of Equilibrium Mixture for $\text{HCo}(\text{CO})_4$ in Supercritical CO_2 at 100°C

The results on the $\text{Co}_2(\text{CO})_8$ system indicate the value of high-pressure NMR studies on supercritical systems. In future work we intend to modify the probe for operation at temperatures $\geq 200^\circ\text{C}$ and will investigate potential dynamic and thermochemical processes in a variety of organometallic catalyst systems in supercritical fluids.

2. Soluble Oxide Catalysis

Methanol is commercially produced by reacting mixtures of carbon monoxide and hydrogen at high temperature and pressure over heterogeneous metal oxide catalysts.¹⁰ Our goal is to better define the role of surface oxygen centers in this process by investigating the chemistry of soluble metal oxide complexes under well-characterized homogeneous reaction conditions. Recently, we demonstrated that hydrogen is activated at nucleophilic oxide centers in the complete absence of a metal center by a low-energy mechanistic pathway.¹¹ In an earlier study, we reported the first homogeneous oxide-based methanol synthesis system.¹²⁻¹⁴ This initial example employed a main group complex hexamethyldisilicon oxide and demonstrated a reaction pathway based on intermediates which were derived directly from the oxide ligand, including formate, hydroxide, methoxide, and oxymethylene. These highly oxygenated intermediates are distinctly different from those previously considered in earlier studies with transition metal carbonyl systems of low oxidation state.^{15,16} Currently, we are investigating the generality of the formate/oxide mechanism by extending these studies to a range of metal oxide complexes. This endeavor requires the use of an appropriate ligand to bring the polar metal oxide and formate functionalities into organic solvents, so that mechanistic analysis is possible. Furthermore, the high-temperature requirements of 180-250 °C for the catalytic methanol synthesis process necessitate a solubilizing ligand with truly unusual thermal and hydrolysis stability. Indeed, the dearth of suitably robust solubilizing ligands has, to date, limited the application of homogeneous metal oxide complexes in synthesis gas catalysis. The tris(trimethylsilyl)methyl ligand is a relatively new species and has been used to prepare peralkylated transition metal complexes with encouraging thermal stability.^{17,18} Accordingly, we have now developed synthetic routes to tris(trimethylsilyl)methyl zinc formate and the corresponding hydroxide complex, both of which exhibit hydrocarbon solubility in excess of 0.1 M. Initial focus has been directed toward soluble complexes of zinc because zinc oxide is an important component of commercial methanol synthesis catalysts.¹⁰

The required starting material, tris(trimethylsilyl)methyl lithium, has been reported¹⁷ to be produced by the metalation of tris(trimethylsilyl)methane in tetrahydrofuran (THF):

¹⁰K. Klier, *Adv. Catal.* **31**, 243-311 (1982).

¹¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1989*, Argonne National Laboratory Report ANL-89/15, pp. 123-126 (1989).

¹²R. J. Klingler, T. R. Krause, and J. W. Rathke, *J. Organomet. Chem.* **352**, 81-94 (1988).

¹³R. J. Klingler and J. W. Rathke, *Organometallics* **5**, 2568-2570 (1986).

¹⁴R. J. Klingler, I. Bloom, and J. W. Rathke, *Organometallics* **4**, 1893-1894 (1985).

¹⁵B. D. Dombek, *Adv. Catal.* **32**, 325-416 (1983).

¹⁶J. W. Rathke and H. M. Feder, *J. Am. Chem. Soc.* **100**, 363 (1978).

¹⁷C. Eaborn, N. Retta, and J. D. Smith, *J. Organomet. Chem.* **190**, 101-106 (1980).

¹⁸S. S. Al-Juaid, C. Eaborn, P. B. Hitchcock, C. A. McGeary, and J. D. Smith, *J. Chem. Soc. Chem. Commun.*, pp. 273-274 (1989).

However, undesirable alkoxide by-products result since the methyl lithium concurrently attacks the tetrahydrofuran solvent. We have thus developed an alternative procedure. In this procedure, bistrimethylsilylmethane is produced by a high-yield coupling reaction, which employs a commercially available organolithium reagent, trimethylsilylmethyl lithium:

This coupled product is activated for further transformation by the introduction of a bromine functionality. The resultant bistrimethylsilylmethane may be brominated in 45% yield employing N-bromosuccinimide:

Significantly, the bromination process proceeds with a degree of selectivity which is unusual for a radical chain process. Thus, the only major organosilicon by-product isolated from the above reaction mixture is simply unreacted starting material, which may be recycled for future brominations. The monobrominated species, bistrimethylsilylmethyl bromide, has been synthesized for comparative purposes by an alternative route and is notably absent from the above reaction product. Furthermore, a high degree of selectivity is noted for bromination at the methylene carbon over the more numerous terminal methyl groups. Subsequently, the dibromide product is converted to tris(trimethylsilylmethyl) bromide in a single step:

The high isolated yield, 91%, for the net process in reaction 12 indicates that the intermediate bromine transfer reaction:

is faster than either of the second-order nucleophilic coupling processes:

Finally, the required lithium reagent is produced by a bromine atom transfer reaction employing trimethylsilylmethyl lithium:

The procedure for producing tris(trimethylsilylmethyl) lithium in reactions 10-16 is more involved than that for reaction 9. However, reactions 10-16 yield a product which is free from all alkoxide contamination. The absence of ether and alkoxide contamination is an important advantage for producing tris(trimethylsilylmethyl) complexes of electropositive metals; and this has recently led C. Eaborn and co-workers¹⁸ to pursue alternatives such as the organomagnesium reagent, $[(\text{Me}_3\text{Si})_3\text{C}]_2\text{Mg}$. The lithium reagent in reaction 16 is more reactive and has been used to produce tris(trimethylsilylmethyl) zinc formate and tris(trimethylsilylmethyl) zinc hydroxide complexes that are sufficiently soluble in hydrocarbon solvents to allow mechanistic investigation. Future effort will be directed toward using this ligand to synthesize soluble hydroxide complexes of other transition metals that are known to exhibit catalytic methanol synthesis activity. In addition, the reactions of tris(trimethylsilylmethyl) zinc formate will be investigated at elevated temperature under mixtures of carbon monoxide and hydrogen in the high-pressure NMR cell.

3. High-Temperature Phthalocyanine Chemistry

We have continued our effort to develop methods for the synthesis of soluble group VIII transition metal complexes of phthalocyanines and to study their catalytic activities.

The *in situ* trimethylsilylation reactions that we reported previously provide a convenient synthesis of the soluble all- α substituted trimethylsilylated phthalocyanines.¹⁹ Although these complexes have good thermal stability at temperatures up to 150°C , loss of trimethylsilyl groups does occur under more severe conditions. We have therefore shifted our study to the corresponding alkyl-substituted phthalocyanines, which have higher thermal stability.

A one-pot synthesis has been developed to prepare 3,6-dipentylphthalonitrile, from which 1,4,8,11,15,18,22,25-octapentylphthalocyanines (R_8PcH_2) may be easily prepared:

¹⁹M. J. Chen, C. M. Fendrick, R. A. Watson, K. S. Kinter, and J. W. Rathke, J. Chem. Soc., Perkin Transac. 5, 1071 (1989).

The 3,6-dipentylphthalonitrile also provides a convenient precursor for a high-yield synthesis of $\text{Co}(\text{R}_8\text{Pc})$ (and possibly also other group VIII metal complexes), as follows:

However, we have not been able to synthesize a $\text{Rh}-\text{R}_8\text{Pc}$ complex directly from 3,6-dipentylphthalonitrile. Instead, $\text{Rh}(\text{R}_8\text{Pc})(\text{PhCN})\text{Cl}$ was prepared from preformed R_8PcH_2 according to

The IR spectrum of $\text{Rh}(\text{R}_8\text{Pc})(\text{PhCN})\text{Cl}$ suggests that benzonitrile is π -bonded to Rh in this complex--an unusual bonding mode for PhCN. This complex provides a good starting material for the synthesis of various $\text{Rh}-\text{R}_8\text{Pc}$ complexes. Simple substitution reactions lead to CO and phosphine complexes:

Reduction of the phosphine complex by excess NaBH_4 forms an Rh^{I} complex, tentatively assigned $(\text{Rh}(\text{R}_8\text{Pc})\text{PR}_3)^+$, which forms a Cl^- bridged Rh dimer when the solution is acidified:

We have not yet detected the hydride complex, $\text{Rh}(\text{R}_8\text{Pc})(\text{PBu}_3)\text{H}$, which may be formed from protonation of the intermediate $\text{Rh}(\text{R}_8\text{Pc})\text{PBu}_3^-$. Presumably, controlled acidification allows the isolation of this Rh-hydride complex. Similarly, alkyl complexes may be obtained by alkylation of the reduced species.

Future efforts will be directed toward the activation of H_2 and CO and the catalytic oxidation of alkanes. Both of these reactions have been reported to occur in structurally related porphyrin complexes of group VIII transition metals. The activation of H_2 and CO may be most effectively accomplished by Rh complexes, while the catalytic alkane oxidations are most likely achieved with Co and Fe complexes.

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 temperatures. Our major focus is on associated and ordered solutions, such as chloroaluminates, silicates, and "ionic" alloys, and on superconducting oxides.

1. Solubilities of Transition Metal Chlorides in Molten Chloroaluminates

Ordered ionic liquids, such as chloroaluminates and silicates, have striking physicochemical properties. For example, at the 50 mol% NaCl-50 mol% AlCl_3 composition, the most ordered composition in this binary system, the ordering can be described in terms of the formation of the chemical species AlCl_4^- and Al_2Cl_7^- . When one also considers the charge ordering in the molten salt NaAlCl_4 , the chemical model of this ordered solution is equivalent to the physical model that can be described in one dimension by ABABAB... The equilibrium constant for the disproportionation reaction

is a measure of the disorder in this system and has very low values that range from 1.06×10^{-7} at 175°C to 5.83×10^{-6} at 355°C .²⁰ In physical terms, these low constants indicate a high degree of order and a very sharp peak in the Darken excess stability function,²¹ with a maximum value of $4.7 \times 10^7 \text{ J mol}^{-1}$ at 175°C at the 50-50 mole percent composition.

One of the most striking properties observed in NaCl- AlCl_3 melts is the very sharp minimum in solubility and maximum in activity coefficients of solutes at the 50-50 mole percent composition. This property is important for the "Zebra" battery system under development for automobile propulsion. This battery uses an NaCl-saturated NaCl- AlCl_3 electrolyte that is also saturated with the relatively insoluble solid FeCl_2 . The FeCl_2 , along with other transition metal chlorides, is expected to have a large maximum in its activity coefficient at the 50-50 mole percent composition. The low solubility of FeCl_2 and its concentration dependence undoubtedly influence the electrochemical kinetics favorably.

To test concepts for describing this property, we have measured the solubilities of solid CoCl_2 in molten NaCl- AlCl_3 mixtures. As can be deduced from Fig. VI-5, the measured solubility of CoCl_2 (filled circles) increases by more than two orders of magnitude in the composition range $X(\text{AlCl}_3) = 0.502$ to 0.669 (where X is mole fraction). One can describe these measurements in terms of the Coordination Cluster Theory (CCT),^{22,23} which is based on a

²⁰L. G. Boxall, H. L. Jones, and R. A. Osteryoung, *J. Electrochem. Soc.* **120**, 223 (1973).

²¹L. S. Darken, *Trans. AIME* **239**, 80 (1967).

²²M. Blander, M.-L. Saboungi, and P. Cerisier, *Metall. Trans.* **10B**, 613-622 (1979).

²³M. Blander and M.-L. Saboungi, "The Coordination Cluster Theory of Solutions," in *Chemical Metallurgy--A Tribute to Carl Wagner*, ed., N. A. Gokcen, *Met. Soc. of AIME*, Warrendale, PA, pp. 223-231 (1981).

physical model. In this theory, the activity coefficients of the solute C, $\gamma(C)$, in a highly ordered binary mixture of A and B can be calculated in the compositional range of interest from a knowledge of the measured activity coefficients of NaCl and AlCl_3 in the solvent and of the (unknown) activity coefficient of CoCl_2 in molten AlCl_3 , $\gamma(\text{CoCl}_2)(\text{AlCl}_3)$ (which is the same for all chloroaluminates). The calculated solubilities are given in Fig. VI-5 by the dashed line with values set to go through the measured data at $X(\text{AlCl}_3) = 0.502$ and 0.669 , indicating an activity coefficient of CoCl_2 in AlCl_3 of 0.35 . The theory provides a very good representation of the concentration dependence of the solubilities.

Fig. VI-5. Calculated and Measured Values of Solubilities and Activity Coefficients of CoCl_2 with Activity Coefficient of CoCl_2 in AlCl_3 [$\gamma(\text{CoCl}_2)(\text{AlCl}_3) = \exp(-1.05)$]

There is yet another description of our experiments, which can be designated as a chemical model. One can characterize this chloroaluminate system as a reciprocal system containing Co^{2+} and Na^+ cations and Cl^- , AlCl_4^- , and Al_2Cl_7^- anions. If we consider the solvent

to be NaAlCl_4 , we can exactly describe the thermodynamics of the dissolution of CoCl_2 by three steps²⁴⁻²⁶:

For these three steps, ΔG_1° is the standard free energy change for the metathetical reaction 24, and ΔG_2^E and ΔG_3^E (reactions 25 and 26, respectively) are the excess free energies of solution of $2\text{NaCl}(\text{l})$ and $\text{Co}(\text{AlCl}_4)_2(\text{l})$ in the solvent at infinite dilution. The sum $\Delta G_1^\circ + \Delta G_2^E + \Delta G_3^E$ is related to the solubility product, K_{SP} , in ion fraction units and to the activity coefficient, $\gamma(\text{CoCl}_2)$ (with the solid as standard state of the solute), by the relation

$$\Delta G_1^\circ + \Delta G_2^E + \Delta G_3^E = -RT \ln K_{\text{SP}} = RT \ln \gamma(\text{CoCl}_2) \quad (27)$$

Values of the solubility product, $K_{\text{SP}} = X(\text{Co}^{2+}) \cdot X(\text{Cl}^-)^2 = \exp(-33.0)$ (where the X's are cation and anion fractions), are essentially constant for all but the composition $X(\text{AlCl}_3) = 0.502$, where the uncertainties in the measurements are greatest. The increase in the solubility of CoCl_2 with an increase in $X(\text{AlCl}_3)$ is related to the formation of Al_2Cl_7^- (reaction 23) and to the decrease in the square of $X(\text{Cl}^-)$ with an increase of the square of $X(\text{Al}_2\text{Cl}_7^-)$. Both the physical model and the simpler chemical model lead to good descriptions of the concentration dependence of the solubilities and provide free energy values that permit one to make predictions of absolute values of the solubilities in all acidic [$X(\text{AlCl}_3) > 0.5$] chloroaluminates.

We plan further measurements with CoCl_2 in basic [$X(\text{NaCl}) > 0.5$] melts and with NiCl_2 in acidic and basic melts. In basic melts, the thermodynamic properties of CoCl_2 can be described in terms of the formation of the solution species CoCl^+ , CoCl_2 , CoCl_3^- , and CoCl_4^- , with the last two species leading to increasing solubilization of CoCl_2 with an increase in the concentration of NaCl .

²⁴M. Blander and E. B. Luchsinger, J. Am. Chem. Soc. **86**, 319 (1964).

²⁵M. Blander, "Thermodynamic Properties of Molten Salt Solutions," in *Molten Salt Chemistry: An Introduction and Selected Applications*, eds., G. Mamantov and R. Marassi, D. Reidel Publishing Co., NATO ASI Series, Dordrecht, Holland, pp. 17-62 (1987).

²⁶M.-L. Saboungi, J. J. Marr, and M. Blander, J. Electrochem. Soc. **125**, 1567-1573 (1978).

2. Structure of Trivalent Molten Salts by Neutron Diffraction

A large number of neutron diffraction experiments have been carried out on molten mono- and divalent salts to determine their structure.²⁷ The isotopic substitution method pioneered by Enderby et al.²⁸ has been used on chlorides to determine the partial structure factors and the pair correlation functions that contain the most pertinent information on the structure. Variety in the structure has been shown to arise as a function of the degree of ionicity of the salts.^{29,30}

There have been very few studies of molten trivalent salts, particularly at the partial structure factor level. In this work, we have investigated the structure factors of AlBr_3 , GaBr_3 , GaI_3 , NdCl_3 , NdBr_3 , NdI_3 , and LaCl_3 at temperatures slightly above their melting points. The Al and Ga salts have a molecular character, with Al_2X_6 or Ga_2X_6 being the predominant molecule within the liquid (where X refers to the halogens). The Nd and La salts, which melt at higher temperatures, are characterized by the presence of a significant amount of short-range order, which exists in the solid and is preserved on melting. In what follows, we will discuss experimental results and model calculations for AlBr_3 and NdCl_3 that illustrate the different kinds of interactions in these salts. Neutron diffraction measurements are planned on isotopically substituted samples to allow a direct experimental determination of the partial structure factors.

a. Structure of a Low Melting Trihalide Salt, AlBr_3

The total structure factor, $S(Q)$, of AlBr_3 was measured at 412 K with neutron diffraction techniques. The main features of $S(Q)$ are the presence of a first sharp diffraction peak at low wavevectors, $Q \approx 1 \text{ \AA}^{-1}$, and the long range of oscillations at high Q . In real space, the pair correlation function $g(r)$ obtained from $S(Q)$ by Fourier transformation shows a prominent sharp peak at $r \approx 2.3 \text{ \AA}$, which can be ascribed to cation-anion (A-X) correlations within the molecules. The coordination numbers obtained were 4.0 for AlBr_3 , 3.8 for GaBr_3 , and 3.7 for GaI_3 . The coordination number of four is expected for A_2X_6 molecules, whereas three is expected of AX_3 . Thus, the AlBr_3 consists of Al_2Br_6 molecules in the melt, and the gallium salts are dimerized only up to $\approx 70\text{-}80\%$, in agreement with earlier Raman scattering studies.³¹ We have used the Reference Interaction Site Model (RISM)^{32,33} to calculate $S(Q)$ under the assumption that the melt consists entirely of A_2X_6 interacting via site-site hard sphere potentials. The parameters needed for this calculation are the molecular geometry, the density of the liquid, and the hard sphere diameters of the atoms in the molecule. The good agreement obtained between measurements and RISM calculations is considered as further proof of the dimerization

²⁷J. E. Enderby and S. Biggin, in *Advances in Molten Salt Chemistry*, Vol. 5, ed., G. Mamantov, Elsevier, New York, p. 1 (1983).

²⁸J. E. Enderby, D. M. North, and P. A. Egelstaff, *Phil. Mag.* **14**, 961 (1966).

²⁹N. D. Wood and R. A. Howe, *J. Phys. C: Solid State Physics* **21**, 3177 (1988).

³⁰N. D. Wood, R. A. Howe, R. J. Newport, and J. Faber, Jr., *J. Phys. C: Solid State Physics* **21**, 669 (1988).

³¹A. Balls, A. J. Downs, N. N. Greenwood, and B. P. Straughan, *Trans. Faraday Soc.* **62**, 521 (1968).

³²H. C. Anderson and D. Chandler, *J. Chem. Phys.* **57**, 1918 (1972).

³³D. Chandler and H. C. Anderson, *J. Chem. Phys.* **57**, 1930 (1972).

of AlBr_3 . The RISM calculations might be improved by considering different potentials than the hard sphere potential.

b. Structure of a High Melting Trihalide Salt, NdCl_3

The total structure factor for NdCl_3 was measured by neutron diffraction at 1100 K and corrected for the magnetic scattering of the Nd^{3+} ions. There is little structure at high momentum transfer, but the first diffraction peak at $Q \approx 1 \text{ \AA}^{-1}$ is still present and is a common feature to all the trivalent molten salts that we have examined. In the case of NdCl_3 , X-ray data were made available to us³⁴ and were used in conjunction with the neutron results to obtain a model structure using the reverse Monte Carlo (RMC) method.³⁵ The RMC method enables one to obtain a three-dimensional structure that reproduces the measurements; from the ionic distributions, one can further probe the ionic arrangements in a trivalent salt system and compute partial structure factors and the radial pair distribution functions. We carried out such calculations for NdCl_3 , and the correspondence between measurements and calculations was excellent. The computations carried out on a system containing 1024 ions inside a box length of 31.52 Å yielded the three partial functions in real and reciprocal space. Furthermore, triplet correlation functions were calculated. In the solid state, NdCl_3 forms a crystal with hexagonal C_{6h}^{2} symmetry. Figure VI-6 shows plots of the six triplet correlation functions for both liquid and crystalline states (the former calculated using RMC, the latter from a distorted lattice). The remarkable similarity between the crystalline and liquid triplet correlations in Fig. VI-6 suggests that the local structure in the melt, although considerably more disordered than in the solid, still retains many of its characteristics.

In conclusion, the structures of trivalent molten salts show interesting differences. Improvements in the intensity and resolution of diffractometers and neutron sources are enabling exploration of lower momentum transfer values. The presence of diffraction peaks at $Q \approx 1 \text{ \AA}^{-1}$ detected in all the salts that we have studied can be related to intermediate-range order.

3. Quantum Chemical Studies

a. High-Critical Temperature Superconductors

The intra-atomic d-d excitations of divalent copper in the high-critical-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ have been investigated by *ab initio* molecular orbital calculations on CuO clusters representing the chains and planes in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$. The assignments of peaks in the optical absorption spectra of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ in the region $<5 \text{ eV}$ have been the subject of some dispute³⁶ and are important in trying to elucidate the mechanism for superconductivity in these new materials. The results of our study indicate that all of the intra-atomic d-d excitations lie in the region 1.4-1.8 eV for divalent Cu. The presence of a π -type

³⁴K. Igarishi and I. Mochinaga, Chiba University, Chiba, Japan, private communication (1989).

³⁵R. L. McGreevy and L. Pusztai, *Mol. Simul.* **1**, 359 (1988).

³⁶S. Uchida, S. Tajima, H. Takagi, and Y. Tokura, in *Mechanisms of High Temperature Superconductivity*, eds., H. Kamimura and A. Oshiyama, Springer-Verlag, Berlin (1989).

oxygen hole (O^-) was found to have little effect on the excitation energies. The results suggest that peaks at higher energy, which have been assigned to d-d excitations in some experimental studies, must be due to some other excitation, such as charge transfer. Future work will include use of the copper oxide clusters to study other electronic excitations such as d-s excitations in $YBa_2Cu_3O_6$ and the effect of π -type holes on the d-d excitations.

Fig. VI-6. Plots of Triplet Correlation Functions for Molten $NdCl_3$ (solid lines) Compared with Those Obtained from RISM Model of the Crystal (dashed lines). The vertical lines show, on an arbitrary scale, the distribution of the triplet angles in a perfect crystal.

b. Development of Very Accurate Quantum Chemical Methods

The development of accurate quantum chemical techniques for the calculation of reaction energies, ionization potentials, proton affinities, and electron affinities of molecular systems and clusters is important in many areas of materials chemistry, including catalysis studies and chemical vapor deposition modeling. A method, referred to as the Gaussian-1 (G1) method, is being developed for this purpose. It uses no experimental input and has no adjustable parameters. It is based on Hartree-Fock theory and incorporates high levels of correlation energy using quadratic configuration interaction and large basis sets. It had previously been successfully applied to compounds containing first-row atoms (Li-F) with an accuracy of 0.1 eV.^{37,38} During

³⁷L. A. Curtiss and J. A. Pople, *J. Chem. Phys.* **88**, 7405 (1988).

³⁸J. A. Pople, M. Head Gordon, D. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989).

the past year, we have used the G1 method to predict energies of species for which experimental thermochemical data are uncertain or not available. The method has helped to identify B_2H_4 and B_2H_5 for the first time^{39,40} and has been used to establish the CH bond dissociation energy in acetylene.⁴¹ In addition, the method has been extended to include compounds containing second-row atoms (Na-Cl). Calculations derived by this method using different basis sets have been compared with well-established experimental data on, for example, SiO, Si_2 , and SiC. The agreement with the experimental data indicated an accuracy of the method of about 0.1 eV, similar to what was found for compounds containing first-row atoms (Li-Cl). This method should prove very useful in making predictions for clusters, ions, etc., where experimental data are limited. This work is being done in collaboration with J. Pople (Carnegie Mellon University) and R. Krishnan (AT&T Bell Laboratories).

The structures and energies of AlX_5^{2-} and AlX_6^{3-} ($X = F, Cl$) have been investigated using molecular orbital theory. In fluoroaluminate melts AlF_6^{3-} is known to be a major component in basic melts, and there is some evidence⁴² for AlF_5^{2-} . There is no evidence for the corresponding chloroanions in chloroaluminate melts, where an excess of $AlCl_3$ gives $Al_2Cl_7^-$ anions. The corresponding $Al_2F_7^-$ anion has not been observed in the fluoroaluminate melts. We calculated structures and heats of formation for AlF_5^{2-} and AlF_6^{3-} with and without Li^+ cations. The energies calculated without the cations indicate that AlF_5^{2-} is more stable. However, when the cations are included, i.e., Li_2AlF_5 and Li_3AlF_6 , the latter is more stable, in agreement with the experimental observations. The structures of these species are illustrated in Fig. VI-7. The corresponding chloride species, with and without cations, were much less stable than the fluoride species, again consistent with experiment. These results can be explained in terms of the larger size of chlorine than fluorine. Quantum chemical calculations were also carried out on $Al_2F_7^-$ and $Al_2Cl_7^-$, with and without cations. In this case, the chloride species was more stable, consistent with the detection of this species in the melt.

C. Interfacial and Corrosion Science

This research program consists of 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) studies of novel catalysis schemes employing molecular sieve materials, and (3) the preparation of high-critical-temperature (T_c) superconducting oxides in thin-film form and fabrication of functional embodiments employing high- T_c materials. Paralleling semiempirical and *ab initio* theoretical research is carried out to support and extend all of the above experimental pursuits.

³⁹L. A. Curtiss and J. A. Pople, J. Chem. Phys. **91**, 4189 (1989).

⁴⁰L. A. Curtiss and J. A. Pople, J. Chem. Phys. **91**, 5118 (1989).

⁴¹L. A. Curtiss and J. A. Pople, J. Chem. Phys. **91**, 2420 (1989).

⁴²W. Haupin, in *Molten Salt Chemistry*, eds., G. Mamantov and R. Marassi, D. Reidel Publishing Co., Dordrecht, Holland, pp. 447-448 (1987).

Fig. VI-7. Structure of Li_3AlF_6 (left) and Li_2AlF_5 (right)

1. Aqueous Corrosion Research

The deleterious effects of aqueous corrosion in practical systems that operate between ambient temperature and the boiling point of water are widely recognized and are generally avoided by appropriate choice of containment materials and/or application of a variety of corrosion inhibition practices. At higher temperatures, such as those existing in light water nuclear reactor (LWR) coolant systems, the corrosion reactions are much more rapid, passive surface layers become less stable, and localized corrosion processes, such as stress corrosion cracking (SCC), are exacerbated by even trace levels of some types of impurities. Under these conditions of high temperature and pressure, much less is understood concerning the mechanistic aspects of the corrosion processes or the synergistic effects of impurities, pH, etc. The overall goal of this research program is to provide an experimental data base against which theoretical and empirical models of aqueous corrosion under LWR operating conditions can be tested over a wide range of temperatures and pressures. Results during the past year are summarized below.

a. Spectroelectrochemical Studies of Aqueous Corrosion

The objective of this effort is to elucidate the relationship between the structural and electronic properties of metal/solution interfaces and the kinetics of metallic corrosion and passivation in aqueous environments. Laser Raman and UV-visible spectroscopies are employed to determine *in situ* the structure and composition of anodically formed corrosion films on metal surfaces. Photoelectrochemical and ac impedance techniques are used to characterize the electronic band structure of the films and to study their transport properties and conduction mechanism(s). Concurrently, dc and ac polarization, cyclic potentiodynamic sweeps, and other transient techniques are employed to further elucidate the interfacial processes involved in the corrosion of metals.

The corrosion and passivation behavior of iron and copper in aqueous solutions containing thiocyanate were investigated to determine the effect of the SCN^- anion on (1) the composition, structure, and electronic properties of the surface films formed and (2) the rates and mechanisms of the associated corrosion reactions. Thiocyanate is of particular interest because it is a pseudo-halide, and halides are common impurities that are known to facilitate metal corrosion and the breakdown of passive films. The thiocyanate anion, however, is a molecular anion that exhibits vibrational frequencies which depend on its environment; hence, its interactions can be probed by monitoring the shifts in these characteristic frequencies. Results to date show that the corrosion and passivation behavior of Cu and Fe are drastically altered by the presence of even small amounts (0.005 to 0.01 M) of SCN^- in borate buffer solutions at room temperature. Corrosion currents are increased four to five times and new surface phases are formed. In the case of iron, breakdown of the preformed passive film occurs following introduction of SCN^- into the solution. Laser Raman spectroscopy showed that the film formed on Cu at 0.2 V vs. a standard calomel electrode (SCE) is CuSCN , while on iron we have obtained spectra attributable to $\text{Fe}(\text{SCN})_2$ and $\text{Fe}(\text{SCN})_3$, depending on anodization potential. In all cases the shift of the C-N vibrational frequency compared to that in solid KSCN is toward higher values, indicating coordination of the sulfur end of the anion in the surface films.

In a collaborative effort involving members of the Materials and Components Technology Division (MCT), Raman spectroscopy, in combination with powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy, has been used to characterize the chemical composition of passive films formed on stainless steel tensile specimens that had been exposed to water at 289° C (LWR operating temperature) over a wide range of pH (3.0-7.0) and corrosion potential conditions (-512 to +230 V). All the samples had been strained to failure in experiments employing the constant extension rate test (CERT) procedure, as part of a program carried out by the MCT Division. The phases identified on each sample in our work by Raman spectroscopy and supporting XRD measurements showed excellent correlation with a recently published potential-pH (Pourbaix) diagram for the Fe-Cr- H_2O system at 289° C.⁴³ The key finding of both studies is that, in the region of the potential-pH diagram where $(\text{Fe}_{3-x}\text{Cr}_x)\text{O}_4$ is both predicted and found to be the stable oxide phase, no evidence of intergranular stress corrosion cracking (IGSCC) is seen in the CERT specimens. The CERT specimens tested at potential-pH conditions outside the $(\text{Fe}_{3-x}\text{Cr}_x)\text{O}_4$ stability region all showed evidence of IGSCC.

In the coming year we will continue our spectroelectrochemical studies of aqueous corrosion on stainless steel. We also plan to examine corrosion and passivation phenomena on metals in nonaqueous solutions with a view toward gaining a deeper understanding of the role of water. Organic solvents like acetonitrile, propylene carbonate, dimethylformamide, etc., with controlled amounts of water will be used. Corrosion kinetics, as well as film composition and properties, will be investigated.

⁴³D. Cubicciotti, J. Nucl. Mater. **167**, 241 (1989).

b. Electrode Kinetic Studies of Aqueous Corrosion

This research examines the effect of temperature on the kinetics and mechanism of charge transfer reactions. In addition to its importance to high-temperature aqueous corrosion, to many energy technologies, and to the electrolytic industries, the charge transfer at high temperatures has become a central issue in electrochemistry. A number of workers⁴⁴ have reported an unexplainable dependence on temperature of the transfer coefficient for complex electrode reactions, and it is of interest to determine whether a simple reaction would also behave anomalously. We have completed our study of the ferrous/ferric redox reaction in a noncomplexing medium (perchloric acid) on an inert gold electrode and found that the apparent transfer coefficient, α , of the reaction is independent of temperature (25 to 275 °C) and has a value of 0.425 ± 0.010 , which is in very good agreement with the theoretically determined value of α based on work described in Sec. VI.C.1.c.

In previous work⁴⁵ we showed that the ferrous/ferric reaction can be strongly catalyzed by trace anionic impurities concentrated at the electrode/solution interface. This year we initiated a study of the catalyzing effect of cationic impurities of the type that form underpotential-deposited metal sub-monolayers on electrode surfaces. The first system investigated was that of copper on gold in scrupulously purified solutions. An approximate doubling of the charge transfer rate was observed at close to monolayer coverages. Since this reaction can now be assumed to be nonadiabatic, a possible avenue exists to elucidate and explain the observed behavior through calculations of the electronic coupling matrix element for a copper monolayer on a gold surface. This computational study is currently being carried out in conjunction with the theoretical effort described in Sec. VI.C.1.c.

In future work we will extend our experimental/theoretical charge transfer studies to more complex reactions of the type that accompany SCC at elevated temperature. The next system to be investigated is the $\text{Cu}^{2+}/\text{Cu}^0$ electrode reaction, which consists of two consecutive electron transfers followed by the incorporation of the copper atom into the metal lattice. (Copper deposition has been identified as one of the most troublesome cathodic reactions occurring during SCC in LWRs.) While this reaction is much more complex than the ferrous/ferric redox reaction, we expect that the first electron transfer step ($\text{Cu}^{2+}/\text{Cu}^+$) will be rate determining, and that we can modify our experimental/theoretical approaches for this case. Electrode kinetic measurements of the $\text{Cu}^{2+}/\text{Cu}^0$ reaction at room temperature will be performed in the near future to lay necessary groundwork for subsequent high-temperature/high-pressure kinetic measurements.

c. Theoretical Studies of Aqueous Corrosion

This research involves the development of microscopic models of electron transfer processes at the electrode/electrolyte interface through the use of a combination of

⁴⁴B. E. Conway, in *Modern Aspects of Electrochemistry*, Vol. 16, eds., B. E. Conway et al., Plenum Press, New York, p. 103 (1985).

⁴⁵M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1987*, Argonne National Laboratory Report ANL-88-19, p. 144 (1988).

molecular dynamics and molecular orbital methods. The work is being done in collaboration with J. W. Halley (University of Minnesota) and is also closely coupled with the experimental kinetic studies in Sec. VI.C.1.b.

During the past year work continued on the theoretical investigation of the ferrous/ferric electron transfer process for a gold electrode at 25-275 °C. There have been few investigations into the importance of electronic effects in outer-shell, heterogeneous electron transfer reactions, and until recently it has been generally assumed that the heterogeneous electron transfer is an adiabatic process. Based on a cluster model of the gold surface/water interface, we have developed a method (using semiempirical molecular orbital theory) for assessing the magnitude of the electronic matrix element for heterogeneous electron transfer between the surface and the solvated iron cations. We have investigated the dependence of the electronic coupling on (1) the distance of the ion from the surface, (2) different approaches of the waters from the first solvation shell of the cation to the adsorbed water layer, (3) the dependence of the results on the cluster size used to represent the surface, and (4) the internal changes of the water molecule structure. This study has shown that the heterogeneous $\text{Fe}^{2+}/\text{Fe}^{3+}$ reaction is nonadiabatic, i.e., it has very weak electronic coupling; therefore, electronic coupling must be included in the molecular dynamics calculations to obtain accurate rates of electron transfer. However, the quantities of interest in the current study, i.e., the temperature dependence of the rate and the activation barrier, are independent of the electronic coupling.

The temperature dependence of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ electron transfer reaction was studied during the past year by molecular dynamics methods, and the calculated results were compared to the results from the experimental kinetic studies described in Sec. VI.C.1.b. The results obtained thus far indicate no anomalous temperature dependence (25 to 275 °C) of the electron transfer rate, in agreement with the experimental results. In addition, the charge transfer coefficient and activation barrier calculated from the molecular dynamics simulations are in good agreement with those obtained from experiment. The study has also revealed insight into the vibrational modes important in the solvent rearrangement which occurs during electron transfer. These results suggest that the single reaction coordinate used in classical Marcus theory is inappropriate for this type of reaction.

In future efforts in this area, we will investigate the $\text{Cu}^{2+}/\text{Cu}^0$ electron transfer reaction by using the theoretical techniques developed over the last several years. As a first step in this study, we have derived *ab initio* ion-water pair potentials for Cu^{2+} interacting with a single water molecule. Pair potentials will also be determined for Cu^+ and Cu^0 with H_2O , and the importance of nonadditivity will be examined. These potentials will be used in the development of a molecular dynamics model for the electrolyte. *Ab initio* methods will also be used to examine the stability of Cu^0 in a water environment and to determine the extent to which neutral Cu^0 affects the electron transfer rate calculation.

d. Synchrotron Radiation Studies of Metal/Solution Interfaces

To complete the interpretation of the kinetic and molecular information derived from the electrochemical, spectroscopic, and theoretical studies described in Sec. VI.C.1.a through VI.C.1.c., there is a need for complementary data on elemental density profiles and ordering behavior within the interfacial corrosion layers that form on metal surfaces and in

the double-layer region adjacent to the metal surface. In particular, it is important to determine the role played by dissolved solution species, pH, and the solvent (water) molecules during the formation of passivation films and the restructuring of the double layer. Techniques based on synchrotron radiation offer many intriguing possibilities for such studies. These possibilities have been assessed, and experiments are planned in user facilities such as the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL) and the Advanced Photon Source to be built and operated by ANL. In this effort, experimental methods are being devised to permit direct *in situ* X-ray investigation of metal/solution interfaces under potential control in an electrochemical cell.

Considerable progress was made on the assembly and testing of a novel electrochemical cell suitable for *in situ* X-ray scattering studies. The geometric embodiment of this cell permits examining a relatively large area (tens of square millimeters) of an electrode/electrolyte interface, while at the same time placing no constraint on the electrolyte thickness and facilitating the application of a uniform electrical field across the electrode surface. Preliminary testing/optimization of the X-ray transmission characteristics of this cell has been performed by Hoydoo You (Materials Science Division) using a recently set up rotating anode facility at ANL.

In collaboration with Hoydoo You and Wen-Bing Yun (Advanced Photon Source Division), we plan to conduct a series of exploratory experiments at an existing synchrotron user facility to investigate the capabilities of the new cell for *in situ* liquid/solid interface studies. These experiments, which should be completed during the coming year, will focus on studying (1) density profiles in corrosion films formed on metals, such as Ni, Fe, Cu, and Zn, as a function of potential, and (2) the morphology of self-assembled molecular films and adsorbed layers on atomically flat surfaces (i.e., distortion of a surface under study is flat to within atomic dimensions). These studies are considered to be forerunners to more detailed investigations of passive film growth, corrosion inhibition by molecular adsorbates, and the structure of the electrical double layer.

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

Ab initio molecular orbital (MO) calculations and inelastic neutron scattering (INS) measurements have been used to examine the effects of the molecular sieve framework on the vibrational frequencies and rotational diffusion of occluded template molecules. The INS spectra of the tetraethylammonium (TEA) cation in the iodide salt and in the chabazite-type cage of SAPO-34 molecular sieve (a silicon-substituted AlPO_4 -34) have been measured by L. E. Iton (Materials Science Division). We have completed MO calculations of the vibrational frequencies of the free TEA cation and assigned modes in the experimental spectra on the basis of these calculations. The results are significantly different from those for tetramethyl ammonium

(TMA) cation, which was studied previously,⁴⁶ including much lower frequencies for methyl group torsions. We are investigating the TEA potential energy surface to determine the barriers to internal rotation and to assess the likelihood of conformational rearrangement during sieve crystallization.

Theoretical studies have been initiated in two new areas. In the first area, *ab initio* molecular orbital calculations are being carried out to investigate the relative Brønsted acid strengths of the framework hydroxyl groups of ZSM-5-type zeolites substituted with B, Al, Ga, Ti, and Fe. These calculated results will be correlated with O-H stretching frequencies measured in infrared spectra. The second area involves local density approximation cluster calculations of near-edge X-ray absorption fine structure (NEXAFS) spectra of molecular sieve materials. These results will allow comparison of cluster models being used to study molecular sieve materials.

b. Studies of Catalysis by Molecular Sieve Materials

In this research effort, we seek to gain new understanding of the catalytic activity and product selectivity demonstrated by molecular sieve cage networks of medium pore size (4 to 8 Å). Infrared spectroscopy is used in conjunction with gas chromatography to provide detailed information on structure-composition-reactivity relationships for a variety of light hydrocarbon reactions on selected aluminosilicate and aluminophosphate framework systems. In the preceding year we found that, when Co(II) is substituted for Al(III) in the framework of certain aluminophosphate (AlPO_4) molecular sieves and the resulting Co(II)-containing AlPO_4 (CoAPO) is calcined in oxygen, the Co(II) is oxidized to Co(III).⁴⁷ Further work with these Co(III)APOs showed that they possess strong oxidizing capability and, for example, can convert methanol to formaldehyde (at 25 °C), NO to NO^+ (at 25 °C), and H_2 to 2H^+ (at ≥ 300 °C). These results suggest that CoAPOs might actually oxidize methane and, in the process, convert the activated methane directly to light hydrocarbons by virtue of the known Brønsted acid catalyzed homologation capacity of such sieve materials. Recent experiments in our laboratory have demonstrated that this is the case. We have found that molecular sieves substituted with cobalt and cobalt/silicon combinations having the AlPO_4 -34 or AlPO_4 -5 structure activate methane starting at ~ 350 °C. At 400 to 500 °C the reaction proceeds more rapidly, with the AlPO_4 -34 and AlPO_4 -5 structures showing comparable activity at all temperatures where products are seen. The highest reactivity observed to date has been achieved with a cobalt substituted AlPO_4 -5 (CoAPO-5), for which yields as high as 60% have been achieved in some experiments. The reaction products (detected by gas chromatography) consist mainly of C_2 and C_3 alkanes and alkenes. Analogous aluminophosphate molecular sieves substituted with magnesium or silicon but containing no transition metal, e.g., MAPO-5, SAPO-34 (M=Mg, S=Si), do not activate methane even at temperatures up to 550 °C. Recent work done by Professor Brenda Shaw and co-workers at the University of Connecticut as part of this project has shown that electrochemical redox activity occurs in CoAPSO-34 microelectrodes at 400 to 500 °C. We have confirmed this activity in our laboratory using somewhat larger electrodes and have been able to sustain the

⁴⁶T. 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).

⁴⁷L. E. Iton, I. Choi, J. Desjardins, and V. A. Maroni, *Zeolites* **9**, 535 (1989).

methane activation process through many effective turnovers at relatively low voltages (3-10 V dc). Aspects of this novel methane-activation process that will be investigated in the future include (1) the reaction efficiency, (2) methods for *in situ* reoxidation of the Co(II) to Co(III), and (3) the catalytic properties of Fe(II)- and Mn(II)-substituted versions of AlPO_4 molecular sieve structures, which we also believe will show methane activation activity.

3. Research on High- T_c Materials

The discovery that certain types of perovskite crystal structures have exceptionally high T_c has spurred a variety of new research activities at ANL. In close collaboration with ANL's Materials Science Division and Materials and Components Technology Division, we have undertaken the following activities: (1) the development of methods for bonding high- T_c ceramics to normal conducting metals for the purpose of adding stabilization and support and (2) the preparation of textured high T_c films by high-temperature ($\sim 900^\circ\text{C}$) oxidation of single-phase liquid alloys (e.g., YbBa_2Cu_3) supported on templating substrates. Progress in each area is summarized below.

a. Bonding of High- T_c Ceramics to Metals

The objective of this effort is to develop promising methods for forming bonds between the high- T_c superconducting ceramic phase and metals or alloys having high electrical and thermal conductivity. This capability would provide a means of (1) manufacturing superconductor/stabilizer assemblies of the type required for high-current-density applications and (2) attaching high- T_c components, such as bus bars and armatures, to a suitable supporting medium. To be effective, the bonded interface between ceramic superconductor and metal must be strong, contiguous, and resistant to temperature cycling; the interfacial electrical resistance must be nil; and the high- T_c properties of the ceramic must not be irreversibly degraded by the bonding process.

A method based on low-temperature thermocompressive diffusion has been developed in our laboratory for bonding $\text{YBa}_2\text{Cu}_3\text{O}_7$ (123) to copper. This method involves the use of metallic bonding foils (typically indium or indium-tin alloys), silver-coated 123 structures, relatively low temperatures (80 to 120°C), and only modest pressure (a few thousand pounds per square inch). Bonded assemblies having a multilayered configuration (copper/bonding foil/silver-coated 123/bonding foil/copper) typically exhibit very low interfacial electrical resistivities ($\leq 10^{-6} \Omega\text{-cm}^2$) and withstand dead weight pulling forces in excess of 3 MPa (500 psi). The bonding method has been successfully applied to 123 in disk, flat-ring, and thin-film form but should also be applicable to other embodiments, to other types of high- T_c ceramics, and to normal conducting metals other than copper (e.g., aluminum). Details related to surface treatment procedures, the advantages of using silver-buffered and silver-loaded high- T_c ceramics, and the interface structure of bonded assemblies have been explored in the course of this work.

b. Preparation of High- T_c Films by Alloy Oxidation

The objective of this research effort is to develop methods for the preparation of high- T_c superconducting ceramic films by oxidation of liquid alloy precursors. Studies at AT&T Bell Laboratories⁴⁸ (Murray Hill, NJ) have indicated that single-phase liquids with the composition MBa_2Cu_3 ($M=Eu$ or Yb) and melting points $<900^\circ C$ can be oxidized to produce textured films of $MBa_2Cu_3O_7$ (123) if the liquid metal is supported on a suitable single-crystal substrate (e.g., $SrTiO_3$ [100]). The resulting high- T_c films showed preferential orientation of the 123 phase a-b planes parallel to the substrate surface and carried critical currents (J_c) in the 10^4 to 10^5 A/cm² range. To improve the potential for practical application of this method, it is desirable to find lower cost substrates, to adapt the liquid phase oxidation procedure for 123 materials to more abundant metals than Eu and Yb, and to extend the technique to the bismuth- and thallium-based high- T_c phases.

The experimental program that we have initiated to explore and exploit the potential of the liquid alloy oxidation method is currently focused on reproducing the AT&T work. We have constructed a high-temperature/high-vacuum (HTHV) apparatus which permits dipping of ceramic substrates into molten alloy mixtures (e.g., $YbBa_2Cu_3$) at temperatures up to $1100^\circ C$ in controlled gaseous environments, oxidation of the adhering liquid alloy film, and annealing of the oxidized film. A series of dipping/oxidation/heat-treating experiments has been done with $YbBa_2Cu_3$ and $YbBa_2Cu_3Ag_3$ alloys (obtained from American Superconductor Corp.). In some of these experiments using $SrTiO_3$ substrates, we have succeeded in producing measurable quantities of textured $YbBa_2Cu_3O_{7-x}$.

The goal of the research on liquid alloy precursor oxidation in the coming year will be to identify a working range of oxygen potential and thermal treatment conditions wherein uniform films of textured $YbBa_2Cu_3O_7$ are reproducibly formed on inert substrates such as $SrTiO_3$, $LaAlO_3$, $KTaO_3$, or MgO . Measurements of T_c , J_c , and Meissner effect will be made on representative samples, and the results will be correlated with synthesis parameters. The importance of substrate crystal habit (oriented versus polycrystalline) on superconducting properties and film texture quality will be investigated. A desirable outcome of our effort in the coming year would be the preparation of textured $YbBa_2Cu_3O_7$ films with T_c near 90 K and J_c approaching 10^5 A/cm².

D. *Geochemistry*

The objective of this effort is to understand (1) the geochemistry of active hydrothermal systems and (2) the thermal and chemical effects of high temperatures on hydrocarbons 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 appropriate field areas. The analytical data are interpreted in terms of the basic geochemical processes that occur in the dynamic natural systems being studied. Potential applications of this work are in nuclear waste management; geothermal energy development; and exploration for minerals, oil, and natural gas.

⁴⁸H. S. Chen, A. R. Kortan, F. A. Thiel, and L. C. Kimerling, *Appl. Phys. Lett.* **55**, 191 (1989).

1. Actinide-Series Disequilibrium Studies of Active Hydrothermal Systems

The extent of radioactive disequilibrium among members of the ^{238}U and ^{232}Th decay series can be exploited for many applications in the earth and environmental sciences. We have been applying actinide-series measurements for investigating the rates and mechanisms of element redistribution and the time scale of hydrothermal activity in several active hydrothermal systems. Our recent work has involved $^{230}\text{Th}/^{234}\text{U}$ age determinations of travertine deposits in the northern part of Yellowstone National Park. The purpose was to gain an understanding of the influence of glaciation upon the underlying hydrothermal system. (Travertines are calcium carbonate deposits, consisting primarily of the minerals aragonite and/or calcite, that can be produced at the Earth's surface where groundwater emerges in a saturated or supersaturated state with respect to the solubility of calcium carbonate.) The use of the $^{230}\text{Th}/^{234}\text{U}$ method for age determinations of travertines ranging in age from 10,000 to 350,000 yr is fairly well established. The use of ^{226}Ra for determining travertine ages <10,000 yr was suggested by Schwarcz,⁴⁹ but little effort appears to have been devoted toward investigating the potential of this method. The principal obstacle encountered in age determinations by the ^{226}Ra method is that one must know (1) the initial amount of excess ^{226}Ra and (2) the integrity of the material with respect to gain or loss of radium since deposition.

During 1989, we completed a study of radium isotopes in thermal waters and travertines from the travertine-depositing hot springs at Mammoth Hot Springs, Yellowstone National Park, Wyoming. The purpose was to investigate the potential applications of radium isotopes for age determinations of young travertines. Essential to this purpose were (1) determining the range of ^{226}Ra activities in modern travertine deposits and (2) understanding the influence of diagenesis (i.e., dissolution-reprecipitation reactions) on the distribution of alkaline earth elements (including radium) within the travertine. Data were collected during the course of this study by chemical and isotopic (Ra, Th, and U) analysis of thermal waters and travertines and mineralogic analysis of travertines. Analytical methods used were radon emanation/alpha scintillation and gamma spectrometry for the Ra isotopes, isotope dilution alpha spectrometry for U and Th isotopes, inductively coupled plasma/atomic emission spectrometry for other elemental analyses, and X-ray diffraction for mineralogic determinations. Travertine samples were collected from the vents of the active hot springs, as well as former vent areas of presently inactive hot springs and a drill core (U.S. Geological Survey's Y-10) through a 75-m thick section of the Mammoth travertine terraces.

Comparison of the chemical and mineralogical compositions of the modern travertines (from the active hot springs) with the older travertines (from the former hot springs and the drill core) revealed two important distinctions: (1) the modern travertine samples primarily consist of the mineral aragonite ($\geq 80\%$), whereas all drill-core travertine samples but one consist entirely of calcite ($\geq 95\%$), and (2) the modern travertine samples have consistently higher concentrations of Sr, Ba, and Ra and lower concentrations of Mg than those of the older travertines. Assuming that all of the travertines formed under similar conditions, we interpreted

⁴⁹H. P. Schwarcz, "Application of U-Series Dating to Archaeometry," in *Uranium Series Disequilibrium: Applications to Environmental Problems*, eds., M. Ivanovich and R. Harmon, Clarendon Press, Oxford (1982).

these observations as indicating that the travertine lost Sr, Ba, and Ra but gained Mg when the aragonitic travertine recrystallized to the more stable calcitic travertine. If so, then radium isotopic data provide constraints on the rate of this process.

Comparison of the activities of three radium isotopes (^{226}Ra , $t_{1/2}=1602$ yr; ^{228}Ra , $t_{1/2}=5.75$ yr; ^{224}Ra , $t_{1/2}=3.64$ d) in thermal waters and modern travertines shows that the relative amounts are identical in both materials. The activities of the radium isotopes are several orders of magnitude greater than those of their parent Th and U isotopes in both waters and travertines, i.e., the radium isotopes are essentially "unsupported." Further, the $^{228}\text{Ra}/^{226}\text{Ra}$ activity ratio in thermal water from the eight hot springs sampled had a narrow range of 0.59 to 0.67. Since radium isotopes are not separated during normally occurring geochemical processes, the only factor having a significant effect upon the ratio of the radium isotopes in the travertine is radioactive decay. Assuming the same initial activity ratio of $^{228}\text{Ra}/^{226}\text{Ra}$ in the travertines (0.62, the mean ratio of the eight springs sampled), we determined that the youngest travertine in which all aragonite had inverted to calcite was 9.0 ± 0.2 yr old at the time of sampling.

The age of a sample of travertine drill core from near the base of the travertine section was determined to be 7700 ± 440 yr by the $^{230}\text{Th}/^{234}\text{U}$ method. This provided an independent constraint by which the depth distribution of ^{226}Ra could be examined with respect to the feasibility of determining the age and deposition rate of this travertine deposit. We predicted the ^{226}Ra activity as a function of depth in the drill core, assuming an initial value equal to the mean ^{226}Ra activity of modern travertines (~ 7 pCi/g) and an age of 7700 yr for travertine at a depth of 72.9 m. The calculated results gave a mean deposition rate of 0.95 cm/yr.

Figure VI-8 is a diagram of the measured and predicted ^{226}Ra activity versus depth below surface in the drill core. It is clear from lines A and B that the measured ^{226}Ra activities below the surface are much lower (approximately 90%) than the predicted activities. This discrepancy is interpreted to result from the loss of radium during the diagenetic inversion of aragonite to calcite, which occurs very near the surface of the deposit during a few year period following deposition from thermal waters. The ^{226}Ra may remain relatively immobile following the initial diagenetic changes, although some local subsurface deposition may occur, as indicated by the anomalously high ^{226}Ra activities measured for certain samples. Thus, the potential for accurate age determinations by the ^{226}Ra method remains limited by the uncertainty in the amount of radium lost during diagenesis and the amount gained through subsurface deposition. However, the rate of travertine deposition may be estimated fairly well from the slope of the best-fit line through the drill core data (line B). This slope is approximately parallel to that of the predicted ^{226}Ra activity versus depth, indicating that the deposition rate was near the predicted one of 0.95 cm/yr. Future studies of Yellowstone travertines will investigate Sr isotope ratios as paleohydrogeologic indicators.

2. Deep Carbon Geochemistry

Our present studies are designed to elucidate the process of organic matter alteration in high-temperature geochemical environments. The results have direct implications to defining the limiting conditions for formation and survival of hydrocarbon compounds in extreme geologic environments. Step-combustion experiments between 200 and 550°C were performed on kerogen (i.e., insoluble organic matter in rocks) from the Green River Shale to determine the

magnitude of isotopic fractionation that may be expected during kerogen metamorphism in sedimentary basins. We also performed several field studies of contact-metamorphosed carbonaceous sediments. We analyzed samples from the 1.6 billion years old sedimentary rocks from the Animikie Basin (Minnesota) for total organic carbon, total carbonate carbon, and isotopic content ($\delta^{13}\text{C}_{\text{organic}}$, $\delta^{13}\text{C}_{\text{carbonate}}$, and $\delta^{18}\text{O}_{\text{carbonate}}$) and also performed isotopic and molecular characterization of extractable organics in these samples. Similar data are being collected for contact-metamorphosed Triassic sediments from the Deep River (North Carolina) and Culpeper (Virginia) Basins.

Fig. VI-8.

Measured and Calculated ^{226}Ra Activity vs. Depth for Samples of Travertine from Mammoth Hot Springs, Yellowstone National Park, Wyoming. Subsurface samples are from the U.S. Geological Survey's Y-10 drill core. Measured data indicated by filled circles. Line A is the predicted ^{226}Ra activity as a function of depth in travertine deposit. This prediction is based on the assumption of 7 pCi/g initial ^{226}Ra activity and 7700 yr age of travertine at 72.9 m depth. Line B is best-fit curve through the drill core data.

Figure VI-9 gives the total yields and isotopic compositions of CO_2 and CO released from the step-combustion experiments on Green River Shale kerogen. A bimodal release pattern was observed for both gases, although CO_2 clearly dominated the overall yield. Note that the fraction collected at the highest temperature in our experiments did not yield the highest $\delta^{13}\text{C}$. It is therefore unlikely that the isotopic profiles resulted from kinetic isotope effects. The $\delta^{13}\text{C}$ profiles probably reflect variable thermal stability of isotopically distinct components of the kerogen.

Two carbonaceous formations from the Animikie Basin were studied: (1) Virginia Formation (lower argillaceous lithosome) and (2) Biwabik Iron Formation (Intermediate Slate unit). Decarbonation of the latter was indicated by the relatively low total carbonate carbon found in samples collected closer to the intrusion. In addition, $\delta^{13}\text{C}_{\text{carbonate}}$ (-13.7 to -3.6 ‰) and $\delta^{18}\text{O}_{\text{carbonate}}$ (12.0 to 23.8 ‰) were variable close to the intrusion. Previous workers⁵⁰ have suggested that carbonate isotopic compositions in the Biwabik Iron Formation reflect a variable degree of metamorphism. In contrast, our combined $\delta^{13}\text{C}_{\text{carbonate}}$ and $\delta^{18}\text{O}_{\text{carbonate}}$ data clearly indicate that this variation is of primary (i.e., depositional) origin and little affected by metamorphism. The total organic carbon content and $\delta^{13}\text{C}_{\text{organic}}$ of variably metamorphosed

⁵⁰E. C. Perry, F. C. Tan, and G. B. Morey, *Econ. Geo.* **68**, 1110-1125 (1973).

samples from the Virginia Formation show no systematic variation with distance from the intrusion (total organic carbon from 0.06 to 2.54% and $\delta^{13}\text{C}_{\text{organic}}$ from -33.3 to -26.1 ‰). In contrast, a clear enrichment of total organic carbon in the Biwabik Iron Formation occurred within the thermal aureole of the intrusion (1.7 to 6.2% within the aureole compared to <1% outside the aureole). This enrichment appears to be accompanied by ^{13}C depletion in the organic carbon fraction. These trends could reflect hydrocarbon mobilization as a consequence of the thermal conditions imposed on the sedimentary units by the emplacement of the Duluth complex.

Fig. VI-9. Yields (double-dashed line) and Carbon Isotopic Compositions (solid line) of CO_2 (left) and CO (right) for Step Combustion of Kerogen from the Green River Shale

Similar studies on samples from the Deep River and Culpeper Basins are in progress. These samples contain more extractable components because of their less metamorphosed character. Isotopic characterization of kerogen and extractable components in these samples will be the focus of future research. These studies will utilize the gas chromatograph/isotope ratio mass spectrometer (GC/IRMS) that will be installed in our laboratory shortly. Our unique GC/IRMS instrumentation will also be employed for isotopic characterization of samples from our step-combustion experiments.

VII. 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 services to the scientific and engineering programs at ANL. In addition, the ACL conducts a research program in analytical chemistry, works on instrumental and methods development, and provides analytical services for governmental, educational, and industrial organizations. The ACL 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 CMT, the principal user, but provides support for all the technical divisions and programs at ANL. The ACL has four technical groups--Chemical Analysis, Instrumental Analysis, Organic Analysis, and Environmental Analysis--which together include about 50 technical staff members.

The Chemical Analysis Group uses wet-chemical and instrumental methods for elemental, compositional, and isotopic analyses of solid, liquid, and gaseous samples. The Instrumental Analysis Group uses nuclear counting techniques in radiochemical analyses for a range of samples (low-level to highly radioactive environmental samples). Other types of analyses done by this group are gas chromatography (GC), X-ray diffraction (XRD) and fluorescence of solids, inert gas fusion of metals, and neutron activation of either liquids or solids. The Organic Analysis Group uses a number of complementary techniques to separate and analyze complex organic mixtures and compounds at the trace level, including synthetic fuels, toxic substances, fossil-fuel residues and emissions, pollutants, biologically active compounds, pesticides, and drugs. The Environmental Analysis Group performs inorganic environmental and hazardous waste analyses and coal analysis.

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.

Analytical Support for Engineering-Scale Studies of Pyrochemical Processes for IFR Fuels

In the electrorefining of uranium and plutonium fuels for the Integral Fast Reactor (IFR), metallic fuel pins (principally U, Pu, Zr) containing fission products 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 conducted in CMT in order to develop models that can predict the recovery of U and Pu, as well as the decontamination of these elements from fission-product elements and process materials. The ACL has contributed to this effort by determining elements of interest in samples from the Cd anode, the halide-salt electrolyte, and the cathode product. Special dissolution procedures were developed for each type of sample matrix, and separation schemes based on solvent extraction and ion exchange were established to isolate the desired elements from matrix components and, subsequently, to separate these elements from each other. Additional analyses by high resolution gamma-ray spectrometry with

a high purity Ge detector were performed on samples to determine ^{241}Am and ^{244}Cm . The purpose was to better understand the behavior of these elements in the electrorefining process.

A "hot" inductively coupled plasma/atomic emission spectroscopy (ICP/AES) instrument continues to be the workhorse for the determination of cations in these types of samples. This instrument is used to determine U and Pu concentrations in samples where 10% uncertainty is sufficient. Whenever higher precision and accuracy are required, the method of choice is mass spectrometric isotope dilution (MSID). Samples containing no plutonium, which are from studies of fission product distribution coefficients in the Cd anode and the electrolyte, are analyzed by a "cold" ICP/AES.

Additional analytical support was provided for studies being conducted in CMT to determine the best waste form for the products of these electrorefining processes. In these studies, the gamma irradiation behavior of various waste forms was determined. Mass spectrometry was used for the determination of hydrogen, nitrogen, and oxygen content of the off-gas as a function of radiation dose rate.

The waste electrorefining salts generated by IFR fuel reprocessing will be contacted with Cd-Li-K alloys 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 to prepare radioactive waste with high compressive strength and low leachability. The leach tests are performed by the standard ANSI6.1 procedure. Ion chromatography is used to measure the amount of Cl^- present, which determines the leach rate from the grout.

During 1989, approximately 320 samples were analyzed for all the CMT engineering groups associated with this program, with almost 210 samples from electrorefining studies, 75 from fission product distribution studies, and 35 from waste studies. Each of these samples required determination of up to ten elements.

DOE Environmental Survey

In early 1986 the DOE initiated a program designed to identify current and/or potential environmental problems and areas of environmental risk at DOE facilities, about 40 sites nationwide. For the last three years the ACL has provided environmental analytical chemistry support in the form of organic, inorganic, and radiological analyses for the sampling teams from ANL and other participating laboratories. The Idaho National Engineering Laboratory (INEL), Oak Ridge National Laboratory (ORNL), and Battelle-Columbus Division/Pacific Northwest Laboratories (BCD/PNL) have been involved in the program in roles similar to ANL in field sampling and analysis. The Oak Ridge Gaseous Diffusion Plant (ORGDP) has provided additional analytical support. The U.S. Environmental Protection Agency Environmental Monitoring Systems Laboratory-Las Vegas (U.S. EPA EMSL-LV) has been providing an independent quality assurance overview; Environmental Monitoring Services, Inc. (EMSI), a consulting firm, has conducted third-party audits; and Nuclear Utilities Services (NUS), a consulting firm, has been providing DOE with technical advice in developing site-specific sampling and analysis plans.

The ACL role includes consulting with and advising the field sampling teams on analysis problems, providing analyses and associated quality assurance/quality control (QA/QC) by methods selected for the program, and developing an analytical methodology suitable for the program in cases where the sample matrix is atypical and/or the types of required data are unique. The methodologies for the organic and inorganic analyses [many of which follow the EPA Contract Laboratory Program Statement of Work (CLP SOW)] and the radiological analyses are coordinated with ORNL, ORGDP, INEL, and BCD/PNL and are published in an Environmental Survey Manual to ensure a consistent and uniform application of methods and treatment of data.

In 1989, the ACL provided analytical support for the Survey and technical analytical support to other participating laboratories, including:

(1) Idaho National Engineering Laboratory

- 180 environmental samples from the Bryan Mound Strategic Petroleum Reserve (Bryan Mound, TX) for inorganic and organic analyses.
- 85 environmental samples from the Stanford Linear Accelerator Center (Palo Alto, CA) for inorganic and organic analyses.
- 75 environmental samples from the Lawrence Berkeley Laboratory (Berkeley, CA) for inorganic and organic analyses.

(2) Oak Ridge National Laboratory

- 9 solidified waste samples from the Lawrence Livermore National Laboratory (Livermore, CA) for inorganic and organic analyses.

To help assure high-quality analytical performance in this program and others, the ACL participated in four multilaboratory programs sponsored by the U.S. EPA and DOE. Each program provided the ACL with sets of either Quarterly or Semiannual Blind Performance Evaluation (PE) Samples for analysis.

During 1989 the ACL received organic and inorganic PE samples quarterly from the EMSL-LV. All scores for ACL analyses were within the acceptable range as determined by the EPA. In addition, the ACL participated in the EPA Water Pollution Study. Semiannual inorganic PE samples were analyzed for cyanide, oil/grease, total dissolved and suspended solids, and a variety of anions. The EMSL-LV reported that ACL's analytical results were in excellent agreement with EPA's known values.

The DOE Environmental Measurement Laboratory (EML) and EMSL-LV coordinated multilaboratory Cross-Check PE Programs and provided radiological PE samples for analysis by the ACL. Water, soil, and air filter samples for radionuclide determinations (e.g., gross alpha-beta, gamma, tritium, radium, uranium, plutonium, neptunium) were received throughout 1989

on a semiannual basis. The ACL did well in these determinations, with each of the radionuclides analyzed being in agreement with reference values.

The ACL has also provided technical support to Science Applications International Corp. (Oak Ridge, TN) in the preparation of Survey draft data documents for the Y-12 Plant (Oak Ridge, TN), the Kansas City Plant (Kansas City, MO), and the Portsmouth Uranium Enrichment Center (Pikeston, OH).

Gas Analysis for Argonne Premium Coal Sample Program

The Argonne Premium Coal Sample Program provides high-quality coal samples from eight U.S. mines for distribution to the coal research community. The program involves processing, packaging, characterization, storage, and distribution of the various coals. It also includes gas mass spectrometric analyses of the cover gas (N_2) in randomly selected sealed ampoules of each coal to determine composition changes over time. The presence of O_2 in the cover gas is of particular concern, but also of interest are changes in the amounts of CH_4 , CO , and CO_2 , since they may signal ongoing chemical or biological degradation of the coal material. To date, the ACL has analyzed the gas from more than 140 such ampoules, with 35 ampoules having been analyzed during 1989. Although trends are apparent in the trace-gas concentrations data from some coals, no significant coal degradation has been detected.

Development of Alternative Analytical Method

The ability of a gas chromatograph/matrix isolation-infrared spectrometer (GC/MI-IR) to aid in characterization of isomeric organic compounds has been demonstrated previously in our laboratory.¹ Other chromatographic techniques are needed to separate those compounds that cannot be separated by normal gas chromatography. It has been demonstrated that supercritical fluid chromatography is well suited for the separation of high molecular weight, polar, or thermally labile compounds. A project was initiated to develop an interface between the ACL's supercritical fluid chromatography (SFC) unit and the matrix isolation-infrared spectroscopy/mass spectrometry system (MI-IR/MS).

After development, we propose to apply SFC/MI-IR/MS to the characterization of toxins and biomolecules present in complex mixtures. The ability to obtain infrared spectra of separated matrix-isolated biomolecules present in complex mixtures and the mass spectra of these same molecules will be useful in identifying the molecules and confirming their structure. Because MI-IR yields very narrow IR bands, and band broadening due to intermolecular hydrogen bonding is absent, any intramolecular hydrogen bonding in a complex biomolecule can be probed.

¹M. J. Steindler et al., *Chemical Technology Division Annual Technical Report, 1988*, Argonne National Laboratory Report ANL-89/15, p. 158 (1989).

Deuterium/Hydrogen Measurements for "Cold Fusion" Studies

Analytical support was provided to those investigating the "cold fusion" phenomenon by performing measurements to characterize the H/D composition of the heavy-water electrolyte and of gases dissolved in the palladium electrode. The electrolyte was analyzed by reacting a small aliquot of the heavy water with hot (450 °C) uranium-metal chips in a closed container and measuring the isotopic composition of the resulting (H_2 , HD, D_2) gas by mass spectrometry. The Pd electrode was degassed, under vacuum, in a specially assembled apparatus that permitted measurement of the rate of gas release from the Pd rod and periodic acquisition of gas samples for mass spectrometric analysis. Outgassing by the Pd was followed at room temperature and at several higher temperatures (up to 600 °C) until the dissolved gases were virtually exhausted. The Pd rod was weighed prior to each temperature change to determine the weight of gases lost. The data obtained permitted characterization of the behavior of these two hydrogen isotopes during outgassing, as well as a measure of the quantity of gas dissolved in the electrode. The electrolyte of this experiment was also analyzed for tritium by using liquid scintillation counting. A baseline analysis was performed (tritium present in the initial solution), and several samples of the electrolyte throughout the experiment were analyzed to determine if any tritium was produced. None was detected above the baseline level.

Purification and Electrodeposition of Ni for Metal Clusters Source

Researchers at ANL studying the reactions and properties of gas-phase metal clusters have found that the best target for producing nickel clusters is one prepared by electrodepositing purified nickel metal on a copper mandrel. The ACL was instrumental in fabricating one such target several years ago by purifying the Ni (using precipitation with dimethylglyoxime followed by ignition of the precipitate to NiO) and electrodepositing a 250-mm layer of the purified nickel on the Cu mandrel. This target was recently exhausted and had to be replaced. Since the Ni involved was a relatively expensive separated isotope (^{58}Ni), the residual Ni on the target was reclaimed by machining the mandrel, which introduced copper as an additional contaminant in the reclaimed Ni. We removed this copper by ion exchange and combined the reclaimed ^{58}Ni with new material prior to purifying it according to the previously used procedures. To give the new target a longer expected lifetime, we were requested to attempt electrodepositing 380 mm Ni rather than the 250 mm applied to the first target. The target produced this time, though thicker than the earlier one, was of poorer quality. Based on lessons learned in this effort, future targets will be restricted to the 250-mm thickness where smooth, uniform, and adherent deposits can be readily achieved.

Characterization/Calibration of Daly Detector on Thermal Ionization Mass Spectrometer

During 1988, we added a Daly scintillation detector to our VG Isotopes Model 54R thermal ionization mass spectrometer (TIMS) to complement the Faraday cup detection system on the original instrument. The Daly detector is about 100 times more sensitive than the Faraday cup and permits isotope-ratio measurements on samples where only tiny quantities (<1 mg) of the element of interest are available or on elements whose ionization characteristics limit the intensity of ion beams achievable with thermal ionization.

In 1989, we carried out experiments to characterize and calibrate the Daly detector for use in measuring uranium isotope ratios. Measurements were performed on a series of NBS uranium isotopic standards to characterize the detector's response over a range of isotope ratios from 1:200 to 200:1. The Daly detector is presently operable in a fully automatic mode with computer-applied corrections. Uranium isotope ratios measured by the external-standard procedure show a between-runs standard deviation of 0.10%, relative; residual bias (after nonlinearity and mass discrimination corrections) is less than 0.01% of the values measured. Future work with the Daly detector will include optimizing analysis conditions (heating sequence, sample loading, etc.) to reduce the run-to-run variations.

Carbon Tetrachloride and Chloroform Monitoring at a USDA Facility

Carbon tetrachloride and chloroform have been extensively used at U.S. Department of Agriculture (USDA) grain storage site at Waverly, Nebraska, for many years. Environmental concerns have resulted in a regular monitoring of these two compounds in air and groundwater. The ACL has performed analyses for these two compounds on monthly (~10) and quarterly (~60) submitted samples. The water samples were analyzed using the CLP Volatile Organic Analysis protocol, while the air samples were analyzed using the NIOSH Method 1003. The results obtained by ACL on the air samples from the Waverly site have formed the basis for USDA selecting an even more sensitive method (Tenax trap absorption/desorption) for air sample analysis. We will provide guidance on sampling and will perform the analytical work with this method.

Analytical Support for Studies of Alkali in Hot Off-Gas from Pressurized Fluidized-Bed Combustors (PFBC)

Alkali metal compounds present in the hot off-gas from PFBC, such as chlorides and sulfates of sodium and potassium, may cause corrosion of the gas turbine used to recover energy released during combustion. Researchers at ANL are developing an analytical alkali sorber bed technique for reliable quantification of the level of vapor-phase alkali in PFBC off-gas on a time-averaged basis so that the effectiveness of different alkali control strategies might be evaluated. In this technique, analytical alkali sorber beds containing activated bauxite or diatomaceous earth are inserted in the primary (activated bauxite) sorber bed that is used to condition the PFBC process stream. After a given test, the analytical sorber beds are contacted with an appropriate leaching solution, and the leachates are analyzed for alkali metals by atomic absorption spectroscopy (AAS) in the ACL. To satisfy the special accuracy requirements ($\pm 2\%$ or better for concentrations below 20 $\mu\text{g/mL}$) of these analyses, the AAS uses controlled acidity for the analytical samples and a high-purity cesium matrix modifier to suppress matrix interferences. Each sample is typically analyzed at several different dilutions to verify the absence of residual matrix effects. During the past year, nearly 250 samples of bauxite leachate and other samples (auxiliary absorber solutions, PFBC feed materials, gases) were analyzed in support of this project.

Infrared Aerosol Analyzer

Concern is increasing about the possible adverse health effects of acidic particles and gases in the air, including the gaseous oxides of sulfur and nitrogen and the corresponding sulfuric and nitric acids in the fine particles suspended in the air. Instruments for real-time analysis of ambient gases are commercially available and have been used routinely for many years. For the particulate matter, however, typical procedures involve collection of samples of the aerosol over long periods of time (many hours or even weeks), with the analysis being conducted afterward in the laboratory, sometimes many days or weeks later.

We have developed a highly sensitive Infrared Aerosol Analyzer (IAA) to provide real-time chemical analysis of ambient aerosol particles.² This portable instrument divides the particulate matter into three different size fractions (coarse, fine, and ultrafine) and analyzes each size fraction separately. Size fractionation and separation of the ambient aerosol are especially important to prevent interaction among particles after collection. The coarse fraction contains basic crustal materials; the fine fraction contains the bulk of the acidic materials, if any are present; the ultrafine particles are the very fresh, newly formed aerosol which, under certain conditions, can contain a high concentration of sulfuric acid. (Mixing of the sizes during sampling or analysis could destroy these differences.) The analysis by infrared spectroscopy simultaneously detects and measures all acidic components of the aerosol, as well as any other constituents that have an infrared fingerprint. This instrument also has the potential for use in a variety of aerosol research projects as well as use as a monitor for industrial and environmental concerns. In 1989 the IAA received one of Research and Development Magazines R&D-100 Awards.

Analytical Support for Rare-Earth Characterization Studies

In one of the Chemical and Engineering Support Studies being conducted for the IFR, the distributions of the more abundant rare earths between the salt phase (as the rare-earth chlorides) and the cadmium solution (as metals) are being compared. In the experiments performed for this work, lanthanum and one other rare earth are dissolved in a pool of cadmium, which is covered with a layer of molten LiCl-KCl eutectic. Samples of the metal and salt phases are withdrawn from the system following stepwise changes in the redox potential (varied by addition of cadmium chloride) or temperature and are analyzed.

Each salt-phase sample is analyzed to determine Li, K, Cd, and the pertinent rare earths by ICP/AES and chloride by argentometric titration. Required ICP/AES detection limits for the rare earths are met by carefully selecting analysis wavelengths and generating profiles of individual emission lines. Each cadmium metal sample is similarly analyzed to determine Li, K, and the rare earths by ICP/AES. Cadmium in the metals is measured by titration with ethylenediaminetetraacetic acid. We presently measure chloride in the cadmium metal samples by silver chloride gravimetry.

²S. A. Johnson, G. T. Reedy, and R. Kumar, "A Real-Time Infrared Aerosol Analyzer," Abstracts, Annual American Association for Aerosol Research Meeting, Reno, NV, October 9-13, 1989, p. 329 (1989).

During 1989, experiments were completed on two rare-earth pairs (La-Nd and La-Eu) and were begun on a third (La-Sm). For europium and samarium, the divalent state of the rare earth is relatively stable, and additional measurements (besides those listed above) were made to determine divalent rare-earth concentrations in selected salt-phase samples. Special care was required for these measurements to avoid air oxidation of the europous or samarous ions during sample preparation or measurement. We developed a procedure wherein the salt sample is dissolved in a nitrogen-sparged solution containing excess ferric [Fe(III)] ion, which is reduced to ferrous [Fe(II)] by the divalent rare earth. The resulting ferrous ion, which is considerably more stable than the divalent rare earth ion, is accurately determined by titration with Ce(IV) using a Ferroin indicator. By performing this titration with a digital autoburet and locating the endpoint with a Dipping-Probe Colorimeter, uncertainties of 1%, relative, are easily achieved. Comparison of the Eu(II) and Sm(II) results from this method with total Eu or Sm concentrations measured by ICP/AES has shown that virtually all Eu in the salt phase exists in the divalent state, while only about 20% of Sm is divalent.

Transuranic Extraction (TRUEX) Process Flowsheet Development

Technology under development in the TRUEX Program involves a solvent extraction process to separate and recover actinides from nitric acid solutions without a need for valence state adjustments. Extraction, scrub, and strip sections in a multistage centrifugal contactor are used in the process and require characterization for elemental composition. Performance of the multistage centrifugal contactor is being tested utilizing simulated nuclear waste streams. These streams typically consist of fission products (Ag, Ba, Cd, Cs, Sr, Pd, Rh, Ru, Ce, Eu, La, Nd, Pr, Sm, Y) and structural or fuel components (Al, Be, Ca, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Sn, Ti, Zr). Data describing element concentrations in various process stages are being acquired to generate and validate computer models of the TRUEX flowsheet. The ACL has analyzed hundreds of samples (almost 500 in 1989) by ICP/AES or other techniques, e.g., laser fluorimetry for U or atomic absorption spectrophotometry (AAS) for Cs, for this effort. The multielement analysis capability of the ICP/AES system, combined with its wide dynamic range for elemental concentrations, is well suited to this type of measurement, although the complicated mixtures involved often present challenging problems pertaining to wavelength selections and handling of spectral interferences. Measurements provided by the ACL have contributed to the accumulation of an extensive TRUEX flowsheet data base in a relatively short time. In turn, this data base has permitted verification of theoretical models and improvements in process performance.

National Acid Precipitation Assessment Program (NAPAP)

Analytical support for the NAPAP of the U.S. Department of Interior continued this year. Marble and limestone test briquettes, exposed to a variety of atmospheric conditions at a number of sites throughout the country, are brought to ANL for sampling and analysis. Hundreds of specimens (approximately 350 during 1989) have been analyzed for fluoride, chloride, nitrate, and sulfate by ion chromatography, and a smaller number have been analyzed for metals by ICP/AES. Substantial elevations in sulfate and nitrate concentrations have been found to occur in

the limestones and have provided a quantitative measure of attack by atmospheric nitrogen and sulfur oxides. Little change in cation concentrations occurs following exposure at the test sites.

Molten Corium-Concrete Interaction (MCCI) Studies

In MCCI experiments, mixtures of uranium oxide, zirconium, steel, fission product elements, and concrete are heated to temperatures simulating reactor meltdown conditions with the objective of studying the vaporization behavior of the elements present and understanding the release of refractory fission products during a degraded-core accident. Samples of solidified melt, aerosols collected by impaction or on filters, and gases were examined to study interaction and transport of the simulated reactor materials. Typically, the solidified melt and aerosol samples were analyzed for Ba, Sr, La, Ca, Al, Mg, Na, K, Fe, Cr, Ni, Zr, Ag, and Ce by ICP/AES, for U by laser fluorimetry or ICP/AES, for silicon by AAS or ICP/AES, and for soluble anions by ion chromatography. Often X-ray diffraction measurements were made to identify particularly interesting phases in selected samples. Gas samples were analyzed by mass spectrometry.

This year, samples from two large-scale MCCI tests involving high-silica concretes were analyzed. The ACL has devised a repertoire of dissolution schemes for these samples, including high-pressure sealed-tube procedures, microwave dissolution procedures, and other special techniques. We put some samples in solution by fusing each with lithium tetraborate at 1000 to 1100 °C and dissolving the resulting material in dilute HCl. Standards for the ICP/AES measurements were prepared in the $\text{Li}_2\text{B}_4\text{O}_7$ flux matrix, and fusion blanks were analyzed with the samples.

Among the results obtained for these tests was evidence that silicon metal was present in addition to SiO_2 in many aerosol samples (an observation explained by disproportionation of gas-phase SiO into Si and SiO_2), and that silicon carbide had formed in some samples. Formation of SiC was unexpected. However, postulating that the SiC arose from gas-phase reaction between SiO and CO_2 helped explain lower-than-anticipated CO_2 concentrations in the gases that were analyzed.

Analytical Support for ANL Geosciences Programs

A wide variety of analytical measurements are performed by the ACL in support of geoscience programs at ANL. These include characterization of groundwater samples by analysis for cations with ICP/AES or atomic absorption techniques, measurement of anion concentrations (F^- , Cl^- , NO_3^- , SO_4^{2-} , Br^- , I^-) by ion chromatography, and determination of pH, alkalinity, or other properties by classical methods. This year, we applied these and other, more-specialized, techniques to measurements on thermal waters and minerals from Yellowstone National Park and to measurements on thermal waters, gases, steam condensates, and gas-sampling absorber solutions from volcanoes in Columbia and Ecuador.

As part of the Yellowstone studies, the ACL was requested to implement procedures to isolate and purify Sr from geological samples for isotopic analysis by methods already in place in our laboratory. We evaluated the effectiveness of several column configurations for the critical

cation-exchange separation of strontium and calcium in typical geological compositions. Elution behavior of the two elements was characterized by ICP/AES analysis of individual eluant fractions from each column. By using longer, narrower columns than those used by others, we were successful in isolating as little as 10 mg Sr in high yield from a matrix containing as much as 50 mg Ca, while needing only about half the volume of high-purity acid solutions that short, wide columns require. Our procedure is now being used for preparing Sr isotopic samples from thermal waters and dissolved travertine (CaCO_3) deposits from Yellowstone hot springs.

A recently developed ^{226}Ra and ^{228}Ra method was used to analyze these Yellowstone samples. Large volumes of water were passed through the special Dowex radium selective resin upon collection, and sent to Argonne where the resins were processed and counted. Short holding times were required to determine ^{224}Ra , which has a half-life of 3.66 days. Other radium isotopes were determined on subsequent countings. Additionally, a radon emanation method was applied to dissolved CaCO_3 deposits from Yellowstone hot springs to determine ^{226}Ra more precisely.

One-Step Separation of Uranium from Mixtures of Cations

Separation of uranium from mixtures containing a variety of other metals is frequently required for effective application of analytical measurement techniques, either for the determination/characterization of the uranium itself or for measurement of the other metals. Most methods for isolating uranium from complicated matrices or for isolating common metals from a uranium matrix involve several steps and, consequently, are time-consuming, prone to contamination, and likely to give poor recovery for the metals of interest. In a collaborative project with the ANL Chemistry Division, we developed a simple, one-step uranium separation based on supported-liquid column-extraction chromatography, which uses a packing prepared from 100- to 120-mesh XAD-7 ion exchange resin coated with 40 wt % diamyl amylphosphonate (DAAP). Uranium is selectively retained on the column from 3 N HNO_3 and eluted with high recovery by 0.01 N HNO_3 . Data obtained in our studies include uranium recovery at the microgram level, column capacity, and retention behavior of a number of common metals and radionuclides.

We have successfully applied this separation to the simultaneous isolation and purification of uranium for mass spectrometric measurement of the U isotopes in a variety of mixtures, including digested environmental materials (e.g., soil, sludge, sediment, tar sand, rock, or bone). In this application, microgram quantities of U may be separated from gram quantities of matrix constituents to give a product sufficiently pure for direct loading on the mass spectrometer filament.

The substantial uranium capacity of the DAAP packing (130 mg U per mL resin) and its virtual nonretention of most other metals make it attractive also for removing uranium interference when determining the other metals in a given mixture. For example, we have used this approach to isolate metal impurities from a uranium matrix for multielement determination by ICP/AES.

Determination of Organic Fluid Fouling in Heat Exchange Systems

The fouling of heat exchange systems is currently being studied using an organic fluid model. The goal is to elucidate the mechanism by which fouling occurs by characterizing soluble precursors in the organic fluid. Samples of heptane spiked with 6% styrene were extracted from organic fluid in a heat exchange system at varying time intervals and analyzed using GC with flame ionization detection and gas chromatography/mass spectrometry (GC/MS). System temperatures ranged from 30 to 180 °C. Results indicated that heptane stability declined after 24 h of loop circulation in the heat exchange system, and the resulting alkane fragments combined with styrene to form propyl benzene and other C₃-benzenes. Styrene formed dimers and trimers by 60 h at the higher temperature. Based on these findings, a hyperconjugation mechanism was proposed for formation of isomeric adducts. Methodology has also been developed to evaluate fouling deposition on the heat exchange system pipe using Fourier transform infrared (FTIR) microscopy, scanning electron microscopy (SEM), and XRD.

Analytical Support for Research on High-Temperature Superconductors

The ACL continued providing extensive analytical support to high-temperature superconductivity programs. Much of this work involves analysis of starting materials, process samples, and products related to fabrication and characterization studies on YBa₂Cu₃O_{7-x} ("123" compound) ceramics or other ceramic compositions. Measurements we perform include determining elemental compositions by ICP/AES, anions by ion chromatography, oxygen coefficients (i.e., the value of x in the formula YBa₂Cu₃O_{7-x}) in selected ceramics by an iodometric method, and phases by X-ray powder diffraction.

Determination of the oxygen coefficient for copper-containing ceramics was established as a new capability within the ACL during 1988. It is based on our modification of a method by Appelman et al.³ and employs an autoburet and special colorimeter to provide optimal precision in the critical titration of iodine with thiosulfate. From the results of replicate measurements performed on the almost 60 samples analyzed during 1989, we have determined that reproducibility of better than ±0.005 in x is routinely achieved for samples weighing from 15 to 40 mg. We are considering modification of the method to accommodate smaller samples so that measurements may be extended to single-crystal superconductors where only 1 mg or less might be available for analysis.

X-ray diffraction is useful for identifying crystalline phases and the presence of amorphous phases and for monitoring the relative purity of samples. Crystalline preferred orientation, which is usually not desirable in phase identification but is desired in some superconductivity preparations, is monitored by observing anomalous intensities for a certain class of reflections in the "123" compound. Lattice constant measurements have also become important with the level of various dopants that are added to superconductive and composite materials in order to influence their physical properties. A change in lattice constants with dopant level indicates

³E. H. Appelman, L. R. Morss, A. M. Kini, U. Geiser, A. Umezawa, G. W. Crabtree, and K. D. Carlson, *Inorg. Chem.* **26**, 3237 (1987).

incorporation of the dopant into the structure; no change in lattice constants could still indicate incorporation into vacancies of the structure.

In addition to supporting research on superconducting ceramics, the ACL also contributes to ongoing work to characterize thin-film superconductors. Elemental compositions of thin films, usually containing only a few micrograms of material, are measured by ICP/AES. Data on the thin films are often reported within a few hours after the samples are submitted so that deposition conditions may be adjusted to give a desired film composition.

Analytical Support Using X-ray Powder Diffraction (XRD) and Scanning Electron Microscopy (SEM)

During this period, 381 XRD and SEM analyses were completed. The SEM is one of the ACL instruments that is available to users at ANL. The SEM facility has a JEOL 35U scanning electron microscope with EEDS II Ortec EDX analyzer and Technics metallic sample coater. Training in use of this instrument is provided, if necessary, by ACL staff.

The ACL has provided XRD analyses to a number of ANL programs (e.g., IFR development, superconductivity basic studies, and electrochemical technology development) for the purpose of phase identification of crystalline materials and, more importantly, phase confirmation of materials after experimental manipulation and treatment.

Computerized Calculation and Reporting of Environmental Levels of Radioactivity Determined by Gamma Spectroscopy

For an analyst, the most time-consuming aspect of gamma spectrometry of samples containing environmental levels of radioactivity is the calculation step. The main reason is the low sample activity, which requires that each energy used for nuclide identification be corrected for room background. A typical sample may contain from 20 to 40 separate energies to be calculated. We have investigated ways of streamlining and simplifying this calculation to eliminate unnecessary data transfer and possible transcription errors and to reduce time spent in calculating and reporting sample data.

We first investigated the use of software on our three gamma spectrometer systems for background correction prior to transfer of the sample data to the CMT VAX computer for analysis by the GAMANAL radionuclide identification program. This approach was quickly abandoned for several reasons, including (1) separate background stripping procedures would be required for each of the three systems, and (2) documentation of the background correction was insufficient to meet the QA requirements of some of the ACL work.

Since all of the gamma spectrometry data are analyzed by GAMANAL on the CMT VAX, we concentrated our efforts on performing the environmental-level calculation on the VAX. Starting with an Excel spreadsheet on an IBM personal computer, we developed a manual entry approach to making the necessary calculations, which we subsequently transferred into the C-CALC Plus spreadsheet on the VAX computer. Since we now had both the nuclide identification file generated by GAMANAL and the spreadsheet on the central VAX computer,

we investigated ways of automatically transferring data from the GAMANAL output to the spreadsheet for calculation. Fortran programming was done to generate GAMANAL output in a format compatible with the spreadsheet. Thus, we are now able to automatically transfer data from the GAMANAL output of sample and background files into the spreadsheet and calculate results very quickly. We are currently investigating the use of VAX macros to further reduce the number of steps in the process and to generate finished reports from the individual sample analysis sheets.

Lansdowne Pennsylvania Project

In the early 1900s, Professor Kabakjian, from the University of Pennsylvania, supplied radium for medical applications on a world-wide basis. Professor Kabakjian accomplished this task by refining uranium ore to extract radium in the basement of his home over a period of several years. Consequently, his work led to widespread contamination of the house, its household contents, and the surrounding property.

During this past year, the Kabakjian property in Lansdowne, PA, has been part of a U.S. EPA Superfund cleanup project. A group of ANL staff coordinated the demolition and decontamination of this site. In support of this project, the ACL developed a reliable method for the determination of protactinium which utilizes a sulfuric acid/hydrofluoric acid system. Historically, analyses by literature methods for the determination of protactinium have been plagued by low and sporadic yields. This element has the tendency to deposit, virtually irreversibly, on the walls of glass vessels or to form colloidal suspensions in most mineral acid solutions. The isotope ^{231}Pa is of interest because it is a direct descendant of ^{235}U and, therefore, serves as an indicator of the ^{235}U content in environmental samples. Implications regarding the history of this site can thus be derived from the ratio of ^{231}Pa to ^{235}U . Because the project included the demolition of the home and the nearby surrounding area, many of the 150 samples analyzed were unusual (i.e., insulation, whole bricks, floor carpeting, etc.), which made for challenging analyses.

Determination of ^{226}Ra and ^{228}Ra in Water and Soil

The radium in soil is the source of radon that is found in homes. The EPA has established 4.0 pCi/L of radon in air as the "level of concern." Radium in soil and rocks contributes to elevated levels of radium in water. Radium in drinking water is regulated by the EPA, where the maximum allowable total radium is 5.0 pCi/L.

We have demonstrated the effectiveness of a newly developed ion exchange method utilizing a radium selective Dowex resin. This method is much faster and less involved than other methods available but requires a large sample size, preferably 20 L. In this method, a water sample is acidified with hydrochloric acid to approximately pH 3 and then processed through the special Dowex ion exchange resin bed. The resin containing the radium is subsequently sealed in a metal can and aged before counting on a NaI detector. The counting data are computer processed by a spectrum analysis program that uses the least squares method.

Soil and crushed rock samples are processed in a similar manner. The samples are sealed in a metal can and allowed to age, during which time ^{226}Ra comes to an equilibrium with ^{222}Rn and its daughters. Counting and data processing are the same as described for water samples. The sensitivity of this method is 0.5 pCi/L for water and 0.1 pCi/g for soil samples when sufficient sample size is available (i.e., 20 L for water and ~200 g for soil). This method for determining the ^{226}Ra and ^{228}Ra is highly desirable since it is fast and accurate and, therefore, cost effective.

At present, this is the method being used for the determination of radium in the EMSL Performance Evaluation samples and in municipal waste samples. In addition, soil and rock samples have been analyzed in an environmental survey of suspected storage sites for uranium ore tailings.

Evaluation of Gas Chromatography/Matrix Isolation-Infrared Spectroscopy for Quantitative Analysis

The purpose of this project, which is funded by the U.S. EPA, is to evaluate the utility of the commercial gas chromatograph/matrix-isolation infrared spectrometer (GC/MI-IR) for quantitative analysis. This instrument, which was developed at Argonne in the ACL, has found several applications as a qualitative tool for identifying compounds that are difficult to identify by other methods such as GC/MS. We ran a series of standard mixtures to determine instrument reproducibility, linearity, and limit of detection. The reproducibility of the response was 40 to 60%, which is poorer than expected. A second phase to this project is to determine the cause of the poor reproducibility in the commercial instrument and find ways to correct it.

Plutonium Residue Recovery (PuRR) Program

Experimental work for determining the most economical process for the recovery of Pu from various types of scrap and residues continued in CMT during 1989. Several different chemical processes have been explored to determine which is the most efficient. These processes utilize a number of different molten salt mixtures along with reductant alloys composed of various combinations of Al, Cu, Ca, Mg, and Zn. The search for a very efficient process for the removal of TRU elements is important in the disposal of the waste effluents, which ideally will be rendered nonTRU waste.

Consistent with this goal, material balances have to be accurate, and reliable analyses of the feed material, salt, and reductants have to be performed. The primary analysis was quantification of elements by ICP/AES and by gamma spectrometry. In addition to the extractants and Pu, elements of interest were Am, B, Cd, Fe, K, Li, Mo, Na, Si, Ta, and Ti. Approximately 130 samples were analyzed in 1989. Gamma spectrometry was chosen for determining plutonium content, primarily because it is a nondestructive method which allows the experimenter to monitor a process and reuse samples if necessary. However, to be reliable within a reasonable uncertainty limit, numerous corrections had to be made for gamma-ray self-absorption due to the sample matrix and packaging materials.

Rocky Flats Plutonium Metal Exchange Program

The ACL has participated in this exchange program for approximately two years since the successful operation of the "hot" ICP/AES instrument in our plutonium laboratory. The primary objective of the program is to provide an independent evaluation for plutonium analysis at participating laboratories and to provide a data base and data review to the DOE on the measurement capabilities of the participating laboratories. The program provides sample materials to participating laboratories for analysis. The plutonium metal is dissolved and chemically separated by anion exchange, and subsequently, the metal impurities are determined by ICP/AES. The impurity measurements from the individual laboratories are statistically evaluated for differences. The ACL has participated in four of these intercomparison studies, and each effort has resulted in metal impurity values that have been consistent with the stated target values being supplied by selected laboratories.

Air Monitoring for Toxic Organics

The ACL is developing modified sampling and analysis procedures, described in U.S. EPA Method TO-14, for ambient air monitoring of toxic organics. This project will require (1) adapting the TO-14 procedures to the specific requirements of EPA Region V; (2) assembling, operating, and validating sampling and analysis equipment; and (3) providing standard operating procedures and training for the validated procedures.

Determination of Herbicides in Water Treatment Systems

The objective of this program is to remove trace organic contaminants from water to improve its quality. The water samples were analyzed by GC/MS for EPA target compounds and up to 80 non-target compounds. This exhaustive characterization required computerized library search and mass spectral interpretation to identify the compounds. The Contract Laboratory Program (CLP) of the EPA requires tentative identification of only up to 20 non-target compounds.

Remote Detection of Agent-Related Chemicals

Fourier transform infrared (FTIR) spectroscopy capability has been established for the remote detection of chemical warfare (CW) agents and their related precursors and degradation products. When released in front of brick walls and other environments, agent-related chemicals (in this case, methanol) have been detected at concentrations of 1.6 ppm for a 1-m pathlength. The objective of this ACL effort is to develop FTIR technology for two scenarios: (1) monitor facilities to determine whether they are producing chemical agents and (2) remotely detect agent from undeclared CW facilities. Remote FTIR spectroscopy uses ambient energy as the infrared source. The instrumentation consists of an interferometer, detector, associated optics, and computerized data system. A vaporizer was developed to allow us to release small quantities of chemicals at low ppm concentrations reproducibly. Future work will include measurements at greater distances for more chemicals.

Analysis of Soil Sample for Explosives and Selected Contaminants

The objective of this work is to validate an FTIR-based method that uses thermal desorption for the qualitative and quantitative analysis of soils for selected pesticides, semivolatile and volatile organic compounds, and high explosives. This work will combine ANL's capabilities in FTIR spectroscopy of gas-phase molecules and trace organic analysis. Initial work in 1989 consisted of redesigning a variable pathlength, heatable cell and thermal desorption unit. Work will continue throughout 1990.

Review of Rocky Flats Plant Laboratories

The ACL conducted an extensive review of Rocky Flats Plant (RFP) chemical analysis activities in support of the RFP Environmental Restoration Program. We assessed the capabilities of four laboratories (two on-site at RFP and two subcontractors) to perform CLP-type analyses. Sample analysis data from three of these four laboratories were evaluated. The laboratory assessments consisted of walk-throughs, records inspection, and employee interviews using checklists derived from the CLP methods. Data were assessed using data acceptability criteria derived from the CLP and were categorized as "valid," "acceptable with qualifications," or "rejected." Five reports were prepared and submitted to both the sponsor (Albuquerque Operations Office) and the reviewed laboratories. The findings of this review have aided RFP in making changes in the chemical analyses in support of their Environmental Restoration Program.

Chemistry of Bottom Sediments from the Chicago River and North Branch Canal, Lake Street to North Avenue

The ACL participated in the analysis of bottom sediments of the North Branch Canal and Chicago River. This study was requested by the United States Army Corps of Engineers (USACE) and resulted from the fact that this organization is in charge of directing and maintaining the commercial navigation that passes through the Chicago River. To facilitate this navigation, the USACE deemed it necessary that this section of the river be dredged. Before these dredgings could be transferred to a landfill, the EPA required that they be analyzed for priority pollutants, including PCBs, volatile and semivolatile organics, metals, and cyanide. Thus, the present study was undertaken to comply with EPA requirements.

Preparation and analysis of these samples were performed using the CLP protocols. The procedures involved extraction of the PCB and semivolatile samples, determination of PCBs using GC with an electron capture detector, and analysis for the semivolatile compounds using GC/MS. Volatiles were determined by a gaseous purge and trap technique, followed by on-line GC/MS analysis. Graphite furnace atomic absorption spectrometry was used to determine for the presence of As, Se, and Tl; the samples were digested in concentrated nitric acid solution, vaporized, and then analyzed by AA spectroscopy. The ICP/AES technique was used for determination of the remaining metals. Cyanide was measured colorimetrically following distillation of the previously acidified samples.

Total PCB contents for all composited samples ranged from below detection limits to a high of 96 mg/kg (dry weight). Mean PCB values for the composited samples taken at each

sampling location (an overall core depth of 7 m) ranged from 5.2 to 45.6 mg/kg (dry weight). The PCB concentrations at most of the sampling stations generally increased with the depth from which the sample was taken.

Samples were analyzed for volatile organic compounds, semivolatile organic compounds, and metal priority pollutants. Volatiles and semivolatiles showed traces of toluene, ethylbenzene, xylene, naphthalene, acenaphthalene, phenanthrene, fluoranthene, pyrene, benzo(a)anthracene, and chrysene.

A Systems Approach to Development of Technology for Verification of Treaties Limiting Chemical Weapons

Progress has been made on bilateral and multilateral treaties to limit chemical weapons (CW). The ACL and other Argonne staff conducted an assessment of the chemical measurement technologies available for verification of treaty provisions relative to CW agents and related compounds. Verification is needed to ensure compliance with several provisions of the treaties, including destruction of stockpiles or prohibitions against manufacture. In this preliminary study, we found a large amount of primary literature on the available technologies but no critical reviews, which should be available for U.S. and international negotiators. We also determined, using assumptions on production technology, that there should be detectable quantities of "signature" chemicals emitted from a production facility; therefore, "fenceline monitoring" appears feasible. In addition, we assessed the current and potential utility of advanced sample preparation, gas chromatography, ion mobility spectrometry, infrared spectroscopy, mass spectrometry, multi-instrument arrays, multivariate signal processing, near infrared spectroscopy, preconcentrators, and electrochemical sensors.

Fourier Transform Infrared (FTIR) Microscopy

The FTIR microscope user facility consists of a Spectra-Tech IRPLAN-II and a Nicolet 60SX FTIR. Applications of this microscope include characterizing changes in plastic pipe as a function of aging and identifying deposits on tubing. The FTIR microscope has also been used to analyze fouling deposition in heat exchangers and to identify organics in coal and water in minerals.

Walter Reed Army Institute of Research (WRAIR) Site Characterization

The WRAIR building is proposed to be built on an uncontrolled landfill site in Forest Glenn, Maryland. Prior to construction of the building, hydrogeological and chemical characterization of this site is required. The ACL has provided assistance to the U.S. Army Corps of Engineers in writing of the sampling and analysis and quality assurance plans for the site. The ACL is managing the total analytical work for this project and will be performing most of the analyses. Analytical work was initiated in 1989. To date, ACL has provided technical assistance on this project in the following areas: development of a sampling plan, specification of analytical procedures, review of data quality, and preparation of a final report.

Advanced Instrumental Methods for Determining Organics in Solid Waste

The main objective of this project, which is funded through the Morgantown Energy and Technology Center (METC), is to apply advanced instrumentation [e.g., GC/MI-IR, supercritical fluid extraction (SFE), and supercritical fluid chromatography (SFC)] to the characterization of organic compounds present in coal waste samples.

Some results of the GC/MI-IR work have been recently published.⁴ The SFE/SFC analyses of coal waste samples demonstrated that SFE using carbon dioxide for a short time (5 to 7 min) extracted compounds of at least as high molecular weight as were extracted using the labor-intensive and time-consuming Soxhlet solvent extraction. The results of SFE/SFC have been submitted for publication.

Environmental Analyses for DOE Sites

The ACL did the following environmental analyses for DOE sites in addition to those done as part of the DOE Environmental Survey:

- **Rocky Flats Plant.** The ACL received approximately 60 environmental samples from the Rocky Flats Plant. These samples were collected by the INEL field sampling team and consisted of waters, soils, and sludges to be analyzed for anions, inorganics in the target analyte list (TAL), and organics in the target compound list (TCL), including volatile and semivolatile organics. These analyses will follow CLP protocols.
- **Argonne National Laboratory-West.** The ACL received environmental samples from ANL-W for analyses in accordance with the protocols of the Resource Conservation and Recovery Act. This work has been initiated with anticipated completion in early 1990.

New Capabilities within the ACL

New capabilities of the ACL established in 1989 include an automated uranium analyzer, a micro ion chromatograph for analysis of small samples, a gel permeation chromatograph for cleanup of environmental samples, two gas chromatographs for determinations of pesticides and PCBs, and a high-efficiency detector for analysis of environmental samples by gamma spectrometry.

⁴J. F. Schneider, L. A. Raphaelian, A. S. Boparai, M. C. Hansen, and M. D. Erickson, *J. Chromatogr. Sci.* **27**, 592-595 (1989).

VIII. COMPUTER APPLICATIONS

The Computer Applications Group provides assistance to CMT staff 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) office automation, (6) information management systems and data-base development, (7) computer operating system maintenance, (8) small and large computer system networking, (9) procurement of automatic data processing equipment, and (10) advisory, educational, and consulting services.

The Computer Applications Group has the responsibility for (1) software maintenance and development for several major minicomputer data acquisition systems, (2) the Division's Local Area VAX cluster consisting of eight VAX's and Macintosh and IBM-compatible personal computer (PC) networks, and (3) hardware maintenance of various small systems and peripherals, including the Division's extensive terminal communications system and local area networks.

Utilization of PC's both for data acquisition/control and modeling in CMT has continued to increase. Over eighty such systems now exist. Group personnel continued work on the computer program portion of the Generic TRUEX Model (GTM) for the CMT Separation Science and Technology Group (Sec. IV.A.1). In 1989, GTM--Mac version 1.1 along with its user manual was released for distribution through the DOE National Energy Software Center. The model, which runs on a Macintosh computer using Microsoft Excel and HyperCard software, calculates a TRUEX solvent extraction flowsheet based on input of a specific feed solution and a specific set of process goals and constraints, and it estimates the space and cost requirements to install a TRUEX process for a specific application. Subsequently, the model was altered to run on an IBM-compatible PC primarily by converting the Macintosh HyperCard user interface to one based on IBM-PC Excel tools. Programming of GTM--Mac version 2.0, which removes some of the limitations found in the earlier release, has begun. Changes were also made to the user interface so that the majority of the code is shared by the Macintosh and IBM-compatible PC versions.

In support work for the Analytical Chemistry Laboratory (Sec. VII), the Computer Applications Group has helped to streamline and simplify use of the GAMANAL radionuclide identification program for gamma spectrometry analysis of environmental samples. Analytical Chemistry Laboratory staff are now able to transfer data from the GAMANAL output of sample and background files into a C-CALC Plus spreadsheet on the Division's VAX 6220 and to then calculate analytical results much faster than previously attainable.

Group staff also continue to support the Analysis and Diagnostic Laboratory (ADL), formerly the National Battery Test Laboratory (NBTL). Operating for over a decade, the ADL evaluates a wide variety of battery systems, some of which require unusual charging or discharging regimes, or feature a local "intelligent controller" that requires unique interfacing to the ADL control system computer (Sec. I.B). The Computer Applications Group is engaged in an ongoing effort to develop software to support the testing of new battery systems as they arrive at the laboratory.

Recent emphasis was given to speeding up data retrieval and analysis by developing the "pointer file" construct, a recording in real time of the location in the sequential data files of the beginning of each cycle of a test, as well as other relevant test information. A second goal has been to make better use of the Division's other computing resources, both hardware and software. Automated procedures have been developed that allow the test operators to activate analysis programs that produce a variety of graphic presentations in a process that combines programs on the ADL's PDP-11 computer and the Division's VAX 6220 and communications via DECnet/Ethernet.

A block diagram of the Divisional computing configuration is shown in Fig. VIII-1. The VAX 6220 continues to provide the primary computing resources for the Division's diverse computing needs. Other members of CMT's VAXcluster are providing computing cycles for the High-Temperature Thermodynamics Group (Sec. VI.B), for scientific workstation applications, and for laboratory automation as replacements for older 16-bit PDP-11 computer systems. Addition of an optical storage subsystem for archival backups is nearing completion. Major software enhancements have included additional capabilities for calendar management and facilities scheduling. The increased use of Adobe PostScript-based laser printers permits taking full advantage of many of the sophisticated graphics and typesetting capabilities of numerous software packages previously installed on the VAX.

Fig. VIII-1. Block Diagram of CMT Computing Facilities

Computer networks continue to grow in importance in the Laboratory's computing environment. Connection of CMT's VAX to the Laboratory-wide Ethernet permits access to local resources such as the Computing and Telecommunications Division's (CTD) Cray and VAX 8700 computer systems and to external networks such as HEPNET (high energy physics), MFENET (magnetic fusion energy network), and ESNET (DOE energy sciences). An NJE interface permits file transfer capability to and from CTD's IBM 3033 batch and time-sharing systems and to the BITNET educational network. Recent installation of Multinet's TCP/IP software now permits direct access to the world-wide Internet. This software supports electronic mail, general file transfer capabilities, and interactive log-ins to other systems on the network, including the CTD IBM computers.

Personal computers connected to the Ethernet are able to use CMT's VAX as a disk, file, and/or print server. This is particularly useful for those systems that are starting to be employed for administrative and graphics applications and for other PC systems which rely on the VAX for data analysis. Major enhancements to DEC's Personal Computing Systems Architecture (PCSA) integration/networking software have significantly reduced memory requirements so that nearly all PC applications can run in a network environment. In addition, PCSA offers multi-windowing capability based on the MIT X-Windows standard; this capability enables a PC user to access several applications running on one or more nodes on the network. Installation of Alisatalk/Alisashare software on the VAX provides many of the same file and print services to the CMT Macintosh community. An integrated system combining all of these network features has recently been installed for the ANL Applied Research and Development Program Office.

To help users become familiar with the many software products and utilities running on the VAX, the Computer Applications Group has initiated a series of biweekly workshops which, together with handout materials, are intended to increase the computer skills of CMT personnel. Plans are being made to expand these workshops to cover PC and networking topics as well.

IX. ADDENDUM.**CHEMICAL TECHNOLOGY DIVISION
PUBLICATIONS--1989**

The Division's publications and oral presentations for 1989 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 — 1989

A. Journal Articles, Books, and Book Chapters

Aqueous Corrosion of Natural and Nuclear Waste Glasses. II. Mechanisms of Vapor Phase Hydration of Nuclear Waste Glasses

T. A. Abrajano, J. K. Bates, and J. J. Mazer
J. Non-Cryst. Solids **108**, 269–288 (1989)

Zambales Ophiolite, Philippines. II. Sulfide Petrology of the Critical Zone of the Acoje Massif

T. A. Abrajano and J. D. Pasteris
Contrib. Mineral. Petrol. **103**, 64–77 (1989)

Zambales Ophiolite. I. Geology and Petrology of the Critical Zone of the Acoje Massif

T. A. Abrajano, J. D. Pasteris, and G. C. Bacuta
Tectonophys. **168**, 65–100 (1989)

Computer Simulation of a Municipal Solid Waste Combustor

S. Ahmed, R. Kumar, and J. E. Helt
J. Air Pollution Control Assoc. **39**, 1328–1333 (1989)

Analysis of Ion-Bombarded and Laser Irradiated Surfaces of ZnS and Zn via Two-Photon High-Resolution Laser-Induced Fluorescence Spectroscopy

H. F. Arlinghaus, W. F. Calaway, C. E. Young, M. J. Pellin, D. M. Gruen, and L. L. Chase
J. Vac. Sci. Technol. **A7**, 1766–1771 (1989)

High-Resolution Multiphoton Laser-Induced Fluorescence Spectroscopy of Zinc Atoms Ejected from Laser-Irradiated ZnS Crystals

H. F. Arlinghaus, W. F. Calaway, C. E. Young, M. J. Pellin, D. M. Gruen, and L. L. Chase
J. Appl. Phys. **65**(1), 281–289 (1989)

Materials for Advanced High Temperature Secondary Batteries

J. E. Battles
Int. Mater. Rev. **34**(1), 1–18 (1989)

Book Review: *Phase Equilibria in Binary Halides*, by V. I. Posypaiko and E. A. Alekseeva

M. Blander
J. Am. Chem. Soc. **3**(12), 4535 (1989)

The Coordination Cluster Theory for Metallic Solutions

M. Blander and M.-L. Saboungi
Alloy Phase Stability, eds., G. M. Stocks and A. Gonis, NATO Advanced Study Institute on Alloy Phase Stability, Kluwer Academic Publishers, Dordrecht, The Netherlands, pp. 285–289 (1989)

Effect of Heat Treatment Time and Temperature on the Properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

I. Bloom, B. S. Tani, M. C. Hash, D. Shi, M. A. Patel, K. C. Goretti, N. Chen, and D. W. Capone
J. Mater. Res. **4**(5), 1093–1098 (1989)

Ion-Dose Dependence of the Sputtering Yield of Ru(0001) at Very Low Fluences

J. W. Burnett, M. J. Pellin, W. F. Callaway, and D. M. Gruen
Phys. Rev. Lett. **63**, 562–565 (1989)

Laser-Induced Fluorescence as a Tool for the Study of Ion Beam Sputtering

W. F. Calaway, C. E. Young, M. J. Pellin, and D. M. Gruen

Chapter 7 in *Handbook of Ion Beam Processing Technology*, eds., J. J. Cuomo, S. M. Rossnagel, and H. R. Kaufman, Noyes Publications, Park Ridge, NJ, pp. 112–127 (1989)

Regiospecific Ortho-Lithiation of Phthalocyanines: A Route for One-Step Synthesis of Highly Soluble Trimethylsilyl Substituted Phthalocyanines

M. J. Chen, C. M. Fendrick, R. A. Watson, K. S. Kinter, and J. W. Rathke

J. Chem. Soc., Perkin Trans. **1**, 1071–1073 (1989)

Homologation of Methanol Catalyzed by Manganese Carbonyl in Tertiary Amine-Methanol Solutions

M. J. Chen and J. W. Rathke

Organometallics **8**(2), 515–520 (1989)

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R. R. Colman, Jr., C. E. Klabunde, H. R. Kerchner, S. A. Richardson, and L. R. Greenwood

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Chem. Phys. **133**, 89–94 (1989)

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L. A. Curtiss and J. A. Pople

J. Chem. Phys. **90**(1), 603–605 (1989)

Further Theoretical Studies on B_2H_4 and B_2H_4^+

L. A. Curtiss and J. A. Pople

J. Chem. Phys. **91**(8), 5118–5119 (1989)

Theoretical Study of B_2H_3^+ , B_2H_3^+ , and B_2H^+

L. A. Curtiss and J. A. Pople

J. Chem. Phys. **91**(8), 4809–4812 (1989)

Theoretical Study of B_2H_4^+ and B_2H_4

L. A. Curtiss and J. A. Pople

J. Chem. Phys. **90**(8), 4314–4319 (1989)

Theoretical Study of the C-H Bond Dissociation Energy of Acetylene

L. A. Curtiss and J. A. Pople

J. Chem. Phys. **91**(4), 2420–2423

A Theoretical Study of the Dissociation Energy of BH Using Quadratic Configuration Interaction

L. A. Curtiss and J. A. Pople

J. Chem. Phys. **90**(4), 2522–2523 (1989)

Theoretical Study of the Ionization of B_2H_5

L. A. Curtiss and J. A. Pople

J. Chem. Phys. **91**(7), 4189–4192 (1989)

Theoretical Studies of CuO Clusters Representing $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$: Investigation of Cu(III) Formation versus Oxide Oxidation

L. A. Curtiss and A. Shastri

High Temperature Superconductivity: The First Two Years, ed., R. M. Metzger, Gordon and Breach Science Publishers, New York, pp. 373–378 (1989)

Influence of Chlorine Ratio and Oxygen Bleaching on the Formation of PCDFs and PCDDs in Pulp Bleaching.
Part I: A Laboratory Study

E. de Sousa, M.-C. Kolar, K. P. Kringstad, S. E. Swanson, C. Rappe, and B. Glas
Tappi J. **72**(4), 147-153 (1989)

PCDFs and Related Compounds Produced from PCB Fires - a Review

M. D. Erickson
Chemosphere **19**(1-6), 161-165 (1989)

Polychlorinated Dibenzofurans and Other Thermal Combustion Products from Dielectric Fluids Containing Polychlorinated Biphenyls

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Environ. Sci. Technol. **23**(4), 462-470 (1989)

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Fusion Eng. Design **11**, 335-357 (1989)

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P. A. Finn, R. G. Clemmer, L. R. Greenwood, A. Lide, D. K. Sze, J. L. Anderson, R. Sherman, J. R. Bartlit, Y. Naruse, and H. Yoshida
Fusion Technol. **15**, 680-686 (1989)

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Fusion Technol. **15**, 1343-1348 (1989)

Measurements of Adsorption in the $\text{LiAlO}_2\text{-H}_2\text{O(g)}$ System

A. K. Fischer and C. E. Johnson
Fusion Technol. **15**, 1212 (1989)

Tritons and Tritides as the Solute and Diffusing Species in Ceramic Tritium Breeders

A. K. Fischer and C. E. Johnson
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Helium-Cooled Lithium Compound Suspension Blanket Concept for ITER

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Synthesis and Sintering of $\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_x$

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Infrared Spectrum of Ruthenium Tetroxide Isotopomers in an Argon Matrix

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The Determination of Impurities in Plutonium Metal by Anion Exchange and ICP/AES

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L. E. Iton, I. Choi, J. A. Desjardins, and V. A. Maroni

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Am. Soc. Test. Mater., Spec. Tech. Publ. **1001**, 515–521 (1989)

Modeling Unusual Tritium Release Behavior from Li_2O

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The Influence of Chlorine Ratio and Oxygen Bleaching on the Formation of PCDFs and PCDDs in Pulp Bleaching.

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E. Papers Presented at Scientific Meetings

Analytical Electron Microscopy of Leached Nuclear Waste Glasses

T. A. Abrajano, Jr., J. K. Bates, and J. P. Bradley

Presented at the 91st Annual Meeting, Am. Ceram. Soc., Indianapolis, IN, April 23–27, 1989

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PYRO—A System for Modeling Fuel Reprocessing

J. P. Ackerman

Presented at the Winter Meeting of the Am. Nucl. Soc., San Francisco, CA,

November 26–30, 1989

Pyrochemistry of Fuel Recovery for the Integral Fast Reactor

J. P. Ackerman

Presented at the Summer National Meeting of the AIChE, Philadelphia, PA, August 20–23,

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Radionuclide Content of Secondary Mineral Phases that form during Glass Reaction

J. K. Bates and W. L. Ebert

Presented at the 92nd Annual Meeting and Exposition of the Am. Ceram. Soc., Dallas, TX,

April 22–26, 1989

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J. E. Battles and L. Burris

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- Acute Lead Exposure and Biological Responses Among U.S. Army Artillery Men
M.-H. Bhattacharyya, D. P. Peterson, S. A. Johnson, J. H. Stebbings, B. D. Goun, I. Janssen, and D. Parmer
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- Ab Initio* Molecular Orbital Study of Bond Dissociation Energies and Ionization Energies of GeH_n , AsH_n , and SeH_n Hydrides
R. C. Binning and L. A. Curtiss
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B. M. Biwer, J. K. Bates, T. A. Abrajano, and J. P. Bradley
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- Thermodynamic Properties of Ordered Liquids: Chloroaluminates
M. Blander
Presented at the 1989 Midwest Thermodynamics Symp., Lake Geneva, WI, May 14–16, 1989
- Calculations of the Chemistry of Coal Combustion Effluents
M. Blander, S. Sinha, A. Pelton, and G. Eriksson
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- Alternative Solid Oxide Fuel Cell Materials
I. Bloom, D. W. Dees, M. C. Hash, and M. Krumpelt
Presented at the EPRI/GRI Workshop, Orlando, FL, October 26–27, 1989
- Supercritical Fluid Extraction—Supercritical Fluid Chromatography of Coal Samples
A. S. Boparai and D. V. Applegate
Presented at the 16th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Chicago, IL, October 1–6, 1989
- Comparison of Supercritical Fluid and Solvent Extracted Coal Using Supercritical Fluid Chromatography
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- Analysis of Activation Products in the Neutron Shield Tank of the Shippingport Reactor
D. L. Bowers and L. R. Greenwood
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- Neutral Emission from ZnS Under Laser Irradiation
W. F. Calaway
Presented at Lawrence Livermore National Laboratory, Livermore, CA, April 11, 1989
- Analysis of Semiconductor Materials Using Resonance Ionization of Sputtered Atoms
W. F. Calaway, J. E. Whiten, J. W. Burnett, M. J. Pellin, C. E. Young, and D. M. Gruen
Presented at the 11th Symp. on Applied Surface Analysis, Cleveland, OH, May 31–June 2, 1989
- Modeling of Aqueous and Organic Phase Speciation for Solvent Extraction Systems
D. J. Chaiko
Presented at the Dept. of Metallurgical Engineering, Michigan Technological University, Houghton, MI, November 7, 1989

- Development of a Process for Treating Red Water by Organic/Inorganic Separation and Biodegradation
D. J. Chaiko, L. Reichley-Yinger, E. R. Orth, E. H. Van Deventer, G. F. Vandegrift, M. Krumpole,
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- Results from the TRUEX Process Verification Studies
D. B. Chamberlain, F. Mrazek, E. H. Van Deventer, K. Barnthouse, C. Conner, J. Dow, M. Internoscia,
A. La'O, R. A. Leonard, J. Stangel, M. Tranovich, and G. F. Vandegrift
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- Peripherally Substituted Phthalocyanines
M. J. Chen, J. W. Rathke, S. Sinclair, and D. W. Slocum
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- Development of Lithium-Alloy/Iron Sulfide Batteries
A. A. Chilenskas
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November 13–17, 1989
- Li/FeS Battery Design for an Electric Van
A. A. Chilenskas and G. Barlow
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- Development of a Centrifugal Contactor for Pyrochemical Processing
L. Chow, R. A. Leonard, T. R. Johnson, and G. F. Vandegrift
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- Size and Cost Estimation for a TRUEX Processing Plant
L. Chow, R. A. Leonard, and G. F. Vandegrift
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- Fuel Cell/Battery Powered Bus System Program
C. C. Christianson
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- The Breeding Blanket Interface (BBI) and the Tritium System Test Assembly (TSTA)
R. G. Clemmer, J. Anderson, J. Bartlit, R. Sherman, D.-K. Sze, P. A. Finn, Y. Naruse, H. Yoshida,
K. Okuno, and M. Enoeda
Presented at the 13th Symp. on Fusion Engineering, Knoxville, TN, October 2–6, 1989
- The Breeding Blanket Interface (BBI): Recent Results for the Solid Breeder and the Aqueous Salt Solution Blanket Concepts
R. G. Clemmer, P. A. Finn, L. R. Greenwood, D. K. Sze, J. R. Bartlit, R. Sherman, J. L. Anderson,
H. Yoshida, Y. Naruse, K. Okuno, and M. Enoeda
Presented at the 13th Symp. on Fusion Engineering, Knoxville, TN, October 2–6, 1989

Theoretical and Experimental Studies of Heterogeneous Electron Transfer

L. A. Curtiss

Presented at the DOE/BES Corrosion Contractors' Meeting, Lawrence Berkeley Laboratory, Berkeley, CA, September 21–22, 1989

Theoretical Studies of Heterogeneous Electron Transfer

L. A. Curtiss

Presented at the DOE/DMS Discussion Meeting on Theory Applied to Materials Science, Gatlinburg, TN, November 14–16, 1989

Ab Initio Molecular Orbital Calculations of Template-Framework Interactions

L. A. Curtiss

Presented at the Conf. on Special Topics on Molecular Sieve Research: Synthesis-Structure-Simulation, Argonne National Laboratory, June 14–15, 1989

Ab Initio Potentials for Metal Ion-Water Interactions and Their Use in Molecular Dynamics Simulations

L. A. Curtiss

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Interfacial Effects in Monolithic Solid Oxide Fuel Cells

D. W. Dees, U. Balachandran, S. E. Dorris, J. J. Heiberger, C. C. McPheeters, and J. J. Picciolo

Presented at the 176th Electrochem. Soc. Meeting, Hollywood, FL, October 15–20, 1989

Electrode Development in Monolithic Solid Oxide Fuel Cells

D. W. Dees, J. J. Heiberger, C. C. McPheeters, U. Balachandran, S. E. Dorris, and J. J. Picciolo

Presented at the AIChE Annual Meeting, San Francisco, CA, November 5–10, 1989

Battery Test and Development Project at the ANL Analysis and Diagnostics Lab for the EPRI Electric Transportation Program

W. H. DeLuca

Presented at the Electric Power Research Institute Transportation Program Review Meeting, Chattanooga, TN, January 24–25, 1989

EPRI Battery Test and Development Project at the ANL Analysis and Diagnostics Lab

W. H. DeLuca

Presented at the Electric Power Research Institute Transportation Program Review Meeting, Argonne, IL, August 24–25, 1989

Ni/Fe Battery Experiences at Argonne National Laboratory

W. H. DeLuca

Presented at the Electric Power Research Institute Nickel-Iron EV Battery Workshop on Hydrogen and Battery Management, Argonne, IL, August 22–23, 1989

Ni/Fe Battery Test Results from ANL Analysis and Diagnostics Lab

W. H. DeLuca

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Preliminary Test Results from the ANL Analysis and Diagnostics Lab on the CSPL 64-V Na/S EV Battery

W. H. DeLuca

Presented at the CSPL Na/S EV Battery Design Review Meeting, Washington, DC, February 28, 1989

Test Results of CSPL Na/S 1/3-EV Battery from ANL Analysis and Diagnostics Lab

W. H. DeLuca

Presented at the CSPL Na/S Program Review Meeting, Albuquerque, NM, October 12, 1989

Continuous Emission Monitoring of Hazardous Waste Incinerators Using Fourier Transform Infrared Spectroscopy

J. C. Demirgian

Presented at the Pittsburgh Conf. & Exposition, Atlanta, GA, March 6–10, 1989

Development of Computer-Generated Data Packages for EPA Analyses

J. C. Demirgian

Presented at the Tenth Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory, April 18, 1989

Development of Computer-Generated Data Packages for EPA Analyses

J. C. Demirgian and M. C. Hansen

Presented at the Pittsburgh Conf. & Exposition, Atlanta, GA, March 6–10, 1989

Electrolytic Separation and Recovery in Caustic of Steel and Zinc from Galvanized Steel Scrap

F. J. Dudek, E. J. Daniels, Z. Nagy, and S. Zaromb

Presented at the Separation Science and Technology for Energy Applications Conf., Knoxville, TN, October 22–26, 1989

The Influence of Gamma Radiation on the Leaching Behavior of Simulated Nuclear Waste Glass in J-13 Solution

W. L. Ebert and J. K. Bates

Presented at the Fourth Int. Symp. on Ceramics in Nuclear Waste Management, Am. Ceram. Soc., Indianapolis, IN, April 23–27, 1989

The Reaction of Synthetic Nuclear Waste Glass in Steam and Hydrothermal Solution

W. L. Ebert and J. K. Bates

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27–December 2, 1989

The Influence of Penetrating Gamma Radiation on the Reaction of Simulated Nuclear Waste Glass in Tuff Groundwater

W. L. Ebert, J. K. Bates, T. A. Abrajano, and T. J. Gerding

Presented at the Fourth Int. Symp. on Ceramics in Nuclear Waste Management, Am. Ceram. Soc., Indianapolis, IN, April 23–27, 1989

The Sorption of Water on Synthetic Nuclear Waste Glass

W. L. Ebert, R. F. Hoburg, and J. K. Bates

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27–December 2, 1989

Analyses for Argonne Premium Coal Sample Program

A. G. Engelkemeir

Presented at the Tenth Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory, April 18, 1989

PCBs in Humans: What We Know and What We Don't Know

M. D. Erickson

Presented at the EPRI 1989 PCB Seminar, San Diego, CA, October 3–6, 1989

One-Step Separation of Uranium from Mixtures of Cations with Diamyl Amylphosphonate Column Extraction

A. M. Essling, E. A. Huff, D. G. Graczyk, and E. P. Horwitz

Presented at the 31st ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10–12, 1989

Desorption of H_2O and H_2 from Steel and $LiAlO_2$ by Temperature Programmed Desorption

A. K. Fischer and C. E. Johnson

Presented at the Fourth Int. Conf. on Fusion Reactor Materials, Am. Nucl. Soc., Kyoto, Japan, December 4–8, 1989

Solid Breeder Blanket Option for the ITER Conceptual Design

Y. Gohar, H. Attaya, M. C. Billone, P. A. Finn, S. Majumdar, L. R. Turner, C. C. Baker, B. E. Nelson, and R. Raffray

Presented at the 13th Symp. on Fusion Engineering, Knoxville, TN, October 2–6, 1989

Hyper- and Hypobaric Processing of Tl-Ba-Ca-Cu-O Superconductors

K. C. Goretta, J. L. Routbort, D. Shi, M. C. Hash, and I. Bloom

Presented at the Fall Meeting of the Materials Research Society, Boston, MA, November 27–December 2, 1989

CW Verification Concepts

D. W. Green

Presented at the Conf. of DOE Technology Research and Development for Arms Control Verification, Los Alamos, NM, August 29–31, 1989

Management Challenges of Getting Started

D. W. Green

Presented at the USDOE Analytical Laboratory Managers Meeting, Livermore, CA, November 14–17, 1989

Measurement of Long-Lived Isotopes and Helium Production in Fusion Materials

L. R. Greenwood

Presented at the Int. Atomic Energy Agency Advisory Group Meeting on Nuclear Data for Radiation Damage Assessment and Related Safety Aspects, Vienna, Austria, September 19–22, 1989

Measurements of Long-Lived Activities Near 14 MeV

L. R. Greenwood

Presented at the IAEA Consultants' Meeting on Activation Cross Sections for the Generation of Long-Lived Radionuclides, Argonne National Laboratory, Argonne, IL, September 11–12, 1989

Radiation Damage Calculations for Compound Materials

L. R. Greenwood

Presented at the Advisory Group Meeting on Nuclear Data for Radiation Damage Assessment and Related Safety Aspects, Vienna, Austria, September 19–22, 1989

Damage Parameters for Candidate Fusion Materials Irradiation Test Facilities

L. R. Greenwood, D. Doran, and F. Mann

Presented at the Workshop on Radiation Damage Calculations for Fusion Conditions, Silkeborg, Denmark, September 28–October 3, 1989

Utilization of Gamma Spectrometry and ICP/AES for the Monitoring of Plutonium Recovery from Intractable Residues

R. R. Heinrich, W. E. Streets, D. L. Bowers, and C. S. Sabau

Presented at the Second Annual Karlsruhe Int. Conf. on Analytical Chemistry in Nuclear Technology, Karlsruhe, Federal Republic of Germany, June 5–9, 1989

The Structure of Molten AlBr_3 , GaBr_3 , and GaI_3 Studied by Neutron Diffraction

M. A. Howe, K. J. Volin, D. L. Price, and M.-L. Saboungi

Presented at the Gordon Research Conf. on Molten Salts and Liquid Metals, Wolfeboro, NH, August 7, 1989

ICP/AES of the Actinide Elements

E. A. Huff

Presented at the Plasma Spectroscopy Task Group Meeting, Am. Soc. for Testing and Materials, Orlando, FL, January 23–29, 1989

Electrochemical Reactions in Submerged Arc Welding with SiO_2 -CaO- CaF_2 Fluxes with High and Low Silica Contents

J. E. Indacochea, M. Blander, and A. Polar

Presented at the Second Int. Conf. on Trends in Welding Research, ASM Int., Gatlinburg, TN, May 14–18, 1989

Electrochemical Transport of Manganese between the Flux and the Weld Metal in Submerged Arc Welding

J. E. Indacochea, M. Blander, and A. Polar

Presented at the Second Int. Conf. on Trends in Welding Research, ASM Int., Gatlinburg, TN, May 14–18, 1989

Research and Development Status of Ceramic Breeder Materials

C. E. Johnson

Presented at the Fourth Int. Conf. on Fusion Reactor Materials, Kyoto, Japan, December 4–8, 1989

Tropospheric Aerosol Measurement Using the Real-Time IR Aerosol Analyzer

S. A. Johnson and R. Kumar

Presented at the Int. Workshop on Space Observations of Tropospheric Aerosols and Complementary Measurements, Hampton, VA, November 15–18, 1989

Management of IFR Wastes

T. R. Johnson, M. A. Lewis, and D. F. Fischer

Presented at the AIChE Summer National Meeting, Philadelphia, PA, August 20–23, 1989

Desorption Activation Energies for Tritium Release from Ceramic Breeders

J. P. Kopasz, A. K. Fischer, and C. E. Johnson

Presented at the Second Symp. on Fabrication and Properties of Lithium Ceramics, Am. Ceram. Soc., Indianapolis, IN, April 23–27, 1989

Enhanced Tritium Release by Solids Modification

J. P. Kopasz, S.-W. Tam, and C. E. Johnson

Presented at the Fourth Int. Conf. on Fusion Reactor Materials, Kyoto, Japan, December 4–8, 1989

An Assessment of Fuel Cells for Transportation Application

M. Krumpelt and R. Kumar

Presented at the Electric Hybrid Vehicle Contractors' Conf., Idaho Falls, ID, September 6–8, 1989

Assessment of Fuel Cells for Transportation

M. Krumpelt and R. Kumar

Presented at the Ninth Battery and Electrochemical Contractors' Conf., Alexandria, VA, November 12–16, 1989

Alternative Electrode Materials

G. H. Kucera, J. L. Smith, and A. P. Brown

Presented at the EPRI/GRI Fuel Cell Workshop, Orlando, FL, October 26–27, 1989

Molten Carbonate Fuel Cell Research

G. H. Kucera, J. L. Smith, and A. P. Brown

Presented at the Fuel Cell Contractors Conf., Morgantown, WV, May 2–4, 1989

Combustion of Char in PFBC and Measurement of Its Alkali-Vapor Emission

S. H. D. Lee and F. G. Teats

Presented at the ICDB Seventh Annual Contractors' Meeting, Urbana, IL, August 1–3, 1989

Pressurized Fluidized-Bed Combustion of Illinois High-Sodium/High-Chloride Coal and Its Derived Char

S. H. D. Lee, F. G. Teats, and E. L. Carls

Presented at the CRSC/EPRI First Int. Conf. on Chlorine in Coal, Chicago, IL, October 9–11, 1989

A New Model for Solvent Extractant in Columns

R. A. Leonard, D. B. Chamberlain, M. C. Regalbuto, and G. F. Vandegrift

Presented at the Sixth Symp. on Separation Science and Technology for Energy Applications, Knoxville, TN, October 22–26, 1989

Gas Generation from the Irradiation of Mortar

M. A. Lewis and D. W. Warren

Presented at the Fourth Int. Symp. on Ceramics in Nuclear Waste Management, Am. Ceram. Soc. Annual Meeting, Indianapolis, IN, April 23–27, 1989

Hydrogen Generation in Mortars Immobilizing Waste Chloride Salts

M. A. Lewis and D. W. Warren

Presented at the Conf. on Scientific Basis for Nuclear Waste Management XIII, Materials Research Soc., Boston, MA, November 27–30, 1989

The Use of Additives for Reducing Hydrogen Yield in Mortar Containing Slag and Chloride Salts

M. A. Lewis and D. W. Warren

Presented at the Conf. on Scientific Basis for Nuclear Waste Management XIII, Materials Research Society, Boston, MA, November 17–30, 1989

Assessment of Inorganic Analysis Data Quality

P. C. Lindahl

Presented at the Eleventh Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory, Argonne, IL, November 9, 1989

ASTM Methods for Trace Element Analysis

P. C. Lindahl

Presented at the Int. Conf. on Trace Elements in Coal, Bowling Green, KY, September 11–13, 1989

Implementing Measures for U.S. EPA Contract Laboratory Program (CLP) Quality Assurance/Quality Control (QA/QC) in the Inorganic Analytical Laboratory

P. C. Lindahl

Presented at the Society for Applied Spectroscopy Atomic Absorption Workshop, Rosemont, IL, April 5, 1989

Assessment of Inorganic Analysis Data Quality in the DOE Environmental Survey

P. C. Lindahl, K. Whaley, V. Fayne, and H. Vincent

Presented at the 31st ORNL-DOE Conf. on Analytical Chemistry in Energy Technology, Gatlinburg, TN, October 10–12, 1989

The Success of a Glovebox System from QA Plans through Audits

R. F. Malecha and G. J. Schreiber

Presented at the Am. Glovebox Soc. Annual Conf., Denver, CO, August 21–24, 1989

Radium in Drinking Water

F. Markun

Presented at the Tenth Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory, April 18, 1989

Spectroscopic Studies of the Reaction of Functionalized Light Hydrocarbons with Silicon- and Cobalt-Substituted AlPO-34

V. A. Maroni

Presented at the Soc. for Appl. Spectrosc. Meeting, Milwaukee, WI, March 15, 1989

The Rate of Hydration of Obsidian as a Function of Relative Humidity, Temperature, and Composition

J. J. Mazer, J. K. Bates, and C. Stevenson

Presented at the Geol. Soc. of Am. Annual Meeting, St. Louis, MO, November 6–9, 1989

A Method for Bonding High- T_c Superconducting Ceramics to Normal-Conducting Metals

J. H. Meiser and V. A. Maroni

Presented at the 175th Electrochem. Soc. Meeting, Los Angeles, CA, May 7–12, 1989

Cold Nuclear Fusion: Some Experiments and Analysis

C. A. Melendres and L. R. Greenwood

Presented at the Cold Fusion Phenomena Workshop, Santa Fe, NM, May 23–25, 1989

Laser Raman Spectroelectrochemical Studies of Metal Corrosion and Passivation in Aqueous Environments

C. A. Melendres, T. Tipton, W. Paden, and W. Ruther

Presented at the Am. Chem. Soc. Meeting, Dallas, TX, April 9–14, 1989

Recent Advances in Electric Vehicle Batteries

J. F. Miller

Presented at the Electrochem. Soc. Meeting, Chicago Local Section, March 2, 1989

Pyroprocessing Equipment and Operations for the IFR Fuel Cycle

W. E. Miller, E. C. Gay, and J. E. Herceg

Presented at the AIChE Summer National Meeting, Philadelphia, PA, August 20–23, 1989

Plutonium Recovery from Residues

T. P. Mulcahey, R. D. Pierce, G. K. Johnson, and D. S. Poa

Presented at the Plutonium/Uranium Recovery Operation Conf., Oak Ridge, TN, October 24–26, 1989

Status of Molten Carbonate Fuel Cell Technology

K. M. Myles and M. Krumpelt

Presented at the 16th Annual Energy Technol. Conf., Washington, DC, February 28–March 2, 1989

Monolithic Solid Oxide Fuel Cell Development

K. M. Myles and C. C. McPheeters

Presented at the Second Space Electrochemical Research and Technology Conf., Cleveland, OH, April 11–13, 1989

Temperature Dependence of the Transfer Coefficient: The Ferrous-Ferric Redox Reaction

Z. Nagy, N. C. Hung, and R. M. Yonco

Presented at the Gordon Research Conf., Ventura, CA, January 16–20, 1989

Double Layer Effects in Electrochemical Corrosion Measurements

Z. Nagy and P. F. Schultz

Presented at the Corrosion '89 Conf., NACE, New Orleans, LA, April 17–21, 1989

Evaluation of Materials for the MHD Steam Bottoming Plant

K. Natesan and W. M. Swift

Presented at the 24th Intersoc. Energy Conversion Eng. Conf., Washington, DC, August 6–11, 1989

Advanced Batteries for Electric Vehicles

P. A. Nelson

Presented at the Fourth Int. Seminar on Lithium Battery Technology & Applications,
Deerfield, FL, March 6-8, 1989

Advanced High-Temperature Batteries

P. A. Nelson

Presented at the Second Space Electrochemical Research and Technology Conf., Cleveland,
OH, April 11-13, 1989

Modeling of Sodium/Metal Chloride Batteries

P. A. Nelson

Presented at the Intersoc. Energy Conversion Eng. Conf., Crystal City, VA, August 6-11,
1989

Evidence for Activation of Methane by Transition Metal-Substituted Aluminophosphate Molecular Sieves

H. T. Nguyen, L. E. Iton, and V. A. Maroni

Presented at the 198th Am. Chem. Soc. Meeting, Miami Beach, FL, September 10-15, 1989

Speciation of Pu(VI) in Near-Neutral to Basic Solutions Via Laser Photoacoustic Spectroscopy

S. Okajima, J. V. Beitz, J. C. Sullivan, and D. T. Reed

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA,
November 27-December 2, 1989

Speciation of Pu(VI) in Near-Neutral Solutions via Laser Photoacoustic Spectroscopy

S. Okajima, D. T. Reed, J. V. Beitz, C. S. Sabau, and D. L. Bowers

Presented at the Second Int. Conf. on Chemistry and Migration Behavior of Actinides and
Fission Products in the Geosphere, Monterey, CA, November 6-10, 1989

Optical Techniques for the Detection of Sputtered Atoms

M. J. Pellin, C. E. Young, W. F. Calaway, and D. M. Gruen

Presented at the Third Topical Conf. on Quantitative Surface Analysis, Salem, MA,
October 21, 1989

Pyrochemical Interface for Plutonium from Slags and Ash

R. D. Pierce, T. P. Mulcahey, and G. K. Johnson

Presented at the Ninth Annual Pyrochemistry Workshop, Alexandria, VA, October 17-19,
1989

Pyrochemical Recovery of Plutonium from Incinerator Ash

R. D. Pierce, T. P. Mulcahey, G. K. Johnson, and D. S. Poa

Presented at the Ninth Annual Pyrochemistry Workshop, Alexandria, VA, October 17-19,
1989

Proposed Experiment to Test Argonne Centrifugal Contactors at Atomic Energy of Canada Research Company

E. L. Plaice, R. A. Leonard, and G. F. Vandegrift

Presented at the Plutonium/Uranium Recovery Operations Conf., Oak Ridge, TN,
October 24-26, 1989Electrodeposition of Uranium Metal by Reduction of Uranium Oxides in Molten LiF-KF-NaF-CaF₂-UF₄

D. S. Poa, L. Burris, R. K. Steunenberg, and Z. Tomczuk

Presented at the 176th Meeting of the Electrochem. Soc., Hollywood, FL,
October 13-20, 1989

Dynamics of Vitreous and Molten Zinc Chloride

D. L. Price, S. Susman, K. J. Volin and M.-L. Saboungi

Presented at the Am. Phys. Soc. Meeting, St. Louis, MO, March 20-24, 1989

Cold Fusion: Experimental Results and the Questions and Answers They Provide

L. Redey

Presented at the Soc. Applied Spectrosc. Meeting, Chicago Section, December 12, 1989

Investigations of Cold Fusion Phenomena and Electrochemistry of the Pd-D System

L. Redey

Presented at the Case Center of Electrochemical Sciences, Cleveland, OH, October 4, 1989

Self-Discharge and Related Phenomena in Li-Alloy/Metal Sulfide Cells

L. Redey and S. L. Marshall

Presented at the 175th Electrochem. Soc. Meeting, Los Angeles, CA, May 7-12, 1989

Electrochemical and Calorimetric Investigations of the Pd-D System

L. Redey, K. M. Myles, D. W. Dees, M. Krumpelt, and D. R. Vissers

Presented at the Cold Fusion Session of the Electrochem. Soc. Meeting, Hollywood, FL, October 15-20, 1989

Investigations of Ni/NiCl₂ Electrodes in Basic Chloroaluminate Melt

L. Redey and D. R. Vissers

Presented at the 176th Electrochem. Soc. Meeting, Hollywood, FL, October 15-20, 1989

Detection and Speciation of Transuranium Elements via Pulsed-Laser Excitation

D. T. Reed, S. Okajima, and J. V. Beitz

Presented at the Metal Speciation and Transport in Groundwaters Workshop, Jekyll Island, GA, May 14-26, 1989

Corrosion Product Identification and Relative Rates of Corrosion of Candidate Metals in an Irradiated Air-Stream Environment

D. T. Reed and V. Swayambunathan

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 2, 1989

Formation of Zintl-Ions in Alkali-Lead Alloys

H. T. J. Reijers, W. van der Lugt, M.-L. Saboungi, and D. L. Price

Presented at the Seventh Int. Conf. on Liquid and Amorphous Metals, Kyoto, Japan, September 4-8, 1989

Formation of Zintl-Ions in Alkali-Lead Alloys

H. T. J. Reijers, W. van der Lugt, C. van Dijk, M.-L. Saboungi, and D. L. Price

Presented at the Gordon Research Conf. on Molten Salts and Liquid Metals, Wolfeboro, NH, August 7-11, 1989

Vaporization of Refractory Fission Products in Severe Reactor Accidents

M. F. Roche, J. L. Settle, L. Leibowitz, C. E. Johnson, R. C. Vogel, and R. L. Ritzman

Presented at the Winter Meeting of the Am. Nuclear Soc., San Francisco, CA, November 26-30, 1989

ICP/AES: A Modern Analytical Tool

C. S. Sabau

Presented at the 14th Annual ARA Congress, Los Angeles, CA, April 20-22, 1989

Clusters in Liquid Alloys

M.-L. Saboungi

Presented at the Thirteenth Midwest High Temperature and Solid State Chemistry Conf., Binghamton, NY, June 18-21, 1989

Heat Capacity and Structure of Compound-Forming Liquids

M.-L. Saboungi

Presented at the Symp. on Structure of Amorphous Materials, Ise-Shima, Japan,
September 11–12, 1989

Structural Implications from Thermodynamics

M.-L. Saboungi

Presented at the Symp. on High Temperature and Materials Chemistry, Berkeley, CA,
October 24, 1989

Structure of Low-Melting Salts

M.-L. Saboungi

Presented at Argonne National Laboratory, Argonne, IL, March 9, 1989

Intermediate Range Order in Molten Salts

M.-L. Saboungi, K. Calkins, H. T. J. Reijers, and D. L. Price

Presented at the Molten Salt Committee Meeting of the Electrochem. Soc. of Japan, Japan,
September 8, 1989

Ordering in Some Liquid Alloys

M.-L. Saboungi, G. K. Johnson, and D. L. Price

Presented at the Sixth Int. Conf. on High Temperatures–Chemistry of Inorganic Materials,
NIST and IUPAC, Gaithersburg, MD, April 3–7, 1989

Structural, Electronic, and Thermodynamic Properties of Liquid Alloys

M.-L. Saboungi, G. K. Johnson, D. L. Price, and H. T. J. Reijers

Presented at the CALPHAD Conf., Stockholm, Sweden, May 28–June 2, 1989

Neutron Diffraction Study of the Structure of Acidic Haloaluminates

M.-L. Saboungi, D. L. Price, K. Calkins, K. J. Volin, H. T. J. Reijers, and M. Blander

Presented at the Seventh Int. Conf. on Liquid and Amorphous Metals, Kyoto, Japan,
September 4–8, 1989

Intermediate-Range Order in Liquid Semiconducting Alloys

M.-L. Saboungi, D. L. Price, J. W. Richardson, K. J. Volin, H. T. J. Reijers, and W. van der Lugt

Presented at the Am. Phys. Soc. Meeting, St. Louis, MO, March 20–24, 1989

The Role of Zintl Ions in the Structure of Liquid Alloys

M.-L. Saboungi, D. L. Price, J. W. Richardson, Jr., K. J. Volin, H. T. J. Reijers, and W. van der Lugt

Presented at the 1989 Annual Meeting of the Am. Crystallogr. Assoc., Seattle, WA,
July 23–29, 1989

Structural, Thermodynamic, and Electronic Properties of Liquid Alloys

M.-L. Saboungi, H. T. J. Reijers, D. L. Price, J. W. Richardson, G. K. Johnson, and W. van der Lugt

Presented at the Seventh Int. Conf. on Liquid and Amorphous Metals, Kyoto, Japan,
September 4–8, 1989

Environmental Quality and the Shift to Alternative Fuels: Progress and Interim Findings of a Department of Energy Study of Transition in Vehicle Power Systems

C. Saricks, J. B. Rajan, and M. K. Singh

Presented at the Am. Inst. Chem. Eng., Philadelphia, PA, August 20–23, 1989

Analysis of Priority Pollutants by Gas Chromatography/Matrix Isolation Infrared Spectrometry/Mass Spectrometry

J. F. Schneider, P. M. Aznavoorian, S. E. Spiro, and I. W. Frank

Presented at the Int. Chemical Congress of Pacific Basin Societies Conf., Am. Chem. Soc.,
Honolulu, HI, December 17–22, 1989

Gas Chromatography/Matrix Isolation-Infrared Spectrometry Applications to the Analysis of Fossil Fuel Mixtures

J. F. Schneider and L. A. Raphaelian

Presented at the Soc. Appl. Spectrosc. Conf., Evanston, IL, February 14, 1989

Evaluation of Gas Chromatography/Matrix Isolation-Fourier Transform Infrared Spectrometry as a Quantitative Technique

J. F. Schneider, K. R. Schneider, and S. E. Spiro

Presented at the 16th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Chicago, IL, October 1-6, 1989

Thermodynamic Predictions of Phosphate Capacities in CaO-Based Melts

S. Sinha and M. Blander

Presented at the Annual Meeting of the Metallurgical Soc., Am. Inst. Mechanical Engineers, Las Vegas, NV, February 27-March 3, 1989

Determination of Organic Fluid Fouling

C. T. Snyder

Presented at the Eleventh Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory, Argonne, IL, November 9, 1989

Quantitation with GC/MI-IR

S. E. Spiro

Presented at the Tenth Analytical Chemistry Laboratory Technical Meeting, Argonne National Laboratory, April 18, 1989

The Rate of Hydration of Obsidian as a Function of Relative Humidity, Temperature, and Composition

C. Stevenson, J. J. Mazer, and J. K. Bates

Presented at the Fall Meeting of the Materials Research Soc., Boston, MA, November 27-December 2, 1989

Strontium Isotopes in Thermal Waters, Travertines and Rocks of the Northern Yellowstone Area

N. C. Sturchio, M. Averill, and E. G. Rauh

Presented at the Seventh Yellowstone Physical Science Symp., Mammoth Hot Springs, WY, September 5-8, 1989

Analysis of Polychlorinated Dibenzofurans and Polychlorinated Dibenzo-*p*-Dioxins in Samples from the Pulp and Paper Industry

S. E. Swanson and C. Rappe

Presented at the 16th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies, Chicago, IL, October 1-6, 1989

Multivariate Statistical Evaluation of Results of Studies of Dioxins from Pulp Bleaching

S. E. Swanson and C. Rappe

Presented at the Ninth Int. Symp. on Chlorinated Dioxins and Related Compounds, Toronto, Canada, September 17-22, 1989

Combustion of Coal-Derived Low-Volatile Fuels in a Slagging Combustor

W. M. Swift and F. G. Teats

Presented at the ICDB Seventh Annual Contractors' Meeting, Urbana, IL, August 1-3, 1989

SO₂-NO_x Control in a Staged Slagging Combustor with Hydrated Lime Injection

W. M. Swift and F. G. Teats

Presented at the Third Int. Conf. on Processing and Utilization of High-Sulfur Coals, Ames, IA, November 14-17, 1989

Is There a Strange Attractor in a Fluidized Bed?

S. W. Tam and M. K. Devine

Presented at the Workshop on Quantitative Characterization of Dynamical Complexity in Nonlinear Systems, Bryn Mawr College, Bryn Mawr, PA, June 22–24, 1989

Interfacial Infiltration Processes in Hot Corrosion—A Generalized Invasion Percolation Approach

S. W. Tam and J. G. Kirklin

Presented at Int. Conf. on High Temperature Corrosion, Les Embiez, France, May 22–26, 1989

Investigations of Hydrogen/ Li_2O Surface Interactions via Quantum Chemical Cluster Methods

S. W. Tam, J. Wright, L. A. Curtiss, and C. E. Johnson

Presented at the Fourth Int. Conf. on Fusion Reactor Materials, Kyoto, Japan, December 4–8, 1989

Interfacial Properties and Thermal Conductivity of Sphere-Pac Beds for Fusion Application

S. W. Tam and C. E. Johnson

Presented at the Second Symp. on Fabrication and Properties of Lithium Ceramics, Am. Ceram. Soc., Indianapolis, IN, April 23–27, 1989

Some Aspects of the Nonstoichiometric and Thermodynamic Behavior of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ System

M. Tetenbaum

Presented at the 1989 Midwest Thermodynamics Symp., Lake Geneva, WI, May 14–16, 1989

Some Aspects of the Nonstoichiometric and Thermodynamic Behavior of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ System

M. Tetenbaum, L. A. Curtiss, B. Czech, B. S. Tani, and M. Blander

Presented at the Spring Meeting of the Materials Research Soc., San Diego, CA, April 24–29, 1989

Oxygen Stoichiometry, Structural Transitions, and Thermodynamic Behavior of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ System

M. Tetenbaum, L. A. Curtiss, B. S. Tani, B. Czech, and M. Blander

Presented at the High Temperature Superconductors—Physics and Materials Science Conf., NATO Advanced Study Institute, Bad Windsheim, Germany, August 13–26, 1989

TRUEX Process Solvent Cleanup with Solid Sorbents

P.-K. Tse, L. Reichley-Yinger, and G. F. Vandegrift

Presented at the Sixth Symp. on Separation Science and Technol. for Energy Applications, Knoxville, TN, October 22–26, 1989

Thermodynamic Properties of the Ternary K-Pb-Sn and Rb-Pb-Sn Alloys

P. Tumidajski, A. Petric, and M.-L. Saboungi

Presented at the Gordon Research Conf. on Molten Salts and Liquid Metals, Wolfeboro, NH, August 7–11, 1989

The Generic TRUEX Model

G. F. Vandegrift, D. J. Chaiko, D. B. Chamberlain, L. Chow, J. M. Copple, D. R. Fredrickson, R. J.

Jaskot, J. D. Kwok, R. A. Leonard, J. B. Rajan, L. Reichley-Yinger, J. Sedlet, I. R. Tasker, and P.K. Tse

Presented at the 13th Actinide Separation Conf., Idaho Falls, ID, May 16–18, 1989

Development of LEU Targets for ^{99}Mo Production and Their Chemical Processing Status 1989

G. F. Vandegrift, J. D. Kwok, D. B. Chamberlain, J. C. Hoh, W. E. Streets, S. Vogler, H. R. Thresh,

R. F. Domagala, T. C. Wiencek, and J. E. Matos

Presented at the Int. Meeting on Reduced Enrichment for Research and Test Reactors, Berlin, Germany, September 10–13, 1989

Advanced Sodium/Metal Chloride Cell Research

D. R. Vissers, S. K. Orth, M. C. Hash, L. Redey, P. A. Nelson, and I. D. Bloom

Presented at the Ninth Battery and Electrochemical Contractors' Conf., Alexandria, VA,
November 12–16, 1989

The Effects of Acid Demineralization on the Sulfur-Containing Compounds Found in an Illinois-Basin High-Sulfur Coal

R. Winans, R. B. McBeth, and J. E. Young

Presented at the Third Int. Conf. on Processing and Utilization of High-Sulfur Coals, Ames,
IA, November 14–17, 1989

Surface Analysis by Resonance Ionization of Sputtered Atoms (SARISA) — Recent Applications and Results

C. E. Young, M. J. Pellin, W. F. Callaway, and D. M. Gruen

Presented at the Ion Beam Analysis Conf., Kingston, Canada, June 26–30, 1989

F. Papers Accepted for Publication

Analytical Electron Microscopy of Leached Nuclear Waste Glasses

T. A. Abrajano, J. K. Bates, and J. P. Bradley

To be published in *Adv. Ceram.*

Stable Isotope Geochemistry of Organic Matter in Animikie Basin Sediments Within the Thermal Aureole of the Duluth Complex

T. A. Abrajano, B. D. Holt, and G. R. Dyrkacz

To be published in *Organ. Geochem.*

Geochemistry of Reduced Fluids Related to Serpentinization of the Zambales Ophiolite

T. A. Abrajano, N. C. Sturchio, and B. M. Kennedy

To be published in *Appl. Geochem.*

Synthesis of Phase-Pure Orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$ Under Low Oxygen Pressure

U. Balachandran, R. B. Poeppel, J. E. Emerson, S. A. Johnson, M. T. Lanagan, C. A. Youngdahl, D. Shi, K. C. Goretta, and N. G. Eror

To be published in *Appl. Phys. Lett.*

Synthesis of Ceramic Superconductors under Low Oxygen Pressure

U. Balachandran, R. B. Poeppel, J. E. Emerson, M. T. Lanagan, C. A. Youngdahl, and S. A. Johnson

To be published in the *Proc. of the Int. Conf. on Superconductivity*

Theoretical Study of GeH_4 , AsH_3 , and SeH_2 : Bond Dissociation Energies

R. C. Binning and L. A. Curtiss

To be published in *J. Chem. Phys.*

Theoretical Study of GeH_4 , AsH_3 , and SeH_2 : Ionization Energies

R. C. Binning and L. A. Curtiss

To be published in *J. Chem. Phys.*

Calculations of the Influence of Additives on Coal Combustion Deposits

M. Blander, S. Sinha, A. Pelton, and G. Eriksson

To be published in *Special Issue of Progress in Energy and Combustion Science in Ash Deposition*

Modeling of Sulfide Capacities in Ternary Slags

B. Chen, R. G. Reddy, and M. Blander

To be published in *J. Minerals, Metals, and Materials*

Autoxidation of Trimethylamine in Aqueous Solutions

M. J. Chen, J. C. Linehan, and J. W. Rathke

To be published in *J. Org. Chem.*

Peripherally Substituted Phthalocyanines

M. J. Chen, J. W. Rathke, S. Sinclair, and D. W. Slocum

To be published in *J. Macromol. Sci.*

Theoretical Investigation of Intraatomic Electronic Excitation Energies of Divalent Cu

L. A. Curtiss and S. W. Tam

To be published in *Phys. Rev. B*

The Influence of Penetrating Gamma Radiation on the Reaction of Simulated Nuclear Waste Glasses in Tuff Groundwater

W. L. Ebert, J. K. Bates, and T. A. Abrajano

To be published in *Adv. Ceram.*

The Characterization of High Critical-Temperature Ceramic Superconductors by Vibrational Spectroscopy

J. R. Ferraro and V. A. Maroni

To be published in *Appl. Spectrosc.*

Properties of LiOH and LiNO₃ Aqueous Solutions

P. J. Gierszewski, P. A. Finn, and D. W. Kirk

To be published in *Fusion Eng. Design*

Radiation Damage Calculations for Compound Materials

L. R. Greenwood

To be published in *Am. Soc. Test. Mater., Spec. Tech. Publ.*

Thermodynamic Properties of the Zeolite Stilbite

D. A. Howell, G. K. Johnson, I. R. Tasker, P. A. G. O'Hare, and W. S. Wise

To be published in *Zeolites*

ICP/AES Actinide Detection Limits

E. A. Huff and D. L. Bowers

To be published in *Appl. Spectrosc.*

Thermodynamic Studies of Mordenite, Dehydrated Mordenite, and Gibbsite

G. K. Johnson, I. R. Tasker, H. E. Flotow, P. A. G. O'Hare, and W. S. Wise

To be published in *Am. Mineral.*

Composition and Spectral Characteristics of Ambient Aerosol at Mauna Loa Observatory

S. A. Johnson and R. Kumar

To be published in *J. Geophys. Res. — Atmos.*

Desorption Activation Energies for Tritium Release from Ceramic Breeders

J. P. Kopasz, A. K. Fischer, and C. E. Johnson

To be published in the *Proc. of the Second Int. Symp. on the Fabrication and Properties of Lithium Ceramics*

A Study of the Thermodynamic and Reducing Properties of Lithium in Cadmium at 773°K

M. A. Lewis and T. R. Johnson

To be published in *J. Electrochem. Soc.*

Laser Raman Spectroscopy in Studies of Corrosion and Electrocatalysis

C. A. Melendres

To be published in *NATO Advanced Study Institute Series*, Kluwer Press, Holland

DC Relaxation Techniques for the Characterization of Fast Electrode Reactions

Z. Nagy

To be published in *Modern Aspects of Electrochemistry*, Vol. 21, Chap. 6, eds., R. E. White, J. O'M. Bockris, and B. E. Conway, Plenum Publishing, New York

Battery Construction, Testing, and Materials

P. A. Nelson and T. D. Kaun

To be published in *Molten Salt Techniques*, Vol. 4, eds., D. Lovering and R. Gale, Plenum Publishing, New York

Inelastic Neutron Scattering from Non-Framework Species Within Zeolites

J. M. Newsam, T. O. Brun, F. Trouw, L. E. Iton, and L. A. Curtiss

To be published in the *Am. Chem. Soc. Symp. Ser.*

Improved Processing of Ceramic Superconductors

R. B. Poeppel, U. Balachandran, J. E. Emerson, S. A. Johnson, M. T. Lanagan, C. A. Youngdahl, and N. G. Eror

To be published in the Proc. of the First Int. Ceramic Science and Technology Congress

Electrochemically Generated Oxygen Contamination in Submerged Arc Welding

A. Polar, J. E. Indacochea, and M. Blander

To be published in Weld. J.

Calorimetric Measurements on Electrochemical Cells With Pd-D Cathodes

L. Redey, K. M. Myles, D. W. Dees, M. Krumpelt, and D. R. Vissers

To be published in J. Fusion Energy

Structure of Liquid Equiatomic KSn and CsSn

H. T. J. Reijers, M.-L. Saboungi, D. L. Price, and W. van der Lugt

To be published in Phys. Rev. B

Formation of Zintl-Ions in Alkali-Lead Alloys

H. T. J. Reijers, W. van der Lugt, M.-L. Saboungi, and D. L. Price

To be published in J. Non-Cryst. Solids

Book Review: *Geology of High-Level Nuclear Waste Disposal*, by I. S. Roxburgh

N. C. Sturchio

To be published in J. Geol.

Radium Isotopes, Alkaline Earth Diagenesis, and Age Determination of Travertine from Mammoth Hot Springs, Wyoming, U.S.A.

N. C. Sturchio

To be published in Appl. Geochem.

Oxygen and Carbon Isotope Ratios in Hydrothermal Minerals from Yellowstone Drill Cores

N. C. Sturchio, T. E. C. Keith, and K. Muehlenbachs

To be published in J. Volcan. Geotherm. Res.

Variations in Chemistry of Acid-Sulfate-Chloride Springs at Nevado del Ruiz Volcano, Columbia, November 1985 through December 1988

N. C. Sturchio and S. N. Williams

To be published in J. Volcan. Geotherm. Res.

Oxygen Stoichiometry, Structural Transitions, and Thermodynamic Behavior of the $\text{YBa}_2\text{Cu}_3\text{O}_2$ System

M. Tetenbaum, L. A. Curtiss, B. Tani, B. Czech, and M. Blander

To be published in *Physics and Materials Science of High Temperature Superconductors*

Atomic Motions in Liquid KPb—A Molecular Dynamics Investigation

K. Foukan, H. T. J. Reijers, D. L. Price, and M.-L. Saboungi

To be published in Phys. Rev. B

Thermodynamic Properties of Liquid Rb-Pb Alloys

P. J. Tumidajski, A. Petric, T. Takenaka, M.-L. Saboungi, and A. D. Pelton

To be published in J. Phys.: Condensed Matter

Thermodynamic Properties of the Ternary Na-Bi-Te and K-Bi-Te Alloys by Electromotive Force Measurements with an Alumina Solid Electrolyte

P. J. Tumidajski and M.-L. Saboungi

To be published in CALPHAD

The Solubility of CoCl_2 in Molten NaCl-AlCl_3

C. Wai, I. D. Bloom, D. Caveny, and M. Blander

To be published in *J. Phys. Chem.*

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To be published in *J. Nucl. Mater.*

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