uranium compounds that were inconsistent with results obtained from other cycles, which led to concern about the currently accepted value for the enthalpy of formation of UO_2. A redetermination of the enthalpy of UO_2 by fluorine combustion calorimetry gave a result in exact agreement with the previously accepted value.

The hydrolysis of UF_6 in excess water produces uranyl fluoride (UO_2F_2), but in small amounts of water other compounds, including UOF_4, $U_2O_3F_6$, and $U_3O_5F_8$, can be produced. Apart from UO_2F_2, no thermochemical data were available for these compounds. A research effort was started to determine the enthalpies of formation for UO_2F_2 and UOF_4 and to estimate values for the other two compounds. The experimental value for UO_2F_2 was in excellent agreement with a critical assessment of the literature data. The standard enthalpies of formation for UO_2F_2 and UOF_4 were -1654.8 ± 2.1 kJ/mol and -1924.6 ± 2.4 kJ/mol, respectively. An interesting result was that UOF_4 begins to decompose to UO_2F_2 and UF_6 at about 500 K.

The double fluoride, $AgUF_6$, was studied for various reasons, one of which was to investigate the relationship of thermochemical results to the oxidation of silver from Ag^+ to Ag^{2+}. The thermochemical values led to the rather surprising result that, thermodynamically, UF_6 is capable of oxidizing Ag^+ to Ag^{2+}:

$$UF_6 + 2\,AgF \rightarrow AgUF_6 + AgF_2$$

Normally, UF_6 is not thought of as a fluorinating agent. Potent fluorinating agents such as ClF_3, BrF_3, and XeF_2 do not fluorinate AgF to AgF_2 due to kinetic constraints. Apparently, the same is true of UF_6.

Some work was done to provide thermochemical information on uranium compounds, which could be used to predict the behavior of uranium in the Nevada Nuclear Waste Site. Because the question being addressed was the behavior of dissolved uranium in contact with concrete at ambient temperatures, the compound, $UO_3{\cdot}2H_2O$ (schoepite), which is the most hydrated form of UO_3, was chosen for the study. The standard enthalpy of formation at 298.15 K, the low-temperature heat capacity, the standard entropy, and the enthalpy increments up to the limit of stability of the material were determined. Information was then derived for the thermochemical values for the decomposition of UO_3 hydrates and the solubilities in acid of $UO_3{\cdot}2H_2O$ and $UO_3{\cdot}0.9H_2O$ as a function of temperature.

Chalcogen (S, Se, Te) Compounds. In spite of the fact that sulfides are used extensively in industry and have been the subject of a great deal of research, much of the existing thermochemical information on inorganic sulfides was seriously in error. In fact, it could not be used for practical applications in some cases. Fluorine combustion calorimetry was well suited to thermochemical measurements on sulfides, which were difficult to perform by more conventional calorimetric methods. The CMT group had been able to obtain reliable data on a variety of sulfides (As_4S_4, As_2S_3, Sb_2S_3, MoS_2, US, US_2, $CuFeS_2$, and K_2S). Plans were made to begin investigations of sulfides of aluminum and tungsten because of their technological importance, and pure and mixed sulfides of cobalt, chromium, manganese, and nickel, which are strategically important materials. The CMT Division was probably the only group that had a capability for measuring thermochemical values for these materials by fluorine combustion calorimetry.

Fluorine-combustion calorimetry was used to measure the enthalpy of formation of GeS_2, which is used in optical and electrical applications. Research on $ZrTe_2$ showed that the compound is quite stable, suggesting that zirconium cladding might act as a getter for fission-product tellurium in a reactor accident.

Because of its use as a desulfurization catalyst and intercalation compound, TiS_2 was of interest, and there was some controversy regarding the existence of a low-temperature transition at about 370 K. In collaboration with workers at the Exxon Corporation and the U.S. Bureau of Mines, the standard molar enthalpy of formation, ΔH^0, and high-temperature enthalpy increments, $H^{\circ}(T) - H^0(298.15\ K)$, were determined. No evidence was found for the transition at 370 K.

Thermochemical data were also obtained on K_2SO_3, $NaLiSO_4$, and $KHSO_5$, which were of commercial or research interest.

In the mid-1980s, the technical community was becoming excited about the subject of "high-tech" materials. A three-day symposium at the American Chemical Society meeting in Chicago in 1985 was devoted to discussions of newly synthesized inorganic compounds, and an entire issue of *Scientific American* (October 1986) concerned these materials and their potential applications. The term "high tech" probably defies an exact definition, but it did include a number of chalcogenide compounds of metals (sulfides, selenides, and tellurides). These compounds have a wide variety of potential applications: (1) high-temperature lubricants, (2) uses in electronics such as semiconductors, thin films, glasses, photoresists, photomicrography, (3) active materials in rechargeable batteries, (4) catalysts, (5) materials in solar-energy conversion, (6) ceramics, (7) materials in extractive metallurgy, and (8) corrosion inhibitors in sulfur-containing atmospheres. In many cases, thermochemical data on these compounds were unreliable or nonexistent, and fluorine-combustion calorimetry was uniquely suited to the purpose of obtaining this information.

In cooperation with Bell Communications Research and with Kenneth Volin and Sherman Susman of ANL's Materials Science Division, the enthalpies of formation of vitreous and crystalline $GeSe_2$ were determined. Molybdenum selenides were of interest because of their use as solid lubricants, electrode materials, and materials for solar-energy conversion. Enthalpies of formation were determined for $MoSe_2$ and Mo_6Se_6.

Vanadium monosulfide was of interest because of its use as a catalyst and its role in the mechanical and other properties of stainless steels. The standard enthalpy of formation of $VS_{1.043}$ was found to be -230.3 ± 2.2 kJ/mol. Tungsten diselenide (WSe_2) was of interest, owing to its use as a high-temperature lubricant. The value obtained for the standard enthalpy of formation of WSe_2 indicated that high-temperature vaporization of the selenide does not lead to the formation of $Se_2(g)$ or $Se(g)$, as others had suggested, and that further studies of the system were needed. The energy of combustion in fluorine of the semiconductor, black phosphorus, together with earlier data from white phosphorus, gave a value of -21.2 ± 2.1 kJ/mol for the transition of α-white to black allotropes of phosphorus.

Theoretical Studies. Larry Curtiss and Dave Chaiko of CMT and John Pople from Carnegie-Mellon University used quantum-mechanical calculations to derive thermochemical data for the N_2H radical, which had not been detected experimentally, but had been postulated as an intermediate species in atmospheric and combustion processes that involved nitric oxide (NO). The calculations showed that N_2H is unstable with respect to dissociation into N_2. Also determined were shifts in the vibrational frequencies of N_2H from those in N_2H_2 and N_2, which should be useful in any experimental attempt to detect the species. The enthalpy and entropy of dissociation were determined from the calculated vibrational frequencies and energy of formation.

Calculations were also made on a complex of water and carbon dioxide that is suspected of being a factor in global warming. *Ab initio* calculations were performed to determine the binding energy, structure, and vibrational frequencies of the $CO_2 \cdot H_2O$ complex, and a set of thermodynamic functions for this entity was generated.

In a cooperative effort with the Physics Division, a new set of thermodynamic functions for dimeric boric oxide (B_2O_2) was generated by a combination of *ab initio* calculations and photoelectron spectroscopy data. The results provided strong evidence that the molecular structure was O=B–B=O, rather than alternative configurations such as B-O-B-O. This work provided thermodynamic functions of improved accuracy for B_2O_2.

Personnel. Pat O'Hare was in charge of the calorimetric work. Other CMT people in this effort were Ward Hubbard, Howard Flotow, Ian Tasker, and Larry Curtiss. The CMT Calorimetry Group decreased in size until 1988, when it disappeared with the departure of Pat O'Hare. Some of the equipment, however, is still being used by other groups.

ELECTROCHEMISTRY

The basic electrochemical studies were concerned with experimental and theoretical investigations of processes occurring at electrodes and in electrolytes. Phenomena such as electrocatalysis, electrochemical corrosion, deposition and dissolution, and complexation in molten salt electrolytes were of interest. The experimental techniques included electrochemical measurements (relaxation and cyclic voltammetry methods), surface analysis (electron spectroscopy, atomic emission spectroscopy, scanning electron microscopy), and spectroscopic measurements (Mössbauer, Raman, UV-visible).

Electrode Kinetics and Electrocatalysis. A study was directed toward those factors that determine the rate and mechanism of the electroreduction of water on carbon-supported iron phthalocyanine (FePc) electrodes. Spectroscopic and electrochemical methods, together with quantum theoretical calculations, were used to correlate electronic structure and catalytic activity. Cyclic voltammetry showed that FePc films on glassy carbon electrodes in 0.05 *M* sulfuric acid solution catalyzed oxygen reduction at first, but became inactive on continued scanning, and then reactivated after about an hour on open circuit. The deactivation was attributed to slow transport of charge carriers within the p-type semiconductor film electrode. Films prepared from solutions of FePc in an organic solvent had a significantly higher activity than those formed by vapor deposition, apparently because the two methods produced different polymorphic forms of the films.

Quantum-mechanical calculations were performed on FePc and its analog, iron porphyrin (FeP), as well as their oxygen adducts. The charge of the iron is about the same in the two molecules, but the electrons are distributed differently. Calculations on the structures of the oxygen complexes of FePc and FeP showed that oxygen in the FePc-O_2 complex binds side-on to the iron with the O-O axis parallel to the FePc plane, whereas the oxygen in the FeP-O_2 complex is bound end-on to the Fe. These differences may determine what makes for a good electrocatalyst (FePc) or a mere oxygen carrier (FeP).

Continued work in this area using rotating ring-disc electrodes indicated that oxygen reduction in the FePc system proceeds by the formation of hydrogen peroxide (H_2O_2), and the loss of catalytic activity on cycling appears to be due to adsorption of peroxide intermediates. *In situ* laser Raman studies of the FePc films on gold and copper electrodes confirmed an earlier conclusion that the FePc was coordinated to water molecules in the solution. *Ab initio* calculations to study the solvation of O_2 by water molecules in solutions indicated that the energy of interaction between H_2O and O_2 molecules is only a few kilocalories, which accounts for the low solubility of oxygen in water. Ensuing studies showed that hydrogen peroxide could be anodically oxidized on the FePc films by a dissolution process that takes place under charge-transfer control.

Meanwhile, theoretical studies continued on the solvation of O_2 and O_2^- in water. These solvation effects were of practical importance because of their role in electrocatalysis. The most probable structure was one that includes both hydrogen-bonded O_2-HOH interactions and electron-donor O_2-OH_2 interactions, according to a newly developed molecular orbital method of calculation.

In continuing investigations of electrocatalysis, laser Raman and cyclic voltammetry techniques were used to study the structure and properties of iron protoporphyrin IX (FePP) as they relate to its catalytic activity in the electrochemical reduction of oxygen. This work was done in collaboration with John McMahon of Williams College. The FePP showed weaker catalytic properties compared to the FePc studies earlier. The conclusion from this work was that the catalytic activity and stability are functions of the molecular electronic structure of the compounds and perturbations caused by interactions with surrounding atoms, molecules, and surfaces.

Metal Dissolution and Deposition. Spectroscopic and electrochemical studies were conducted on anodic corrosion and passivation of metals in aqueous and molten salt environments. The anodic polarization of Fe, Co, Ni, Cu, Ti, Ta, and Mo in molten LiCl-KCl was measured at temperatures of 375 and 450°C. The corrosion-passivation behavior was similar to that found in aqueous systems, which was somewhat surprising. The oxides of Fe, Co, and Cu were reversibly reproducible, but those of Ta, Ti, Ni, and Mo were not. Consequently, Fe, Co, and Ni were suggested as possible cathodes for secondary batteries having molten salt electrolytes.

Many of the reactions involved in electrode kinetics studies are so fast that special measuring techniques are necessary. Several improvements were made in the equipment and the data-gathering methods. A galvanostatic double-pulse technique was used to investigate the kinetics of nickel in LiCl-KCl, LiCl-RbCl-$CaCl_2$, and LiBr-KBr-CsBr eutectic melts. The exchange current density of the reaction ranged between 0.1 and 1.7 A/cm^2.

Spectrochemical methods were applied to the identification of anodic corrosion films on silver in 0.05 *M* sulfuric acid. The dominant phase was Ag_2SO_4, but a new phase, $Ag_7O_8SO_3$, which had not been reported previously, was also observed. The conversion of Ag_2SO_4 to higher oxides *i.e.*, Ag_2O and AgO, was slow from an electrokinetic viewpoint. Anodic films on silver in 0.05 *M* Na_2SO_4 were basically the same as those found in H_2SO_4.

The formation of anodic corrosion films on nickel in 0.05 *M* NaOH solution at room temperature was studied by cyclic voltammetry and *in situ* laser Raman spectroscopy. An anodic film that formed on the nickel corresponded most closely to "hydrated" Ni_2O_3. Studies were also made of nickel in aqueous borate media. Infrared studies were conducted on anodic corrosion films formed on iron. Laser Raman spectroscopic and X-ray diffraction techniques were used to identify coatings found on Type 304 stainless steel that had been subjected to tensile tests in the Materials Science and Technology Division. Raman bands that could be attributed to Fe_2O_3 and Fe_3O_4 were observed in test samples that had been exposed to solutions containing dissolved oxygen as an impurity, and this result was confirmed by X-ray diffraction.

In collaboration with the Materials Science and Technology Division, a cell and electrolyte-recirculation system was constructed to conduct simultaneous spectroscopic and electrochemical studies of aqueous corrosion at high temperature and pressure (300°C and 10 MPa). Cyclic voltammetry studies of nickel in 100 ppm Na_2SO_4 solution at 25 to 290°C indicated that passivity of the nickel disappeared above about 100°C and pitting corrosion occurred above 250°C. At potentials near the region of oxygen evolution, the presence of Ni_2O_3 was noted. This study also included an evaluation of the use of AC impedance measurements to obtain further electrochemical information.

A study was made of lead in dilute Na_2SO_4 solution. Cyclic voltammograms showed typical anodic dissolution/passivation behavior. The passive film at low and high temperatures was $PbSO_4$, and at intermediate temperatures it was $PbO{\cdot}PbSO_4$. Laser Raman spectroscopy and X-ray diffraction were used to characterize the types of compounds that could conceivably form as lead corrosion products. The various forms (β- and γ-NiOOH, $Ni_2O_3{\cdot}2H_2O$, $Ni_3O_4{\cdot}xH_2O$, and NiO_2) were thought to differ only in the degree of structural disorder and the nature of intercalated molecules, ions, *etc.*

An effort was devoted to the electrode kinetics and mechanistic aspects of metallic corrosion in aqueous media. The processes are basically electrochemical and involve anodic oxidation of a metal accompanied by reduction of a component in the solution, and the anodic oxidation is often the rate-controlling step. Stress-corrosion cracking is a manifestation of this type of process that has been a problem in light water reactors. A capability was developed for investigating high-temperature, high-pressure electrode kinetics. Among various reference electrode designs that were tested, a palladium/hydrogen pH-sensitive (pseudoreference) electrode gave experimental results close to the theoretical values at 90 atm pressure and a temperature of 250°C. Deviations were observed at lower temperatures, probably due to decreased hydrogen permeability of the palladium.

In 1985, a high-temperature, high-pressure test loop that incorporated a built-in, fast-pulse electrochemical cell was built and placed in operation, and several working-electrode, counter-electrode combinations and reference electrodes were designed, built, and tested. The palladium/hydrogen electrode was tested further and found to be a stable reference electrode suitable for electrochemical relaxation measurements at high temperature and pressure. A cooperative program was initiated with John Halley of the University of Minnesota in which he was to perform molecular-dynamics calculations and the CMT workers were to provide experimental data. The initial experiments were made on relatively simple systems, including Fe^{2+}/Fe^{3+} and Cr^{2+}/Cr^{3+} redox reactions on a gold electrode.

A cyclic-voltammetry investigation of the Fe^{2+}/Fe^{3+} couple showed that the overall rate of the reaction increased fourfold between 25 and 150°C, an increase typical of diffusion-controlled reactions. In these measurements, ultra-clean media were required to avoid interferences, and a computer model was developed to sort out the diffusional effects from the surface reaction kinetics. Also, *ab initio* molecular orbital calculations were used to develop potential energy functions for hydrated transition metal cations, which can be used to provide calculations of electron-transfer rates.

These studies also included the development of computer models to estimate the effect of the structure of the interfacial solution layer on the transient electrode kinetics measurements, and a model to determine the effect of mass transport on the calculation of corrosion rates from electrochemical polarization measurements.

Because of the role of adsorbed molecules on surfaces in corrosion and other electrochemical reactions, some *ab initio* studies were conducted on this phenomenon. The studies emphasized computation of the energetics of surface processes and dealt with shifts in vibrational frequencies, binding energies, binding sites, ionization energies, and charge-transfer effects of the adsorbed molecules. Collaborative work was performed with

Professor John A. Pople of Carnegie-Mellon University, in which interactions of lithium and beryllium with water were investigated. The beryllium atoms were in clusters of one to five. A dramatic increase in the interaction energy occurred when the cluster size reached three beryllium atoms, with no further major changes as it went from three to five. The water molecules preferred corner binding sites over edges or faces of the clusters. An investigation of water interactions with Mg and Na atoms showed that they, like Li and Be, form complexes with H_2O that have metal-oxygen bonds with charge transfer to the metal atoms.

Personnel. Among the personnel in the electrochemical studies were Ira Bloom, Alan Brown, Dennis Dees, Mike Krumpelt, Ralph Loutfy, Carlos Melendres, Zoltan Nagy, Laszlo Redey, Jack Settle, and Bob Yonco.

OTHER SPECTROSCOPIC AND STRUCTURAL STUDIES

In the previous chapter, mention was made that many metal halides form gaseous complexes with "acidic gases" such as $AlCl_3$ or $FeCl_3$, which enhance their volatility by factors as large as 10^{14}. Such complexes may have practical utility for chemical separations, metallurgical processes, high-efficiency lamps, and lasers. This program consisted of spectroscopic and thermodynamic measurements to find new vapor-phase complexing agents and vapor species and to determine their electronic, vibrational, and structural properties. George Papatheodorou played a leading role in much of this work.

In 1980, spectrophotometric investigations were conducted on gas-solid reactions of $FeCl_2$ and $ErCl_3$ with $AlCl_3$, $GaCl_3$, and $InCl_3$ as the carrier gases, and *ab initio* molecular orbital calculations were made on the complexes $BeF_2 \cdot AlF_3$, $MgF_2 \cdot AlF_3$, and $AlF_3 \cdot BeF_2 \cdot AlF_3$. The calculations indicated that the cation MF^+ can move relatively easily about the nearly spherical anion AlF_4^- to form corner-, edge-, or face-bridged structures. The most stable structure for the complex $AlF_3 \cdot BeF_2 \cdot AlF_3$ was two edge-type bridges. In general, there was a preference for edge-type, two-fluorine bridging in these systems.

A statistical mechanical model was developed to calculate the entropies and free energy functions of vapor molecules. Only the atomic masses and a characteristic interatomic distance are needed for the calculation, which was tested successfully for the gaseous MX_n species where $n = 1\text{-}6$, and homonuclear clusters of 2-7 atoms.

Ab initio molecular orbital calculations were made on the bonding energies of $LiOH \cdot H_2O$, which was suspected of being an important species in the vapor of high-pressure molten carbonate fuel cells.

INTERFACIAL CHEMISTRY

Ab initio studies were initiated in 1984 on the properties of molecules adsorbed on surfaces. The idea behind these studies was to add a theoretical component to the various experimental efforts on aqueous corrosion and interfacial chemistry. Shifts in the vibrational frequencies, binding energies, binding sites, ionization energies, and charge-transfer effects of adsorbed molecules were investigated.

Zeolite Catalysis. In 1984, work was started on the surface chemistry of zeolites, which are aluminosilicate minerals having an open structure. Due to this open structure, they can function effectively as catalysts. Spectra of several types of zeolites were obtained by dusting or impacting zeolite particles on the surfaces of ATR (attenuated total internal reflection) elements. This technique permitted *in situ* measurements of gas adsorption/desorption processes and chemical surface reactions. *Ab initio* studies were also begun on molecules adsorbed on surfaces with emphasis on the energetics of surface processes.

Diffuse reflectance studies were concentrated on the reactivities of two iron-modified versions of ZSM-5 and offretite, which are synthetic zeolites that have potential utility as molecular-shape-selective catalysts. Protonated sites of differing stability were examined by means of deuterated probe molecules (D_2O and CH_3OD). Analysis of the infrared band positions of reactants and products in the zeolite structure provided new information on the role of the various protonated sites in hydrogenation and dehydrogenation reactions. The O-H and C-H stretching vibrations revealed further information on the reactions involved in hydrocarbon reforming within the zeolite.

By 1986, significant progress had been made in the use of Fourier transform infrared (FTIR) diffuse reflectance spectroscopy to investigate the reactivity of synthetic zeolites toward light hydrocarbons. These studies were augmented by adding a gas chromatograph to the diffuse-reflectance cell so that the reaction products could be identified simultaneously with the FTIR spectra. This arrangement shed new light on the effect of temperature on carbon-hydrogen bond scission in the catalytic conversion of alcohols to gasoline-type hydrocarbons. The catalyst used for this purpose was a synthetic zeolite, H-ZSM-5.

Investigations continued on the vibrational dynamics of zeolite framework structures. Twelve different structures were by then analyzed fully, providing the theoretical groundwork for detailed lattice dynamics calculations. Potential energy functions were then determined on several well-studied model systems having a rutile structure. A valence force field model involving only three parameters resulted in very good fits to observed vibrational data for several dioxides and fluorides having the rutile structure.

Ab initio molecular orbital calculations were used to investigate rotational barriers and vibration frequencies of organic templating cations used in the crystallization of synthetic zeolites. The use of organic bases such as tetraalkylammonium hydroxides greatly increased the number of gel/solution synthesis possibilities for producing microporous materials such as zeolites. The role of these organic materials, however, was not well understood, and the subject was investigated by researchers at the Materials Science Division and the Intense Pulsed Neutron Source along with those in CMT. Molecular orbital calculations were performed on the energies of the conformational rearrangements required for tetrapropylammonium ion to serve as a template for the zeolite ZSM-5.

Continuing work with the combined infrared spectroscopic and gas chromatographic techniques was directed toward the catalytic reactions of several light hydrocarbon reactions on aluminosilicate and aluminophosphate framework systems, the interactions of light alcohols and Brönsted acid sites of H-ZSM-5, and the catalytic properties of silica- and cobalt-substituted zeolites.

In 1988, a systematic study was conducted on the catalytic properties of a series of aluminum phosphate ($AlPO_4$) molecular sieve structures. A group of low-molecular-weight organic oxygenates (light alcohols, ethers, aldehydes, and esters) was used to observe reactant selectivity effects and any homologation behavior. The key factors affecting homologation proved to be pore directionality, pore connectivity, the nature of the functional groups of the reactant, and the presence of pre-existing carbon-carbon bonds in the reactant.

Further structural studies of the effects of molecular sieve frameworks on the vibrational frequencies and rotation of diffusion of occluded template molecules were continued. Results from *ab initio* molecular orbital and inelastic neutron scattering techniques indicated that cobalt-substituted aluminophosphate molecular sieves possess a strong oxidizing capability, converting methanol to aldehyde, and that cobalt/silicon substitutions can activate methane, which is homologated to C_2 and C_3 alkanes and alkenes.

Personnel. The CMT people involved in this work included Vic Maroni, who spearheaded the effort, Larry Curtiss, Torben Brun, Bob Kleb, Jim Newsam, Bob Beyerlein, and D. E. W. Waughan.

SPECIAL BASIC RESEARCH INVESTIGATIONS

The following are several basic research studies that were related to areas of practical interest. In some cases, basic investigations were necessary to support certain aspects of the applied programs. Other studies were exploratory studies of subjects that might lead to future applied programs.

Gas-Condensed Phase Equilibria. Equilibria between gases and liquids or solids in complex multicomponent systems are important in several energy technologies, including magnetohydrodynamics and coal combustion, desulfurization, and gasification. The objective of this program was to generate computer programs and database information to examine the chemistry of these complex systems.

In the condensation of alkali sulfates in combustion gases, Na_2SO_4-K_2SO_4 solutions were found to condense at somewhat higher temperatures than Na_2SO_4 alone, but to form a liquid at much lower temperatures. Thus, under typical burner conditions, a much larger fraction of the alkali sulfate condenses to form corrosive liquids rather than the less corrosive solids. A second conclusion was that the presence of dolomite as an entrained solid greatly increases the possibility that corrosive sulfate liquids, rather than solids, could be formed in turbines and condensers. (As mentioned elsewhere, dolomite is used in fluidized-bed combustion systems to remove SO_2 from the off-gases.)

This work was then expanded to incorporate reciprocal molten-salt solution theories to handle more complex systems such as mixtures of Na^+, K^+, Ca^{2+}, Mg^{2+}/SO_4^{2-}, Cl^-, and CO_3^{2-}. In 1987, a computer program was used in a collaborative study with the ANL Materials and Components Technology Division to calculate the condensed and gaseous products in the combustion of high-sulfur coal. Under both oxidizing and reducing conditions, the condensed phases were saturated with silica (SiO_2), and the major gaseous carriers of sodium and chlorine were NaCl and HCl, respectively. Silicates were the major phase of the condensates at temperatures above about 1327°C, and the concentrations of sulfates (under oxidizing conditions) and sulfides (under reducing conditions) increased with decreasing temperature. These results are considerably different from the assumptions that had usually been made in the past about the compositions of corrosive deposits from coal combustion or conversion.

Impurity Interactions in Liquid Metals. A study was directed toward the reactions of nitrogen with selected metallic elements in liquid lithium because nitrogen was known to play a key role in corrosion and mass transfer in chromium-containing steels used for containment of liquid lithium blankets in the magnetic fusion program. The systems under study were Li-Cr-N and Li-Ca-N.

Scanning electron microscopy and ion-microprobe mass analyses, together with sampling and wet chemical analyses, were completed, and the results were combined with earlier resistometric data to gain a better understanding of the mechanism of the reaction of chromium with nitrogen in liquid lithium. The data supported the proposed formation of Li_9CrN_5 in the solutions. The solubility of this compound is significantly higher than that of chromium metal, which could account for the enhanced corrosion and mass transfer observed in lithium-stainless steel systems.

Precipitation techniques, based on the formation of nitrides that are less soluble than Li_3N, were also investigated as a means of reducing nitrogen levels in liquid lithium. Experiments with calcium additions indicated a finite solubility for the compound LaCaN and an equilibrium between that compound and Ca_3N_2. These results indicated that the nitrogen levels could be controlled in a range of 100-1000 ppm by weight through careful adjustment of the calcium activity in the lithium.

Sulfide Species in Molten Salt Solvents. The properties of sulfide species formed in molten salt electrolytes were germane to the chemistry of high-temperature electrochemical systems, including the metal sulfide-based batteries. Electronic-absorption, resonance-Raman, and electron-spin-resonance spectra were obtained for species formed in molten $CsCl\text{-}AlCl_3$ solutions containing different S/Al ratios. The results showed that the S_3^- radical was the predominant sulfur species, and that this radical tends to form adduct-type molecular ions such as $AlCl_3{\cdot}S_3^-$.

Other investigations were concerned with the structural and chemical behavior of polyhalide and polysulfide anions in molten alkali halides of the type used in batteries with chalcogen positive electrodes. Identification of the charge-bearing species and elucidation of mechanisms for capacity loss and self-discharge were important to the applied battery program. A spectrophotometric study of solutions of $Li_2S\text{-}FeS_x$, where x is between 1 and 2, depending on the state of charge of a $LiAl/FeS_2$ battery, provided firm evidence for the existence of at least two sulfide-containing species.

Physical Chemistry of Minerals and Materials. The aim of this research was to elucidate the dissolution and transport characteristics of certain 3d transition metals such as Cr, Mn, Ni, and Cu in nonaqueous media. This area of research had a potential for eventual applications, including the recovery of these strategically important metals from naturally occurring deposits or industrial by-products.

In a solvent-extraction type of separation, Co^{2+} dissolved with equal concentrations of Fe^{3+}, Ni^{2+}, and Cr^{3+} in a low-melting (150°C) carboxylate eutectic phase and was extracted selectively into a dodecane phase containing bis-(2-ethylhexyl) phosphinic acid. This result demonstrated the possibility of using ligand-exchange reactions in solvent-extraction separations.

Experiments were conducted with molten LiCl-KCl eutectic as a solvent for two polysulfide ore concentrates from iron-cobalt-copper-nickel mineral deposits in Missouri and Idaho. Additions of acidic post-transition metal halides (*e.g.*, $BiCl_3$, $HgCl_2$, $SnCl_2$, and $ZnCl_2$) were effective in dissolving most of the ore-bound transition metals.

Continuing studies were performed on anion/cation coordination chemistry in low-melting molten salts containing organic anions. The ligand field spectra of 3d transition metal ions were studied in formate, acetate, and thiocyanate eutectics. Octahedral coordination was seen in all cases. The tendency toward octahedral coordination was attributed to crystal-field effects, while formation of complexes with low negative charge was believed to result primarily from electrostatic effects. A highlight of this work was the synthesis and characterization of a unique halocarboxylate salt that had metastable fluid properties at room temperature. Further studies led to a glassy alkali metal trifluoroacetate (TFAc) that formed a metastable liquid at temperatures as low as 22°C. This salt, of the composition CsTFAc-NaTFAc-KTFAc (50-25-25 mol%), remained fluid for long periods of time at room temperature in an anhydrous condition, but crystallized if traces of water or other impurities were present. Electronic absorption spectroscopy was used to examine the structural properties of the TFAc anion and to investigate the coordination chemistry of 3d transition metals (V^{3+}, Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) in TFAc solutions. The ligand field absorption spectra were similar to spectra of the same cations in aqueous solutions, but the molar absorptivities were 2 to 20 times higher.

Lixiviation studies were conducted on naturally occurring oxides and sulfides of the transition metals. Molten LiCl-KCl alone was not effective for this purpose, but successful lixiviation by LiCl-KCl occurred when acidic metal halides such as $BiCl_3$, $HgCl_2$, $SnCl_2$, and $ZnCl_2$ were added. Molten LiCl-KCl by itself, however, was successful in recovering metals from oxide mattes produced by roasting sulfide ore.

An electrolytic reduction was performed on LiCl-KCl solutions of transition-metal ions leached from ore samples. Complete electrodeposition of cobalt was achieved with a current efficiency near 100%, using graphite electrodes.

These studies were then directed toward sea-based minerals. Pacific sea nodules containing about 30 wt% Mo, 7 wt% Fe, and smaller amounts of Ni, Co, and Cu, all in oxide form, were treated with two candidate extraction salts, LiCl-KCl eutectic and NaCl-KCl-$MgCl_2$ eutectic. The latter extracted close to 100% of the Mn, Fe, Ni, Cu, and Co from the nodules, while the LiCl-KCl extracted only about 50% of the Mn, Cu, and Co. Cyclic voltammetry showed that cobalt can be electrodeposited from molten alkali halides with nearly 100% coulombic efficiency.

Taken together, the results of this work suggest the possibility of a compact pyrochemical processing plant to recover these metals at the site of the deep sea mining operation.

Further work was done in which equilibrations of nodule material and molten NaCl-KCl-$MgCl_2$ were sparged. Chlorine gas and hydrogen chloride (HCl) were produced by the lixiviation reaction. Manganese, cobalt, nickel, and copper were all extracted as divalent ions, and the iron was trivalent. The sequences of reactions involved were established by absorption spectra, X-ray diffraction, and chemical analysis.

In larger-scale experiments (50 g of nodule, 250 g of salt), iron and copper were recovered as $FeCl_3$ and $CuCl_2$ by volatilization at 450-500°C. (A complex vapor species, $FeCuCl_5$, appeared to be involved in the volatilization.) Nickel, and then cobalt, were recovered as the metals by electrolysis, leaving only manganese in the salt. Preliminary tests indicated that the manganese could be precipitated as an oxide by a controlled reaction with oxygen. This processing scheme was the subject of one of the *Industrial Research Magazine* IR-100 awards for 1985.

These studies, initiated and directed by Vic Maroni, were done by Bob Yonco and some temporary personnel.

Electrochemical Reactions in Submerged Arc Welding. Underwater arc welding of steel plate entails high currents and DC voltages (*e.g.*, 500 A and 30 V) which result in electrochemical reactions at the surfaces of the weld pool and the weld wire that is fed in. The weld wire is usually anodic while the weld pool and base plate are cathodic. The purpose of these studies was to determine mechanisms for alteration of the weld metal chemistry that would improve the quality of the welds.

After arc welding with SiO_2-MnO-FeO fluxes, the weld wire would be exposed to a relatively high oxygen partial pressure, and a half-cell reaction can be written as

$$nO^{2-} + M \rightarrow MO_n + 2\,ne^-$$

where M is a metal at the weld wire-slag interface, and n is related to the valence of M in the oxide. (For steel, M would be largely iron.) This reaction produces an oxide which finds its way into the slag and the weld metal. Experimental results for the oxygen content of the weld metal were consistent with the proposed mechanism.

The cathodic reactions result in reduction and deposition of metal (*e.g.*, Fe, Si) at the interface. The relative amounts of the species in the deposits depend upon the possible oxidation-reduction reactions between the various metals and oxides. An analysis of experimental results indicated that both the electrochemical and back reactions were important.

The underwater welding studies were initiated by Milt Blander. Art Pelton was involved in the work, but most of the effort was supplied by temporary personnel or people outside the Division.

SOLID OXIDE SUPERCONDUCTORS

In the 1980s, a discovery was made that a new class of materials consisting of copper oxide and oxides of certain Group II and III metals such as barium and the rare earths exhibited superconductivity at temperatures approaching 100 K (-173°C). This was an exciting development in that superconductivity had been limited previously to metals at temperatures below about 10 K (-263°C), which required liquid helium or hydrogen as a coolant. Because of the much higher T_C value (the temperature below which the material is superconductive) of the new oxide systems, sufficient cooling can be achieved with liquid nitrogen, which is much less expensive and more readily available.

This development stimulated much interest and sparked a variety of new research initiatives at Argonne. The Chemical Technology, Materials Science, and Components Technology Divisions entered into a collaborative effort on the following activities: (1) measurements and analysis of the vibrational densities of states of the high-T_C materials; (2) *ab initio* and semiempirical molecular orbital studies of $(Cu\text{-}O)_n$ clusters similar to those found in the high-T_C structures; (3) synthesis of high-T_C phases by oxidation of metallic precursors; (4) X-ray diffraction studies of single-crystal high-T_C phases; and (5) bonding of high-T_C ceramics to metals.

Infrared, Raman, and theoretical group methods were used to look at the vibrational densities of a variety of perovskite-type structures, including some with high T_C values. The predicted number of phonons was compared with the experimental data. Several phonons of $La_{1.85}Sr_{0.15}CuO_4$ and $YBa_2Cu_3O_{7-x}$ were observed and assigned unambiguously to the structure.

Molecular orbital calculations indicated the likelihood of mixed valence states of the different Cu sites in $YBa_2Cu_3O_{7-x}$ which fall in the ranges of 2.5-3.0 and 2.0-2.5 and may cause structural features that result in superconductivity. The superconducting phase for $T_C = 94$ K appeared to have an oxygen stoichiometry near 7.0.

Studies were continued on the connection (if any) between phonon behavior and high-temperature superconductivity. Results from $La_{2-x}M_xCuO_4$ (where M = Sr, Ba) showed an excellent fit between a valence-bond-type force field model and the four Raman-active phonons and two of the seven infrared-active phonons.

Attempts were made to fabricate superconducting ceramic materials in bulk and coating forms by oxidizing mixtures of metals corresponding to the stoichiometry of the desired oxide product. The initial results suggested that superconducting films could be fabricated on metal precursors if the conditions were controlled carefully. The most successful bonding procedure involved the use of indium foils with $YBa_2Cu_3O_7$ disks that had been sputter-coated with silver. A composite of the same ceramic material + 10 vol% silver sandwiched between two copper disks had an interfacial electrical resistivity of about 10^{-6} ohm-cm^2. Several additional assemblies of this general type were fabricated with good results. In 1989, preparations were started for a research effort on the preparation of high-T_C superconducting ceramic films by the oxidation of liquid alloy precursors.

Individuals who worked on various aspects of this program were Vic Maroni, Milt Blander, Ira Bloom, Alan Brown, Wally Calaway, Larry Curtiss, Dieter Gruen (Chemistry Division), Mark Hash, Stan Johnson, Carlos Melendres, Shiu-Wing Tam, Ben Tani, and Marv Tetenbaum.

ENVIRONMENTAL CHEMISTRY

The Environmental Chemistry Program continued in the 1980s with the same basic objectives: that is, determine the mechanisms involved in the formation of atmospheric sulfate and nitrogen-bearing aerosols, and improve the instrumental capability to conduct the studies.

Characterization of Atmospheric Aerosols. Although chemical analysis of aerosol particles can be accomplished by analytical techniques such as neutron activation, X-ray fluorescence, and atomic absorption, identification of the actual chemical species is not so straightforward. Methods had been developed for collecting time- and size-classified atmospheric particles, which provided some information on sources and mechanisms of formation.

The Attenuated Total Internal Reflection (ATR) instrument described in the last chapter was field-tested and found effective even with very short sampling times, *i.e.*, about one minute. The instrument combined inertial impaction for sample collection with an infrared detector that used multiple internal reflection to achieve very high sensitivity. Tests were conducted both at ground level and aboard aircraft. A typical sample covered only about 10% of the impactor surface, so the individual aerosol particles did not interact with one another. The capability of the device was evaluated in a weeklong series of airborne field experiments conducted around a power plant near Centralia, Washington. During traverses of the aircraft through the plume from the stack, a single traverse six miles from the stack produced a sample sufficient for analysis even though the plume itself was very clean.

The sensitivity of the Fourier-transform infrared (FTIR) spectroscopic method for condensed-phase nitrate was extended to the sub-microgram level. A band at 1384 cm^{-1} was useful for nitrate levels down to about 0.1 µg. A less sensitive band at 2430 cm^{-1} was better suited to higher levels (>40 µg).

A study was also conducted on determinations of the bisulfate ion, which has major absorption bands at 1205 and 600 cm^{-1}. A procedure was developed whereby the bisulfate ion could be measured quantitatively, which made possible a quantitative measure of the acidity of acid sulfates present in the aerosols.

In 1981, work was started on the use of X-ray diffraction to identify the crystalline phases in the fine-particle fraction of the aerosols. X-ray diffraction patterns were obtained and interpreted for 50-µg samples of aerosols in the 0.3-1.0 µm size range. Samples taken at Argonne and at State College, PA, showed that $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, $3(NH_4NO_3)\cdot(NH_4)_2SO_4$, and $2(NH_4NO_3)\cdot(NH_4)_2SO_4$ were frequently observed species. Numerous other double salts of ammonium and sulfate that contained metallic ions such as lead and calcium were also found. Some complexing of natural species and those generated by human activities may have occurred. Atmospheric scientists had not considered this possibility previously.

Work continued on the effects of collection time and particle size on the nature of aerosol particles. Particles of different sizes had very different chemistries, different sources and mechanisms of formation, and different behavior in the atmosphere. In general, the submicrometer particles were formed by gas-to-particle conversion, contained carbon and compounds of ammonia and sulfuric and nitric acids, had a relatively long residence time in the atmosphere, and tended to be regional in their occurrence. Larger particles, on the other hand, were formed mostly by mechanical processes, contained self-derived species such as carbonates and silicates, had fairly short residence times, and tended to be of local origin.

Sulfate Formation. Atmospheric sulfates, which are present in varying amounts in suspended particulate matter and in rain or snow, are composed of (1) primary sulfates formed within sources of emission to the atmosphere and (2) sulfates formed in the atmosphere, primarily by the oxidation of SO_2. Oxygen isotopy was used to investigate mechanisms by which these sulfates may be formed. The resulting information was expected to be useful in formulation of pollution-control strategies.

There are numerous pathways by which primary and secondary sulfates could be formed, which complicates research on the subject. Initial studies were aimed at the oxygen isotopy of sulfur dioxide to sulfate reactions that were amenable to laboratory simulation. The early results indicated that primary sulfates resulting from the formation of SO_3 at elevated temperatures, followed by hydrolysis, could be distinguished from other atmospheric sulfates.

Mechanisms of primary sulfate formation were studied by comparing the oxygen isotopies of sulfates formed from SO_2-air-water vapor mixtures at temperatures of 450-600°C in the presence of three different catalysts: platinum, Fe_2O_3, and charcoal. The results indicated that, of all the sulfate formed in this temperature zone in the exhaust chambers of power plants and other combustion systems, only the sulfates that are produced through the intermediate formation of gaseous SO_3 have a relatively high ^{18}O content. Application of the oxygen isotopy technique to samples of precipitated water and suspended aerosols at Argonne in 1976-1978 produced data on the relative percentages of primary sulfates in the two types of samples. In general, the percentage of primary sulfate in the precipitated water did not show a strong seasonal variation, but in the aerosol samples the level was about 10% in the summer and 30-40% in the winter. This work showed that the oxygen isotopic technique could be very useful in assessing the relative contributions of "local" *vs.* "distant" sources of sulfur emissions at a receptor site.

When the oxygen-isotopic technique was used to determine the scavenging effect of rain on sulfate in a power-plant plume, the results showed that rain was about 300 times more effective in removing primary sulfates than in removing the SO_2. In the power-generating units, about 48% of the scavenged sulfates originated as SO_3. In the exhaust from a diesel engine, about 60% of the total sulfate was SO_3-derived primary sulfate.

Oxygen isotopic studies were conducted on the effect that diurnal variations in the oxygen isotope ratios ($^{18}O/^{16}O$) in water vapor has on the ratios in atmospheric sulfates. Field experiments, contrary to earlier results, indicated no consistent differences in the day and night samples. Also, no excessive enrichment of ^{18}O was found in water vapor samples collected on charcoal.

One of the questions involved in the atmospheric-pollution studies was the degree to which hydrogen peroxide (H_2O_2) might be responsible for the oxidation of SO_2 to sulfate, and whether this oxidation limits the aqueous-phase formation of sulfuric acid. This subject was of interest to the U.S. Environmental Protection Agency because it might show whether efforts to reduce atmospheric formation of sulfuric acid and its subsequent deposition should focus on the reduction of H_2O_2 rather than SO_2 in the atmosphere. A determination was made of the dependence of the $^{18}O/^{16}O$ ratio in the sulfate on that in the H_2O_2 by which sulfate was formed by aqueous oxidation of SO_2. A relationship was derived whereby the relative importance of the H_2O_2 oxidation in the atmosphere could be assessed by measuring the isotopic ratios in the sulfate, water, and H_2O_2 of rainwater. Some preliminary results were obtained on rainwater.

Nitrogen Chemistry. The initial objective of this study was to determine the vapor-liquid equilibria for the system NO_x-H_2O-SO_x-NH_3 at compositions that could be present in the ambient environment, with special attention to compositions involved in acid rain. The program included the development of instruments for measuring individual nitrogen oxides at low concentrations in a mixture. One such instrument was a chemiluminescent NO_x analyzer, which is based on a chemiluminescent reaction between NO (nitric oxide) and O_3 (ozone). The instrument was developed to a stage where it could be used in air at atmospheric pressure, but further work was needed to adapt it to the vapor-liquid equilibrium studies.

An interesting application of this device was its use to investigate the production of NO and NO_2 by lightning in a thunderstorm. By correlating the NO_x measurements with other chemical and meteorological data, the amount of NO_x generated in a single lightning flash was estimated to be 1×10^{26} molecules/flash.

The catalytic effect of nitrogen oxides on the conversion of sulfur dioxide to sulfuric acid was studied by means of a computer model that supposed a sequence of reaction steps with known or estimated rate constants. The parameters in the model were evaluated using part of the experimental data, and then the model successfully calculated the kinetic data from the rest of the experiments.

Ammonia is a ubiquitous species in the atmosphere that has a role in the neutralization of acid gases and particles formed by industrial and automotive pollutants. It may also be a source of nitrate in the atmosphere through oxidation by various mechanisms. Preliminary results indicated that NO is produced by the photochemical oxidation of ammonia.

One of the reaction systems of interest was the conversion of SO_2 to sulfate in the presence of H_2O and O_2, and possibly the influence of NO_2 and $HONO_2$. When gas mixtures of NO_x, H_2O, and O_2 were prepared for this work, the NO_2 concentration decreased much more rapidly than would be expected on the basis of rate constants published for the homogeneous NO-NO_2-HONO-$HONO_2$ system. When surface reactions of the nitrous and nitric acids were taken into account, however, the calculated results agreed well with the experimental data. These experiments indicate that heterogeneous reactions may have an important effect on the NO_x-SO_x interactions under certain conditions.

Carbon Studies. Carbon was of major interest as a component in atmospheric aerosols, and also in other areas of materials science. Therefore, an investigation was begun on the reactions of carbon with a variety of gases, including SO_2 and NO_2. The carbon was deposited on the internal reflection units in the FTIR spectrometer either by sputtering or by deposition as carbon black from a methane flame. Unlike the flame-deposited carbon, the sputtered carbon was quite reactive when exposed to SO_2 or NO_2. After exposure to air, to a CO_2-O_2-SO_2 mixture, and then to air again, absorption bands corresponding to CO, sulfite ion, sulfate ion, and NO_3 were measured. This technique permitted detection of gases such as SO_2, CO_2, CO, and H_2O

vapor simultaneously with the solid-phase material.

Personnel. In the 1980s, Romesh Kumar became the Group Leader of this program, replacing Paul Cunningham who had also been the Section Head in charge of the Analytical Chemistry Laboratory. Members of the group included Dave Drapcho, Ben Holt, Bill Hubble, Ron Isaacson, Stan Johnson, Wally Kremsner, Teresa Lang, Eugene Nielson, and Stan Siegel. Tony Engelkemeier, Don Graczyk, and Ben Tani of the Analytical Chemistry Laboratory, and Louis Fuchs of the Chemistry Division, also contributed significantly to this effort.

GEOCHEMISTRY OF THERMAL SYSTEMS

This was a new basic research program that originated in 1985. Its objective was to investigate specific chemical phenomena in geothermal systems through detailed chemical and isotopic analyses of rock, minerals, water, and gases sampled from appropriate geological sites. The resulting data were used to characterize the dynamic processes that occur with time in these natural systems. This type of information could prove useful in practical areas such as nuclear waste isolation, geothermal energy exploration and development, and exploration for minerals, oil, and natural gas. In some respects, this work was similar to the environmental and zeolite studies in that the compositions of the materials and/or the physical conditions for their formation often show considerable variability in natural systems. These factors create a challenge in the interpretation of data and mathematical modeling, but do not preclude an ability to generate an understanding of these systems and to make certain predictions concerning their future behavior. The arsenal of analytical methods used in these studies included neutron activation, inductively coupled plasma/atomic emission spectrometry, atomic absorption spectrometry, electron microprobe analysis, mass spectrometry, and alpha spectrometry.

An interesting analytical sampling technique was developed whereby fluid inclusions in a polished mineral specimen could be released by a laser and analyzed in a noble gas isotope ratio mass spectrometer. Before analysis, the samples were subjected to neutron irradiation to produce isotopes of Ar, Kr, and Xe from selected elements such as K, Ca, Cl, Ba, Br, U, and I, which can then be analyzed together with the naturally occurring gases in the same inclusions.

Uranium and Thorium Series Disequilibrium Studies. The first studies were made on samples of drill cores from the Biscuit Basin Rhyolite Flow in Yellowstone National Park. Data from one core were consistent with a model of single-stage uranium addition involving water/rock mass ratios as high as 10^5 or more. Results from the other core showed much less uranium mobility. Preliminary dating studies of ^{238}U hydrothermal precipitates, which were conducted in collaboration with Carl Binz of Loras College, Dubuque, Iowa, suggested that none of the samples was older than 200,000 years. The ^{238}U disequilibrium among its decay series members was used to determine the time scale of hydrothermal activity as part of the Continental Scientific Drilling Program (CSDP). The sites of interest were at Yellowstone, Wyoming; Valles, New Mexico; and Long Valley, California. Samples were collected in 1986 from Yellowstone, Long Valley, and the caldera at Valles. Most of the veins were older than 300,000 years, which was the resolution of the technique. Analyses of ^{226}Ra in Yellowstone samples suggested that a redistribution of radium and barium had occurred.

In 1987, large-volume thermal water samples were collected from 13 hot springs and geysers in Yellowstone and analyzed for radium, thorium, and uranium to determine the geochemical behavior of these elements, as well as their potential application as tracers and indicators of groundwater flow rates in hydrothermal systems. Studies (still under the CSDP) continued in 1988 with investigations of the disequilibrium between ^{226}Ra and ^{230}Th in drill core samples of hydrothermally altered rhyolite from Yellowstone. The ^{226}Ra/^{230}Th ratios showed that the cation compositions of samples were consistent with an ion-exchange equilibrium between zeolites and coexisting thermal waters. Data were obtained on equilibrium constants and diffusivities. The zeolite-water exchange appeared to have been operating for at least 8,000 years.

The ^{230}Th/^{234}U method was well established for determining the age of travertines from 10,000 to 350,000 years. The use of ^{226}Ra for determining lower travertine ages was investigated to determine the potential usefulness of this method. These studies, conducted on thermal waters and travertines from Mammoth Hot Springs in Yellowstone Park, indicated that ^{226}Ra activities at depths to 70 m below the surface were much lower than expected. Nevertheless, the rate of travertine deposition (about 1 cm/yr) was accurately estimated from the slope of the best-fit curve in plots of the ^{226}Ra activity *vs.* depth.

Oxygen and Carbon Isotopic Studies. Studies of oxygen isotope distribution were completed in a collaborative effort with K. Muehlenbachs of the University of Alberta. In the initial investigations, some disequilibrium was observed between thermal water and most solid phases. Further work with silicate and carbonate samples from Yellowstone showed that the ^{18}O/^{16}O ratio in minerals decreased with depth, reflecting the thermal gradient. Most SiO_2 minerals had ^{18}O/^{16}O ratios higher than equilibrium values predicted from the temperatures and the thermal water compositions. This effect was attributed either to deposition of the minerals at higher temperatures or to water with a high ratio. The ^{18}O/^{16}O ratio decreased with increasing sample age. The investigators speculated that the initial deposition of amorphous SiO_2 occurs relatively rapidly after a new fracture opens and allows a flow of SiO_2-supersaturated water. When the flow decreases or stops, equilibration takes place with SiO_2 deposition.

Hydrothermal Energy and Volcanism. A catastrophic eruption of the Nevado del Ruiz volcano in Colombia occurred on November 13, 1985. In a cooperative effort with Prof. S. Williams of Louisiana State University and Dr. Y. Sano of the University of Tokyo, thermal water and gas samples were taken from the Nevado del Ruiz volcano and several other Central American volcanoes. In water samples taken from hot springs at the Nevada del Ruiz volcano, a significant increase in the SO_4/Cl ratio occurred about 13 months after the eruption, and then decreased to the normal value within a month. The change may have resulted from the input of a pulse of magmatic SO_2, but there was no change in the ^{34}S/^{32}S ratio.

Deep Carbon Geochemistry. The introduction of magmatic heat into potential source rocks for oil and gas may cause significant hydrocarbon deposits in situations where such deposits would not be produced by conventional oil- and gas-forming processes. The compositions, quantities, and mobilities of hydrocarbons released by magmatic heat are not well known and cannot be predicted from currently available data.

Analyses were initiated on samples from approximately 1.6-billion-year-old sedimentary rocks of the Animikie Basin that were intruded by magmas of the Duluth complex in northern Minnesota. The analytical studies were performed on carbon and carbon isotopes, including characterization of kerogen fractions. The results suggested that large-scale mobilization of hydrocarbons might have occurred in this formation. In another study, step-combustion experiments at temperatures between 200 and 550°C generated data that would be useful in determining the degree of fractionation of carbon isotopes that may occur in high-temperature geological environments.

Personnel. In general, this was a highly collaborative effort that involved many outside individuals and organizations. The Principal Investigator was Neil Sturchio. Martin Seitz had a part in the initial stage of the program. Teofilo Abrajano, John Bohlke, a postdoctoral appointee, and Ben Holt (STA) also contributed to the effort. Much of the effort was supplied by the Analytical Chemistry Laboratory.

Analytical Chemistry Laboratory

The Analytical Chemistry Laboratory (ACL) entered the 1980s with a staff of about 25 people and Paul Cunningham as Manager. In 1982, as mentioned earlier, Paul departed for Los Alamos and Dave Green took over the operation. At that time, about two-thirds of their work was for the Division, notwithstanding the fact that the ACL had been designated as a central facility for the entire Laboratory. Like many of the other programs in the Division, ACL was subject to a financial squeeze in 1982, which resulted in the loss of two staff members. Because the work load was somewhat variable, however, the ACL was able to use the services of well-qualified, part-time analytical chemists who had retired or were available for other reasons to even out the load at a relatively low cost. After that time, the group grew steadily, reaching a manpower level of about 50 by the end of the decade.

In 1980, an organic analysis facility in Building 221 had just been completed, in which a primary consideration was for safety in handling carcinogenic, toxic, or flammable materials. The facility was equipped with a computerized chromatographic-mass spectrometry system.

The capabilities of ACL for various types of work were increased in the early 1980s by the acquisition of several new pieces of equipment, including a thermal ionization mass spectrometer; an inert gas fusion system for hydrogen, oxygen, and nitrogen analyses; a pulsed nitrogen laser unit for determinations of uranium in soil and groundwater; an inductively coupled plasma/atomic emission spectrometer; and an energy-dispersive X-ray analyzer to be used with the scanning electron microscope. Various other equipment upgrades and acquisitions continued throughout the 1980s, with emphasis on increased use of computers for automation and data processing.

The ACL consisted of three groups as of 1982:

1. A Chemical Analysis Group that was involved primarily with wet chemical and instrumental analysis.
2. An Instrumental Analysis Group that dealt mostly with nuclear decay counting, mass spectrometry, gas chromatography, neutron activation, inert gas fusion, and isotopic analysis.
3. An Organic Analysis Group that conducted analyses of complex organic mixtures, including fossil fuels, toxic materials, pesticides, and drugs.

Later on, in about 1988, a fourth group, called the Environmental Analysis Group, was added to respond to the growing amount of environmental research in the Division.

The capabilities of ACL were heavily publicized in the early 1980s to attract more work both from other ANL divisions and from outside sources. At the time, the two major efforts were on the proof-of-breeding program in CMT and work for the Energy and Environmental Systems (EES) Division. Large efforts were also required on the TRIO experiments in the nuclear fusion program, analysis of Integral Fast Reactor fuel for oxygen and hydrogen, and support for the TRUEX program, all discussed earlier.

The ACL began doing a substantial amount of work for outside (non-ANL) organizations that included the Environmental Protection Agency (EPA), the Nuclear Regulatory Commission (NRC), General Public Utilities (GPU), Fermilab, the Commonwealth Edison Company, the University of Illinois, the Gas Research Institute, the National Park Service (NPS), and others.

The following is a recap of most of the work performed by ACL in the 1980s. Many of these items were mentioned in the previous technical discussions; other items were not reported previously because they were funded directly from sources other than CMT.

Proof of Breeding Project
Preparation of Isotopic Standards for the Applied Physics Division
Workshops for Division of Educational Programs
DOE Environmental Survey (of about 40 DOE sites)
Detector Upgrade of Thermal Ionization Mass Spectrometer
Accelerator Mass Spectrometer Dating with Calcium-41
Development of Masked Multichannel Scaler (MMS)—subject of an IR-100 Award from *Industrial Research Magazine*
Analytical Support for Region V EPA Projects
Multiple Analyses of Uranium Alloys for the ANL Program on Reduced Enrichment for Research and Test Reactors
Gas Analysis for Argonne Premium Coal Sample Program
TRIO Program (Fusion Reactor Blanket Studies)
New Method of Isolating and Purifying Uranium for Isotopic Analysis
Analysis of High-Temperature Semiconductors
Analytical Method for Organic Carbon in Lake and River Sludges
Groundwater Analysis for Geosciences Programs
Enriched Uranium Booster Target Project
Loss of Cooling Accident Project
Molten Corium-Concrete Interaction Program
Development of a Dioxin Cleanup Method
Pyrochemical Process for Integral Fast Reactor
High-Sulfur Dry Scrubber Test
National Acid Precipitation Assessment Program (National Park Service)
Spent Fuel Leaching Tests
Americium Certified Reference Samples for New Brunswick Laboratory
TRUEX Process Flowsheet Development
Energy from Municipal Waste Program
Performance of Fuel in a High-Burnup LWR Reactor
Polyurethane Foam Pyrolysis Studies
Quantitation PCB/Pesticides in Environmental Samples
Fourier Transform Infrared Microscopy
Advanced Instrumental Methods for Analyzing Organics in Solid Waste
Analysis of Dioxins from Municipal Waste Incineration
Characterization of Organics in Solid and Sludge Wastes from Emerging Energy Technologies
Plastic Pipe Program
Rocky Flats Plutonium Metal Exchange Program
Determination of ^{226}Ra and ^{228}Ra in Water
Determination of Protactinium in Environmental Samples
X-Ray Diffraction of Superconducting Materials
Environmental Radiochemistry
Plutonium Residue Recovery Program
Advanced Mass Spectrometry Capability
Analysis of Dioxins from Municipal Waste Incineration
Chemistry of Bottom Sediments of the Chicago River
Technology for Verification of Treaties Limiting Chemical Weapons

This list, although not all-inclusive, illustrates the variety and scope of the ACL programs. The organization of ACL at the end of the 1980s is shown in Table 5-10.

Table 5-10. Organization of the Analytical Chemistry Laboratory in 1989

Dave Green, Manager
Fred Martino, Assistant

Amrit Boparai
Peter Aznavoorian
Gerald Baudino
Susan Bussey (STA)
Jack Demirgian
Laura Lamoureux
Gerry Reedy (STA)
John Schneider
Christine Snyder
Stephen Swanson
Yifen Tsai (STA)
Ronald Wingender (STA)

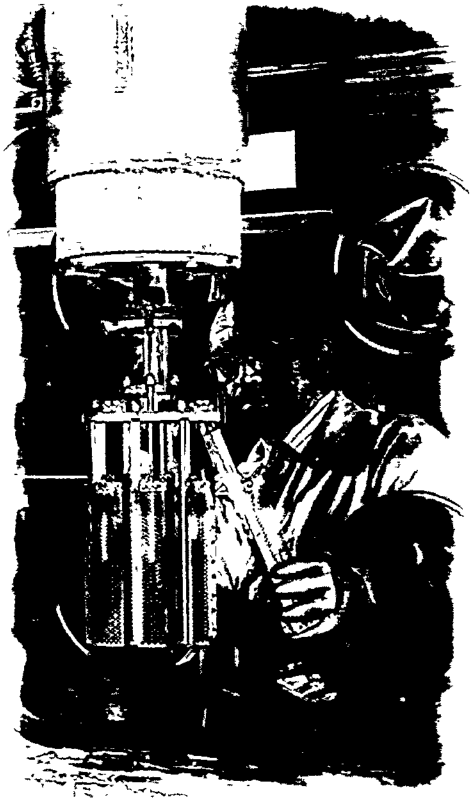
Don Graczyk
Tony Engelkemeier
Alice Essling
Howard Flotow (STA)
Irene Fox
Doris Huff (STA)
Ed Huff
Everett Rauh
Laury Ross (STA)
Florence Smith
Charles Stevens (R.A.)

Bob Heinrich
Del Bowers
Harvey Goodspeed (STA)
Francis Markun
Carmen Sabau
Stan Siegel (STA)
Elane Streets
Ben Tani
Tony TenKate
Lesa Wetter

Pete Lindahl
Ralph Bane (STA)
Ken Jensen (STA)
Jane Marr
Steven Newnam
Lynn TenKate

Admin. Asst.: Vanessa Arzate
Secretaries: Lilia Barbosa
Alice Birmingham
Virginia Strezo
(Janet Steinquist was the lead secretary up to 1989.)

1990 - 1998: INTO THE FUTURE



1990-1998

(top) Samples being prepared for atomic absorption analysis.

(bottom, left) Inert atmosphere glove-box facility for investigating molten metal/molten salt processes and for preparing radioactive wastes for disposal.

(bottom, right) Apparatus developed for treating a wide variety of spent nuclear fuels.

6

1990-1998: Into the Future

The year 1998 marks the 50th anniversary of the Division, and we have regarded that year as the cutoff date for this history. (The work in the technical programs is generally reported up to the end of 1997.)

As the United States entered the 1990s, the economy was healthy, and it appeared that there might be some respite from military conflicts, but, once again, that was too good to be true. On August 2, 1990, Iraq invaded Kuwait, and the U.S., with the approval of its allies, responded with a military action that sent the Iraqis back home. Other foreign military involvements included an effort to protect the delivery of relief supplies to Somalia, and peacekeeping duties in Haiti and Bosnia. By 1991, the Soviet Union had broken up into the Commonwealth of Independent States, and Boris Yeltsin was elected president of the Russian Republic on July 10 of that year. On February 1, 1992, Presidents Bush and Yeltsin issued a joint statement that the Cold War was over.

In the 1992 U.S. presidential election, Bill Clinton and Al Gore defeated incumbents George Bush and Dan Quayle, which gave the Democrats control of the administration and both houses of Congress. In 1994, however, the Republicans captured majorities in the House and Senate. Clinton and Gore were reelected over Bob Dole and Jack Kemp in the 1996 election, while the Republicans maintained control of Congress. During the mid-1990s, the political atmosphere became highly charged, and some of the activities of the Clinton administration (referred to as "Whitewater") were under investigation by Special Prosecutor Kenneth Starr. The 1998 election resulted in a small gain in House seats for the Democrats, but both houses remained under Republican control.

The economy flourished in the 1990s, with a skyrocketing stock market. Although some nuclear reactors had been shut down, total nuclear power production was increased due to higher outputs and plant factors. In the computer market, IBM (International Business Machines, Inc.) cut 25,000 jobs as a result of a $6 billion loss. By the 1990s, IBM had lost its dominance of the computer industry, and Microsoft, Inc., was rapidly taking its place.

At Argonne, Laboratory Director Alan Schriesheim decided to resign in June 1996. He was succeeded by Dr. Dean Eastman, who resigned in July 1998. As of December 1998, Associate Laboratory Director Frank Fradin was serving as acting Laboratory Director. In the Chemical Technology Division, Martin Steindler resigned as Division Director in 1992, and was replaced by Jim Battles, who served in that capacity until 1994, when Jim Laidler assumed that responsibility.

The experimental work in the Division in the 1990s was mostly a continuation of existing projects, although the recycling of IFR fuel was phased out, and more emphasis was placed on environmental problems, such as the treatment of nuclear and other hazardous waste materials.

NATIONAL AFFAIRS

In the 1990s, the U.S. economy was in good shape, with reasonable interest and inflation rates and a low unemployment level of about 5.5%. The stock market was healthy, and underwent a boom in which the Dow Jones industrial index exceeded 9,000 in 1998. The market showed signs of faltering in 1998, however, due to world-wide economic problems that had arisen primarily in Asia. One matter of growing concern was the rapidly increasing national debt (about 5.5 trillion dollars in 1997). Both political parties espoused a balanced budget, but their opinions differed over priorities. The decade was marked by anomalous weather conditions, including severe flooding in several areas, which was attributed to the El Niño heating effect in the Pacific Ocean.

As the nation entered the 1990s, its foreign affairs appeared to be going well. General Noriega of Panama surrendered on January 3, and the United States signed an arms control agreement with the Soviet Union. On August 2, 1990, however, Iraq suddenly invaded and occupied the monarchy of Kuwait, a tiny, but oil-rich country. The U.S. immediately launched "Operation Desert Shield," in which over 230,000 troops were sent to Saudi Arabia and were followed by another 200,000 when President Saddam Hussein continued the Iraqi military buildup. The U.S. action was sanctioned by a U.N. Security Council resolution. A ground war called "Desert Storm" began on February 24. The Iraqi forces were soundly defeated within 100 hours. Bush elected not to extend the fighting to Baghdad, leaving Hussein, as it turned out, to continue his mischief. In 1992, the U.S. sent troops to Somalia to protect the delivery of relief supplies, but the operation was limited and relatively ineffective, with a final evacuation of the troops in 1995. A U.S.-led multinational military force was sent to Haiti in 1993 in a peacekeeping mission to reinstate President Aristide after he had been ousted by a military coup. In 1995, the U.N. sent 60,000 troops, including 20,000 Americans, to Bosnia in a peacekeeping effort. In Russia, both the economy and the government were in bad shape, and the people had difficulty in adapting to a capitalist system after generations of totalitarian rule. It seems likely that the present regime will remain in power, but the situation remains tenuous.

At the beginning of the decade, the White House was occupied by George Bush, his popular wife, Barbara, and his dog, Millie, who was credited with writing a book. Dan Quayle was Vice President, and the Democrats controlled both houses of Congress. The 1992 election was a contest among Bush, Bill Clinton, and third-party candidate Ross Perot. Some pundits attributed Clinton's victory to Perot, whose campaign apparently siphoned a substantial number of conservative voters away from Bush. The Democrats retained control of Congress. Although Clinton was a popular president, the 1994 mid-term election was a landslide victory for the Republicans, who captured both houses of Congress and many state governorships. Clinton and Vice President Albert Gore were reelected in 1996, and there was little change in the makeup of Congress. During these power shifts in Washington, relationships between the Democrats and Republicans became more acrimonious as both parties struggled to keep or gain power and to promote their different ideologies. Clinton and his administration were accused of a series of wrongdoings known collectively as "Whitewater," and Kenneth Starr was appointed as a Special Prosecutor to investigate the charges. At the present time, the matter has not been resolved. Both houses of Congress remained under Republican control in the 1998 election, but the Democrats gained five or so seats in the House of Representatives.

Although the U.S. space program also felt the effect of federal belt tightening, NASA made a number of remarkable achievements in the 1990s. The Hubble Space Telescope, which could make astronomical observations free from atmospheric effects, was launched in 1990. After the main lens was found to be defective, crew members of the space shuttle *Endeavor* made the necessary repairs in 1993.

During the period 1990-1997, the U.S. space shuttles *Columbia, Atlantis, Discovery,* and *Endeavor* completed a total of nearly fifty missions that involved military applications, satellite launchings, a wide variety of scientific experiments, and other activities. The Russians had a similar program involving seventeen space shuttles designated *Soyuz TM-9* through *TM-25.* In the mid-1990s, the U.S. teamed up with the Russians in manning the Russian Space Station MIR, which was about nine years old at the time and has been showing its age by a series of scary, but not fatal, mishaps. In addition to the manned space missions, the U.S. and other countries deployed several unmanned space probes. Some of the satellites were used for military and communications purposes; most were used to obtain all kinds of information on space phenomena, including the poles of the sun, short wavelength and magnetic effects, ultraviolet radiation, moon mapping, weather effects, X-ray sources in the Milky Way (stars, pulsars, black holes), asteroids, comets, auroras, solar winds, and radio signals. Two probes of particular interest to the public were used to explore the surface of Mars. The result was a series of fascinating pictures and chemical analyses of some of the rocks. A somewhat startling revelation toward the end of the 1990s was evidence that large quantities of water (as ice) may be present on the back side of the moon.

ENERGY AND THE ENVIRONMENT

The total consumption of energy in the United States in 1995, and the amounts used for electric power generation are shown by source in Table 6-1. Coal is the source of about 55% of the energy used for power generation, and the tonnage per year continues to increase. Petroleum and natural gas account for a larger percentage of the total energy use because of industrial and domestic heating and transportation consumption. Somewhat surprisingly, nuclear, in spite of a decreasing number of reactors in operation, increased by about 17% in the period 1990-1995 due to upgraded performance and higher plant factors. Despite their popular appeal, solar and wind contributions are negligible.

Perceptions about energy and the environment both by the public and by many scientists were changing significantly during the 1990s. According to some experts (*ANS Fuel Cycle and Waste Management Division Newsletter,* Spring 1998), sources of fossil energy (coal, oil, gas) and nuclear energy (uranium and thorium) are being found to exceed greatly the amounts previously believed to be available. Their conclusion was that development of better technologies to produce electricity cannot be justified on the basis of resource depletion. At the same time, a White House panel (*Chemical & Engineering News,* May 5, 1998) stated that the Nation has no coherent energy policy and may be losing out in a multibillion dollar global energy market. Both groups felt that U.S. research and development on energy, including nuclear, is seriously underfunded. Energy research funding in the U.S. decreased in real dollars by about 75% between 1978 and 1996, and is less than half of that in Japan. Concerns about global warming by greenhouse gases (mainly CO_2) seem to have softened slightly the antinuclear attitude by some environmental groups, although they still raise questions about nuclear proliferation and waste disposal.

If resource depletion is not a problem, there appears to be less justification for improved breeder reactors such as the IFR, although they may have significant advantages in safety, reduction or elimination of long-lived transuranic elements, and low waste volumes. An ongoing debate continues as to whether existing LWR designs, advanced LWRs, LMFRs , LMFBRs, or some other type should be the reactors of the future.

Table 6-1. U.S. Energy Consumption in 1995 by Source

Source	Total		Power Generation	
	10^{15} Btu	%	10^9 kWh	%
Petroleum	34.6	38.3	61	2.0
Natural Gas	22.2	24.6	307	10.2
Coal	19.6	21.7	1,653	55.2
Nuclear	7.2	8.0	673	22.5
Hydroelectric	3.4	3.8	296	9.9
Biofuels	2.8	3.1	-	-
Other[a]	0.5	0.5	6	0.2
Total	90.3	100.0	2,995	100.0

[a]Other renewable sources (geothermal, solar, wind, etc.).

Dr. Lawroski may have put his finger on the problems of the IFR when he once said it was probably 25 years ahead of its time. Nuclear fusion power is an attractive concept, and its principles are well understood, but its practical application remains an elusive goal. Whichever of these reactor systems may be selected for future use, the Chemical Technology Division is well positioned to do development work on its fuel cycle—it has had experience with all of them.

With respect to the environment, a great deal of progress has been made on the reduction of air, water, and land pollution. Although much remains to be done, many of the problems have been identified, and solutions are being implemented. For several years, loss of ozone in the stratosphere has received a great deal of attention, and chlorofluorocarbons have been banned from general use in the U.S. and most other countries. The chemistry of interactions between chlorine compounds and atmospheric ozone is complex and poorly understood, so it is difficult to determine what measures, if any, should be taken. The emphasis now, however, has shifted toward global warming due to CO_2 in the atmosphere. It is not entirely clear that global warming exists, and if it does, whether it is a result of CO_2 produced by human activities. The official position of the U.S. government is that global warming is, indeed, a threat, and that immediate action must be taken to reduce CO_2 emissions.

Nuclear waste disposal has been an ongoing national problem for both technical and political reasons. The Federal Government has not yet been able to make good on its promise to accept and dispose of commercial nuclear wastes in exchange for a tax that was levied for this purpose on all the nuclear power that has been produced to date. These wastes are currently being stored underwater as spent fuel assemblies at various locations. Yucca Mountain in Nevada was selected as a site for permanent burial of nuclear wastes, but it has become controversial on both political and technical grounds, and no alternatives have been deemed acceptable at the present time. There are also differing points of view about the acceptability of various physical and chemical forms of nuclear wastes for permanent storage. Nuclear waste forms and the suitability of geological formations for this purpose are a major program in the Chemical Technology Division. Other studies in the Division have concerned the separation of transuranic elements, which have very long half-lives (*i.e.*, 10^5 years or so), and fission-product elements, which decay to acceptable levels in a few hundred years. Such a separation might simplify the nuclear waste disposal problem.

The Division has been involved in a wide variety of other environmental research activities such as air pollution, municipal waste incineration, and disposal of non-nuclear hazardous wastes. The coal combustion, fuel cell, and battery programs in CMT have all been aimed primarily at providing technologies for cleaner air.

THE LABORATORY

In 1996, Argonne National Laboratory celebrated its 50th anniversary. One of the events associated with this anniversary was the publication of a history of the Laboratory, *Argonne National Laboratory, 1946-96,* by Jack M. Holl, University of Illinois Press, Urbana and Chicago, 1997. Any ANL employee who reads this scholarly, yet very readable, history is bound to develop a fuller appreciation of the extraordinary efforts of the Laboratory Directors and other upper management people to keep the organization afloat through crisis after crisis. Argonne was not alone in facing these problems of budget cuts, repeated changes of perceived national needs, political wind shifts, and new technological challenges; the other national laboratories had similar problems. Another readily available source of information about Argonne's history, as well as its current status, is an ANL home page on the Internet at www.anl.gov.

The Reagan budget cuts of the 1980s hit the Laboratory hard. The number of full-time ANL employees dropped from over 5,000 in 1980 to less than 3,700 during that period, but then increased again to nearly 5,300 by 1994. The big research plum that nearly everybody wanted a part of was the Superconducting Super Collider (SSC), which was to have been a huge project. Argonne's lack of success in getting in on a significant piece of this action was probably a blessing in disguise. The SSC project, first to have been located in Illinois, and then in Texas (President Bush's home state), finally collapsed due to political controversy along with technical and financial difficulties. Meanwhile, Drs. Schriesheim, Fradin, and others began developing a very broad basis of support from universities, industries, and the DOE for the Advanced Photon Source (APS) to be located at ANL. This synchrotron had a wide appeal because it would be primarily a users' facility and could be used for a remarkably wide range of research areas covering the gamut from the most basic studies to immediate applied problems. The APS has become a reality and now operates as an independent entity, under the leadership of Dr. David Moncton, within the ANL organization. Another initiative that was pushed hard by Drs. Charles Till and Yoon Chang was the Integral Fast Reactor (IFR), which was basically an advanced version of EBR-II technology. This program was being pursued quite successfully until 1993, when it was halted abruptly by the new Clinton administration. At the beginning of his presidency, Clinton announced that "We are eliminating programs that are no longer needed, such as nuclear power research and development." He did compromise, however, in that continuing work was allowed on the actinide recycling program and the processing of fuel from EBR-II, which was to be decommissioned. This, in effect, ended Argonne's long history of reactor research and development.

In June 1996, Dr. Schriesheim resigned after 12 years as the Laboratory Director. He was replaced by Dr. Dean Eastman, who had received a Ph.D. from the Massachusetts Institute of Technology in the field of electrical engineering. Dr. Eastman had been in various research and R&D management positions at IBM and had held concurrent positions as a visiting professor at MIT and the University of Chicago. In July 1998, Dr. Eastman resigned, and, as of this writing, Dr. Frank Fradin, who had served for many years as an Associate Laboratory Director for Physical Research at ANL, is serving temporarily as the Laboratory Director.

THE DIVISION

In 1995, as a part of the improvements in the general appearance of Building 205, and, in particular, the exhibit in the lobby, a new logo, shown below at the left, was adopted for the Division. This design, which was selected from several proposed by Media Services, has more visual impact than the previous triangular logo (below right) designed by Martin Steindler in about 1986. In the new logo, the "atom" represents the nuclear programs being conducted in the Division, the lightning bolt suggests the various electrochemical programs, and the flask symbolizes the Analytical Chemistry Laboratory. Another assertion of the Division's identity appears on the Internet as the home page **www.cmt.anl.gov**. The Analytical Chemistry Laboratory also has a home page: **www.cmt.anl.gov/acl/acl.htm**.

CHEMICAL TECHNOLOGY DIVISION

CHEMICAL TECHNOLOGY
APPLIED SCIENCE
BASIC SCIENCE
PROCESSES
DEVICES
DIVISION

Organization

A number of changes occurred in the upper management of the Chemical Technology Division, as indicated in Table 6-2. The terms of service in this table are only approximate because changes in the assignments did not normally take place at the beginning or end of a year.

Martin Steindler announced his resignation as Division Director in 1992, and was replaced by Jim Battles, a metallurgical engineer with a Ph.D. from Ohio State University. Jim had been involved in various CEN/CMT research and development programs over many years and had served in several managerial positions, including Associate and Deputy Division Director. In 1994, Jim stepped down with retirement in mind and was succeeded by Jim Laidler, who had earned a doctorate in Materials Science at the University of Virginia. He then held managerial positions at Hanford in the area of

Fig. 6-1. James Battles

Fig. 6-2. James Laidler

nuclear fuel reprocessing before and after a stint in the Army, followed by a position at ANL in Dr. Till's office before he joined the CMT Division.

The position of Deputy Division Director was eliminated when Jim Battles became the Division Director. During the course of the 1990s, the Division had to be rather nimble in reorganizing its structure to accommodate major changes in the technical programs that were dictated by the funding agencies. By 1998, the structure of the Division seemed to have stabilized, so it now consists of the Administration and four technical departments: (1) Nuclear Technology, (2) Electrochemical Technology and Basic Science, (3) Waste Management, and (4) the Analytical Chemistry Laboratory.

Table 6-2. CMT Upper Management Changes in the 1990s

Year	1990	1991	1992	1993	1994	1995	1996	1997	1998
Division Director									
Martin Steindler	X	X	X						
Jim Battles				X	X				
Jim Laidler						X	X	X	X
Deputy Division Dir.									
Paul Nelson	X	X							
Jim Battles			X						
Associate Division Dir.									
Jim Battles	X	X							
Dave Green	X	X	X	X	X				
Jim Laidler				X	X				
Chuck McPheeters						X	X	X	X
Mike Myles			X	X	X	X	X	X	X
Assistant Division Dir.									
Ron Breyne	X	X	X	X					
Karen Larsen					X	X			
Mike Boxberger							X	X	X

As of 1998, the administrative functions of the Division continue to be the responsibility of Mike Boxberger, assisted by Sofia Napora, Patricia Halerz, and Martha Teitlus. Leo Morrissey handles the Financial and Procurement Services with the help of Lauren Ambrose, Vanessa Mendez, Judy Popik, and Heidi Terdic. Mike Slawecki is the Manager and Janice Muller the Deputy Manager of the Facilities and Support Services Group, which includes Kurt Alford, Ronald Tollner, and Irma Zepeda. Jan is also the Division Environmental Compliance Officer. Ray Wolson is the Safety Officer, assisted by John Rajan and Gale Teats. Dick Malecha and Art Frigo manage the Engineering Design Group, which includes Dan Preuss and Yolantha Siegfried. Roberta Riel is the Quality Assurance Representative. The Computer Group, headed by Steve Gabelnick, consists of Glen Chapman, Jacqueline Copple, Joe Kulaga, and John Osudar. Joe Harmon, assisted by Maria Contos, continues as the Manager of the Editorial Services Group.

Personnel

During the period 1990-1998, the personnel level of CMT (all categories) decreased from about 260 to 235. During this same period, the percentage of Special Term Appointees (STAs) increased from about 14 to 20, which means the level of effort decreased somewhat more than the total figures would suggest, because STAs are generally part-time employees. Extensive use was made of temporary personnel such as the STAs, postdoctoral appointees, students, visiting professors, and other scientists. Several programs were staffed almost entirely by temporary people. There was also much collaborative work with people from other ANL divisions and outside organizations.

When one considers the loss or reduction in funding for some of the major CMT programs in the 1990s, such as the IFR, batteries, fuel cells, fossil fuel research, and fusion power, the Division appears to have survived remarkably well. The age distribution of people in the Division has been such that retirements have been peaking in the 1990s—it seems as if another retirement party is announced almost weekly.

The women in the Division who perform the secretarial and administrative tasks tend to be unsung heroines in that their names are not mentioned in the publications, which are the final products of the Division's work. Table 6-3 lists those who were in the Division through 1998.

Dr. Laidler instituted a loose-leaf *Members of the Chemical Technology Division* book, which was an inspired idea. This has proved helpful to everybody, but especially to new employees and to part-time people who do not have daily contacts with other members of the Division. Oftentimes one recognizes names that appear on reports and elsewhere and recognizes faces in the hallways, but has no other easy way of connecting them. One of the items to be listed on these sheets is outside interests. Perhaps one can gain a bit of insight into the types of people in CMT from this information. Because of some differences in the ways of categorizing such activities, an accurate count is difficult, but Table 6-4 gives a general idea of what many CMT people like to do in their spare time. Other activities that received five responses each were boating & canoeing, flying, softball, dancing, photography, and hunting. Many respondents listed home repair and maintenance, but that is often neither optional nor recreational.

In Retrospect

It may be appropriate at this point to reflect on some of the changes that have transpired over the past 50 years. Several long-term members of the Division were asked to offer their views on this subject. One of the most striking things about the Division when it was

Table 6-3. Secretaries and Other Administrative Assistants

Lauren Ambrose
Jody Bailey
Lilia Barbosa
Norma Barrett
Alice Birmingham
Joyce Bringle
Mary Burke
J. Butler
Laurie Carbaugh
Janet Carothers
Loretta Cescato
Dianne Cheek
Maria Contos
Marilyn Elison
Elaine Estand
Anita Franchini
Guadaluipe Franchini
Sherry Grisko
Patricia Halerz
Marian Harkins
Mary Ann Hejny
Helen Hill
Christine Johnson
Linda Lane
Stephanie Malak
Susan McKinney
M. McLaughlin
Vanessa Mendez
Jan Muller
Sofia Napora
Marilyn Osborn
Maria Pacholok
Judy Popik
Mary Powell
Debbie Rausch
Roberta Riel
Lysbeth Rizzi
Sue Rura
Kay Shields
Gina Schierbeek
Carol Stogsdill
Marietta Strachan
Virginia Strezo
Wendy Strle
Martha Teitlus
Heidi Terdic
Donna Tipton
Sandra Tummillo
Cindy Wesolowski
Mary Lou White
Irma Zepeda

Table 6-4. Outside Interests of CMT People

Reading	40	Volunteer Work	20	Basketball	9
Music (general)	36	Tennis/Raquetball	18	Theater/Movies	9
Traveling	33	Computers	16	Music (classical)	9
Bicycling	30	Swimming/Scuba	15	Sailing	8
Hiking/Walking	28	Golf	14	Bowling	8
Gardening	27	Woodworking	14	Volleyball	8
Camping	24	Cooking	14	Drawing/Painting	7
Church/Bible	24	Sewing/Crafts	14	Ultimate Frisbee	7
Skiing	24	Running	12	Soccer	6
Fishing	22	Cars	10		

first formed and in the early fifties is the ages of the employees. The people in upper management were in their 20s and 30s, as were most of the other staff. Those people represented a large peak in the age distribution curve that persisted through the years until it was finally diminished by retirements and other factors. One item of interest that arose in the interviews with the CMT staff was that, particularly in the earlier days, there were certain "movers and shakers" who had a major effect on the work of the Division. Among those who were mentioned specifically were Hal Feder, Milt Levenson, Carl Crouthamel, and Elton Cairns.

When the Division was formed, it had a single mission—to develop solvent-extraction processes for the decontamination and recovery of uranium and plutonium from spent reactor fuels. The scope of the mission was then expanded to include fluoride volatility and pyrometallurgical processes, and at about the same time, to processes for feed materials and waste handling. Diversity continued in a variety of directions, including reactor safety, materials chemistry, and new analytical methods. The EBR-II project was a large Laboratory-wide undertaking in which the Division was heavily involved in the fuel recycling. Sodium chemistry and technology and reactor safety became major programs. At about that time, pressure developed to redirect the Division's efforts toward environmental programs, which resulted in the work on batteries, fuel cells, fusion power, and coal combustion. The Analytical Chemistry Laboratory became a separate entity within the Division. The nuclear work that continued was directed largely toward the processing of fuel from EBR-II, which was being decommissioned, and waste processing; some work continued on separations chemistry and contactor development. Basic research has continued at a modest level through most of the history of the Division. Computers and other solid-state electronics have had a profound effect on the way work is done, both in the scientific and administrative parts of the Division. At first, computers were used almost exclusively for mathematical calculations, and, as languages such as Basic, Fortran, Cobol, Pascal, and others were developed, many people began writing their own programs. Further development of hardware and software greatly expanded the utility of computers to include word processing, spreadsheets, graphics, design, and a host of other applications up to the present stage, which includes rather easy-to-use features such as e-mail and the Internet, as well as very powerful, highly sophisticated systems that can be interconnected with supercomputers at other sites. Mathematical modeling is a useful tool for describing and understanding all kinds of phenomena and operations, and it has been used extensively in CMT programs. The complex Gaussian molecular orbital calculations that have been made almost routinely by Larry Curtiss and others in the Division would have been impossible just a few years ago. Another area of great importance to the work in CMT is the development of new instruments and other equipment based on computer technology, especially for analytical chemistry.

Complaints are often heard about the increasing degree of micromanagement, particularly by the funding agencies. When management systems such as PERT (Program Evaluation and Review Technique) were introduced, many felt that it was fine for building a submarine or a bridge, where all the tasks were predictable and could be placed in a schedule network. The research people complained that in their work, such management systems required "inventing on schedule," which was not possible. Nevertheless, milestone schedules became a part of the promises one had to make to procure funding, and there was a tendency to be overoptimistic in order to sell the program. Over the years, management by the funding agencies became more heavy-handed, with many requirements concerning safety, training, and a host of other items, and inspections have become more common. All of this tends to make experimental work slower and more difficult, and probably discourages spontaneity.

But for those who yearn for the "good old days," there were other unpleasantries in getting the work done. Nearly all of the work was classified, which meant keeping notebooks and other records in locked files. Because many people throughout the building were working with radioactive materials, everybody had to wear special shoes or shoe covers, and nearly every lab had hand and foot counters. Food and coffee were not allowed in the offices. Group meetings and reports were weekly, and attendance at weekly seminars was compulsory. Associate Division Directors, and often the Division Director, attended the group meetings, and they were not shy about criticizing your work. There was no air conditioning except as needed for sensitive equipment.

TECHNICAL PROGRAMS

Electrochemical Technology

In the 1990s, CMT continued its investigations of various types of batteries and fuel cells for electric vehicles, load-leveling, and other energy-storage applications. This work consisted of research and development on promising systems, performance and lifetime testing, post-test cell examinations and diagnostics, modeling studies, technology transfer to industrial firms, and technical management functions for the Department of Energy (DOE).

LITHIUM ALLOY/METAL SULFIDE BATTERIES

By 1990, the technology of lithium alloy/metal sulfide batteries had matured to the point that the DOE felt it was time to push them into practical application through a variety of joint agreements with industrial firms that would expedite technology transfer into the private sector. The Li/FeS technology had developed to the small battery level, while that of the higher-performance Li/FeS_2 system was ready for scale-up to full-size cells for electric vehicle batteries.

Industrial R&D Contracts. A new industrial R&D contract was negotiated between DOE and SAFT America whereby SAFT would develop lithium/iron sulfide batteries for electric vehicle propulsion. In support of this three-year, cost-shared effort, CMT was to provide technology transfer to SAFT, technical management for DOE, and the necessary R&D to solve any critical technical problems. The contract called for delivery of three full-size Li/FeS electric van batteries for laboratory and in-vehicle testing. In addition, SAFT was to design, fabricate, and test full-scale Li/FeS_2 cells, using the CMT technology.

In 1991, the General Motors Corporation, Ford Motor Company, and Chrysler Corporation formed a partnership designated as the U.S. Advanced Battery Consortium (USABC), to accelerate the development of advanced batteries for electric vehicles. This consortium was then extended to the electric utility industry through an agreement between USABC and the Electric Power Research Institute (EPRI); this partnership pooled its resources with those of DOE. These events resulted in a major restructuring of the DOE battery R&D program, which, in turn, caused a realignment of the CMT efforts so as to support the USABC objectives. The technologies that CMT discussed with USABC included lithium/sulfide, sodium/sulfur, nickel/metal hydride, and lithium/polymer battery systems. The sodium/nickel chloride system was added to the list due to a recent technical breakthrough by CMT that had markedly increased the performance of the nickel chloride electrode.

Through most of the 1990s, the Division continued to provide technical management and support to the USABC. In 1993, CMT was awarded two contracts, in the form of Cooperative Research and Development Agreements (CRADAs) by the USABC—one for developing bipolar Li/FeS_2 batteries and the other for testing advanced batteries in the Analysis and Diagnostics Laboratory. Performance targets for the Li/FeS_2 batteries were an energy density of 300 Wh/L, a power density of 600 W/L, a lifetime >1000 charge-discharge cycles, and a cost <$100/kWh.

In-House Research and Development. The in-house development work on Li/metal sulfide batteries in the 1990s was devoted almost entirely to the bipolar Li-alloy/FeS_2 cells and batteries for electric vehicle applications. A conceptual battery design is shown in Fig. 6-3, and Fig. 6-4 is an exploded view of the internal components of the system. The bipolar cells have a uniform

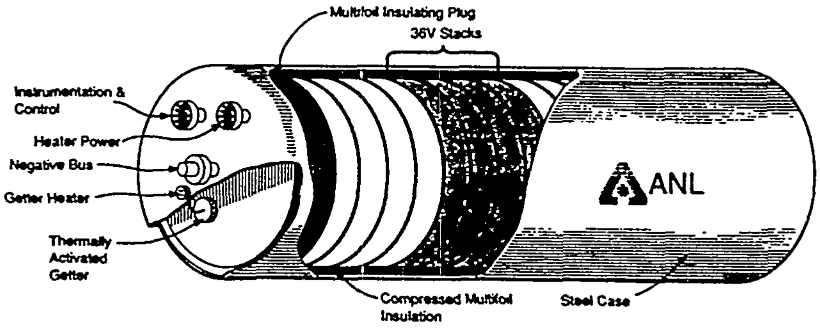


Fig. 6-3. Design of Li/FeS$_2$ Battery

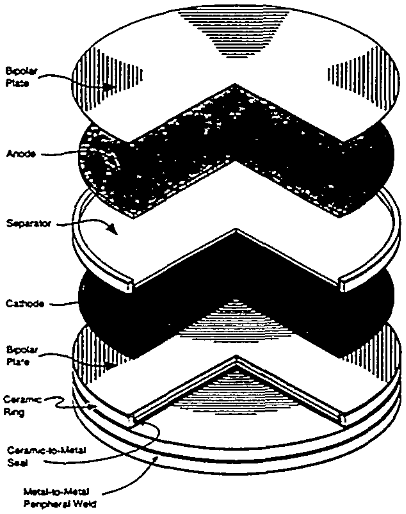


Fig. 6-4. Design of Li-Alloy/ FeS$_2$ Bipolar Stack

current distribution across the electrode surfaces, and this type of battery configuration has a low impedance. Calculations showed that the lower hardware weight of bipolar cells would increase the specific energy by 50% and the specific power by more than 100%. The extensive experience that had been gained previously on electrode materials, separators, electrolytes, construction materials, thermal insulation for batteries, and other items in the prismatic cells was directly applicable to the bipolar cells. One major challenge remained, however, in developing electrically insulating, hermetic seals to join the rims of the circular cells used in the bipolar system. A concentrated effort on this problem by Tom Kaun and his colleagues finally met with remarkable success. The remaining in-house work on bipolar batteries consisted mainly of scaling up the peripheral seals to full-size cells and various incremental improvements in the other cell components to increase performance and lifetime and to lower the cost.

Optimization studies were made on the electrode separators, which consist of MgO powder in a matrix of the molten salt electrolyte. Physical and electrical properties of the powder separators were investigated as a function of MgO content, electrolyte composition (LiCl-KCl, LiF-LiCl-LiBr, LiCl-LiBr-KBr, or LiF-LiBr-KBr), and temperature. Following these tests, the LiCl-LiBr-KBr (25-37-38 mol%) electrolyte was used in most of the cells at an operating temperature of 425°C. Because the long-term durability of MgO powder separators was of some concern, evaluations were conducted on a composite rigid separator consisting of MgO and chalcogenide pressed powders sandwiched between porous metal plates. These separators performed well and showed good chemical and physical stability.

The major effort was on development of the peripheral seals for the bipolar cells. To produce the seal, a ceramic ring was sealed to molybdenum on one side to form the FeS$_2$ electrode housing, and a steel assembly was sealed to the other side of the ring to form the lithium-electrode alloy housing. New sealant materials were developed, which were electronic insulators, bonded tenaciously to the metals and ceramics, and were resistant to chemical attack by the materials in the cell. The seals also had to have a graded coefficient of expansion to match those of the steel and molybdenum. A sealed bipolar Li/FeS_2 cell (3-cm dia) operated over 450 cycles and 2,000 h while retaining >90% of its original capacity.

Four of these cells were combined into a stack to form a module. The cells performed well, and the "lithium-shuttle" mechanism prevented overcharging of cells with no external charge equalization. In a bipolar stack, cells normally fail eventually by short circuiting, in which case the short-circuited cell ceases to function, but simply becomes an electronic conductor between the adjacent cells. The result is a small voltage loss, but the battery can continue to operate.

The next major step was to scale up the bipolar cells. A new project, funded jointly by the State of Illinois and DOE, was initiated with the objective of fabricating and testing a prototype bipolar Li/FeS_2 battery made up of 15-cm-dia cells having capacities of 50 to 75 Ah. A stack of 22 cells would constitute a 36-V module, and modules would be series-connected to form a 220-V electric vehicle battery. The calculated performance of a General Motors Impact, in which a bipolar Li/FeS_2 battery was substituted for the advanced lead-acid battery then used in the vehicle, could provide a range of 250 miles and accelerate from 0 to 60 mph in 8 seconds.

The CMT program on lithium-alloy/metal sulfide batteries was phased out in the late 1990s because the technology had reached a stage where commercial development by industry was appropriate.

Personnel. The development work on lithium/metal sulfide batteries was under the general direction of Don Vissers. Most of the modeling and evaluation studies were done by Paul Nelson, and Al Chilenskas continued to work on battery engineering and design as an STA after he retired.

Others who contributed to this program were Vincent Battaglia, Ira Bloom, Dennis Dees, Mark Hash, Gary Henriksen, Andrew Jansen, Tom Kaun, Frank Mrazek, and Laszlo Redey.

SODIUM/METAL CHLORIDE BATTERIES

The sodium/metal chloride battery system uses a molten sodium negative electrode, a β''-alumina solid electrolyte, and a solid metal chloride such as $NiCl_2$ or $FeCl_2$ as the positive electrode. The positive electrode has a secondary electrolyte (catholyte) of molten $NaAlCl_4$. This type of cell can be represented as:

$$Na//\beta''\text{-}Al_2O_3//NaAlCl_4/NiCl_2/Ni$$

The operating temperature is around 260°C. Although the Na/$NiCl_2$ system has a high theoretical specific energy of 790 Wh/ kg, the performance of existing single-tube cells was rather anemic, with a specific energy of 100 Wh/kg and a specific power of 100 W/kg. Preliminary modeling studies of the system showed that the surface area of the solid electrolyte needed to be increased to reduce the current density, and that the performance of the metal chloride should be increased.

A concerted effort was focused on ways to increase the performance of the $NiCl_2$ cathode. The following cell was used for these studies:

$$Al/NaAlCl_4\text{, additives}/Ni/NiCl_2$$

The aluminum electrode served both as a counter and reference electrode because of its well-defined chemistry and fast kinetics. The results indicated that the soluble nickel species was present, and it also made the cell construction simpler. By fabricating the nickel electrode with larger and more uniform porosity, its specific impedance was decreased to about one-half of that in state-of-the-art cells. The performance properties of porous electrodes were also investigated with a complete Na/β''-alumina, $NaAlCl_4/NiCl_2/Ni$ cell.

During charge, the nickel electrode developed a poorly conductive surface layer of the $NiCl_2$ product. An addition of 2 wt% sulfur (based on the weight of the chloroaluminate salt) to nonporous nickel electrodes resulted in a marked improvement in the capacity, impedance, and coulombic efficiency.

The electrochemical studies, which included techniques such as current-interrupted galvanic cycling and cyclic voltammetry, were complemented by direct microscopic examinations of the morphological changes that occurred in the electrodes. The data from these studies were used to develop a mathematical model of the electrochemical processes that were involved. Finite-element calculations were made on 22 cases involving a variety of design variables.

The Chemical Technology Division provided technical management and support for a contract that DOE had negotiated with Beta Power, Inc., to develop conceptual designs for high-performance Na/MCl_2 batteries. Two such designs had the potential of achieving 150 Wh/kg at the 3-h discharge rate and 150 W/kg at 80% depth of discharge, and a new contract was placed to develop the batteries for electric vehicle applications.

In 1991, a significant breakthrough was made in the form of a "synergistic" $NiCl_2$ electrode in which the usable capacity was increased by a factor of five, and the impedance was reduced to one-third of that of a baseline $Ni/NiCl_2$ electrode. The tests also showed that the operating temperature could be reduced as low as 153°C with good performance. The improved performance was effected through a combination of additives and morphological modifications. Calculated battery performance data based on the new CMT cell design indicated that the $Na/NiCl_2$ batteries could meet the mid-term USABC objectives for electric vehicles, and that bipolar cells, if developed successfully, would come close to meeting the extremely stringent long-term goals (specific energy, 200 Wh/kg; specific power, 400 W/kg).

A detailed study of the solubility of $NiCl_2$ in the chloroaluminate electrolyte indicated that the solubility can be decreased by adjusting the basicity of the system and through the use of additives. By applying this information to cell designs, research cells exceeded 500 cycles with no significant performance degradation. In addition, static, cycling, and stress-corrosion tests indicated that Ni-200 could be used safely for cell housings and current collectors. These improvements in the cell designs also permitted much faster recharging times (1-2.5 h *vs.* 10-15 h). At this juncture, the major improvements in $Na/NiCl_2$ battery technology attracted the interest of the Hughes Aircraft Co. and Eagle-Picher Industries, Inc., who fabricated some sealed cells.

By 1994, CMT had brought the $Na/NiCl_2$ technology to the stage where it could be transferred to industry. For electric cars, this system offers several advantages:

1. It has a wide range of operating temperatures (150-400°C).
2. It stores more energy per unit weight of nickel than other nickel battery systems (<2 kg/kWh *vs.* about 6.3 kg/kWh).
3. It has a high degree of overcharge protection and long cycle life.
4. The cells can be hermetically sealed and are environmentally safe.
5. The cells fail by short circuits, permitting continued operation of series-connected stacks.

6. The raw materials are abundant and relatively inexpensive.

Laszlo Redey, Jai Prakash, and Andy Jansen conducted these research studies.

OTHER ADVANCED BATTERIES

Lithium-Polymer Electrolyte Batteries. In 1992, a research program was started on the lithium-polymer electrolyte (LIPE) battery. In a CRADA arrangement with the 3M Company and Hydro-Québec, the CMT Division was to provide technical support of the development of LIPE batteries. These batteries are all-solid-state electrochemical devices that consist of ultra-thin (<100-μm) layers that are laminated together, and they operate at moderate temperatures (typically 60-80°C). The negative electrode in usually lithium but may be a lithium alloy or lithium-carbon. The electrolyte is generally a polyether such as polyethylene oxide (PEO) containing a dissolved lithium salt. The positive electrode is a composite of electrolyte (to provide conductivity) and some active material, most often a metal oxide or sulfide (*e.g.*, VO_2, MnO_2, or TiS_2).

The objective of this research was to develop a suitable reference electrode for cells of this type. A reference electrode is essential in analyzing the processes occurring within an electrochemical cell. It carries no current, but provides a constant potential against which the potentials of operating cell electrodes can be measured individually. This is a powerful diagnostic tool for studying the electrochemical reactions occurring at the individual electrodes. Development of a reference electrode for the LIPE cells was a challenging task because it had to satisfy several requirements—it had to be reversible with fast kinetics, chemically compatible with the system, and long-lived. It also required a geometry that was suitable for the thin electrodes of the cell. To pursue these objectives, an inert atmosphere glove-box facility was set up for fabrication and testing of the LIPE cells.

Lithium was an obvious candidate for the negative electrode, and several types of lithium or lithium-alloy reference electrodes were evaluated. Screening tests were conducted, in which lithium-tin alloy showed the best performance. These reference electrodes had to be deposited on a stainless steel substrate as ultra-thin (50-1000 Å) tin layers. Electrochemical tests were then performed in a cell in which the electrolyte material was PEO that contained dissolved lithium trifluoromethane sulfonate ($LiCF_3SO_3$) salt. The cell can be represented as

$$Li/PEO_{10}\text{-}LiCF_3SO_3/Li_xSn$$

where x is 8 or 10. During a coulometric titration in which lithium was transferred into the tin electrode, three voltage plateaus were observed. The third plateau, with a potential of 0.53 V *vs.* lithium, showed excellent stability over two weeks of monitoring.

Development of alternative cathodes was also a part of the LIPE project. In the operation of a lithium-polymer electrolyte cell, lithium ions are repeatedly inserted into and withdrawn from the transition metal oxide structure of the positive electrode. This process tends to produce structural changes in the metal oxide matrix, particularly under conditions of overcharge or overdischarge, so the cell operating conditions must be carefully controlled during cycling. Post-test analyses and other detailed studies of the cells were made, including modeling. Performance data based on tests of state-of-the-art materials, including α-MnO_2 positive electrodes, translated into a projected specific energy of 180 Wh/kg. Any further information on the design and performance of these batteries is considered proprietary.

Dennis Dees was the leader of the group working on lithium-polymer electrolyte batteries, which also included Khalil Amine, Vincent Battaglia, Rex Gerald, Gary Henriksen, Andrew Jansen, Christopher Johnson, Arthur Kahaian, Keith Kepler, Robert Klingler, Gene Nielson, Jai Prakash, Laszlo Redey, Mike Thackeray, Robert Turner, and John Vaughey.

Lithium-Ion System. Rechargeable "lithium-ion" batteries are becoming popular as power supplies for various consumer electronic devices such as laptop computers, camcorders, and cellular phones, and are also believed to have potential application to electric vehicles. The electrochemical process that occurs in these batteries, which operate at room temperature and generate about 4 V, involves the shuttling of lithium ions between two electrodes during charge and discharge. The purpose of this research was to determine if Li-Mn-O spinels can be used in place of the present $LiCoO_2$ cathodes, which are costly and considered hazardous.

The focus of the work was on (1) identification and characterization of Li-Mn-O phases that would be formed as lithium is inserted into, and extracted from, the cathode during discharge and charge and (2) methods of preparing cathode material of the desired composition. A portion of the Li-Mn-O phase diagram in the composition region of interest is shown in Fig. 6-5. The compositions that an electrode would have during charge and discharge lie on the tie line between $LiMn_2O_4$ and $Li_4Mn_5O_{12}$, and can be represented by the general formula $Li_{1+\delta}Mn_{2-\delta}O_4$ (δ between 0 and 0.33). Lithium can be extracted from, and inserted into, $Li_xMn_2O_4$ at approximately 4 V *vs.* metallic lithium when x is between 0 and 1.

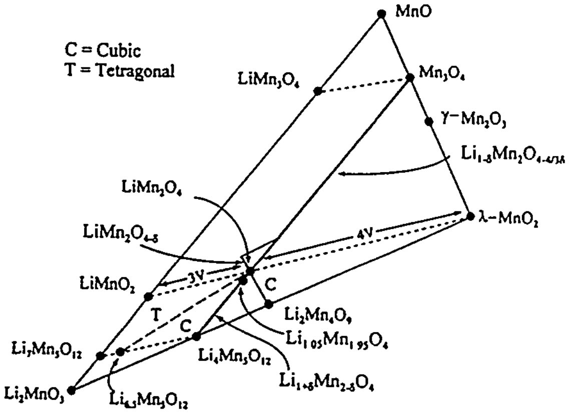


Fig. 6-5. Partial Phase Diagram of the Li-Mn-O System

Synthesis of single-phase $LiMn_2O_4$ spinel is not a simple process. When cubic $LiMn_2O_4$ is heated to 1200°C, it forms a number of different phases and crystal structures. The pertinent reactions were studied systematically by X-ray diffraction, thermogravimetric analysis, and differential thermal analysis, and a suitable temperature sequence for preparing single-phase, stoichiometric $LiMn_2O_4$ was developed.

Detailed structural studies were made on α-MnO_2, which is a potentially attractive positive electrode material for 3-V lithium secondary batteries. The CMT researchers substituted the water component in $MnO_2 \cdot H_2O$ with Li_2O to fabricate "lithia-stabilized" electrodes, which have significantly superior performance over the parent α-MnO_2. The structures of hydrated, dehydrated, and lithiated α-MnO_2 were determined by the Rietveld profile refinement technique and time-of-flight neutron diffraction data. Structural studies were initiated on the Li-V-O system, which also shows promise as an insertion-type electrode. Initial results were promising and this work is continuing.

Contributors to the lithium-ion battery research were Khalil Amine, Roy Benedek, Dennis Dees, Gary Henriksen, Andrew Jansen, Christopher Johnson, Keith Kepler, Michael Manimelto, Michael Thackeray, and John Vaughey. Dennis Dees was the leader of this effort.

High-Power Energy Storage System. In 1997, a new CMT program was started on a high-power energy-storage device that could be coupled with a fuel cell in a hybrid vehicle. Integration of the galvanic properties of lithium battery "insertion" electrodes and the high surface areas of supercapacitors to form a lithium-ion based galvanic stack may be a method to achieve this end. Testing of a $Li_4Ti_5O_{12}/LiCoO_2$ cell couple gave promising results, and a conceptual design for 400-V galvanic stack based on a $Li_4Ti_5O_{12}/LiNi_{0.82}Co_{0.18}O_2$ system was developed. The design comprised a stack of 144 spirally wound cells divided into 18 modules enclosed in a thermally controlled jacket. The $Li_4Co_5O_{12}/LiCoO_2$ cells have shown excellent lifetimes in excess of 112,000 cycles. Work on this system is continuing with emphasis on modeling studies and further optimization of the electrode materials.

Khalil Amine was Project Manager for the high-power lithium ion battery program. Others working on the project were Vincent Battaglia, Andrew Johnson, Mike Thackeray, and John Vaughey.

Nickel/Metal Hydride System. The nickel/metal hydride battery is a promising contender to replace the popular nickel/cadmium batteries because of its superior performance, low impedance, and absence of toxic cadmium. It also avoids the shape-change vagaries of the cadmium electrode. The cell reaction for a nickel/metal hydride battery can be represented as

$$MH_x + xNiO(OH) \leftrightarrow M + xNi(OH)_2$$

where M is a rare earth alloy such as $LaNi_5$, with partial substitution of the La or Ni by a small amount of Sn, Mn, Co, Al, or possibly other metals. The present versions of Ni/MH batteries are afflicted by hydrogen-management problems associated with charge-discharge cycling and self-discharge, active material deterioration, and long-term capacity loss due to corrosion of the MH electrode.

A combination of electrochemical and neutron-diffraction studies was used for *in situ* investigations of the cells. Neutron diffraction revealed the locations of deuterium (a hydrogen isotope) in the molecular structure. A special quartz tube cell was designed to minimize background scatter caused by the construction materials, electrolyte, and the presence of remaining protons. A commercial $NiO(OH)/Ni(OH)_2$ electrode was deuterated and used as the positive electrode. The electrolyte was 15% KOD/D_2O. The electrochemical properties of the MH electrodes and Ni/MH cells were measured by interrupted galvanic cycling.

Three alloys were investigated: $LaNi_5$, $LaNi_{4.88}Al_{0.12}$, and $LaNi_{4.4}Al_{0.6}$. The $LaNi_5$ electrode had a low, but stable capacity. The $LaNi_{4.4}Al_{0.6}$ had the highest capacity and a small capacity drop. The $LaNi_{4.88}Al_{0.12}$ had a high initial capacity, but poor stability. The capacity-loss mechanism proved to be corrosion of the aluminum by the caustic electrolyte.

The *in situ* neutron diffraction measurements employed the General Purpose Powder Diffractometer at the ANL Intense Pulsed Neutron Source (IPNS). The data indicated that $LaNi_5$ and its derivatives have a hexagonal space group structure containing two crystallographically distinct nickel sites, Ni(1) and Ni(2). In aluminum-substituted $LaNi_5$, the aluminum substituted selectively on the Ni(2) sites.

As of 1997, the CMT work on Ni/MH batteries had become limited to testing in the Electrochemical Analysis and Diagnostic Laboratory (EADL).

The limited amount of research that ANL was allowed to do on the Ni/MH cells was performed by Laszlo Redey, along with Vincent Battaglia, Andrew Jansen, Dan Simon, and temporary and part-time personnel.

ELECTROCHEMICAL ANALYSIS AND DIAGNOSTICS LABORATORY

The EADL continued its mission of testing and evaluating advanced battery systems for applications such as electric vehicles and utility load-leveling. During the 1990s, evaluations were performed for the Department of Energy (DOE), the Electric Power Research Institute (EPRI), the U.S. Advanced Battery Consortium (USABC), and others. The resulting information was used by these organizations to identify the most promising avenues for further research and development. Test results were also useful in generating a database for modeling of projected battery performance.

Performance and Life Evaluations. A very brief summary of test results from six types of electric vehicle battery in 1990 is shown in Table 6-5. Where two sets of values are listed, the data are for batteries from different manufacturers and/or of different designs. The specific energies translate into ranges of 47 to 154 miles for a van having a 695-kg battery.

Although some of these batteries are suitable for specialized practical applications such as fork lifts and golf carts, none of them even come close to matching the power, range, and price of a typical family car powered by a gasoline engine. It was clear that a major technological breakthrough would be required to achieve widespread acceptance of electric automobiles.

Tests were continued on sodium/sulfur batteries from Powerplex Technologies, Inc., Chloride Silent Power, Ltd., and ASEA Brown Boveri. Operating temperatures for the sodium/sulfur system were in the range of 310 to 340°C. By 1992, the cycle life of these batteries was in a range of about 600-800.

The zinc/bromine batteries were supplied by the Studiengesellschaft fur Energiespeicher und Antriebssysteme (SEA) Research Group for Energy Storage and Propulsion Systems in Austria, which had licensed the technology from the Exxon Corp. and improved the original Exxon design.

Table 6-5. Summary of 1990 Test Results from Electric Vehicle Batteries

Technology	Specific Energy,[a] Wh/kg	Peak Power,[b] W/kg	Battery Life,[c] cycles
Sodium/Sulfur	81 79	150 90	>200 >200
Zinc/Bromine	75	53	>300
Nickel/Metal Hydride	54	182	289
Nickel/Cadmium	55	191	>250
Nickel/Iron	56 51	92 111	370 >200
Lead-Acid	36 33	125 87	370 715

[a] Measured at 3-h discharge rate.
[b] From driving profile discharge at 50% depth of discharge.
[c] For 100% depth of discharge cycles (">" indicates ongoing test as of December 1990).

The zinc/bromine system exhibited reasonably good specific energy (75 Wh/kg), but low specific power (53 W/kg). Two disadvantages were a need to conduct an electrochemical maintenance procedure after every six or so cycles, and certain safety issues.

Performance tests were conducted on nickel/cadmium battery modules manufactured by SAFT (Industrial Storage Battery Division) in France. This battery had the highest peak-power capability of any of the systems (191 W/kg) and completed more than 1,018 driving cycle discharges. It was then sent to EPRI for further evaluations. Two other batteries from SAFT having capacities of 200 and 80 Ah were tested for the fuel cell/battery bus project discussed later. These units chalked up 9,084 and 4,104 cycles, respectively, which correspond to >75,000 and 35,000 bus miles.

Two types of advanced nickel/iron batteries from Eagle-Picher Industries with capacities of 220 and 179 Ah were evaluated. The larger module had a lifetime of 370 cycles. Several additional nickel/iron batteries from Eagle-Picher were then placed on test. The longest operating module completed 918 cycles.

Tests continued on lead-acid batteries from several sources: Sonnenschein Battery Co.; Chloride Motive Power; Johnson Controls, Inc.; Bell Computer, Inc.; Electrosource, Inc.; GNB Industrial Battery Co.; Yuasa/Exide, Inc.; Optima Batteries, Inc.; and Hawker Energy Products, Inc. Of the lead-acid batteries tested, Electrosource modules achieved the highest specific energies (43 and 36 Wh/kg), an Electrosource module had the highest peak power (171 W/kg), and a Yuasa/Exide module showed the longest cycle life (494 cycles).

Performance data were obtained in 1990 on 3.6-Ah (C-size) nickel/metal hydride cells from the Ovonic Battery Co. The thought was that these cells might be scaled up to an electric vehicle battery. The cells exhibited the highest volumetric energy density (186 W/L) of any battery system examined to that time. The specific energy and peak power were 54 Wh/kg and 182 W/kg, respectively, but their longest lifetime was 289 cycles. The following year, tests of cells scaled up to 25 Ah showed an impressive peak power of 200 W/kg, but the lifetimes of these cells were limited to about 500 cycles. In 1997, a new CRADA with the Advanced Battery Consortium was started to evaluate Ni/MH cells and modules from USABC battery cost reduction contracts with GM-Ovonics and SAFT.

Tests were also conducted on Li/FeS cells from SAFT of America, Inc. The specific energy and peak power were 66 Wh/kg and 64 W/kg, and the lifetime was 163 cycles.

Post-Test Analysis. A joint failure analysis was conducted on a 19-kW Na/S battery that had been fabricated by Chloride Silent Power and tested at ANL for 241 cycles. Examination of 17 failed cells showed that most of the failures resulted from cracks in the glass seal between the β″-alumina solid electrolyte and an α-alumina top cap. The examinations also showed that the use of sodium safety cans alleviated, but did not prevent entirely, a potential for failure propagation due to loss of the sodium seal. A cell that had suffered from discharge polarization during cycling was examined by radiography, which indicated that the polarization was caused by a reduced sodium level in the electrolyte annulus. A maldistribution of sodium on the electrolyte surface could result in high localized current densities. Post-test examinations of Na/S batteries from Chloride Silent Power under a CRADA with USABC were completed in 1994.

Examinations were performed on failed cells from a 36-V Li/FeS module fabricated by Westinghouse Naval Systems Division and tested at ANL for 141 cycles. The cause of failure proved to be short circuits due to deposition of metallic iron in the separators. Difficulties with thermal management of the module had exacerbated the problem; most of the failures were in the central portion of the module, where the temperature had risen more than 50° over the normal operating temperature of 450°C.

Thermal Li/FeS_2 cells from Sandia National Laboratories were also examined to investigate failures resulting from Li_2S deposits within the separators of these primary cells. The Sandia thermal cells consisted of an FeS_2 cathode, a MgO powder separator, molten LiCl-KCl electrolyte, and a Li-Si anode. Microscopic examinations showed that Li_2S deposition was affected by a variety of factors mostly related to the compositions of the cell constituents. Further basic studies of the system were recommended.

Post-test evaluations were made on a prismatic Li/FeS_2 cell built and operated through 434 cycles by SAFT, America. Declining capacity and coulombic efficiency were attributed to expansion and extrusion of the positive electrode material into the MgO powder separator, which caused a partial short circuit. Other findings, however, were positive—there was little or no corrosion of the molybdenum components, and formation of aluminum intermetallic compounds with nickel and stainless steel components in the negative electrode was minimal.

A Ni/Fe module from a battery pack built by Eagle-Picher for in-vehicle testing in 1983 was removed from testing after 66,000 actual and equivalent miles of operation. Capacity decline of the module was totally attributable to voltage reversal of one cell caused by degradation of the iron plates through local overcharge.

Much of the effort on post-test examinations was directed to lead-acid batteries from various manufacturers. A module from Chloride EV Systems, Ltd., that had undergone 715 cycles was subjected to post-test analysis, which showed that its declining performance was caused by high levels of antimony and poor adhesion between the grids and the active materials. Two valve-regulated lead-acid (VRLA) technologies for utility cycling applications were evaluated: (1) gelled-electrolyte modules from Johnson Controls, Inc., and (2) absorbed-electrolyte modules from GNB Battery Co. Failure of the Johnson Controls unit resulted from a manufacturing defect that caused corrosion of a strap for the positive plate lugs. The GNB batteries had a longer lifetime and failed through corrosion of the positive electrode grids. A study of stibine (SbH_3) emissions during operation of the GNB batteries showed that only minor ventilation was needed to avoid a toxicity problem. Other post-test examinations of various lead-acid batteries showed that positive grid corrosion was the most common mode of failure. Overcharge and variations in the oxygen-recombination efficiency were factors in the corrosion process.

The post-test analytical and diagnostic work by CMT achieved growing recognition for its excellence, and, in 1993, the USABC chartered ANL to draft a procedural outline for the standardization of post-test analyses. In 1997, the ANL post-test analysis activities had declined and that laboratory was closed. At the time of this writing, however, a facility for the testing of advanced fuel cells was about to go into operation.

Evaluations and Studies. In 1997, evaluations were conducted on an electric vehicle battery pack from Chrysler Corp., which was constructed from Ovonic Ni/MH modules. A study was conducted for DOE on the technical status of foreign electric vehicle batteries. In addition to the performance and lifetime evaluations, Argonne has supported the Advanced Battery Consortium by having representatives on the Ovonic Nickel/Metal

Hydride Working Group and the Battery Testing Procedures Tiger Team, as well as various other USABC planning and evaluation groups. In 1998, evaluations were continued on the cost reduction programs and the lithium-polymer battery development program.

Personnel. The battery testing and evaluation activities were managed by Bill DeLuca. Others involved in the effort were Brandon Cole, Kenneth Gillie, Roger Hogrefe, John Smaga, Tony Tummillo, and Carl Webster.

FUEL CELL RESEARCH AND DEVELOPMENT

The DOE continued to insist that Argonne's primary role in the fuel-cell area be the technical management and evaluation of industrial research and development contracts, with small in-house programs on supporting research. This in-house work consisted mainly of materials studies and mathematical modeling of fuel-cell systems. By 1990, the Argonne scientists and engineers had established the basic designs and feasibility of molten carbonate and monolithic solid oxide fuel cells, but further work was needed to improve performance and lifetime and to scale up the systems for practical application. As in the battery program, the advent of polymer electrolytes opened the possibility of a new type of fuel cell, and work in this area was started in 1992.

Monolithic Solid Oxide Fuel Cells. As indicated in the previous chapter, the monolithic solid oxide fuel cell (MSOFC) is made up of two multilayer composites, one being the anode/electrolyte/cathode and the other being the cathode/interconnect/anode. The anode is nickel, the cathode is strontium-doped lanthanum manganite, and the electrolyte is yttria-stabilized zirconium oxide (YSZ). The electronically conductive intercell connector material is strontium-doped lanthanum chromite. The nickel anode is in the form of a Ni-YSZ cermet.

In 1988, Allied Signal Aerospace/AiResearch began development work on the MSOFC with technical support from ANL, and this support continued into the 1990s. Long-term effects on the cell components were evaluated by accelerated tests at elevated temperatures (1000-1200°C) in air for 1000 h. A small increase in the cathode resistance was observed, but not considered to be a serious problem. Since the MSOFC would be expected to operate with coal gas or natural hydrocarbon fuels that contain low-ppm concentrations of sulfur, the effect of sulfur on anode performance was evaluated. The interfacial resistance increased significantly with H_2S concentrations in the low-ppm range. Follow-up studies on the free energies of H_2S reactions with ZrO_2 and Y_2O_3 indicated that such reactions were thermodynamically possible, but thermogravimetric experiments showed that they did not occur, probably because of kinetic factors.

A major disadvantage of conventional fuel cells is that they require hydrogen as the fuel. Attempts to use methanol or ethanol fuel by adding special catalysts have met with only limited success. One scientific wag put it succinctly: "All they have to do is to solve three problems with the methanol fuel cell—the anode, the cathode, and the electrolyte." The situation may be different, however, for solid oxide fuel cells, which operate at temperatures of 800-1000°C. At these temperatures, potential fuels such as hydrocarbons, alcohols, and natural gas can reform on the nickel cermet anode to form electrochemically active species such as hydrogen and carbon monoxide. Exploratory experiments were conducted in which a polarization curve (voltage *vs.* current density) was measured for a solid oxide fuel cell using hexadecane as the fuel. The curve was similar to those for hydrogen fuel but showed a voltage reduction that was attributed to a high water content in the fuel stream. The water was added to support the internal reform reaction and to suppress the formation of tars and coke through cracking reactions. Subsequent studies were made on the operation of lower-temperature (500-700°C) solid oxide fuel cells with methanol as the fuel. The performance was nearly the same as that with hydrogen. Thus, it was established that solid oxide fuel cells can operate with fuels other than hydrogen but may have problems with sulfur in natural fuels and with the formation of carbonaceous deposits in the case of hydrocarbons. Work that was done on sulfur-tolerant anodes indicated that $La_{0.7}Mg_{0.3}CeO_{3.35}$ and $La_{0.8}Nb_{0.2}CeO_{3.7}$ show promise for this purpose.

There was an interest in decreasing the operating temperature of MSOFCs to 500-800°C so that metal components could be used in the cells, thereby increasing design flexibility. Theoretical considerations suggested that certain perovskites might have sufficient ionic conductivity to serve as electrolytes at 600°C, and the conductivities and ionic transference numbers were determined for six compositions of Sr-Zr-O or Sr-Zr-Sn-O. Although these materials have the oxygen substoichiometry needed for a fuel cell, the conductivities were still too low to be practical. In a preliminary study of orthophosphates, tests of strontium-doped $LaPO_4$ showed that materials of this type might be promising candidates. Studies were then conducted on Bi_2O_3-Al_2O_3 compounds, along with incorporation of Bi_2O_3 into a refractory host lattice ($LaAlO_3$). Conductivities of $Bi_2Al_4O_9$ and La-Al-Bi-O mixtures were determined, using platinum electrodes and humidified H_2/O_2 gas at 500-800°C. The conductivities were of the order of $10^{-2}\ \Omega^{-1}cm^{-1}$ with ionic transference numbers of about 0.65. This conductivity, although below the goal, is about the same as that of yttria-stabilized zirconia, the present electrolyte material. Some preliminary studies were performed on ceria-based and bismuth aluminate systems as potential solid electrolytes.

The sealants in a solid oxide fuel stack, in addition to forming gas-tight seals along the edges of each electrode and between the manifold and stack, must be chemically and thermally stable at 1000°C and compatible with H_2, O_2, water vapor, and the cell materials. Initial studies of two commercial cements showed them to be unacceptable because they contained silicon and had regions of porosity. Reactive glasses were then synthesized and evaluated. The results showed that the nature of surface reactions of the glasses with the cell components was more important than an exact match in coefficients of expansion. At the cell edge, the sealant can be relatively rigid because it has to tolerate the thermal expansion behavior of, at most, only two different cell ceramics. At the stack-to-manifold junction, however, a somewhat compliant seal is required to accommodate the thermal expansion of four ceramics plus the manifold. Fifteen novel sealants having varying degrees of rigidity were synthesized, bonded to ceramics typical of the fuel cell, and tested by heating to 1000-1350°C. Optical and scanning electron microscopy showed that two were superior—a rigid cementitious material and a glass-ceramic composite that was expected to be somewhat compliant. Further thermal and electrical testing showed that the composite material formed a rigid, elastic, gas-tight seal. Further work culminated in successful glass-ceramic sealants based on a five-component oxide system: SrO, La_2O_3, Al_2O_3, SiO_2, and B_2O_3. These seals were subjected to long-term tests for materials compatibility, physical integrity, and electrical properties. Samples of the high-temperature sealants were sent to several fuel-cell manufacturers for evaluation and received favorable reviews.

A model developed in 1990 that simulated the electrochemistry and thermal hydraulics of an MSOFC stack with a cross-flow design yielded the temperature distribution and the fuel and oxidant compositions for the entire system. This model could also simulate operation with different fuel gases, such as hydrogen, coal gas, and methanol. In 1991, much of the electrochemical modeling work was transferred to the University of Oklahoma.

Molten Carbonate Fuel Cells. The molten carbonate fuel cell (MCFC), as mentioned previously, consists of a porous nickel anode, a porous nickel oxide cathode, a liquid Li_2CO_3-K_2CO_3 electrolyte in a $LiAlO_2$ matrix, and appropriate metal separator sheets. Anode material studies continued on $LiFeO_2$ and MnO, which had been shown earlier to be stable in the anode environment and to have bulk resistivities at 650°C of 0.2 and 20 Ω-cm, respectively, which are in an acceptable range for use in the anode. Cell tests of doped and undoped $LiFeO_2$ were conducted at 140-650°C in a stream of humidified anode gas. Niobium doping did decrease the resistivity with a minimum at a Nb/Fe mole ratio of 0.06. The performance was also improved by a new method of synthesizing $LiFeO_2$ with starting material of a higher surface area. Further full- and half-cell tests were made with $LiFeO_2$ anodes (undoped and doped with Mn, Co, and Ni), and Nb-doped CeO_2. Polarization curves (voltage *vs.* current density) indicated that none of these electrodes performed as well as the state-of-the-art Ni-Cr anode, and none could sustain a current density higher than about 80 A/cm^2. In the case of CeO_2, the electrode performance decreased on exposure to the reducing atmosphere but could be restored temporarily by exposure to an oxidant.

A large proportion of the development work on the MCFCs was on the cathode. Tests were made both with 25 cm^2 full-size cells and with diagnostic half-cells. Effort was focused on $LiFeO_2$ cathodes as a thermodynamically stable replacement for NiO, which had been experiencing lifetime-limiting dissolution/precipitation problems. The performance of $LiFeO_2$ electrodes appeared to be restricted by slow reaction kinetics. Modification of the synthetic method for $LiFeO_2$ to increase the surface area resulted in some, but not sufficient, improvement in the performance. An increase in the total surface area of the cathode, with little attention to the pore structure, produced some improvement in the performance, but it was probably limited by access of gas to the bulk electrode, which depends on the pores. The best-performing electrode in full-cell tests was Co-doped $LiFeO_2$. Data on the kinetics of the reactions suggest that different mechanisms are involved in the operation of NiO and $LiFeO_2$ electrodes. As a result of ensuing detailed studies on the effects of temperature, oxygen partial pressure, carbon dioxide partial pressure, electrolyte thickness, and electrolyte composition, a new oxidant mixture (95% air-5% CO_2) was selected. With this oxidant, the performance of Co-doped $LiFeO_2$ cathodes in half-cell tests at 675°C was similar to that of NiO electrodes at 650°C. Tests of $LiFeO_2$ cathodes with other dopants (Cu-, Mn-, Ni- and Mg-doped Li_3MnO_3) resulted in less improvement than that from the cobalt-doped material. Seebeck coefficient measurements led to the conclusion that the alternative cathode must be a p-type conductor with little or no electronic component.

There was an incentive to increase the normally ambient operating pressure of MCFCs to about 10 atm to increase the power density. The increased chemical activities of the gases at the higher pressures shorten the life of the NiO cathode, which is a major reason for seeking alternative cathode materials. The resistivities of $LiFeO_2$, $LiCoO_2$, and NiO are about 300, 1, and 0.1 Ω-cm, respectively. Thus, to match the performance of NiO, the resistivities of the two alternative materials would have to be decreased significantly. Individual dopants did not accomplish this goal, but a new, proprietary double dopant was found, which reduced the resistivity from 300 to about 0.3 Ω-cm. This double dopant improved the performance of $LiFeO_2$ and $LiCoO_2$ cathodes over a wide range of cathode-gas compositions. At this stage, NiO and the two doubly doped cathode materials showed about the same performance, and lifetime became the issue. The relative lifetimes of NiO, doubly doped (D.D.) $LiFeO_2$, and $LiCoO_2$ were evaluated, using mixtures of CO_2 and O_2 as the cathode gas. The results, shown in Fig. 6-6, as well as other data, indicated that both $LiCoO_2$ and $LiFeO_2$ have a longer life than NiO.

Although $LiCoO_2$, with a low resistivity of about 1 Ω-cm, could serve as a longer-lived direct substitute for NiO, its high material cost could prevent its large-scale use.

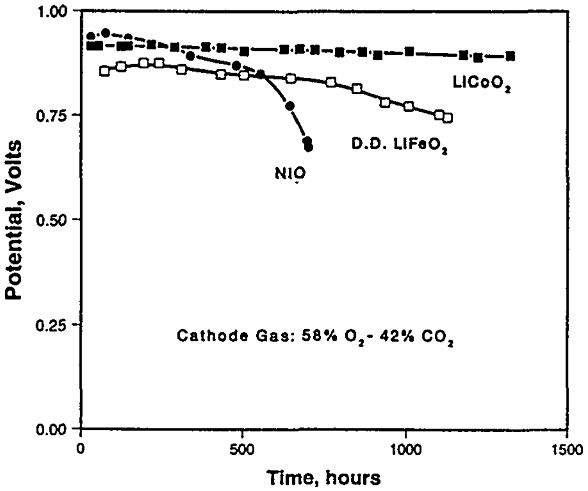


Fig. 6-6. Potential *vs.* Operating Time for Experimental Cathodes in MCFCs

Therefore, attention was directed toward lowering the resistivity of $LiFeO_2$ (300 Ω-cm). By adding a combination of cation substituents, the resistivity of a $LiFeO_2$-based material (designated "Material 1") was lowered to 1.3 Ω-cm at 650°C, close to the desired value for a MCFC. This material appeared promising for use in a practical fuel cell, but a remaining problem was identified when preliminary studies indicated that it had a higher creep rate than the lithiated NiO used in state-of-the-art cells.

Some work was done on ways to reduce the solubility of the NiO cathode by modifying the 70 mol% Li_2CO_3-30 mol% K_2CO_3 electrolyte. Additions of $CaCO_3$ lowered the solubility of NiO and decreased the corrosion rates of stainless steel cell components, but $CaCO_3$ segregated during cell operation due to concentration polarization, thereby removing it from further consideration. Cells having Li_2CO_3-K_2CO_3 electrolyte tended to form short circuits during extended operation at high current densities due to segregation of the electrolyte. Recent studies with carbonate-wetted $LiAlO_2$ strips and 100-cm^2 cells have indicated that it may be possible to minimize this problem by using a Li_2CO_3-Na_2CO_3 electrolyte.

As of this writing, the current molten carbonate fuel cell consists of a porous nickel anode, a semi-fluid $(Li,K)_2CO_3$ + $LiAlO_2$ electrolyte, and a metal bipolar plate. An ongoing effort is being made to develop alternative cathodes, non-segregating electrolytes, and more corrosion-resistant cell components.

Polymer Electrolyte Fuel Cell. As of 1992, CMT was becoming more involved with the technical management of DOE-supported research and development of the polymer electrolyte fuel cell (PEFC) and the phosphoric acid fuel cell (PAFC) for transportation applications. Some in-house work that was supported on the polymer-electrolyte program involved research on the proton-exchange membrane fuel cells (PEMFC), which consist of a carbon-supported platinum electrode for oxidation of hydrogen fuel, an identical cathode for reduction of oxygen, and a polymer electrolyte membrane that transports hydrogen ions from the anode to the cathode. Because of the interest in renewable fuel sources, the hydrogen fuel gas was obtained by the reforming of alcohols, and it contained substantial amounts of CO_2 and traces of CO. At the relatively low operating temperature of 80°C, these impurities decrease the efficiency of the platinum catalyst and, therefore, the power output. The high cost of the platinum catalyst was an incentive to decrease the amount that was needed.

The initial research was aimed at platinum-based alloys that would decrease the amount of platinum while retaining the high electrochemical activity for hydrogen oxidation. The candidate alloys were first screened for catalytic activity under simulated operating conditions of a cell. They were exposed to CO-containing electrolyte just long enough to reach a platinum surface poisoning about equivalent to that of a platinum electrode operating on reformer output. The promising alloys were then placed in an actual cell, and the potential resulting from a current pulse was measured as a function of time. This procedure permitted separation of the reaction kinetics from other effects contributing to the measured potential. The results showed that platinum alone was the best anode when operating with pure hydrogen, but with CO in the fuel stream the alloy was superior to platinum.

An evaluation was made of two methods for fabricating polymer electrolyte cells: in one method, the electrolyte was impregnated into the electrodes; in the other, the electrolyte was mixed directly with the platinum catalyst used in the anode ("ink technique"). Two different gas-flow configurations (serpentine and waffle) were also examined. The results showed that the ink technique and the serpentine gas-flow pattern gave better performance.

In 1995, the emphasis was shifted to the direct use of methanol fuel in a PEFC without a need for reforming. Such cells were having problems with high anodic polarization, methanol crossover across the electrolyte membrane, and a reduced cell voltage due to mixed cathode potentials. A study was undertaken on the effect of ruthenium on the electronic structure of platinum and its electrocatalytic behavior in oxidizing methanol. The methanol crossover problem results from its solvation of the protons that carry the cell current. Work was started on the possibility of using a basic system where hydroxide is the conducting ion, and it moves in the opposite direction, so there is no chance of methanol transfer.

The major obstacle to developing a polymer electrolyte fuel cell that operates directly on methanol has been the low electrocatalytic activity of the anode catalyst for the methanol oxidation reaction. In 1997, a systematic study of platinum-based alloy catalysts showed that Pu-Ru alloys gave the best results.

Fuel Reformer Technology. In 1990, a study was conducted on fuel reformers to assess the state of the art for converting alternative fuels (methanol, ethanol, and compressed and liquefied natural gas) into a hydrogen-rich gas mixture for powering fuel cells in automotive applications. The existing reformers did not have the start-up and dynamic response capability required for a stand-alone fuel cell unit in an automotive application. In a separate project, the State of Illinois and DOE agreed to sponsor a program at ANL to develop reformer technology to convert ethanol to hydrogen for use in fuel-cell-powered vehicles.

A search was begun for catalysts to enhance the ethanol-steam reaction

$$C_2H_5OH + 3\ H_2O \rightarrow 2\ CO_2 + 6\ H_2$$

This is the ideal reaction. In actuality, some other reactions are involved, which lead to the formation of methane (CH_4). A Ni-Al-Zn catalyst gave a higher gas production rate, but a Cu-Zn-Ni catalyst produced a higher concentration of hydrogen and less methane in the product gas. Further studies of this reaction with a nickel-based catalyst showed that a high hydrogen yield with a low CH_4 concentration would be possible through the use of a water-gas shift converter after the reformer.

A possible alternative to the ethanol-steam reaction is partial oxidation. Methanol, for example, undergoes the reaction

$$CH_3OH + 1/2\ O_2 \rightarrow 2\ H_2 + CO_2$$

With a Cu-Zn-O catalyst, the methanol began to reform at about 150°C, and 100% conversion was achieved at 350°C. In 1994, a bench-top [10 kW(e)] methanol reformer based on partial oxidation was built and tested. The catalyst was copper zinc oxide (in the oxidized form). Startup was rapid, and the reaction product composition of 50% H_2, 20% CO_2, and <5% CO_2 was typical. This reformer was much lighter and smaller than existing units and was a radical departure from current reformer technology at that time. The next step was to look at the partial oxidation reforming of hydrocarbon fuels.

An idealized general reaction can be written for partial-oxidation reforming of a generic hydrocarbon fuel:

$$C_nH_mO_p + x\,(O_2{+}3.76N_2) + (2n{-}2x{-}p)\ H_2O$$
$$\rightarrow nCO_2 + (2n{-}2x{-}p{+}m/2)\ H_2 + 3.76x\ N_2$$

where x is the oxygen/fuel molar ratio. Conventional catalysts (including Fischer-Tropsch types) and a new class of proprietary catalysts developed by CMT scientists were tested to determine their effectiveness in promoting this reaction. The best performance was obtained with the Argonne catalyst. This catalyst was then tested with a variety of hydrocarbons that are typically present in gasoline. The results were very good. For example, partial-oxidation reforming of iso-octane at 630°C resulted in nearly complete reaction of the isooctane and a hydrogen concentration over 60%. Similar experiments were done with pipeline natural gas, which typically contains over 90% methane. Partial-oxidation reforming of natural gas at 690°C with the ANL catalyst left only 0.5% of the methane unreacted, and the hydrogen concentration was 70%. This research on reforming catalysts has been highly productive and is continuing. Work is also in progress on methods of removing CO from the reformate by a regenerative sorption process that uses CuCl-impregnated porous materials such as bauxite.

Modeling Studies. Mathematical modeling was used extensively in all of the fuel cell programs, and it took many forms. Detailed modeling was used to characterize the electrochemical and chemical reactions and rate-controlling kinetic factors in the electrodes and electrolytes. Engineering-type modeling involving mass and heat transfer, current and voltage distribution, flow patterns and pressure drops, and other properties of that type were used to optimize cell and stack designs. Finally, systems analysis studies of practical applications such as integrated systems involving reformers, fuel cells, and batteries for bus propulsion were a form of modeling.

The following are specific examples typical of the modeling work in the fuel-cell programs. Modeling of the MSOFC thermochemistry and thermal hydraulics characterized the temperature distribution, fuel and oxidant compositions, energy efficiency, fuel utilization, and power density for cells fueled by hydrogen, coal gas, and methanol. A modeling study was used to determine the factors affecting the electrochemical kinetics of the reactions in the MSOFC. In another study, the efficiency of fuel cell/battery-powered buses was determined as a function of fuel and oxidant flow rates. A computer simulation was developed for polymer electrolyte fuel cells used in a bus propulsion system. In the molten carbonate fuel cell program, the effectiveness of distributed manifolds having different flow patterns was evaluated by modeling. Finally, a generic steam reformer for methanol was modeled to determine its behavior under various operating conditions.

Technical Management. The CMT Division, through the ANL Electrochemical Technology Program, provided support to the DOE Office of Transportation Technologies and to the DOE Office of Buildings Technologies in the form of technical management of R&D contracts with industrial developers of fuel cells and related components. This activity involved the preparation of work statements, proposal evaluations, and progress reviews.

Because of the large number of contracts and wide scope of the work, the following is only a brief summary of these activities. An Allied Signal Aerospace/AiResearch program on monolithic solid oxide fuel cells extended into the 1990s. A major activity was the Fuel Cell Bus Project, which was supported jointly by DOE and the California South Coast Air Quality Management District (SCAQMD) and managed jointly by CMT and Georgetown University. The objective of this program was to demonstrate an urban bus powered by a methanol-fueled phosphoric acid fuel cell combined with a battery. Two industrial contractors were selected: Booz-Allen & Hamilton, Inc., and Energy Research Corp. In the second phase of this project, H-Power Corp. was contracted to assemble and test fuel cell/battery systems prior to their installation in buses. Subcontractors on the H-Power team included Transportation Manufacturing Corp., Bus Manufacturing USA, Inc., Booz-Allen Hamilton, Inc., Fuji Electric Co., and Soleq Corp. In 1994, this program resulted in the first U.S.-built bus powered by a fuel cell, and H-Power Corp. built two more buses in 1995. These buses are still in operation.

Polymer electrolyte fuel cells (PEFC) were also of interest for transportation applications. The Allison Gas Turbine Division of General Motors Corp. built and tested a 10-kW PEFC in 1993 during the first phase of a three-year contract. Supporting subcontractors included Los Alamos National Laboratory, Dow Chemical Co., Ballard Power Systems, General Motors Research Laboratories, and General Motors Advanced Engineering Staff. Ford Motor Co. had an ongoing contract to develop a 50-kW PEFC fuel-cell stack, which included subcontracts with International Fuel Cells and Mechanical Technology, Inc. Chrysler also had a contract for similar work, using Pentastar Electronics, Inc., as a subcontractor.

Arthur D. Little had a major role in the development and engineering of reformer systems for converting ethanol and natural gas into hydrogen for fuel cells, and they engaged SETA Corp. in environmental assessments of fuel-cell-powered vehicles, and Engineering Systems Management in life-cycle and cost comparisons. Other miscellaneous contracts included Ovonics work on nickel/metal hydride batteries and investigations of thermoelectrochemical power sources by the Delco-Remy and Hughes Aircraft divisions of General Motors Corp. In 1996 six new contracts were issued to Energy Partners, Texas A.&M. University, International Fuel Cells, Allied Signal, Arthur D. Little, and Vairex Corp. to develop innovative designs and materials to improve the performance of PEFC systems.

Personnel. The fuel cell programs in the 1990s were under the general purview of Mike Myles and directed by Mike Krumpelt. Ira Bloom was the leader of the solid oxide fuel cell work, which also included David Carter, Dennis Dees, Rajiv Dosi, Mark Hash, Tim Kueper, Frank Mrazek, Deborah Myers, and Xiaoping Wang. The research on molten carbonate fuel cells was led by Gene Kucera and involved Ira Bloom, Alan Brown, Kevin Byrne, Gary Henriksen, Sheldon Lee, Mike Roche, Jim Smith, and Joe Stapay. Research on the polymer electrolyte fuel cell was conducted by Shabbir Ahmed, Khalil Amine, Ira Bloom, Deborah Myers, and Tony Tummillo under the leadership of Romesh Kumar. Technical assessments and modeling were performed by Shabbir Ahmed, Ira Bloom, Gary Henriksen, Ted Krause, Mike Krumpelt, Romesh Kumar, Jim Miller, Deborah Myers, Walt Podolski, and Bill Swift.

Fossil Fuel Research

The fossil fuel research program, often referred to by people in the Division as the "coal program," continued into the 1990s, but waned rather quickly in the early part of the decade, due to loss of funding, until it had disappeared by the mid-1990s.

FLUIDIZED-BED COMBUSTION STUDIES

As described earlier, fluidized-bed combustion is a process for burning coal under atmospheric or pressurized conditions in a fluidized bed of limestone or dolomite, which removes most of the SO_2 from the off-gases during combustion. As of 1990, studies were in progress on the following:

1. Loss of metal from heat exchanger surfaces.
2. Materials performance in a fluidized-bed cogeneration air heater.
3. Alkali vapor emissions from pressurized fluidized-bed combustion (PFBC).
4. Combustion of cleaned coals.
5. Use of Illinois limestones to reduce SO_2 and HCl emissions during combustion of Illinois coal containing high levels of sulfur and chlorine.

Metal Loss in Fluidized-Bed Combustors. Loss of metal from heat-transfer tubes in FBCs was an ongoing problem that was frustrating efforts to commercialize this technology. The following organizations joined into a cooperative effort to address this problem: DOE, ANL, Electric Power Research Institute (EPRI), Illinois Center for Research on Sulfur in Coal (CRSC), Tennessee Valley Authority (TVA), ASEA Babcock PFBC, Foster Wheeler Development Corp. (FWDC), and ABB Combustion Engineering Systems (ABB/CE). The objective was to develop models and computer codes to predict hydrodynamics and metal loss of tubes in fluidized beds, and to translate these models into designs and operating conditions that would minimize metal loss. The ANL divisions involved in this effort were CMT, Energy Systems (ES), and Materials and Components Technology (MCT).

Data from fluidized-bed experiments at the University of Illinois at Urbana-Champaign (UI-UC) and at FWDC were used in ANL-developed models to analyze the fluidized-bed hydrodynamics. Babcock and Wilcox (B&W) developed a three-dimensional model. Room-temperature (no combustion) tests by FWDC characterized the erosion and hydrodynamic behavior in which the conditions could be altered by changing the geometry of the equipment. The data were analyzed at ANL to evaluate bubble formation and its effect on erosion patterns. In the experiments at UI-UC, particle velocity was determined by use of a radioactive tracer particle. By putting together all this information, it was possible to calculate the directional distribution and velocity distribution of the particles impinging on the tube surfaces. Bubble velocities in the fluidized bed were computed from differential pressure measurements in the FWDC experiment and were found to agree with computed values. Babcock and Wilcox then completed a three-dimensional hydrodynamic model, which was validated by comparing its output with that from the ANL two-dimensional model.

Experimental work then continued, with testing of a "cold-model" fluidized bed at FWDC and studies of erosion and particle velocity at UI-UC. In the UI-UC work, particle velocities of soda-lime glass beads were determined by the tracking technique, and the unsurprising conclusion was that the high erosion regions of the immersed tubes coincided with those of high particle speed and high hitting frequency. The experimental data from FWDC and UI-UC were compared with predictions from hydrodynamic and erosion models (FLUFIX/MOD2 and EROSION/MOD) developed at ANL. The maximum erosion rates in the FWDC experiments were determined to be 0.5 mm/1,000 h for aluminum tubes and 2.9 mm/1,000 h for polyvinyl chloride (PVC) tubes. Similar, but not identical, results were obtained by UI-UC.

Atmospheric Fluidized-Bed Cogeneration Air Heater Experiment. Argonne managed the Atmospheric Fluidized-Bed Cogeneration Air Heater Experiment for DOE. The ANL divisions involved with this project were CMT and MCT. The purpose of the project was 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). Rockwell International was awarded a contract for experimental testing of heat-exchanger tube bundles in a DOE-owned AFBC unit in El Segundo, California. Test specimens of a wide variety of alloys were supplied by ANL and three organizations under subcontracts with Westinghouse Electric Corp. The objective of the tests was to determine metal-loss information that would permit lifetime projections for the alloys in the AFBC environment. The tests had a duration of about 2,000 h, and the temperature was approximately 880°C. Oxygen partial pressures, which were normally about 10^{-3} Pa, were measured by means of a cell with an yttria-stabilized zirconia solid electrolyte. In general, the results of these tests showed that deposits of the bed material on the alloy surfaces caused significant, sometimes catastrophic corrosion. The same alloys, however, had acceptable corrosion rates when their surfaces were free of such deposits.

The overall conclusions of this investigation were the following:

1. Some stainless steels and other alloys exhibited little corrosion.
2. Long-term (3,000-h) laboratory tests revealed that others underwent catastrophic corrosion at sustained low oxygen partial pressures and in the presence of bed-material deposits.
3. Some alloys were susceptible to unacceptable corrosion when in contact with the bed material.
4. Among the weldments, a variety of fillers had acceptable corrosion resistance.
5. Of the coated specimens, aluminized coatings were very poor. In general, the development of crack-free coatings was difficult.

6. Among the cladding alloys, Type 310 stainless steel on Type 304 stainless steel or Alloy 800H exhibited superior performance.

Regenerable Activated Bauxite Sorbent Alkali Monitor. Vapor-phase alkalis in the PFBC exhaust can corrode the turbine-blade materials. Earlier work had shown that a time-averaged value of the alkali-vapor concentration in the exhaust gas could be measured by using an analytical activated-bauxite sorber bed. The adsorbed alkalis were recovered by water leaching and analyzing the solution by atomic absorption spectrometry. The objective of this work was to develop a regenerable activated bauxite sorber alkali monitor (RABSAM) for *in situ* measurement of the alkali vapor in the PFBC exhaust gas. The commercial-grade activated bauxite that was used contained some clay impurities that could react with the alkali vapors. These impurities were deactivated by impregnating fresh activated bauxite with NaCl solution, followed by heat treating, water leaching, acid leaching, and Soxhlet extraction with deionized water.

Lithium chloride (LiCl) was then considered as a possible substitute for NaCl because it is more reactive than NaCl and would decrease the amount of non-chloride sodium produced by deactivation of the clay impurities. Test results showed that the clay materials in raw activated bauxite were completely deactivated by impregnating the material with 6 *M* LiCl solution, followed by heat treatment at 700°C for about 50 h.

Two test runs were made, using fresh activated bauxite treated by the LiCl-solution technique, preconditioned at 895-900°C and 10 atm for 3.5 h with a simulated PFBC off-gas containing no NaCl vapor. The preconditioned material was then tested for NaCl capture efficiency under essentially the same conditions as the preconditioning step, but with the addition of 5-9 ppm (by weight) NaCl. Each test run was for 10 h. The NaCl capture efficiencies were 94.5% in the first test and 96.7% in the second one. Surprisingly, under similar test conditions "fresh" (untreated) activated bauxite had a capture efficiency of >99%. The conclusions from these tests were that (1) the treated activated bauxite behaves similarly to untreated activated bauxite in terms of the capture mechanisms for NaCl vapor in simulated PFBC off-gas, and (2) exposure to NaCl vapor in the off-gas might almost completely deactivate the clay impurities in the untreated activated bauxite.

Measurement of Alkali Metal Vapor/Aerosol in FBC Exhaust Gases. Illinois has the largest bituminous coal deposits of any state in the union. Unfortunately, Illinois coal, although abundant, is "dirty," with a high sulfur content (much of it around 3%) and other undesirable impurities such as chlorine. The specific objective of this effort, which was sponsored by the Illinois Center for Research on Sulfur in Coal, was to evaluate the alkali-vapor corrosivity of PFBC off-gas generated by burning Illinois coals of high-chlorine, high-sulfur content. Two typical Illinois coals were burned in the ANL laboratory-scale fluidized-bed facility, and the alkali-vapor emission was measured by the activated bauxite sorber technique. The results showed that sodium was the major alkali metal species present, and that the alkali metal concentrations were 2.5 times greater than the specified limit of 24 ppb for an industrial gas turbine. It was clear that further work was needed to develop a method to control alkali vapors for turbine protection and that the effectiveness of washing procedures to remove sodium compounds from coal should be evaluated.

A joint project between ANL and Sargent & Lundy was undertaken to determine the effect of coal washing on emissions, costs, and amounts of solid-waste products for an

80-MW(e) circulating fluidized-bed combustor. Tests were conducted by burning these coals in the ANL laboratory-scale FBC facility at atmospheric pressure. A Sargent & Lundy evaluation of the results, when applied to the 80-MW facility, indicated that washing the coal resulted in a greater than 50% reduction in SO_2 emissions, and that 95% sulfur removal was possible for both coals with a limestone sorbent. Nitrogen oxide (NO_x) emissions from the washed coal were about 33% less than those for the untreated coal, and both values were below the acceptable standard. Washing the coal would also reduce by 69% the solid-waste handling burden and area of run-off pond needed. In fact, laboratory analyses showed that toxic metal concentrations in the storage area or leachate would not exceed acceptable levels. A cost analysis based on this information indicated that a plant using washed coal would have an economic advantage.

Because of the success of the ANL activated-bauxite technique for determining the alkali-vapor content of exhaust gases from fluidized-bed combustion units, it attracted interest from several organizations. At the request of a Swedish firm, ABB Carbon, ANL was contracted to measure the alkali vapor/aerosol content of off-gases from a 15-MW(t) Component Test Facility in Finspong, Sweden. The results of these tests were considered proprietary and were not reported. A similar request from Electric Power Development Co. and Ishikawajima-Harima Heavy Industries Co. in Japan involved measurements of the alkali metal/aerosol content of off-gases at the Wakamatsu 71-MW(e) PFBC Demonstration Plant in Kitakyushu City, Japan. The necessary instrumentation was designed and built and sent to Japan along with a documentation of the operating procedure. In the U.S., ANL was contracted to measure the alkali vapor/aerosol content of flue gas from an atmospheric circulating fluidized-bed combustor fabricated by Ahlstrom Pyropower. This was a subcontract to Ahlstrom Pyropower's contract with the Illinois Clean Coal Institute. Tests with three Illinois No. 6 coals indicated time-averaged concentrations of 49, 47, and 44 ppb, which are about twice the acceptable limit of 24 ppb for turbine use. Further tests showed that in-bed getter materials (emathlite and kaolin) reduced the levels to 19 and 23 ppb, respectively.

Evaluation of Illinois Limestones for Reducing SO_2 and HCl Emissions. In this CRSC study, Illinois limestones and dolomites were evaluated for reducing SO_2 and HCl emissions from the ANL fluidized-bed combustor (FBC) with a 15-cm dia. The test was under excess air conditions typical of a single-stage, bubbling-bed, pressurized FBC. The sorbents were a Fredonia limestone, a Racine/Sugar Run dolomite, and a Racine dolomite from Illinois quarries. The fuel was a Herron No. 6 coal, which contained 2.6 wt% sulfur, and the operating conditions were 8 atm absolute pressure, 3.5% O_2 in the fuel gas, 0.9-m bed height, Ca/S mole ratios of 0.75 to 4.6, and temperatures of approximately 800-900°C. The sulfur retention ranged from 67.4% with the Fredonia limestone at a Ca/S ratio of 1.3 to a high of 98.0% with the same limestone at a Ca/S ratio of 4.6. As expected, the sulfur retention increased markedly with increasing Ca/S ratio, but only slightly with increasing temperature. The two dolomites were more effective than the limestone.

Continuing studies showed that these results were consistent with the physical characteristics of the sorbents, as determined by mercury porosimetry and nitrogen BET measurements of surface area and pore-size distribution. Measurements of HCl in the flue gases during the combustion tests indicated that the sorbent was not effective in reducing HCl emissions, which was an expected result.

The Fredonia limestone sorbent was also tested under fuel-rich combustion conditions, *i.e.*, an air/fuel ratio <1.0. Sulfur retention, which varied from 80 to 90%, increased with increasing Ca/S ratio and with decreasing air/fuel ratio. An important conclusion from these findings is that a staged FBC may offer significant environmental and operational advantages over conventional FBC systems.

Selection of Non-Alkali-Adsorbing Components. During the on-line, time-averaged measurements of alkali-vapor concentrations in PFBC off-gases, the results were found to be distorted through capture of the alkali vapor by the Type 304 stainless steel sampling line. A joint study was undertaken with the MCT Division to investigate this phenomenon and to identify materials that do not interact with the alkali vapors and would therefore be suitable for sampling lines and other components such as valves, piping, filters, and separation membranes. Thermogravimetric analysis (TGA) was used to evaluate candidate materials, which included Fe-, Ni-, and Co-based alloys as well as noble-metal-coated and ceramic-lined alloys. After the thermogravimetric analysis, the specimens were examined in detail by scanning electron microscopy (SEM) coupled with energy-dispersive X-ray analysis (EDAX) and Auger electron spectroscopy. In nearly all cases, an oxide scale had formed on the surfaces of the specimens. Coatings of noble metals (Pt, Au, Ag) did not prevent the scale formation. Aluminizing of the alloys followed by heating in air produced a coating that remained intact after the 100-h exposure to the baseline PFBC environment. In none of these cases was any sulfur found in the surface layers.

Parametric Study of N_2O Emissions from FBC. The amount of nitrous oxide (N_2O) present in FBC off-gases and the effect of operating conditions on the amount were not well known. Nitrous oxide was thought to be one of the pollutants contributing to the greenhouse effect and depletion of ozone in the upper atmosphere. Some confusion existed as to whether it was subject to emissions regulations; moreover, the analytical method used to determine NO_x emissions compliance is not sensitive to N_2O. A parametric study was done with the laboratory-scale (15-cm-dia) FBC at ANL to shed more light on N_2O emissions.

Two Illinois coals from Kerr-McGee Coal Co. and Peabody Coal Co. were burned in the FBC, and the N_2O emissions were measured by means of an on-line infrared analyzer and gas chromatograph. The SO_2 and NO_x levels were also determined. Measurements were made over a range of temperatures, excess air levels, fluidizing velocities, and pressures. The results were as follows:

1. The N_2O concentration decreased substantially as the temperature was raised.
2. The concentration increased with increasing excess air.
3. Increased residence time (the inverse of fluidizing velocity) tended to decrease the N_2O emissions.
4. Increasing pressure appeared to increase the N_2O levels somewhat.
5. Increasing the SO_2 level (by decreasing the sorbent feed rate) tended to increase the N_2O level.
6. In general, N_2O levels observed in these experiments ranged from about 40 to 150 ppm.

Personnel. Full-time members of CMT who worked on this program were Erv Carls, Sheldon Lee, Walt Podolski, Bill Swift, and Gale Teats. Several members from other divisions and Shelby Miller, an STA, also contributed to the effort. Swift was in charge of the work during the 1990s.

MAGNETOHYDRODYNAMIC STUDIES

Chemical Technology continued as the lead division for the ANL program on magnetohydrodynamics (MHD); the work on materials was done jointly with the MCT Division, and the mathematical modeling was a joint effort with the ES Division.

Materials Evaluations. Work continued on the development of open-cycle MHD systems in an effort to improve the electrical efficiency of coal-fired power plants and to reduce their environmental impact. Although the primary objective of the MHD plant is to extract heat from the combustion gases to produce high-pressure steam, it must also separate the seed material (usually a potassium salt) from the ash and recover it for reuse, preheat the primary combustion air to about 700°C or higher, lower nitrous oxide (N_2O) concentrations to acceptable levels, and inject secondary air to complete combustion of the fuel. The fuel-rich mixture leaving the topping cycle at about 2000°C enters a steam-bottoming cycle similar to that in a conventional coal-fired power plant.

Corrosion of boiler tubes by sulfur and alkalis in the combustion gases is a concern in conventional coal plants, and the problem is magnified in MHD plants because of the higher alkali content of the gases. Laboratory autoclave tests were performed to study the corrosion of candidate materials for components of the bottoming cycle of an MHD plant. Examinations were conducted on specimens of tube materials used in long-duration (2000-h) proof-of-concept tests with Illinois No. 6 coal in the low mass flow train (LMFT) at the Coal Fired Flow Facility (CFFF). The CFFF, which was operated for DOE by the University of Tennessee Space Institute, simulated the MHD bottoming cycle. Analyses of deposits on the tube samples taken at various times and locations indicated that the chemistry of the deposit did not change significantly with variations in the K_2/S ratio in the potassium seed material. The deposits in all locations were predominantly soluble potassium sulfate with no carbonate or bicarbonate. Of the materials tested, Type 310 stainless steel showed the least corrosion, while Types 304 and 316 were attacked severely.

Materials-evaluation studies were also made on the topping cycle. A piece of a cooling panel made of SA 387, a low chromium-molybdenum steel, that was tested for 250 h showed no sulfur in the gas-side scale, even though the coal being burned contained 3.6 wt% sulfur. Among 11 candidate alloys that were corrosion-tested for cooling circuits in the MHD channel, tungsten-copper alloys showed the best resistance. Tests were also made on the corrosion resistance of boron nitride and silicon nitride insulating materials in a potassium environment at temperatures of 538 and 760°C. Also measured were the electrical conductivities of the specimens before and after exposure to the potassium. The boron nitride was attacked and its conductivity increased markedly, whereas the silicon nitride showed no ill effects. Therefore, silicon nitride appears to be the material of choice.

Power Train Modeling. The Component Development and Integration Facility (CDIF) is an engineering-scale test facility for MHD topping cycle components that is operated by MSE, Inc., for DOE. In an effort to interpret and understand the MHD generator operation at CDIF, the CMT and ES Divisions began a joint effort to develop and use computer-generated simulations to investigate flow patterns and nonuniformities (*e.g.*, in temperature and plasma conductivity) in the major components of the MHD power train.

The combustion code that was developed solved transport equations for multiple gaseous species and solid particles of various sizes. Conservation laws were used in conjunction with rate equations governing the mass, momentum, chemical species composition, turbulent kinetic energy, and turbulent dissipation for a two-phase reacting flow. A sample calculation was made by using both the combustion and channel codes to simulate the second-stage combustor and MHD channel at CDIF. Results were obtained for the predicted properties (power, conductivity, and velocity) of the plasma flow in the MHD channel.

Personnel. Bill Swift and Dai-Kai Sze of CMT were involved in the MHD work, but most of the experimental effort was provided by individuals from the Energy Technology (ET) and Technology Development (TD) Divisions.

Hazardous and Mixed Waste Research

This program was concerned with the management and disposal of a wide variety of troublesome waste materials, including municipal wastes, toxic materials, and transuranium radioactive wastes that had been produced during defense-related work at DOE sites. Jim Cunnane, Jim Helt, and George Vandegrift had management responsibilities for these programs.

MODELING STUDIES

A mathematical model was developed to simulate the pyrolysis and combustion of municipal solid waste (MSW) in a water-wall mass burner. This process involved the heatup, pyrolysis, and burnout of the waste material as it was moved by a traveling grate from the inlet of the incinerator to the exit. The model permitted calculation of the temperatures and mass-flow profiles over the length of the bed. The model showed that: (1) the grate length in the reference design was longer than necessary to heat the material to the pyrolysis temperature, (2) an increased solids feed rate caused a slowdown of the heating and conversion process, and (3) bed height had a negligible effect on the solids heating rate. The simulations also showed that the solids processing rate could be increased by reducing the length of the burnout zone and by distributing the air flow, so it was kept low in the heatup and reaction zones to permit rapid heating and conversion of the solids. A two-dimensional model was considered to be a good beginning for the study, and the researchers concluded that to proceed to the next level more data were needed on the pyrolysis and combustion behavior of MSW components such as plastics, hemicellulose, *etc.* Mechanisms of the combustion reactions of char also needed to be included.

During the combustion process, radiant heat from the flame zone heats up the bed as it is carried across the grate, then the moisture in the MSW is vaporized and carried up into the flame zone by the air flowing in from under the grate. The rate of drying can be expressed by an Arrhenius function and depends upon the temperature and the moisture content. With a further rise of temperature, the cellulose fraction of the MSW begins to pyrolyze, yielding several gases (hydrogen, water, carbon oxides, and methane), which are transported into the flame zone by the air. Pyrolysis of the cellulose also yields a char (carbon) and ash residue in the bed. After a review of the literature on char combustion, empirical equations were developed to estimate the rate of char combustion, which turned out to be higher that the rate of cellulose pyrolysis. Consequently, char combustion was a minor consideration in the combustor design. The main investigators in this program were Jack Demirgian, Christine Snyder, and Milton Haas.

MICROWAVE-ASSISTED DETOXIFICATION

Safe and effective disposal methods were needed for chlorinated hydrocarbons such as 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE), which had become a major hazardous waste problem at DOE Defense Program sites. The objective of this project was to evaluate the technical and economic aspects of using microwaves to detoxify these materials by converting them to easily disposable compounds such as CO_2, CO, HCl, H_2O, and H_2. In previous studies, a 6-kW, 2.45-GHz microwave generator with a 2.1-cm-dia quartz reactor was used to produce an oxygen/argon plasma (20.13% oxygen) for investigation of the oxidative degradation of TCA and TCE. Destructive removal efficiencies of 95.9-98.3% were achieved by a single pass of the stream through the reactor. In the case of the TCA, however, a significant portion of the chlorine was not totally converted to the desired products.

Experiments were then conducted in which water vapor was added to the argon/oxygen with the idea that hydrogen in the water would tend to remove the chlorine as HCl, and the oxygen would remove carbon as CO or CO_2:

$$C_2H_3Cl_3 + 4\ H_2O \leftrightarrow 2\ CO_2 + 4\ H_2 + 3\ HCl$$

Single-pass destructive removal efficiencies were >97% for TCA.

This work continued with a study of the reaction of TCA and oxygen, using a 7-kW microwave generator. The operating conditions were varied (O_2/TCA molar feed ratios from 1.5 to 165 and microwave power inputs from 300 to 600 W). The TCA conversion ranged from 75% at 300 W and an O_2/TCA ratio of 1.5 to >99% at 600 W and a ratio of 150. The products of this reaction with excess oxygen and high microwave power input (600 W) were CO_2 and HCl. A reduction of the O_2 concentration or power input resulted in the formation of soot, CO, and hydrocarbons. In the case of TCE, power inputs of 600-800 W and O_2/TCE molar ratios of 13 to 190 gave conversions of >96%. Because the TCE contains insufficient hydrogen to convert all the chlorine to HCl, the excess chlorine is removed as Cl_2. This problem was solved by adding water vapor to the oxygen in the argon plasma. With the water addition, the only reaction products were CO_2 and HCl.

In 1992, work was started on a modification of the process whereby an air plasma with water as a co-reactant was substituted for the argon/oxygen mixture. (One potential application of the process was to detoxify air streams containing volatile organics that were generated by air stripping of contaminated soils.) A major concern with this approach, however, was the possibility that NO_x could be a problem because nitrogen fixation from air is more likely at the high plasma temperatures than at the more modest temperatures in a conventional thermal combustor. This project, however, was terminated at the end of 1992.

Jim Helt, Ravi Varma, and Ted Krause were responsible for much of this work.

AQUEOUS BIPHASE PROCESSES

When a suitable combination of soluble inorganic salts and water-soluble polymers such as polyethylene glycol (PEG) is added to water, the system separates into two liquid phases with the polymer phase on top and the salt phase on the bottom. In some respects, this kind of a system, which is called an "aqueous biphase," is similar to the combination of aqueous and organic solvents used in solvent-extraction processes. Separations in biphase systems, however, generally depend upon differences in the distribution of insoluble solids, rather than soluble species between the liquid phases. Very fine (colloid-size) solid particles, when suspended in an aqueous biphase system, will seek one phase or the other, depending on the particle interactions with the particular solvent. The water-soluble polymers used in biphase separations, unlike the organic compounds used in solvent-extraction processes, are nonflammable, inexpensive, nontoxic, and biodegradable.

The initial objective of this research was to develop a scheme for the recovery of plutonium from solid wastes stored at DOE sites to levels where the plutonium concentration would meet or exceed "economic discard limits," and the recovered plutonium would be compatible with existing plutonium recovery processes. As the work progressed, however, several other potential applications of aqueous biphase separations became apparent.

Preliminary Studies. The initial experiments showed that single-stage separation factors $>10^6$ could be obtained between silica and a wide variety of metal oxides. For example, with a biphase system consisting of 15% PEG/7.5% Na_2SO_4 at pH = 3, >99.99% of metal oxides such as Fe_2O_3 and Al_2O_3 partitioned to the Na_2SO_4 (bottom) phase, and >99.99% of the silica particles partitioned to the PEG-containing (top) phase. The partitioning behavior of the solid particles depended upon a number of variables, including the heat of immersion (ΔH_i), the pH of the system, the nature of the bonding of sorbed species, and the effects of surfactants.

Plutonium Recovery. The plutonium wastes usually consisted largely of silica or graphite resulting from foundry operations. To prepare the solid waste material for the biphasic extraction, it was first wet ground to a particle size of approximately 1 µm. The heterogeneous nature of the plutonium-bearing solid wastes and their physical properties were such that most of the PuO_2 was expected to be in the form of micron-size grains after the ultrafine grinding step. In the initial plutonium studies, polymeric Pu(IV) was used as a stand-in for particulate PuO_2. (Detailed characterization studies had shown that these two forms of plutonium shared the same chemical and physical properties that are of importance in this type of separation.) Preliminary studies of the partitioning behavior of monomeric Pu(IV), polymeric Pu(IV), and micron-size PuO_2 particles between 15% PEG/7.5% Na_2SO_4 and 15% PEG/15% $(NH_4)_2SO_4$ showed that efficient plutonium recovery should be possible in alkaline solutions (pH >3).

Experiments were then conducted with polymeric Pu(IV) and silica or graphite, which are the major constituents of foundry residues and incinerator ashes. In a test with SiO_2 ground to 0.2-1.0 µm, the silica distributed to the upper (PEG) phase and the Pu to the lower phase, with a separation factor of $>10^6$ in a single-stage separation. In a similar experiment with graphite (1-2 µm), the graphite distributed strongly to the PEG phase, but the plutonium polymer apparently tended to adsorb on the graphite particles and accompany the graphite into the PEG phase. Through the use of a suitable surfactant, however, the partition coefficient of plutonium was decreased from 4.0 to 0.04, thereby increasing the separation factor to a value of $>10^4$.

In addition to selective partitioning between the liquid phases in these systems, selective flocculation occurs at high ionic strengths. In the 15% PEG/7.5% Na_2SO_4 system, CeO_2 particles became flocculated in the salt phase, and the SiO_2 particles flocculated in the PEG phase. Solid-liquid separations were then achieved readily either by mild centrifugation or by microfiltration. When the two phases were centrifuged in the same tube, the solids appeared as sharply defined bands at the bottom of the tube.

The foregoing observations suggested that several options were available for designing a process flowsheet for plutonium recovery from process wastes. Samples of such wastes were obtained from the Rocky Flats Plant, Los Alamos National Laboratory, the Hanford site, and the Savannah River Laboratory. To aid in the flowsheet development, phase diagrams were determined for PEG/salt systems of interest. A flowsheet for the aqueous biphase separation (ABS) process would include wet grinding of the waste material to a micron-size level to liberate the refractory PuO_2, selective partitioning between the two immiscible aqueous phases, a solid-liquid separation, and recycle of the aqueous phases. The goal was to recover most of the plutonium in a concentrate that was only 1-5% of the initial waste volume. When the concentration of the extractant was increased, the plutonium-containing particles distributed to the PEG phase with partition coefficients up to about 300, and the particles without plutonium remained in the salt phase.

Uranium Recovery. Aqueous biphase separations were also considered for possible use in remediation of uranium-contaminated soil, a typical example being soil at the DOE Defense Production Facility at Fernald, Ohio. The objective of such a process was to remove sub-micron particles of UO_2 from the clay soil and recover a uranium concentrate having a volume less than 2 to 4% of that of the feed, and to leave a "clean" soil fraction containing less than 35 pCi of uranium per gram of soil.

Laboratory experiments were conducted by use of a model system consisting of kaolinite and submicron-size UO_2. When feed containing 200,000 ppm uranium was suspended in a 15% PEG/10% Na_2CO_3 system and scrubbed several times with a Na_2CO_3 solution, the recovered clay product contained 45 ppm uranium, which was below the 35 pCi/g limit. Batch extractions were then made with a <50-μm size fraction of Fernald soil, which represented about 70-80% of the total. "Clean" soil containing about 125 ppm uranium was recovered from the top (PEG) phase, while the uranium concentrated in the bottom in a volume equal to about 1% of the initial soil volume. These results suggested that the goal of 50 ppm uranium or less in the soil was achievable through the use of countercurrent extractions and pretreatment of the soil by attrition scrubbing.

Further test-tube-scale tests were conducted with the Fernald soils. The ABS process worked reasonably well with soils collected near the incinerator at Fernald, but those samples from storage areas did not respond as well.

In 1993, scale-up tests were made with uncontaminated clay feeds, in the pilot-plant facilities of the Otto H. York Co. in Houston, Texas. Clay was fed into a Karr column (2.54-cm ID and 3.6-m high) at a rate of 70 g/h. The column used countercurrent feed solutions of 30% PEG and 20% Na_2CO_3. The results indicated that a full-scale column could achieve solid throughputs of about 600 to 1200 kg/h, which should make this type of processing less expensive than landfill disposal. In a pilot-scale test with the Fernald soil in the Karr column in 1994, the uranium content of the soil was reduced from 471 mg/kg to about 78 mg/kg. Electron microscopy revealed that some of the uranium particles had remained in the soil. Because one of the major concerns with the process was the capital equipment and processing costs for separating the soil product from the effluent stream, the possibility of using flocculants was investigated with some success.

A preliminary process flowsheet was then developed for uranium removal from soils by an ABS system having a capacity of 20 ton/h of dry soil. The treatment cost was projected as $120/ton.

Waste Pretreatment. A collaborative effort was undertaken with Northern Illinois

University to investigate the use of biphasic systems for the extraction of long-lived radionuclides such as technetium-99, iodine-129, and selenium-75 from caustic high-level liquid wastes. Initial experiments were performed to examine the ability of aqueous PEG solutions to extract iodide and pertechnetate (TcO_4^{2-}) selectively from simulated supernatant solutions in the underground waste storage tanks at the DOE Hanford site. Because of the high ionic strengths of the caustic waste solutions, aqueous biphasic systems could be generated simply by adding aqueous PEG solutions directly to the waste solutions.

Tests were conducted with three Hanford waste-tank simulants. In all cases the separation was rapid, and the single-stage separation factors for pertechnetate ranged from 79 to 26,500, depending on the anionic species in the system. In general, separation factors were higher in the presence of polyvalent anions such as carbonate (CO_3^{2-}). These results indicated that it should be possible to achieve technetium decontamination factors well above 10^3 in a multistage, countercurrent extraction. Neither irradiation nor temperature appeared to affect the partition coefficients of the technetium.

Either PEG or PPG can be used to form the biphasic systems. Separation factors for technetium in the PPG system, listed in Table 6-6, are considerably higher than those in the PEG system. The high separation factor between pertechnetate and nitrate (NO_3^-) is significant because that has always been recognized as a particularly difficult separation.

Metal Separations. The biphasic systems used in most of the separations consisted of immiscible PEG and salt solutions. Some inorganic salts that promote biphase formation are the sodium and potassium salts of sulfate, carbonate, phosphate, and hydroxide. A major problem that arose in using biphasic separations for metal-ion extraction was an inability to recover solutes efficiently from the polymer-rich phase by back-extraction. This problem was solved by a discovery that the metal complex could be extracted efficiently from the PEG phase by a water-immiscible alcohol such as n-butanol at an elevated temperature (60-80°C). The partition coefficient for PEG in the butanol-water system was typically about 15, while that for the salts was 10^{-3} or less. Although the PEG partition coefficient is marginal, mass transfer of the PEG into the alcohol causes a large volume change, which results in >99.4% PEG recovery. The PEG can then be recovered by back-extraction into a dilute salt solution at 20°C. When this procedure is incorporated into a process flowsheet involving actinides, the actinide product is concentrated in a small volume of low-salt solution, which is suitable

Table 6-6. Separation Factors for Pertechnetate in PPG Systems

Ionic Species	Separation Factor
NO_3^-	1,049
NO_2^-	2,297
CO_3^{2-}	3,148
Na^+	2,576
$Al(OH)_x^{3-x}$	10,500