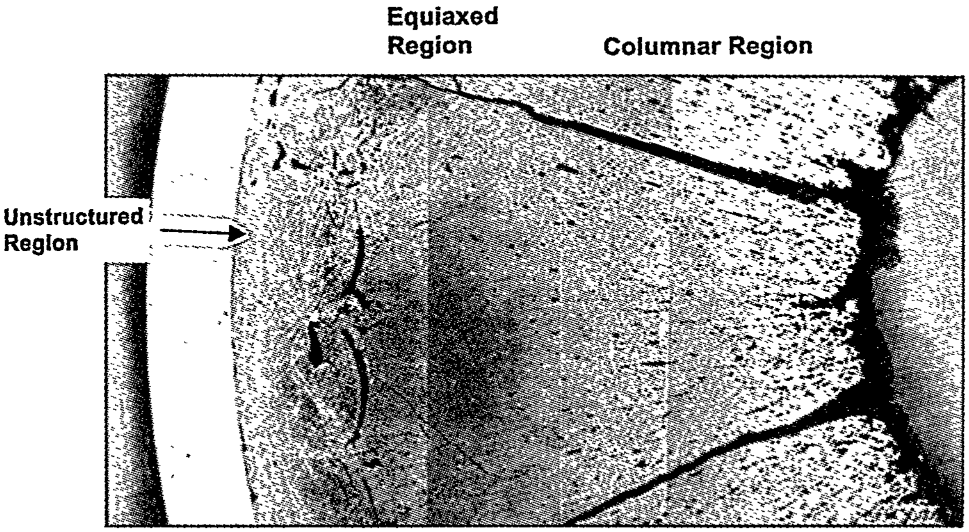


Fig. 4-26. Cross Section of Irradiated UO_2-PuO_2 Fuel Pin. Courtesy of Oak Ridge National Laboratory.

mixed oxides crystallize into columnar grains that radiate outward from the center. The resulting densification of the fuel causes a central void to form. Beyond the columnar grains is a region of equiaxed grains, and beyond that and near the cladding is an unstructured region of the original fuel.

In early work, an electron-probe microanalyzer, which accomplished microsampling and micro-analysis directly, was used to determine point-to-point concentrations of the elements across a fuel pin. This instrument cannot detect elements in the low mass range from hydrogen to carbon and has low sensitivity for elements carbon through oxygen. The capability of the electron-probe microanalyzer was supplemented in 1972 by acquisition of an ion-probe microanalyzer (IMMA), which provided a capability for determining the distribution of the whole range of elements with good sensitivity (ppm range). With this instrument, a small sample area (down to 3 μm) was ionized by a monoisotopic beam impinging on the sample surface. The secondary ion beam, comprising the sputtered sample ions and some of the scattered primary ion beam, is collected in a double-focusing mass spectrometer where element masses can be identified and their concentrations determined.

Oxygen Distribution in Irradiated Fuel. The solid-state diffusion of oxygen resulting from the thermal gradient drives oxygen toward the outer edge of the fuel, thereby establishing an oxygen gradient that is a function of the total oxygen content and the temperature gradient. The most important single property of a mixed-oxide fuel is the oxygen potential, which governs the chemical form of the fission products, their chemical activity (and, hence, the extent of fuel-cladding interactions), and in the event of a cladding rupture, the extent of sodium-fuel reaction.

A new method, based on the distribution of molybdenum in the fuel, was developed for calculating the oxygen potential at points in the fuel, mainly along a radius. The basic concept of the method was that at each point in the fuel (along the temperature gradient), a local equilibrium exists between the oxidized and reduced forms of a fission product, which functions as a "redox" indicator. For a variety of reasons, the Mo-MoO_2 system was chosen, resulting in the following equation:

$$\Delta G(O_2) = \Delta G^{\circ}_{f}(MoO_2) \\ + RT \ln [a(MoO_2)/a(Mo)]$$

where $\Delta G(O_2)$ represents the oxygen potential, $\Delta G^{\circ}_{f}(MoO_2)$ is the standard free energy of formation of MoO_2, a(Mo) is the activity of molybdenum in a noble metal inclusion, and $a(MoO_2)$ is the activity of MoO_2 in the oxide matrix. This equation was found to work well in the columnar grain region, but in the cooler fuel regions, cesium molybdate (Cs_2MoO_4) forms, and the MoO_2 activity is no longer proportional to its concentration in the oxide matrix.

Behavior of Cesium. Considerable research was devoted to the behavior of cesium because of its high volatility and resultant mobility in oxide fuels. The transport and reactions of fission-product cesium in a fuel element may affect the performance of fuel pins in several ways, one of which is restriction of the axial flow of fission gases (xenon and krypton) to the plenum of the fuel element. In-pile experiments indicated that gas-flow restrictions develop in the region of the interface between fuel and blanket sections. This gas-flow restriction was attributed to the deposition of cesium uranate (Cs_2UO_4). The prevention of fission-product gas flow could cause the pressure to build up in the fuel region and eventually rupture the cladding.

The reaction of cesium to form cesium molybdate competes with that to form cesium uranate. Thermodynamic calculations led to the conclusion that, if the oxygen-to-metal (O/M) ratio is much less than 2.00 (hypostoichiometric, *e.g.*, 1.97), there will be a tendency for the cesium to migrate to the fuel-blanket interface. If the O/M ratio is greater than 2.00 (hyperstoichiometric, *e.g.*, 2.10), formation of cesium uranate in the fuel can be expected. This could lead to swelling of the cladding. If the O/M ratio is close to stoichiometric, the cesium will tend to remain in the fuel as cesium molybdate.

The chemical reaction of gaseous cesium with uranium oxide to form Cs_2UO_4 is the following:

$$2\ Cs(g) + O_2(g) + UO_2(s) \rightarrow Cs_2UO_4(s)$$

where the oxygen pressure and uranium oxide activities are for hyperstoichiometric UO_2. The amount of Cs_2UO_4 formed is limited by the amount of oxygen available above that needed to form stoichiometric UO_2. The rate of reaction of cesium with hyperstoichiometric UO_2 as a function of temperature and the initial O/U ratio is shown in Fig. 4-27.

Studies of irradiated cladding showed that oxygen-containing fission products such as cesium uranate can accelerate intergranular attack of the stainless steel cladding. Although the level of attack was not too serious, understanding and controlling the formation of such compounds were important. Darrell Fee developed a model of cladding attack based on the reaction of cesium with the protective layer of Cr_2O_3 on the cladding surface to form cesium chromate (Cs_2CrO_4), which is non-protective. Once the protective Cr_2O_3 layer on the stainless steel is breached, which occurs slowly and is temperature-dependent, the subsequent rate of attack depends only on the rate of generation and release of oxygen formed as the fuel is fissioned. Cesium chromate forms on the cladding when the

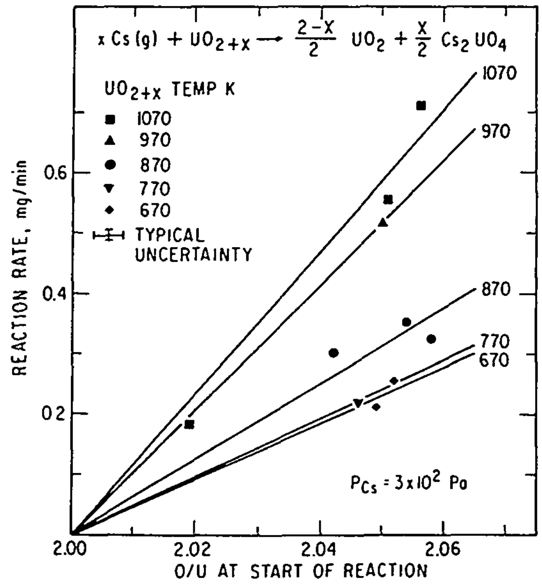


Fig. 4-27. Effect of Temperature and O/U Ratio on Reaction Rate of Cesium with UO_2

cesium equilibrium pressure of the fuel exceeds the equilibrium cesium pressure on the cladding. Thus the distance between the two curves shown as the shaded area in Fig. 4-28 represents the driving force for cesium chromate formation and, thus, cladding attack. The model accurately predicted the in-reactor attack of LMFBR fuel cladding.

Chemistry of GCFR Fuels. When the Clinch River Breeder Reactor was cancelled in the late 1970s, attention turned to the behavior of mixed oxide fuels in a Gas-Cooled Fast Reactor (GCFR). This work relied heavily on the LMFBR base technology, but there are significant differences between an LMFBR and a GCFR. Unique to the GCFR are the use of vented fuels, roughened cladding to promote heat transfer, a helium coolant, and direct contact of the primary coolant with the steam generator.

Again, cesium chemistry occupied center stage because of concern about deposition of cesium uranate at the fuel-blanket interface, restricting axial flow of the fission-product gases and their release to the helium coolant. A major accomplishment was the elucidation of the Cs-U-O phase diagram (Fig. 4-29) by Darrell Fee and Carl Johnson. Of the ten possible cesium uranates, only three, Cs_2UO_4, $Cs_2U_2O_7$, and $Cs_2U_4O_{12}$, can exist in equilibrium with hyperstoichiometric UO_2 and liquid/gaseous cesium in the temperature range of 600-1000°C.

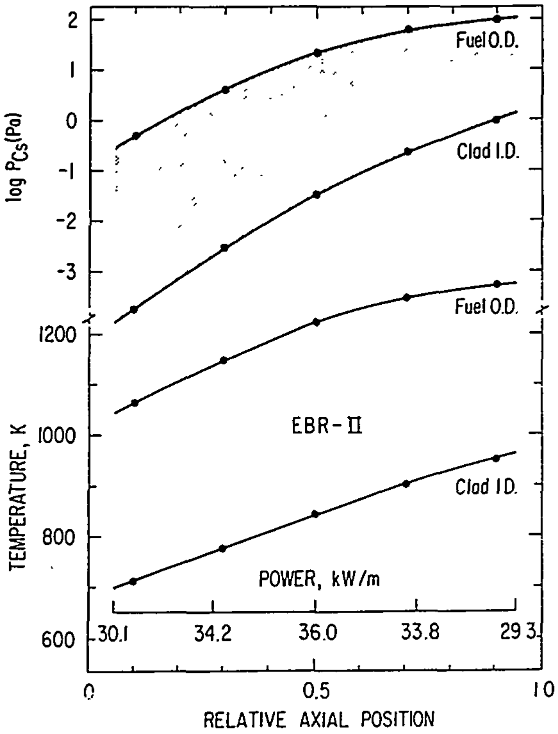


Fig. 4-28. Temperatures and Equilibrium Cesium Pressures in EBR-II Fuel Pin

Molten Salt Chemistry

Throughout almost the entire history of the Chemical Engineering, and, later, the Chemical Technology Division, the research and development programs have involved the use of molten salts. Among these programs were pyrochemical and fluoride volatility fuel reprocessing, high-temperature batteries, fuel cells, fusion blanket processing, the coal-combustion and magnetohydrodynamics work, and the current programs on electrometallurgical processes. In addition to these applications, molten salts were often used as solvents in basic research studies where more conventional aqueous or organic solvents could not be used for one reason or another. In

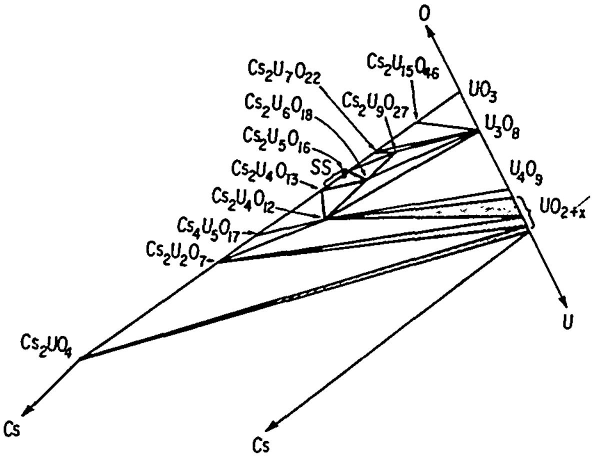


Fig. 4-29. Cesium-Uranium-Oxygen Phase Diagram

the early 1970s, the focus was largely on molten-salt electrolytes for high-temperature batteries, but the scope then expanded into the basic chemistry of salts involved in the fuel cell, coal, and fusion programs.

PHASE EQUILIBRIA

In 1970, researchers in the battery program were investigating candidate systems suitable for use in lithium/chalcogen cells of the general type Li/MX/C, where Li was lithium or a lithium alloy, MX was a molten alkali metal halide salt containing lithium ions, and C was one of the chalcogens (sulfur, selenium, or tellurium). Theoretically, a lithium/sulfur cell would have provided the highest voltage and capacity, but attempts to operate such cells were unsuccessful for several reasons. Elemental lithium presented the problems of solubility in the electrolyte, which resulted in self-discharge due to electronic conductivity of the salt, a tendency to plate out on any metal surfaces at negative potential in addition to the electrode during recharge, and corrosion by chemical reduction of ceramic insulators. As pointed out previously, alloying the lithium with aluminum solved these problems. In evaluating the chalcogens for the positive electrode, consideration had to be given to the phase relationships among the molten halide electrolyte, the elemental chalcogens (S, Se, or Te), and the reaction product (Li_2S, Li_2Se, or Li_2Te). Multicomponent electrolytes, such as LiF-LiCl-LiI, had to be used because they were liquid at reasonable temperatures. (Ternary phase diagrams of the systems LiF-LiCl-LiI and NaF-NaCl-NaI had been developed previously by Carl Johnson and Ellen Hathaway.) A phase diagram, to represent the positive electrode in a Li/LiF-LiCl-LiI/S cell, would have five components, LiF, LiCl, LiI, S, and Li_2S. Because the electrolyte composition is invariant in composition, however, a binary or ternary salt can be regarded as a single phase, making possible pseudoternary systems comprising the salt, Li_2S, and S.

Implicit in the phase-diagram studies are mutual solubilities of the components. Solubilities of Li_2Se were measured in LiCl-KCl, LiF-LiCl-LiI, and LiBr-RbBr eutectics as a function of temperature. All showed the usual straight-line log (solubility) *vs.* 1/T plots, and the solubilities were the same for salts having all-lithium cations. With LiCl-RbBr, the solubility was lower. The solubility of selenium in LiBr-RbBr was about the same as that of Li_2Se (0.03 mol% at 365°C), but the selenium solubility from mixtures of Se and Li_2Se was considerably higher (1.5 mol%), probably due to the formation of selenides. Reverse experiments on the solubility of molten halide salt in Se and Li_2Se-Se mixtures showed very low values, a favorable result from a practical viewpoint. Companion studies of sulfur and Li_2S in LiBr-RbBr showed low solubilities of 0.3 and 1.5 mol%, respectively, but Li_2S-S mixtures resulted in values of 8-10 mol%—a bad omen for the use of sulfur as a positive electrode material.

Paul Cunningham, Ellen Hathaway, Stan Johnson, and Vic Maroni conducted studies of the pseudoternary phase diagrams employing emf, differential thermal analysis (DTA), and chemical analysis techniques. Isothermal sections of the systems Li_2Se-Se-(LiBr-RbBr) and Li_2Se-Se-(LiF-LiCl-LiI) are shown in Figs. 4-30 and 4-31. Further investigations were conducted on the solubilities of the molten salts and Li-Li_2S in each other, using emf measurements. The results elucidated some details of the pseudoternary phase diagrams and provided thermochemical data that resulted in a standard free energy of formation of -94.0 kcal/mol for solid Li_2Se at 360°C.

Several other phase-equilibrium studies that related to various applied programs were conducted by different individuals: CaI_2-$CaCl_2$, CaI_2-CaF_2, and CaI_2-$MgCl_2$ by Ram Sharma; LiI-KI and LiI-RbI by R. Sridhar and

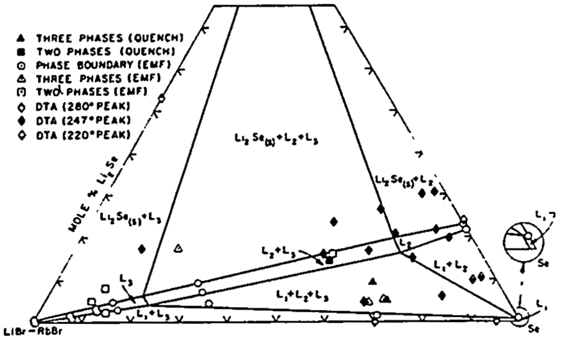


Fig. 4-30. Phase Diagram for Li_2Se-Se-(LiBr-RbBr) System at 360°C

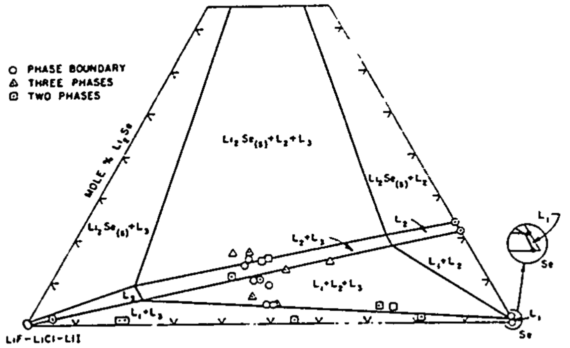


Fig. 4-31. Phase Diagram for Li_2Se-Se-(LiF-LiCl-LiI) System at 390°C

Carl Johnson; $LiF-AlF_3$, $NaF-AlF_3$, and $Li_3AlF_6-Na_3AlF_6$ by Marie-Louise Saboungi; the reciprocal ternary system $Na-NaOH-Na_2O-NaH$ by Mike Myles and Fred Cafasso; and Li-LiH, Li-LiD, and Li-LiT by Ewald Veleckis, Vic Maroni, and Bob Yonco. Marie-Louise Saboungi, Jane Marr, and Milt Blander determined the solubility of FeS in LiCl-KCl, and Marie-Louise Saboungi and Al Martin measured the stability of "J-phase" ($LiKFe_{24}S_{26}Cl$) as a function of molten salt composition. Gene Kucera and Marie-Louise determined the solubility of MgO in $CaO-CaCl_2$.

MOLTEN SALT SPECTROSCOPY

Two phosphorus compounds, P_4S_7 and P_4Se_3, were of interest as positive electrode materials for electrochemical cells. Vic Maroni and Bob Schablaske investigated the structures of liquid and solid P_4S_7. Five of the sulfur atoms were present in P-S-P bridges, and two were in the terminal P-S bonds. Bands for the two stretching modes expected for the terminal P-S bonds were found in the solid, but not in the liquid. This observation suggested that the terminal sulfur atoms might have been dissociated in the molten state or might have become cross-linked with terminal atoms on adjacent molecules, a behavior proposed earlier for P_4S_{10} molecules. Apparently, the "P_4S_5" internal cage structure remained intact in the liquid state. Raman studies of solid P_4Se_3 produced results consistent with previous studies in the literature.

The Raman spectrum of the iodate ion, IO_3^-, in molten nitrates was examined as part of a program to explore possible methods of removing fission-product iodine from off-gases in scrub towers. Iodate is one of the major reaction products from the reaction of iodine with nitrates. Melts containing the iodate were prepared by heating 15 mol% I_2O_5-85 mol% MNO_3 mixtures, where M was Li, Na, Rb, Cs, Ag, or Tl. Three Raman bands attributable to IO_3^- were observed in all cases. Changes of the cation in the above sequence produced downward shifts in the symmetric stretching frequencies, which indicated that the cation polarization effects on the IO_3^- and NO_3^- ions were similar. Vic Maroni and Ellen Hathaway did that investigation.

Vic Maroni studied the structures of divalent metal ions in molten halide salts, including the systems $LiCl-MgCl_2$, LiCl-KCl-5 mol% ZnI_2, and LiCl-KCl-5 mol% $ZnCl_2$. The zinc iodide and chloride produced identical spectra consistent with the presence of $ZnCl_4^{2-}$, which indicated that the zinc was tied up as chloride. This result explained the high removal efficiency of iodine by LiCl-KCl cover salt used in zinc decladding and the low vapor pressure of ZnI_2 over the melt. In the case of magnesium, $MgCl_4^{2-}$ was shown to be the predominant monomeric species, and the complete Raman spectrum of $MgCl_4^{2-}$ was characterized.

Several other materials were examined by Raman infrared, emission-spectrum, and/or X-ray methods: tungstates, molybdates, $NaNH_2$, KCl-$SnCl_2$, KX-PbX_2 (where X= Cl and Br), and molten carbonates. Vic Maroni, John Bates, Paul Cunningham, and Ellen Hathaway were responsible for most of this work.

Although not strictly molten-salt chemistry, another area that received attention was the characterization of vapor species related to the above systems. George Papatheodorou played the major role in this work, but several others were involved. An interesting phenomenon that had been observed earlier was that trivalent metal halides such as the chlorides and bromides of aluminum, gallium, indium, and iron form volatile complexes with normally non-volatile halides, thereby enhancing their volatility. This effect was primarily of theoretical interest, but could have practical implications for chemical separations, crystal growth, or high-power gas lasers. The objectives of research in this area were to find new vapor complexes and to determine their structure, thermodynamic properties, and mode of formation.

Spectrophotometric and vapor-density measurements were made on the pairs $CoCl_2$-$InCl_3$, $PdCl_2$-$InCl_3$, $PdBr_2$-$AlBr_3$, and $SmCl_3$-$AlCl_3$ at temperatures and pressures of 180-825°C and 10-1200 kPa. Equilibrium constants were determined for the reactions, which were of the type

$$CoCl_2(s) + In_2Cl_6(g) \rightarrow CoIn_2Cl_8(g)$$

Raman and resonance Raman spectra of several gaseous species, including $CuIn_2Cl_8$, $CuAl_2Cl_8$, $CuCl_2$, and $InAlBr_4$, were determined. Another interesting and potentially useful aspect of these reactions is that they can be used to chlorinate transition metal and lanthanide oxides to the chlorides by addition of $AlCl_3$. The complex chloride vapor species can then be used to recover high-purity chlorides or to effect chemical separations. Solid uranium dioxide was chlorinated by this technique, using Al_2Cl_6 vapor and chlorine at 300°C to produce solid UCl_5, which was then transported as a UCl_5-Al_2Cl_6 vapor complex from which high-purity U_2Cl_{10} crystals were deposited. This work was then continued, using $FeCl_3$, $AlCl_3$, and $POCl_3$ as "carrier" gases, and research was aimed at a systematic characterization of the thermodynamics of the complexing reactions. Mixtures of UO_2 and ThO_2 were chlorinated, and the products were separated as UCl_3 and $ThCl_4$. Enhancement of the volatility of $ErCl_3$ by $AlCl_3$, $GaCl_3$, and $InCl_3$ was also examined.

THEORETICAL STUDIES

By the mid-1970s, a large body of data on phase equilibria in molten salts had been generated both in the basic and applied programs of the Division, and still more information was available from the literature. Nevertheless, much was still missing, especially for ternary and higher systems, in terms of phase diagrams and especially thermodynamic properties. Milt Blander and Marie-Louise Saboungi made a significant contribution toward improving the situation by invoking theoretical concepts to correlate the existing data and to predict the behavior when experimental data were missing or incomplete.

Their first effort, in 1974, was to use a thermodynamically self-consistent empirical extension of conformal ionic solution (CIS) theory to calculate liquidus phase diagrams for charge-asymmetric ternary reciprocal systems. Eight such systems were calculated, and the results agreed well with the limited experimental data that were available. Their conclusion was that the theory could be a significant aid in calculating phase diagrams *a priori*, in judging and correlating experimental data, and in minimizing the amount of experimental data needed to construct ternary phase diagrams. The conformal ionic solution theory was used to derive an expression for the total excess free energy of mixing for additive ternary systems. In some cases, the solution properties of ternary systems could be predicted solely from measurements of the subsidiary binaries.

The studies were then extended to incorporate molecular dynamics (MD) computer simulations for deriving the macroscopic and microscopic properties of classical charged particles from intermolecular potentials. Equations derived by this approach resulted in predictions of thermodynamic properties of molten-salt solutions that agreed closely with experimental measurements.

Marie-Louise Saboungi, Harold Schnyders, Mel Foster, and Milt Blander applied the CIS theory to the prediction of liquid-liquid miscibility gaps in reciprocal molten salt systems and found excellent agreement with experimental data for the system Na, Ag||NO_3, Br obtained by Blander and Gene Kucera. Thermodynamic calculations were used to determine the solubility products for sulfides of Ag, Cu, Cr, Fe, Mg, Mn, Na, Pb, Ti, and Zn, which were of interest to the battery program, and a computer-assisted analysis was conducted on the phase diagrams in the $NaF\text{-}AlF_3\text{-}LiF\text{-}CaF_2\text{-}MgF_2\text{-}Al_2O_3$ system, which is important in the aluminum industry.

Liquid Metal Chemistry

Most of the extensive studies that involved the chemistry of liquid metals in the 1970s were closely connected with the battery, fuel-reprocessing, sodium technology, and fusion programs and have been mentioned previously. The systematic investigations of solubilities and thermodynamic properties of various solutes in liquid metals that had been going on in Irv Johnson's group were concluded. Data were obtained by Irv, Bob Yonco, and John Heiberger on dilute solutions of lanthanum, cerium, and praseodymium in liquid zinc and in liquid cadmium. Also in Irv's group, Bob Yonco, John Heiberger, and Jack Fischer investigated solutions of neptunium in liquid magnesium, and Mike Krumpelt studied the thermodynamics of neptunium solutions in liquid cadmium. Ram Sharma made measurements on the systems magnesium-lead and magnesium-tin, and Mike Myles determined the phase diagram of the system copper-magnesium-calcium. These investigations, along with those performed earlier, provided a large, systematic data base on the solubilities and thermodynamic properties of liquid metal solutions, primarily those of zinc and cadmium.

Marie-Louise Saboungi and Jane Marr computed isothermal cross-sections of the ternary phase diagrams for the systems Al-Li-Mg and Ca-Li-Mg, using solution theory based on statistical mechanics and thermodynamics. Although some uncertainties about the subsidiary binaries and other input information precluded entirely unequivocal results, this type of analysis proved to be a powerful tool for generating complex phase diagrams with a minimum amount of experimental effort.

Further experiments and theoretical studies were directed to the solubilities of gases in liquid metals. This subject was of practical interest to the applied programs, particularly fusion energy and sodium technology, but was also intriguing from a basic viewpoint in that a better understanding of the unusual solvency properties of liquid metals might be gained by looking at the simplest of solutes, the noble gases. Ewald Veleckis, Bob Blomquist, Wally Kremsner, George Redding, and Bob Yonco had obtained experimental data on the solubilities of helium, argon, and xenon in liquid sodium. Their results were used in a theoretical study based on bond energies and surface-tension considerations. The general conclusion was that the first nearest neighbor interaction in a liquid metal is attractive (positive bond energy), and the second neighbor interaction is repulsive (negative bond energy).

Other Basic Research

NUCLEATION STUDIES

A small study was undertaken by Milt Blander on bubble nucleation in liquids to gain a better understanding of one mechanism for contact vapor explosions that occur in industry and could be hazards in nuclear reactors and the transmission of liquefied natural gas. The limits of superheat for 17 cryogenic hydrocarbons ranging in volatility from ethane (b.p., -88.2°C to cis 2-butene (b.p., 3.7°C) were measured and were about 0.885 of the critical temperature. The limits of superheat for mixtures were linear functions of the mole fractions.

An analysis of contact vapor explosions of hydrocarbons showed a definite correspondence between the explosiveness of hydrocarbons poured on a hot substrate and the conditions based on nucleation theory that closely approach the limit of superheat of the hydrocarbons. Jim Eberhart and Wally Kremsner were also involved in these studies.

METEORITIC STUDIES

In the early 1970s, Milt Blander instigated a combination of theoretical and experimental studies on the chemical processes involved in the origin of chronditic meteorites with the objective of developing clues as to the early history of the solar system and possible precursors leading to the formation of planets. This work in the Chemical Engineering Division was performed by Milt Blander and Gene Kucera. Also involved in the program were Lou Fuchs of the ANL Chemistry Division, H. N. Planner and Klaus Keil of the University of New Mexico, and L. S. Nelson and N. L. Richardson from Sandia Laboratories. The National Aeronautics and Space Administration (NASA) supported the work.

The concepts under study were based on the constrained equilibrium theory, which leads to predictions of the chemistry of meteorites and planet precursors. Chrondules are millimeter-sized spherical bodies found in the matrices of chrondites, the largest class of meteorites. They appear to be silicate droplets that crystallized rapidly within the chrondites, which crystallized 4.6 billion years ago. To investigate the way in which the spherulites were formed, experiments were performed on the crystallization of metastable, supercooled Mg_2SiO_4-SiO_2 mixtures.

Small beads of $MgSiO_3$ were formed by melting the material on loops of iridium wire, using a CO_2 laser in a furnace. Each bead was then held at a temperature ranging from 970 to 1346°C and then remelted by the focused laser beam. During recooling in the furnace, the metastable, supercooled droplets crystallized with a characteristic brightening caused by the heat of fusion. Some of the chrondules that formed a glass were devitrified by heating.

Thin, polished sections of the spherules were examined by optical microscopy and an electron microprobe. The microprobe analyses indicated that the SiO_2 content of the material had decreased from the original value of 60 wt% to values between 44 and 56 wt%. The only crystalline material detected by X-ray was forsterite (Mg_2SiO_4); the residual amorphous material was undoubtedly a glass. Based on the size of the spherules and the cooling conditions, the onset of crystallization was estimated to have been between 985 and 1346°C.

The micrographic examinations of the thin chrondule sections showed a variety of crystal morphologies. By combining this information with other data on furnace temperatures, nucleation temperatures, and the phase diagram of the $MgSiO_4$-SiO_2 system, Blander and his co-workers were able to correlate the crystal morphology, size, and texture with the degree of subcooling. A comparison of these spherulites with those in the chondrites showed many similarities, and indicated that those in the chrondites had crystallized at temperatures in excess of 600°C and, most likely, above 900°C.

These observations place limitations on current theories of the origin of chrondules. For example, if they were formed by direct condensation of metastable supercooled liquids, they could have formed in a nebula of solar composition at pressures as low as 10^{-3}-10^{-4} atm. If formed by impact melting during a collision of a "meteorite" with another body, the chrondules must have been in a thermal blanket at high temperatures after the collision.

A wealth of information was also obtained from a study of the carbonaceous Allenda chrondite. The mineralogy and textures of 20 calcium-aluminum-rich inclusions from this chrondite indicated that they had crystallized from a liquid formed either by impact or direct condensation.

Another group of researchers had found anomalous oxygen isotope compositions in the calcium-aluminum-rich inclusions in the Allende meteorite, and concluded that the inclusions could never have been liquid, contrary to their textural appearance and to the constrained equilibrium theory. When their isotopic data were normalized relative to a consistent standard, the data did not support their conclusions but were consistent with the liquid droplet model and constrained equilibrium theory.

THERMAL CONDUCTIVITY OF ASSOCIATING GASES

Associating gases were known to have enhanced thermal conductivities and heat capacities, which could be useful in heat-transfer or power cycles. Thermal conductivity measurements were performed on a number of associating vapors to (1) characterize the types (size) of polymers present and gain a fundamental understanding of the factors that influence bond strength, (2) determine the thermodynamics of the individual association reactions and, hence, the extent of such reactions, and (3) determine the magnitude of the thermal conductivity augmentation. In addition to the experimental work, *ab initio* molecular orbital calculations were performed on various species to gain a better understanding of the process and provide a basis for comparisons of the experimental results.

The initial thermal conductivity measurements were made on H_2O, D_2O, acetone, 2,2,2-trifluoroethanol, and acetic acid vapors, using a thick hot-wire cell in the ranges of 0.07-2.0 atm and 47-143°C. The pressure dependence of the thermal conductivities for all five substances indicated that dimers were the only significant polymeric species. The enthalpies of association ranged from -3.36 to -4.75 kcal/mol for the first four species, but the value for acetic acid was -15.55 kcal/mol. The strong association of acetic acid suggests that it, or a derivative such as CF_3COOH, might be a good candidate for a heat-transfer or power-cycle working fluid.

A new thermal conductivity apparatus was constructed for use at pressures up to 500 kPa and temperatures up to 250°C, and additional measurements were made on various fluoropropanols, a fluorobutanol, pyridine, trifluoroacetric acid, and a methanol-water mixture. In the methanol-water mixtures the results indicated the presence of a methanol-water dimer and trimer, methanol tetramer, and water dimer. Trifluoroacetic acid associated very strongly, with a high thermal conductivity similar to that of acetic acid. The methanol-water system with a 2:1 trimer species also showed strong association (an enthalpy of -10.43 kcal/mol). The work on associating gases was performed primarily by Dave Frurip and Larry Curtiss.

FLUID CATALYSIS

Fluid catalysis involves the catalysis of a desired reaction in a system of two immiscible liquids. Hal Feder and Jerry Rathke began a program on this subject in 1977. The reactions that were being investigated have potential application in fuel conversion, energy storage, or feedstock manufacture. The objective was to elucidate the kinetics whereby homogeneous organometallic catalysts activate small molecules such as CO and direct their subsequent reactions into specific paths. According to one of the progress reports, "intimate details connecting the molecular structures of the catalysts, the nature of the intermediate species, and the thermochemical kinetic parameters of each reaction step are sought by a combination of techniques including chemical, spectral, and isotopic studies at high-temperature and high-pressure conditions." Due to space considerations, the intimate details are left to the imagination of the reader. Particular attention was directed toward synthesis gas, which consists mainly of hydrogen and carbon monoxide and is a principal reactant in the industrial production of numerous organic chemicals. Because it is potentially available from any carbonaceous material (*e.g.*, coal, wastes, biomass), it could become a key chemical intermediate for production of fuels or organic chemicals from new sources. One of the areas of work in this program concerned the use of a soluble mononuclear metal complex to catalyze the reaction of carbon monoxide and hydrogen. A particularly exciting development was the discovery of a new system for homogeneous conversion of methanol to ethanol. This system has the potential practical advantages that the ethanol itself is not homologated to higher alcohols, and that the main byproduct is carbon dioxide rather than water, so the ethanol product is anhydrous.

One branch of this research effort was to explore new ways of using homogeneous catalysts that would enhance the separability of the catalysts and the reaction products. Three approaches were identified: (1) partition catalysts (two immiscible liquid phases with controlled partition of the catalyst between them), (2) supported catalysts (catalyst anchored by strong bonds to solid oxides or porous polymers), and (3) surfactant catalysis (catalytic centers attached by covalent bonds to lipophilic or lipophobic entities in such a way as to produce micelles or bilayer membranes).

ENVIRONMENTAL CHEMISTRY

In 1973, Paul Cunningham and Stan Johnson undertook a program of environmental studies related to atmospheric pollution, and, later on, Ben Holt and Romesh Kumar joined the effort. The Analytical Chemistry Laboratory was also a major contributor. The objectives were to gain an understanding of the chemistry of airborne particulate matter, with emphasis on the mechanisms and kinetics for the formation of primary (at the source) and secondary (in the atmosphere) sulfates, nitrates, and other pollutants. This effort involved the development of air-sampling devices, instruments, and analytical techniques to characterize atmospheric aerosols, in addition to laboratory experiments to investigate the formation of pollutants.

Infrared (IR) spectroscopy was selected as the primary method of analysis, and, in the initial studies, air samples were taken at ANL and in Chicago. The results indicated that the smaller particles (<1 μm dia) were composed mainly of ammonium sulfate [$(NH_4)_2SO_4$], whereas the larger particles consisted of carbonates, silicates, and surface nitrates with almost no ammonium sulfate. The sulfate was believed to have come from a heterogeneous oxidation of SO_2 to SO_3, which then reacted with ammonia.

Two possibilities were proposed for the oxidation of sulfur dioxide: (1) a homogeneous oxidation of SO_2 to SO_3, and (2) a heterogeneous reaction in which the SO_2 was first sorbed on a cloud droplet or aerosol particle and then oxidized to sulfate. Because the isotopic ratio of O-18/O-16 in the product was significantly different for these two oxidation mechanisms, it was possible to identify which mechanism was predominant in a particular case.

Air samples were taken by two methods, inertial impaction, in which the particles impinged on a collection surface, and filtration. Introduced in 1977 was IR Fourier-transform analysis, which greatly increased the sensitivity and accuracy of the analyses and permitted determinations of nitrate, acidic and neutral sulfate, ammonium ions, and total hydrocarbons on particle samples collected by impactors or filters. A multiple internal reflection technique was then adopted, which greatly increased the sensitivity and made possible very short sampling times for polluted industrial and urban air as well as power plant plumes. These advances in sampling and analytical techniques made it possible to analyze specimens directly on the collectors with no intermediate handling.

Laboratory experiments were conducted in a flow reactor system in which seed aerosol, reactive gases (O_3, SO_2, NO, NO_2, and NH_3), and ultraviolet light could be introduced in a controlled way to simulate typical or extreme conditions for particulate formation.

Much of the environmental work was done in cooperation with other organizations. In 1975, ANL field studies were partially supported by the Midwest Interstate Sulfur Transport and Transformation (MISTT) study. In the summer of 1975, samples were collected in St. Louis, MO, and in two rural locations in central Illinois. The total sulfate was lower in the rural areas, but the acidity was higher. In 1976, ERDA implemented the Multistate Atmospheric Power Production Pollution Study (MAP3S), which leads one to wonder if acronyms are raging out of control when their letters have to be exponentiated. Samples were collected at College Town, PA; Charlottesville, VA; Rockport, IN; and Uptown and Roquette, NY. In general, there were wide variations in sulfate activity, and the nitrate levels were very low. The aerosol acidities were higher in the Eastern states than in the Midwest.

Two items that were beginning to be addressed at the end of the 1970s were (1) a need for data on liquid-vapor phase equilibria in the system NO_x-SO_x-H_2O-NH_3 to gain a better understanding of nitrogen behavior in the atmosphere, and (2) the role of SiO_2, which is believed to be produced by the reoxidation of SiO resulting from the reduction of SiO_2 by hot carbon char during coal combustion. Over 25% of the submicron particulate in samples from the Southwest proved to be SiO_2.

The use of dolomite to control sulfur dioxide emissions in coal combustion plants was mentioned earlier. Some supporting basic chemistry studies in that area were conducted by the Environmental Chemistry Group. In the regeneration of spent dolomite, two competing reactions occur in the reduction of calcium sulfate by hydrogen, one producing calcium sulfide and the other, calcium oxide. The sulfide was the predominant product, but the oxide was more desirable from a process standpoint. Introduction of as little as 1% water vapor caused the reaction to produce only calcium oxide.

Studies of the dolomite-SO_2 reaction were undertaken to evaluate the effect of structural disorder in the dolomite on the reaction rate. Experimental methods for defining the magnitude of morphological disorder (porosity, surface area, *etc.*) were well established, but a quantitative determination of structural disorder of a reacting solid in terms of defects, dislocations, stacking disorder, cleavage, *etc.*, as compared to an ideal, well-ordered crystal was a difficult problem. X-ray diffraction and high-voltage electron microscopy were selected as possible investigative techniques. In studies of the conversion of dolomite to the half-calcined product, the conversion yield at 640°C was about 15% after several hours, but at 800°C the yield was close to 100% within 20 min. This result suggested that the higher temperature might have caused additional structural disorder, but X-ray could not confirm this due to the complexity of the system. The electron-diffraction and electron-microscopic studies of half-calcined dolomite and 50% sulfated material showed numerous disorder features. Further detailed basic studies on dolomite and its sulfated products were not planned because the complexity of the systems seemed to preclude definitive results.

Analytical Chemistry Laboratory

The creation of the Analytical Chemistry Laboratory (ACL) as a separate entity within CEN in 1971 was mentioned earlier in the discussion of the Division's organization. The stated functions of ACL at the time were the following:

1. To provide assistance to scientists and engineers in solving analytical problems that were outside their area of expertise or that required specialized equipment.
2. To perform routine analyses, thereby using the Laboratory's resources efficiently.
3. To conduct research and development studies, as required, to provide the ACL with the capabilities to meet the needs of the Laboratory's programs.

In the late 1970s, about two-thirds of the work by ACL was for CEN programs; the remainder was scattered widely among other ANL divisions, the main ones being the Chemistry and Materials Science Divisions. The workload was approximately 1,500 jobs per year, which required more than 16,000 separate analyses. The staff amounted to about 30 people.

In 1977, ACL received direct support from DOE for a development program on instruments to identify and measure organic environmental contaminants. The instrument that was developed consisted of a gas chromatograph, time-of-flight mass spectrometer, and computer system. In 1979, a plutonium analytical facility, which had been under construction for several years, became operational. This facility was used primarily for work involving plutonium-containing wastes.

The ACL had a major role in nearly all of the research and development programs in CEN, not only in performing analyses, but also serving in an advisory capacity, and, in some cases, lending personnel to work within particular programs. It is probably no exaggeration to say that few, if any of the major research and development programs in CEN could have been conducted successfully without the participation of the ACL.

Nuclear Safeguards

In June 1970, at the request of AEC's Office of Safeguards and Materials Management, the Division began work aimed at developing general design criteria for safeguarding Special Nuclear Materials (SNM) in nuclear facilities. Heading the group organized for this effort was Dr. Stephen Lawroski, the former Director of CEN. Members of the group included Leonard Link, John Loeding, Charles Bean, and Wally Seefeldt. The materials covered by SNM were plutonium, uranium-233, and uranium highly enriched with U-235. Some attention was also given to protection of facilities handling low-enrichment uranium.

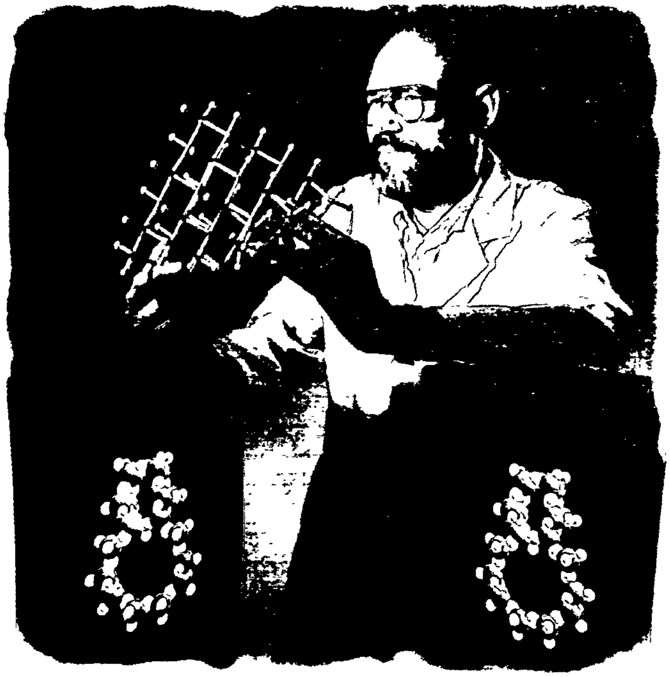
In the mid-1970s, this work came under the aegis of the newly formed Nuclear Regulatory Commission (NRC), and the group began to assist the Office of Standards Development of NRC with the preparation of safeguards measures. These measures were designed to deter, prevent, or respond to (1) the unauthorized possession or use of significant quantities of nuclear materials through theft or diversion and (2) sabotage of nuclear facilities. The two basic safeguards measures were physical protection and materials control and accounting. The Division's program provided background information, rationale, and technical data for NRC criteria, guides, and reports in support of these safeguards objectives. The criteria were the basis for NRC's rules and regulations; the guides defined the rules and identified acceptable ways of complying with them; the reports helped the licensee to understand the regulations and guides.

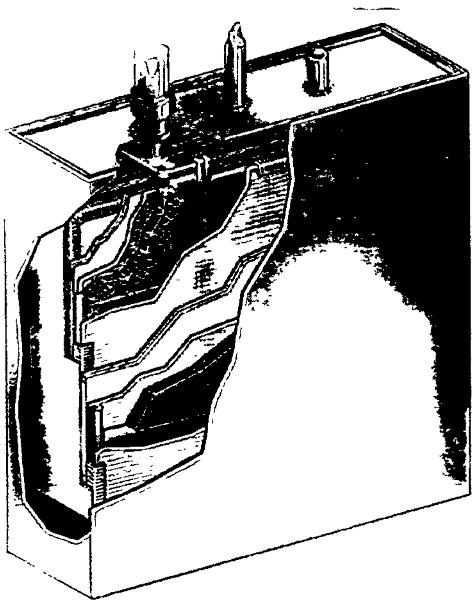
The output of the group was a set of draft criteria, guides, and reports for use by NRC. The NRC prepared all final versions for publication. Included in the output of this group were the following:

1. Draft criteria for design and startup of processing plants.
2. Three guides on security clearance requirements.
3. Three guides on holdup of SNM in equipment, design and placement of physical barriers, and materials-protection contingency measures at processing and fabrication plants.
4. Reports on factors affecting theft vulnerability and on protection of hazardous materials such as by-product fission products and small quantities of SNM.
5. A study of the feasibility of dynamic inventory in fuel fabrication and processing plants and of potential methods for accomplishing such an inventory.
6. A report on bullet-resistant materials to aid licensees in design and construction of control rooms and central alarm stations for nuclear facilities, *e.g.*, reactors and processing plants.

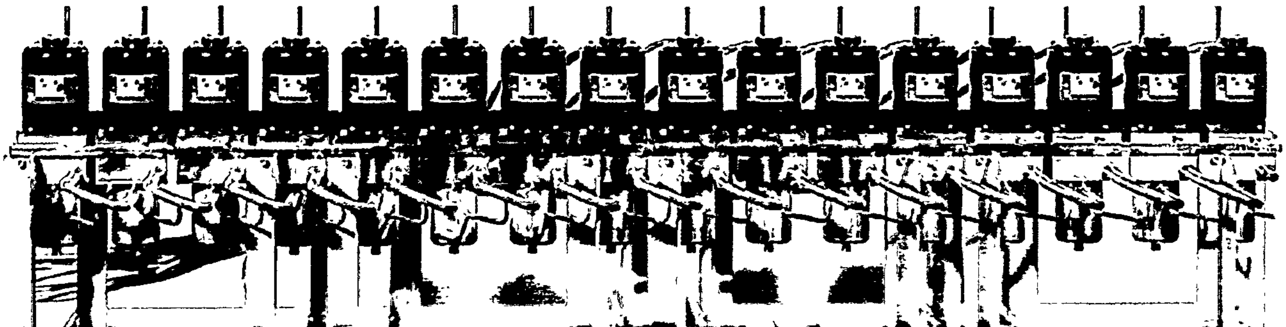
This program came to an end in 1977 when the contract for performing it expired.

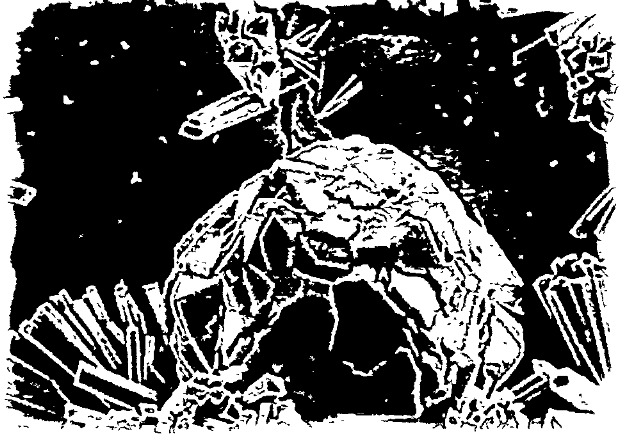
FROM TEST TUBE TO PILOT PLANT





1980-1990: CMT – NEW NAME, NEW MISSIONS





A 50 YEAR HISTORY OF THE CHEMICAL TECHNOLOGY DIVISION

1980-1990

(top, left) Molecular models used in basic science studies of materials properties.

(top, right) Prismatic design developed for lithium/iron sulfide cell intended for electric-vehicle application.

(bottom) Bank of centrifugal contactors, which are used to remove transuranic elements from a waste stream through differences in the distribution of the waste components between immiscible aqueous and organic phases.

(bottom, right) Micrograph showing surface of waste glass sample after corrosion testing to study its long-term behavior under conditions relevant to geologic disposal.

5

1980-1990: CMT—New Name, New Missions

At the beginning of 1980, the morale of the nation was depressed by the continuing hostage situation in Iran and an unfavorable economy. President Jimmy Carter was soundly defeated by Ronald Reagan in the 1980 election. Reagan and his Vice President, George Bush, served two terms, and in 1988 Bush defeated Michael Dukakis in a race for the presidency.

Although the United States was not technically involved in a war in the 1980s, neither was it entirely at peace. Unrest was rampant throughout the world with assassinations, hostage taking, and hijacking, and the U.S. was involved in several limited military actions. The Cold War continued with Reagan taking a strongly anti-Communist stance (the "Evil Empire") until 1985 when he met with Mikhail Gorbachev, which relaxed the tension somewhat, and the Berlin Wall was opened in 1989, about seven months after a disastrous explosion and fire at the Chernobyl nuclear power plant. The Communist regime in the Soviet Union was beginning to crumble.

In the U.S., nuclear utilities were still constructing power plants and putting them in operation, but no orders were placed for new plants. Public confidence in nuclear power had been shaken by the accidents at Three Mile Island and Chernobyl. In addition to the perceived safety problems, the disposal of nuclear wastes became a major issue that was at least as much political as it was technical.

During the 1980s, scientific research and development was subjected to severe budget cuts, not only by the U.S. government, but also by industries attempting to improve their profitability. The decline in financial support was accompanied by decreasing enrollments of university students in science and engineering courses.

At Argonne, Dr. Alan Schriesheim replaced Dr. Massey as Laboratory Director on May 10, 1984. The Laboratory, by this time, had shifted its emphasis strongly toward environmental and alternative energy research in accordance with changes in the DOE priorities. Several new divisions or groups had been formed at Argonne to handle the new programs. Within the Division, the level of effort on high-temperature lithium alloy/metal sulfide batteries decreased significantly, and a greater emphasis was placed on nuclear technology. A major nuclear initiative was the Integral Fast Reactor (IFR), which combined an EBR-II-type metal-fueled reactor with an on-site electrometallurgical fuel recovery and recycle system.

Les Burris, who continued as Director of the Chemical Engineering Division until 1984, was succeeded by Dr. Martin Steindler, a chemist and long-term member of the organization. On July 19, 1982, the Chemical Engineering Division was renamed the "Chemical Technology Division" (CMT) to reflect more accurately the nature of its work. Another long-term ANL tradition ended in the 1980s when the emergency telephone number was changed from "Dial 13" to "911," which had become a national standard.

The 1980s was a difficult period for the CMT Division, as well as many other research organizations, because of shifting national priorities, funding uncertainties, and other pressures. During the course of the decade, the number of full-time personnel in the Division decreased by about 40%.

NATIONAL AFFAIRS

The people of the United States entered the 1980s with a feeling of despair about the hostages in Iran and worries over an economy gone awry. The inflation rate was 12%, unemployment in "rust belt" cities had reached 15-20%, and the prime lending rate was 15%. The country was sliding into a recession that persisted well into 1982. Morale was diminished further by Operation "Eagle Claw," a clandestine military attempt to rescue the hostages from the embassy in Teheran and remove them from Iran by airlift. Not only was the feasibility of the operation questionable, but poor planning and execution led to its complete failure with eight American fatalities and five injuries. The Iranians responded by dispersing the hostages to ensure that any further such attempts would be futile. The American public was heartsick over the situation, and people tied yellow ribbons around trees to express their frustration.

The faltering economy, the hostage situation, and several other factors set the stage for a decisive defeat of Jimmy Carter and Walter Mondale by Ronald Reagan and George Bush in the 1980 presidential election. Reagan came on with an optimistic attitude, confidence about the future, and a strong sense of patriotism. The hostages were released two days before his inauguration, which further enhanced his popularity. But the euphoria was short-lived. On March 30, only two months after his inauguration, Reagan was shot in an assassination attempt by John W. Hinckley, who was pronounced not guilty by reason of insanity. Reagan's press secretary, James Brady, and two secret service officers were also wounded. On August 3, the U.S. air controllers went on an illegal strike and were fired summarily on August 11 by Reagan's orders. This event had a chilling effect on the union movement throughout the U.S.

Reagan and Bush were reelected by a landslide vote in the 1984 contest against Walter Mondale and Geraldine Ferraro. In the 1988 election, George Bush and Dan Quayle defeated Michael Dukakis and Lloyd Bentson, giving the Republicans a 12-year tenancy in the White House.

In the early 1980s, the "cold war" with the Soviet Union was still the primary concern in American foreign policy. Reagan was strongly anti-Communist and felt that the U.S. should deal from a position of strength. One of his top priorities in office was to increase the size and power of the U.S. military forces. Terrorist activities and limited military actions seemed to have replaced all-out wars around the world. Argentina, in 1982, attacked the Falkland Islands and was defeated by the British, with the U.S. providing only logistic support. In 1983, a truck bomb killed 237 U.S. Marines, who were assigned to a peacekeeping mission in Beirut, Lebanon. Just six months earlier, 50 people had lost their lives in an attack on the American Embassy in Lebanon. In October of that same year, the United States mounted an attack on the island of Grenada over a concern that Cubans were building an airstrip there for shipment of communist arms to Nicaragua and El Salvador. In spite of overwhelming firepower, 133 Americans were killed or wounded. Reagan was almost obsessive about the leftist Sandinistas who had taken control of Nicaragua in 1985, and strongly supported the Contra guerrillas who were attempting to overthrow the Sandinista regime. A covert operation in which proceeds from arms sales to Iran were diverted to aid the Contras resulted in the so-called "Iran-Contra" affair, which surfaced in 1987 and culminated in congressional hearings that featured Marine Lt. Col. Oliver North, Jr. North and arms dealer Richard Secord were convicted, but North's conviction was later overturned in an Appeals Court. Reagan denied any knowledge of the operation and escaped unscathed, which was one of the reasons he was dubbed the "Teflon President." Also in 1987, Iraqi missiles killed 17 Americans on the

U.S.S. *Stark*. Iraq issued an apology. The Iranians, in an attempt to block oil shipments through the Gulf of Iran, laid mines and built gun emplacements, which provoked skirmishes with the U.S. Navy that erupted into a crisis when the cruiser, U.S.S. *Vincennes*, mistakenly shot down a civilian Iranian airliner with a loss of 290 lives. The last U.S. military action in the 1980s was an attack on Panama to free it from dictatorial control by strongman Gen. Manuel Noriega, who had been indicted by the U.S. on drug-dealing charges.

Numerous other instances of terrorism, such as plane hijackings and hostage taking, occurred throughout the 1980s. Three nuns and a lay worker were shot in El Salvador in 1981, and a South Korean Boeing 747 was shot down by the Russians, killing 269 passengers. Indira Gandhi, Prime Minister of India, was assassinated by Sikh terrorists, and anti-Sikh riots ensued with an estimated 1,000 deaths in 1984. In 1985, a TWA airliner was hijacked by two Shiite Moslems, the cruise ship *Achille Lauro* was hijacked with one American fatality, terrorists seized an Egyptian Boeing 737 with 59 killed in a rescue attempt, and nine were killed at airports in Rome and Vienna. In 1988, Soviet and Kuwaiti planes and an Aegean cruise ship were hijacked with further loss of life. The biggest blow to the U.S. was the bombing of a Pan Am Boeing 747 over Lockerbie, Scotland, which killed 259 passengers and nine on the ground. Besides the terrorism, concern was growing about the escalation of chemical and nuclear weapons. Israel bombed an Iraqi nuclear facility in 1981, Iraq bombed an Iranian nuclear plant in 1985, Libya used chemical weapons on Chad in 1987, and Iran and Iraq used chemical weapons on each other in their border war of 1988.

The 1980s were marred by several major accidents. In 1984, a toxic gas leak from a Union Carbide plant in Bhopal, India, resulted in 2,000 deaths and 150,000 injuries. A chartered plane carrying U.S. military personnel crashed in Newfoundland in 1985, killing 248 U.S. soldiers. In 1989, the Exxon tanker *Valdez* ran aground in Prince William Sound, Alaska, releasing 11 million barrels of crude oil. The decade was topped off by the Chernobyl disaster in 1989.

The Soviet Union underwent some wrenching changes, starting with the successive deaths of several leaders: Leonid Brezhnev in 1982, Yuri Andropov in 1984, and Konstantin Chernenko in 1985, who was replaced by Mikhail Gorbachev. Reagan, who had been adamant about any negotiations with the Communists up to that time, met with Gorbachev on November 19, 1985, and the tension began to thaw. It was during this period that Reagan said, "Mr. Gorbachev, tear down that wall!" Relations started to improve gradually, and the Berlin Wall was finally opened to the West in 1989.

The U.S. continued its space program, with emphasis on the Space Shuttles. Original launchings of the four shuttles were *Columbia* (4/12/81), *Challenger* (4/4/83), *Discovery* (8/30/84), and *Atlantis* (10/3/85). The shuttle flights became almost routine until January 28, 1986, when the *Challenger* exploded 72 seconds after lift-off, killing all seven aboard. This was a severe shock to the American public, compounded by the fact that one of the casualties was a school teacher, Christa McAuliffe, whose participation had been highly publicized, and many children witnessed the accident on television. The explosion was attributed to an O-ring failure in the propulsion system, and further shuttle flights were postponed until the *Discovery* was launched on September 9, 1988. An unmanned space probe, *Magellan*, which was launched on May 4, 1989, to explore Venus, used radar to generate a geological map of the planet.

Reagan and Bush both seemed to be basically neutral on the issue of nuclear power, which Carter had opposed. Carter had been more concerned about future energy sources for the U.S., and had encouraged research and development work on conservation and alternative technologies to meet the need. The national laboratories were funded to conduct research and development in these areas, with an emphasis on the use of subcontracts and other working agreements to transfer the new technologies to industry as they became available. Reagan had an opposing viewpoint on this matter. He felt that private industries should fulfill these needs themselves, using their own resources. An example of this approach was a reduction of annual government funding from about 155 to 35 million dollars for solar energy research. Reagan, intent on decreasing federal expenditures, brought in a Budget Director, David Stockman, who achieved notoriety by studying the budget in great detail and coming up with specific funding cuts for nearly every activity in the government. The one area of research and development funding that remained healthy was national defense, but about 80% of that money was diverted toward weaponry procurement rather than technology development.

Significant changes were also occurring in the economic and business institutions of the country. Strong emphasis was placed on bottom-line profits for the next quarter or two with little thought given to long-range strategies. Corporate takeovers and severe downsizing became prevalent. Once the oil crisis of 1979, the recession of 1982, and the high interest rates of the 1970s had subsided, the U.S. underwent a period of rapid economic expansion. The only major concerns were the ongoing rapid increases in the national debt and trade deficits. The emphasis on short-range profits at the expense of long-range planning by industry caused the downsizing or complete elimination of many corporate research laboratories. This was a particularly serious problem in view of foreign competition. In 1960 about 17% of the 47,000 U.S. patents were issued to foreign holders. By 1987, the figure was about 49% of the 88,000 U.S. patents. Although these figures are not necessarily a quantitative measure of the problem, they illustrate a trend. The fates of many corporate research laboratories were exemplified by a subcontract that the CMT high-temperature battery group had with the Carborundum Company's research organization to develop and supply boron nitride cloth separators for lithium alloy/iron sulfide cells. The Carborundum research organization had an excellent reputation and lived up to it by developing an innovative process for boron nitride fiber production and forming the fibers into a variety of felts and woven cloths on the scale required by the battery program. At this point, the Carborundum Company was taken over by the Kennecott Copper Corp., which absorbed most of the Carborundum research activities into the Kennecott Labs. Within a matter of months, Kennecott was taken over by Sohio and the process was repeated. Even the large, highly respected corporate research laboratories, where major discoveries such as the transistor were made and Nobel-prize winning basic research was done, became the Rodney Dangerfields of the corporate world. One exception to this trend was in the computer industry, where much highly competitive research was done, but much of that consisted of short-range efforts toward incremental extensions of the existing technology.

Similar observations could be made about U.S. universities and colleges. The public perception of science and technology seemed less favorable than in the past. The proportion of American university and college students majoring in the sciences had dropped by about 40% in the 1980s. The reason for that is not obvious, but self-interest would suggest to a student entering college that exiting with an MBA would be more likely to lead to a higher salary and better employment opportunities than would a Ph.D. in one of the sciences, and in considerably less time. The prevailing conventional wisdom that a person entering the work force will have to make six or seven career changes during his or her lifetime is a disincentive to spending the ten years or so beyond high school that are required to become a research scientist in some specialty. In the graduate schools, foreign students who constituted about 50% of the total in science and engineering took up much of the slack. Some of the foreign students returned to their native countries, while others remained permanently in the U.S. and have now become a large proportion of the nation's practicing scientists and engineers. The universities also felt the brunt of reduced federal funding in the 1980s. Research grants and contracts were reduced or eliminated in many cases, and funding for facilities was hard to find.

Thus, all three of the nation's major research and development institutions—industry, the universities, and the national laboratories—were feeling the financial crunch of the 1980s. Two major reductions in force, one near the end of 1981 and the other in mid-1982, decreased the manpower at Argonne from about 5200 to 4200.

Although the 1980s were not a particularly sanguine period in general, they had their bright spots, among which were "firsts" that were achieved by several women. Sandra Day O'Conner was the first woman appointed to the Supreme Court (1981), Dr. Sally K. Ride was the first woman astronaut in space (1983), Dr. Kathryn D. Sullivan was the first to walk in space (1984), Geraldine Ferraro was the first woman to run on the national ticket for Vice President of the United States (1984), and Hanna H. Gray was the first female president of the University of Chicago. Apparently President Gray's first introduction to the Argonne site was when she was to be honored at a reception on a hot, humid summer day in the cafeteria building. A tornado alert sounded, and everybody was herded into the basement where they sweltered while standing under water pipes dripping with condensation. Apparently, she found the situation somewhat amusing, at least in retrospect.

THE NUCLEAR INDUSTRY

By 1980, nuclear power had become a controversial issue, partly because of concerns such as safety, nuclear proliferation, and radioactive waste storage, and partly because of uncertainty about its economic competitiveness. People on both sides of the nuclear issue raised many complex questions, for which there were no unequivocal answers. Few if any plans were being made for new nuclear power plants after 1979, but many plants were still under construction and scheduled for startup in the 1980s and 1990s. The more significant ones are listed in Table 5-1.

The waning interest in nuclear power was reflected by the fact that several major universities in the U.S. were phasing out their nuclear engineering departments, which, in some cases, included research reactors.

THE DIVISION

Dr. Walter Massey continued in the position of Laboratory Director at Argonne until May 10, 1984, when he was succeeded by Dr. Alan Schriesheim. Schriesheim had earned a Ph.D. in physical organic chemistry at Pennsylvania State University and had been General Manager of the Technical Department in the Corporate Research Laboratories of the Exxon Research and Engineering Company. Dr. Schriesheim was the first Laboratory Director with a background primarily in industrial research, which was no doubt a major asset in the competitive environment of the 1980s. He had a purposeful, thoughtful manner and seemed very interested in receiving input from the staff. He maintained a schedule of breakfasts with senior technical personnel with no particular agenda, just to talk over whatever was on their minds. Another aspect of his administration that requires mention was

Table 5-1. Power Reactors Started up in the 1980s and 1990s

		Type	MW(e)	Start
Arkansas Nuclear One 2 (Russellville, AR)	Energy Operations, Inc.	PWR	836	3/80
North Anna 2 (Mineral, VA)	Virginia Power	PWR	897	12/80
Joseph M. Farley 2 (Dothan, AL)	Southern Nuclear Operating Co.	PWR	860	7/81
Sequoyah 1 (Soddy-Daisy, TN)	Tennessee Valley Authority	PWR	1148	7/81
Salem 2 (Salem, NJ)	Pub. Serv. Electric & Gas Co.	PWR	1106	10/81
McGuire 1 (Cornelius, NC)	Duke Power Co.	PWR	1129	12/81
Sequoyah 2 (Soddy-Daisy, TN)	Tennessee Valley Authority	PWR	1148	6/82
Susquehanna 1 (Berwick, PA)	Penn. Power & Light Co.	BWR	1082	6/83
San Onofre 2 (San Clemente, CA)	So. Cal, Ed. & San Diego G. & E.	PWR	1070	8/83
St. Lucie 2 (Hutchinson Island, FL)	Florida Power & Light Co.	PWR	839	8/83
LaSalle County 1 (Seneca, IL)	Commonwealth Edison Co.	BWR	1078	1/84
Virgil C. Summer (Parr, SC)	So. Carolina Electric & Gas Co.	PWR	885	1/84
McGuire 2 (Cornelius, NC)	Duke Power Co.	PWR	1129	3/84
San Onofre 3 (San Clemente, CA)	So. Cal. Ed. & San Diego G. & E.	PWR	1080	4/84
LaSalle County 2 (Seneca, IL)	Commonwealth Edison Co.	BWR	1078	10/84
WNP-2 (Richland, WA)	Wash. Pub. Power Supply Syst.	BWR	1157	12/84
Susquehanna 2 (Berwick, PA)	Penn. Power & Light Co.	BWR	1091	2/85
Callaway (Fulton, MO)	Union Electric Co.	PWR	1171	4/85
Diablo Canyon 1 (Avila Beach, CA)	Pacific Gas & Electric Co.	PWR	1073	5/85
Catawba 1 (Clover, SC)	Duke Power Co.	PWR	1129	6/85
Grand Gulf (Port Gibson, MS)	Energy Operations, Inc.	BWR	1173	7/85
Byron 1 (Byron, IL)	Commonwealth Edison Co.	PWR	1105	9/85
Waterford 3 (Taft, LA)	Energy Operations, Inc.	PWR	1075	9/85
Wolf Creek (Burlington, KS)	Wolf Creek Nucl. Oper. Corp.	PWR	1160	9/85
Palos Verde 1 (Wintersberg, AZ)	Arizona Public Service Co.	PWR	1221	1/86
Limerick 1 (Pottstown, PA)	PECO Energy Co.	BWR	1055	2/86
Diablo Canyon 2 (Avila Beach, CA)	Pacific Gas & Electric Co.	PWR	1087	3/86
Millstone 3 (Waterford, CT)	Northeast Utilities	PWR	1149	4/86
River Bend (St. Francisville, LA)	Energy Operations, Inc.	BWR	936	6/86
Catawba 2 (Clover, SC)	Duke Power Co.	PWR	1129	8/86
Palos Verde 2 (Wintersberg, AZ)	Arizona Public Service Co.	PWR	1221	9/86
Hope Creek (Salem, NJ)	Pub. Serv. Electric & Gas Co.	BWR	1031	12/86
Clinton (Clinton, IL)	Illinois Power Co.	BWR	930	4/87
Alvin W. Vogtle 1 (Waynesboro, GA)	Georgia Power Co.	PWR	1162	5/87
Shearon Harris (New Hill, NC)	Carolina Power & Light Co.	PWR	860	5/87
Byron 2 (Byron, IL)	Commonwealth Edison Co.	PWR	1105	8/87
Beaver Valley 2 (Shippingport, PA)	Duquesne Light Co.	PWR	833	11/87
Perry 1 (North Perry, OH)	Cleveland Electric Illum, Co.	BWR	1205	11/87
Palos Verde 3 (Wintersberg, AZ)	Arizona Public Service Co.	PWR	1221	1/88
Fermi 2 (Newport, MI)	Detroit Edison Co.	BWR	810	1/88
Nine Mile Point 2 (Scriba, NY)	Niagara Mohawk Power Co.	BWR	1080	4/88
Braidwood 1 (Braidwood, IL)	Commonwealth Edison Co.	PWR	1120	7/88

South Texas Project 1 (Palacios, TX)	Houston Lighting & Power Co.	PWR	1250	8/88
Braidwood 2 (Braidwood, IL)	Commonwealth Edison Co.	PWR	1120	10/88
Alvin W. Vogtle 2 (Waynesboro, GA)	Georgia Power Co.	PWR	1162	5/89
South Texas Project 2 (Palacios, TX)	Houston Lighting & Power Co.	PWR	1250	6/89
Limerick 2 (Pottstown, (PA)	PECO Energy Co.	BWR	1055	1/90
Seabrook (Seabrook, NH)	No. Atlantic Energy Serv. Co.	PWR	1150	7/90
Comanche Peak 1 (Glen Rose, TX)	Texas Utilities Co.	PWR	1150	8/90
Comanche Peak 2 (Glen Peak, TX)	Texas Utilities Co.	PWR	1150	8/93

the activities of his wife Beatrice, who was responsible for many improvements in the overall appearance of the Laboratory. The cafeteria was remodeled with various enhancements, including trees among the tables, and the lobbies and other public areas of many of the buildings were redecorated. By the time the numerous improvements in the appearance of the buildings and grounds were completed, just about all of the last vestiges of the "military base" appearance of Argonne were gone, and the site had more the appearance of a university or corporate research campus.

The Associate Laboratory Directors most concerned with the programs in the Chemical Engineering Division were Dr. John J. Roberts (Energy and Environmental Technology) and Dr. Charles E. Till (Engineering Research and Development).

As of 1980, the upper management of the Chemical Engineering Division comprised the following:

Division Director:	Leslie Burris
Deputy Division Director:	Donald S. Webster
Associate Division Directors:	Duane L. Barney Fred A. Cafasso Martin J. Steindler
Assistant Division Directors:	Ronald L. Breyne Herbert L. Brown, Jr.

Paul Nelson and Al Jonke do not appear on this list because they were in Associate Laboratory Directors' organizations at the time, but both returned to CMT, whereupon Paul replaced Don Webster, who had retired, as the Deputy Division Director, and Al returned to his position as an Associate Division Director. Because of the many programmatic changes in the 1980s and the numerous reorganizations to accommodate these changes, Section Heads, Group Leaders, Program Managers, *etc*., are not listed here, but are mentioned in the section on technical programs.

When the Chemical Engineering Division was formed in 1948, its work consisted largely of engineering research and development work on solvent-extraction processes for the recovery of spent reactor fuels. By 1980, the Division had undergone two major stages of diversification from that original mission. The first stage was a move into other nuclear areas such as nuclear safety, materials research, and basic research on the properties of reactor materials. The second stage involved non-nuclear research and development of all types of energy sources, a mission that ERDA had assigned to all the multipurpose national laboratories. The Division's activities at the time fell into three general categories: (1) process and equipment development through engineering-scale demonstrations, (2) applied chemistry, and (3) basic research in a variety of areas, some of which were related to the applied technology programs.

The distribution of funding in 1981 was approximately as follows: electrochemical technology (batteries and fuel cells), 62%; fusion power technology, 15%; coal combustion technology, 15%; basic energy sciences, 8%.

In view of this diversification, the time was ripe for the Division to adopt a more descriptive name, and, after a period of considerable agonizing by Les Burris and others, the name "Chemical Technology Division" was selected. There was some concern over the fact that a long-standing and highly respected group at Oak Ridge also had that name, but that did not seem to create a problem. Consequently, on July 19, 1982, CEN became CMT. The change was announced in a memorandum from John Roberts, which is reproduced in Fig. 5-2. A few people grumbled that the new name was not compatible with basic research, but it stuck with no apparent ill effects.

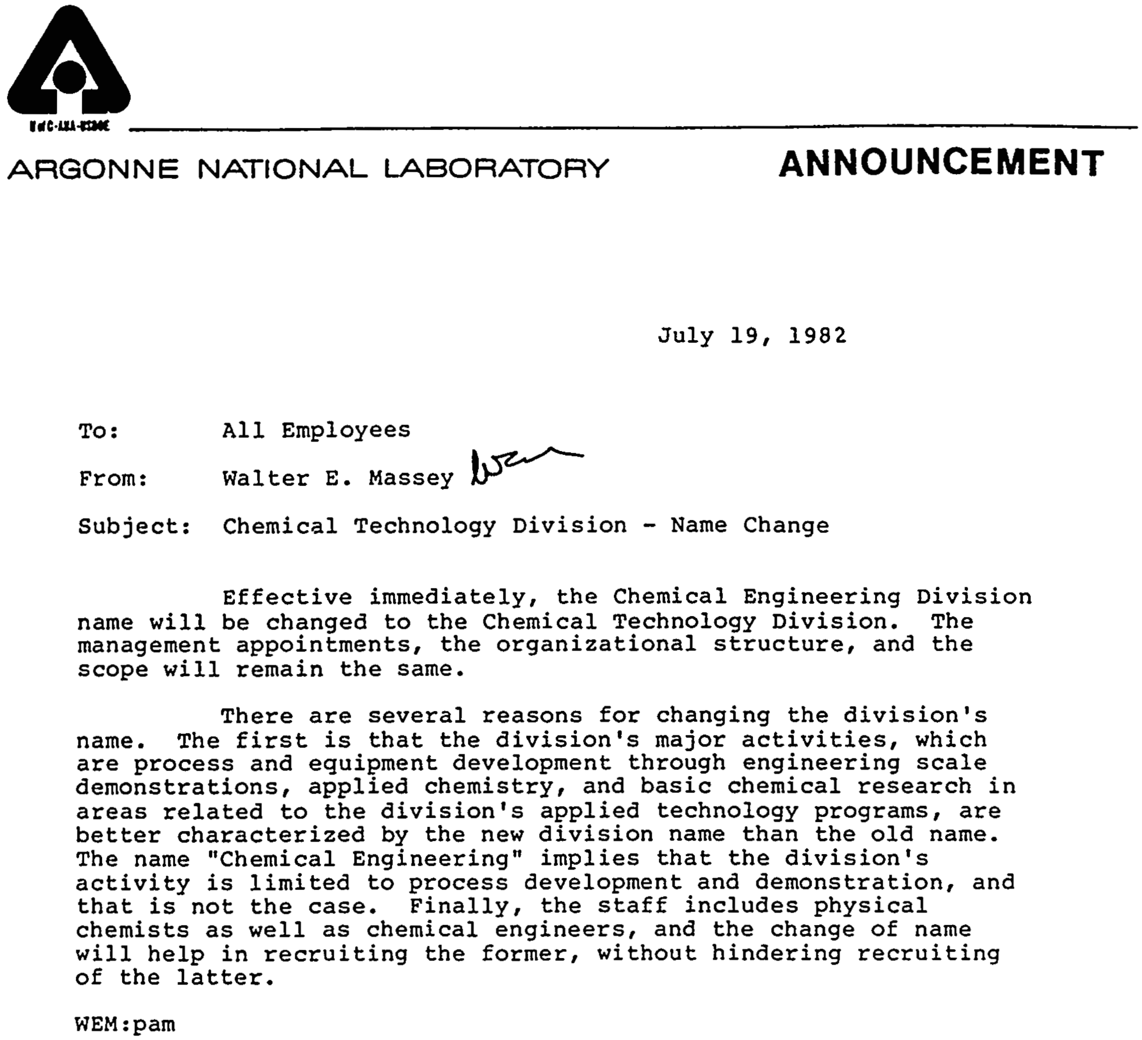
In 1984, Les Burris, after eleven years as Division Director, decided it was time to step down, and he was succeeded by Dr. Martin J. Steindler, who had started to work in the Division in the early 1950s after receiving a Ph.D. from the University of Chicago. Martin, after being initiated into the Division by working for Hal Feder, had been the lead player in much of the work on fluoride volatility processes and was responsible later for most of the nuclear work after the fuel-reprocessing programs had ended. It is an interesting fact that, even up to the present time, each engineer who has been the Division Director was succeeded by a chemist, and each chemist has been succeeded by an engineer. (Jim Battles is a Metallurgical Engineer.)

Fig. 5-1. Martin Steindler

As indicated earlier, budget cuts required a significant reduction in force at CMT from about 280 in 1980 to approximately 170 in 1989. One factor that alleviated the situation somewhat was that most of the staff members who had joined the Division in the late 1940s and early 1950s were reaching, or at least approaching, retirement age. The Laboratory offered attractive early retirement packages to those who were in the appropriate age brackets. There was an exodus of several upper management people from the Division. Don Webster retired in 1982 and Al Jonke in 1985. Duane Barney transferred to Washington, DC, on special assignment as an ANL employee. Fred Cafasso, in 1984, left the Division to accept an upper management position in the Chemistry Division. Numerous other people in the Division either retired or found work elsewhere, some in other divisions at Argonne. The tight funding situation in the Division was made worse by the fixed costs such as building maintenance, accounting, library, and utilities, which could not be reduced significantly.

The management situation in the Division tended to be fluid, with the various programs starting and stopping and several key people leaving. After the dust had settled, the upper management of the Division ended up as follows in 1989:

Division Director:	Martin J. Steindler
Deputy Division Director:	Paul A. Nelson



ARGONNE NATIONAL LABORATORY **ANNOUNCEMENT**

July 19, 1982

To: All Employees

From: Walter E. Massey

Subject: Chemical Technology Division - Name Change

Effective immediately, the Chemical Engineering Division name will be changed to the Chemical Technology Division. The management appointments, the organizational structure, and the scope will remain the same.

There are several reasons for changing the division's name. The first is that the division's major activities, which are process and equipment development through engineering scale demonstrations, applied chemistry, and basic chemical research in areas related to the division's applied technology programs, are better characterized by the new division name than the old name. The name "Chemical Engineering" implies that the division's activity is limited to process development and demonstration, and that is not the case. Finally, the staff includes physical chemists as well as chemical engineers, and the change of name will help in recruiting the former, without hindering recruiting of the latter.

WEM:pam

Fig. 5-2. A New Name for the Division

Associate Division Directors: David W. Green
Carl E. Johnson

Assistant Division Directors:
Ronald L. Breyne
Herbert L. Brown, Jr.

Responsibility for the Technical Editing Group, which had been under Gwen Kesser, was given to Joe Harmon in 1980. Those who served under Joe as technical editors at various times during the 1980s include Susan Barr, Dave Hamrin, Richard Keener, Penelope Raptis, and John Simmons. Maria Contos and Valerie Gaines were secretaries. Maria and Joe, in cooperation with the Computer Applications Group, instituted a system for computerized record keeping of all the Division's publications. Without that system, it would have been very difficult, if not impossible, to have written this volume. As of

1989, the Technical Editing Group consisted only of Joe and Maria. Unfortunately, the volume of work did not decrease in proportion to the size of the group.

The other supporting groups in the Division remained intact for the most part, albeit at reduced levels. As with the research and development groups, the workload was eased somewhat by the use of part-time retirees or other employees hired on Special Term Appointments (STAs).

Because the secretaries and clerks have an essential role in the operation of the Division, but do not normally receive personal recognition in publications, we have done our best to list in Table 5-2 all those who were in the Division at some time in the 1980s.

Helen Hill managed the Division office throughout the decade as the Director's secretary, first under Les Burris, and then under Martin Steindler. Marilyn Osborn was the Deputy Director's secretary, under Don Webster, and then Paul Nelson. Stefanie Chapman worked for Fred Cafasso, Lucille Jensen for Martin Steindler, Sherry Grisko for Duane Barney, Doris Worthington for Al Jonke, Judy Popik for John Ackerman, Cindy Wesolowski for Carl Johnson, Jan Steinquist for Dave Green, and Loretta Cescato for Jim Battles. Jan Muller was given additional administrative responsibilities in Herb Brown's office. Anne Melton, who had worked for Everett Proud and then Ron Breyne, retired in 1981. Others in Ron's office were Sofia Napora, Maria Colunga, Laurie Malak, Cindy Mau, Debbie Morgan, Teresa Clark, Debbie O'Rourke, Guadalupe Franchini, Heidi Rudolph, and Laurie Ammerpohl.

Table 5-2. Secretaries and Clerks in the CMT Division in the 1980s

- Lauren Ambrose
- Laurie Ammerpohl
- Margaret Anderson
- Vanessa Arzate
- Lilia (Mojica) Barbosa
- Jacqueline Bertoletti
- Alice Birmingham
- Marlene Bukowski
- Mary Burke
- Susan Bykowski
- Laurie (Malak) Carbaugh
- Janet Carothers
- Loretta Cescato
- Stefanie Chapman
- Teresa Clark
- Maria Colunga
- Maria Contos
- Valerie Crudup
- Nancy Deloria
- Linda Ellis
- Elaine Estand
- Guadalupe Franchini
- Dorothea Gabrovic
- Valerie Gaines
- Sherry Grisko
- Guadalupe Guzman
- Marian (Gardner) Harkins
- Helen Hill
- Lucille Jensen
- Kerri Kilian
- Wendy (Donnelly) Lamb
- Dawn Landis
- Teresa Lang
- Lee Legerski
- Charlotte LeGrand
- Stephanie (Malm) Malak
- Cindy (Mau) Meurer
- Deborah Morgan
- Janice (Lewin) Muller
- Sofia (Gawenda) Napora
- Deborah O'Rourke
- Marilyn Osborn
- Peggy (McBride) Parks
- Judith Popik
- Roberta Riel
- Heidi Rudolph
- Kathleen Shields
- Janet Steinquist
- Carol Stogsdill
- Virginia Strezo
- Wendy (Zanelli) Strle
- Audrey Taylor
- Donna Tipton
- Sandra Tummillo
- J. Van Dahm
- Denise Voss
- Coleen Weeks
- Cynthia Wesolowski
- Cynthia Wilkinson
- Kathy Willis
- Doris (Michalek) Worthington

The Division did not escape Mrs. Schriesheim's aggressive beautification program, and it was probably a good thing. Building 205, after 50 years of hard use, was ready for a cosmetic upgrade, and the Division management was agreeable to the idea. In the public areas, lighting was modernized, floors were retiled, walls were painted, and broken plaster was repaired. Some of those things had been done before, but not all at once. The overall effect was impressive; one had the feeling of being in a brand new building. A major item in the upgrading was the Division library, which had been relocated to the east end of L-Wing in the 1960s when Dr. Vogel moved the Division Office to A-Wing. The library, which occupies about 2,000 square feet, and had undergone only a few changes since that time, was completely revamped in 1985-86 to satisfy Mrs. Schriesheim's decorating requirements and Martin Steindler's insistence on functionality; it is now an efficient, attractive place to work.

The morale of the personnel in the 1980s was obviously affected by the budget cuts and layoffs, but perhaps even more so by increasing micromanagement of the programs, especially by DOE. There were more and more program reviews, on-site inspections, and reporting requirements, as well as hundreds of new regulations relating to safety, quality assurance, personnel matters, environmental concerns, and other areas. At the same time, DOE was requesting many technical studies and evaluations that had to be done with existing personnel, often on short notice. Few would argue with the good intent of most of the individual items, but, taken as a whole, they required large amounts of additional paperwork and time. The increasing tendency toward micromanagement of the national laboratories eventually reached a level where it became a national issue.

One rather plaintive comment heard frequently from scientists and engineers during this period was that "research just isn't fun anymore." The threat of program funding cuts and layoffs, along with the heavy monitoring, and often, criticism of their work, seemed to suggest that their efforts were unappreciated and probably unworthy of support. The Laboratory Directors and Division Management worked hard to attract new programs and were successful enough that a bad situation did not become a lot worse. By the end of the 1980s, things had stabilized somewhat with the Division reduced in size.

With respect to computers, the 1980s was an exciting period for members of the Division, as well as the rest of the world. IBM (International Business Machines Corp.) came out with the first desktop personal computer ("PC") in 1981, which was immediately cloned by several other manufacturers. The PC machines were based on MS-DOS (the Microsoft Disk Operating System) up until the mid-1990s. The Apple Computer Company developed a competitive line called Macintosh, which used a graphical interface with icons, which many people found easier to use than the PC machines. Apple computers were more popular for use in schools due the their ease of operation, and Apple dominated that niche of the market for many years. On the other hand, more software was becoming available for the PCs owing largely to Microsoft's aggressive marketing. The two systems were not compatible, and each had its proponents, sometimes with a nearly religious fervor. It was a bit reminiscent of the battle between "Beta" and "VHS" when videocassette tape recorders first came on the market. Both PCs and Macs found their place in the Division as more desktop computers were acquired.

By 1980, the Division had experienced a major growth in laboratory automation, data acquisition, instrument control, and data reduction. Much of the commercial equipment that was being used was packaged with internal computers. Most of the individual systems used in the experimental work were of the PDP-11 family. To centralize these activities, a VAX 11/780 was procured in December 1980. The VAX and PDP units are manufactured by the Digital Equipment Corp. A PDP-11/44 served as a "front end" for connection of computers in the laboratory programs to the VAX, and the VAX provided for direct connection of individual terminals to the ANL Central Computing Facility. The VAX and associated equipment were installed in a climate-controlled enclosure on the service floor under A-Wing.

In 1981, the Computer Group began to explore office automation for administrative functions such as personnel, budget, and procurement, and in 1982 the system became available for almost everybody's use. By the end of the year, 132 terminals were in use in the laboratories and offices. Software packages became available, including (1) MASS-11 for word processing, (2) DIGICALC for spreadsheet work, (3) $\mathrm{T_EX}$ for typesetting purposes, (4) BASIC and PL-1 language compilers, and (5) electronic mail.

At this point, nearly everybody had access to terminals and user-friendly software. MASS-11 on the computer gave the secretaries many more options than had been available on the single-purpose word processors. Some staff members began writing report drafts, memos, *etc.*, on the computer and giving them to a typist in electronic form for proper formatting and corrections. The final step had been taken in the transition from typewriter and carbon paper to computer.

By the end of 1983, the Computer Group consisted of seven CMT staff members and three full-time consultants, and the VAX was being used by more than 250 people. That same year, the publications file program was completed. To meet the needs of the Nuclear Fusion Group, the VAX was connected to a Cray mainframe at Lawrence Livermore National Laboratory. As the system continued to grow, a divisional local area Ethernet system was installed to provide more bandwidth. Connections were extended to thousands of other organizations and the Internet.

Programs such as Proof of Breeding, the National Battery Test Laboratory, TRUEX work, and the high-temperature thermodynamic studies of materials were heavy computer users, and a MicroVAX-II was acquired in 1985 for the high-temperature work. In 1988, the 7-year-old VAX was replaced with a VAX 6220, which had nearly three times the capacity of the older system. Toward the end of the 1980s, the computer terminals began to be replaced by desktop personal computers, which use the VAX as a disk, file, and/or print server. A block diagram of the CMT computing facilities as of 1989 is shown in Fig. 5-3. From about 1987 on, laser printers were used almost exclusively, along with Adobe Post-Script software. Very high-resolution output could be obtained with typesetting software.

Throughout the decade, the Computer Group, under Steve Gabelnick's leadership, was involved in a wide variety of activities:

1. Laboratory data acquisition and control
2. Computer modeling and simulation
3. Post-analysis of experiments
4. Graphic interpretation
5. Division information management and database development
6. Operating system maintenance
7. Computer networking
8. Equipment procurement
9. Advisory, educational, and consulting services

Members of the Computer Group included the following: Steve Gabelnick, Glen Chapman, Jacqueline Copple, Msiri Kazadi, Bob Kessie, Joe Kulaga, Bob Land, Carl Meyer, and John Osudar.

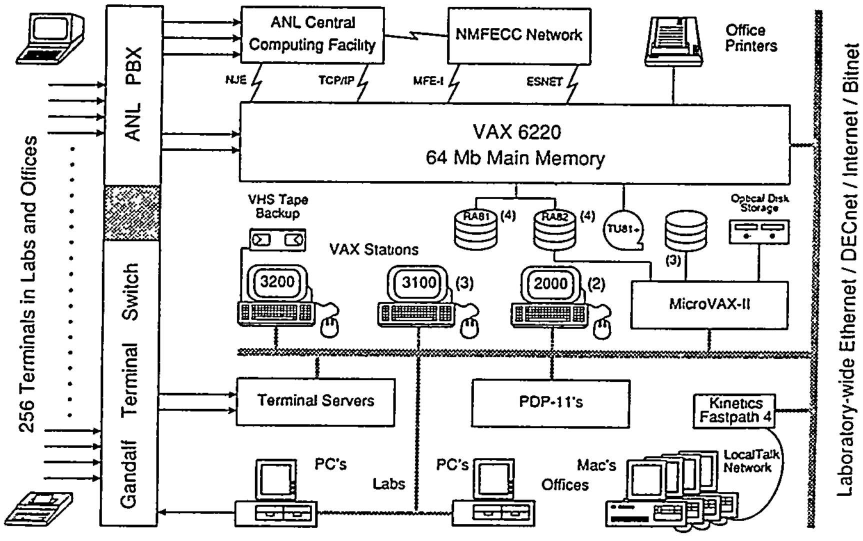


Fig. 5-3. Block Diagram of CMT Computing Facilities

TECHNICAL PROGRAMS

As the Division entered the new decade, the technical programs remained essentially unchanged for a year or two until the Reagan budget cuts and new DOE priorities began to take their toll. In 1981, the DOE made a decision to transfer overall management responsibility for the high-temperature battery program from CMT to Sandia National Laboratories and Lawrence Berkeley Laboratory and to reduce the funding severely for the Li-Al/FeS battery research and development at ANL. At the same time, there was a more gradual, but steady reduction of effort in the ANL and contractors' work on aqueous battery systems. The fuel-cell program remained relatively healthy, and the major emphasis was shifted from molten carbonate to solid oxide fuel cells. The remaining solar energy work was transferred out of the Division in 1982. The fossil fuel program and magnetohydrodynamic studies continued throughout the 1980s, as did the applied physical chemistry and basic research work.

Several programs were initiated on hazardous waste management and various aspects of nuclear technology, including separations of reactor fuel constituents, high-level active waste repositories, an electrometallurgical process for recycling fuel from the proposed Integral Fast Reactor (IFR), and methods for recovering plutonium residues from a diversity of other materials.

In the 1980s, several major trends were evident in the Division's programs. The overall budget and personnel were reduced drastically. There was a significant shift of effort from electrochemical programs to nuclear technology. The individual programs tended to be smaller, with less emphasis on industrial contractors, outside management activities, and end-use demonstrations, and more emphasis on research and development.

Lithium-Alloy/Iron Sulfide Batteries

The primary effort in the advanced battery work was on the lithium-aluminum/iron monosulfide (Li-Al/FeS) cell because of its performance and reliability. Cells using iron disulfide (FeS_2) instead of the monosulfide were also of interest due to their potential for higher performance, and the emphasis had begun to shift toward that system by the end of the decade.

The failure of the 20-kWh Mark I battery module in 1979 brought about a revised strategy and schedule for the development of lithium alloy/iron sulfide cells, as shown in Table 5-3.

Because a major objective of this program was to transfer the technology to industry, approximately 60% of the funding was expended through industrial subcontracts. Two major cell and battery development contracts were with battery manufacturing firms, Eagle-Picher Industries, Inc., and Gould Inc. Other related contracts were negotiated with the Carborundum Division of the Kennecott Copper Corp., General Motors Research Laboratories, Rockwell International, the Institute of Gas Technology, and the University of Florida.

ELECTRODE CHEMISTRY

As of 1980, previous work had shown that iron monosulfide (FeS) and iron disulfide (FeS_2) were both promising materials for positive electrodes, and a lithium-aluminum alloy containing about 50 at.% lithium (LiAl) was the favored negative electrode material, although there was also some interest in lithium-silicon alloys. A LiAl/FeS cell undergoes the following overall reaction:

$$2\ LiAl + FeS \rightarrow Li_2S + Fe + 2\ Al$$

which exhibits a voltage plateau at about 1.33 V and a theoretical specific energy of about 460 Wh/kg of active materials. A LiAl/FeS_2 cell discharges by the overall reactions:

$$2\ LiAl + FeS_2 \rightarrow Li_2S + FeS + 2\ Al$$
$$2\ LiAl + FeS \rightarrow Li_2S + Fe + 2\ Al$$

with voltage plateaus at 1.67 and 1.33 V, respectively, and a theoretical specific energy of approximately 680 Wh/kg. In the case of the lithium-silicon electrode, which is normally started at a composition corresponding to $Li_{3.25}Si$, a series of compounds

Table 5-3. Development Schedule for Lithium/Iron Sulfide Batteries

Year	1983	1986	Post 1990
System	Li-Alloy/FeS	Li-Alloy/FeS	Li-Alloy/FeS_2
Specific Energy,[a] Wh/kg			
Cell	100	100-125	160-225
Battery		80-100	130-180
Peak Specific Power,[b] W/kg			
Cell	125	150-250	240-350
Battery		120-160	190-360
Lifetime, Deep Discharges[c]			
Cell	500	1000	1200
Battery		800	1000
Battery Heat Loss, W		75-150	50-100

[a] At a 4-hr discharge rate.
[b] Peak power sustainable for 20 s at 0 to 50% state of discharge.
[c] End of life defined as 20% capacity loss or a coulombic efficiency below 95%.

is formed as lithium is removed during discharge:

$$Li_{3.25}Si \rightarrow Li_{2.33}Si \rightarrow Li_{1.71}Si \rightarrow Si$$

Cells with FeS or FeS_2 positive electrodes and $Li_{3.25}Si$ negative electrodes have specific energies about 10% higher than those with LiAl negative electrodes. Based on these considerations, the negative electrode work was broadened to include Li-Si and Li-Si-Al as well as Li-Al as the active material.

A special test cell was designed so as to apply current perpendicular to the electrode face, causing the current distribution to be one-dimensional, varying only through the thickness of the electrode under test. This one-dimensional-electrode (ODE) cell was used for studies of galvanostatic (constant-current) cycling, current interruption, electrode-potential relaxation, and high-intensity current pulsing. The current-interruption data provided values for the area specific resistance (ASR) of the electrode, which is in units of ohm-cm^2, and is a useful value in the engineering design of practical cells.

Studies were continued on FeS and FeS_2 positive electrodes. The discharge process for the FeS electrode, which appears simple at first glance,

$$2\,Li + FeS \rightarrow Li_2S + Fe$$

turned out to be much more complex when it was examined in detail. Several chemical and electrochemical reactions are involved, but these are the overall reaction paths:

$$\begin{gathered} FeS \rightarrow \text{J phase } (LiK_6Fe_{24}S_{26}Cl) \\ \text{J phase} \rightarrow \text{X phase } (Li_2FeS_2) \\ \text{J phase} \rightarrow Li_2S \\ FeS \rightarrow Li_2S \\ \text{X phase} \rightarrow Li_2S \end{gathered}$$

The "J" and "X" phase designations, which were acquired through some arcane process during their characterization by X-ray diffraction, are used extensively in the literature on lithium/iron sulfide batteries. Emf studies of these reactions resulted in a fairly good thermodynamic characterization of the FeS discharge process, and, together with literature data, produced values of -102.5 and -99.9 kcal/mol at 700 and 800 K, respectively, for the free energy of formation of Li_2S.

Current-interruption techniques were used to investigate voltage-loss processes (mainly electrode polarization) that were limiting cell performance. The results proved valuable in mathematical modeling work and in cell design optimization.

A common problem in conducting electrochemical studies on systems involving molten salt electrolytes is the lack of a suitable reference electrode. Laszlo Redey and Don Vissers found that the Ni/Ni_2S_3 couple makes an excellent reference electrode for molten halide salt systems. Tests of the electrode showed a linear response of the emf to the logarithm of the sulfide ion concentration, and this Nernstian response was in excellent agreement with that predicted theoretically for a two-electron reaction. The usefulness of this electrode was improved further by incorporating a thermocouple to provide corrections to the emf during temperature changes. The potential versatility of this electrode for various applications was recognized nationally through an IR-100 Award by *Industrial Research Magazine.*

Studies were also conducted on FeS_2 positive electrodes, which discharge by the following sequence of phase changes:

$$\begin{aligned} &FeS_2 \rightarrow Li_3Fe_2S_4 \rightarrow Li_{2+x}Fe_{1-x}S_2 \\ &\rightarrow Fe_{1-x}S \rightarrow Li_2FeS_2 \rightarrow Li_2S + Fe \end{aligned}$$

Emf measurements were made on the first reaction ($FeS_2 \rightarrow Li_3Fe_2S_4$), using a specially designed cell, with the following result:

$$E\,(V) = 1.5558 + 0.0004785\,T\,(°C)$$

An interesting quirk of this reaction is the positive temperature coefficient, which indicates an entropic heat absorption during discharge that could simplify heat management of a practical battery. Additional solubility data were obtained on the Li-Fe-S phases formed in the FeS_2 electrode.

The ODE cell was used to conduct extensive measurements on various types of electrodes (Li-Si, Li-Al, Li-Al-Si, FeS, FeS_2, NiS, and others) and several different electrolyte compositions. Nearly all of the early work had been done with LiCl-41.2 mol% KCl molten salt electrolyte, which is a eutectic composition that melts at 352°C. This electrolyte has two serious shortcomings. (1) Because of its high melting temperature, it requires high cell operating temperatures approaching 400°C or higher. (2) Its KCl content is sufficiently high to cause the formation of J-phase, which inhibits the kinetics of the FeS discharge reaction in a cell. Formation of J-phase can be suppressed in two ways. One way is to increase the temperature, and the other is to decrease the potassium ion content of the electrolyte. Cells were operated with electrolytes of various compositions in an effort to improve their electrochemical performance and/or decrease the operating temperature. An experimental investigation to seek molten salt systems having lower melting temperatures revealed several combinations of alkali metal halides (*e.g.*, LiF, LiCl, LiBr, KCl, KBr, CsCl, CsBr) that had adequately high lithium ion concentrations along with melting temperatures in the general range of about 235 to 350°C. Consideration had to be given, however, to other factors such as solubilities of the active materials, stability toward reduction by the Li-Al electrode, and corrosion or other interactions with the cell hardware.

MATERIALS ENGINEERING

In a high-performance electrochemical cell, the electrodes contain highly aggressive compounds, which place severe limitations on the choice of materials for cell components such as the separator, current collectors, housing, insulators, and other components. Chemical compatibility and mechanical stability were evaluated by two methods: static immersion tests in mixtures that simulated the positive and negative electrodes, *i.e.*, FeS/LiCl-KCl and LiAl/LiCl-KCl, and tests in 50-Ah cells. Nickel proved to be very corrosion resistant in the FeS static tests, but was attacked in the cell tests. The attack, however, could be reduced greatly by adding iron powder to the electrode. The same situation prevailed with low-carbon steel. The beneficial effect of iron powder additions was quantified later by accelerated static immersion tests.

Some work was done on protective coatings applied to low-cost substrate materials, most often, low-carbon steel. Coatings of Ni, Ni-Mo, Cr, and TiN-TiC appeared promising for FeS electrodes, and no corrosion was observed with LiAl electrodes coated with TiC, TiN, or TiC-TiN. Tests of low-carbon steel electrodes, electroless and electroplated with nickel, showed a reduction of the corrosion rate in FeS electrodes, but their long-term integrity appeared questionable.

At the Li-Al electrode, deposition of aluminum on low-carbon steel resulted in a brittle, intermetallic reaction layer, which limited the lifetime of the component. A galvanic deposition study was made by coupling a low-carbon steel electrically to an aluminum electrode in LiCl-KCl electrolyte and measuring the current at temperatures of 470-530°C. The rate showed an Arrhenius temperature dependence, *i.e.*, $G = G_0 \exp(-Q/RT)$, where the activation energy, Q, was 21.4 kcal/mol, and the galvanic deposition rate constant was 1.65×10^{-2} g/(cm^2 sec). Diffusion-rate measurements of aluminum in nickel and low-carbon steel at 475°C indicated diffusion coefficients of 3.4×10^{-11} and 2.4×10^{-11} cm^2/sec, respectively. The predominant phase for the aluminum/steel couple was $FeAl_3$, and in the aluminum/nickel couple there was an inner zone of Ni_2Al_3 and an outer zone of $NiAl_3$. When the rate data for deposition and diffusion were combined, the results showed that the overall aluminum reaction rate was controlled by the initially slower galvanic deposition and was linear, but once a certain transition time had been reached, the rate was limited by diffusion and was parabolic.

By 1983, materials work in the lithium-aluminum/iron sulfide program had broadened to include other areas such as sodium/sulfur and glass electrolyte cells, so further work is discussed under those topics.

CELL DEVELOPMENT

Li-Al/FeS Cells. Engineering modeling studies were conducted to generate mathematical correlations of performance and lifetime with cell design parameters and operating variables. These correlations were obtained through multiple regression analyses of test data from previously operated cells. Specific energies were predicted for up to 800 cycles of 84 Li-Al/FeS multiplate cell designs. The results were used to identify cell designs most likely to meet the Mark II cycle-life goals, *i.e.,* less than 20% decline in specific energy over 500 cycles.

The Mark IA cells had shown a significant capacity decline during cycling (typically 20% within 80 cycles). An effort was undertaken to provide design recommendations that would reduce the rate of capacity loss in Li-Al/FeS cells. By inserting a reference electrode into an engineering-scale bicell, the charge/discharge characteristics of the positive and negative electrodes could be monitored individually. The results indicated that the capacity fading problem had been caused by a capacity decline of the negative (Li-Al) electrode, and that the problem could be nearly eliminated by a high lithium content of more than 60 at.% in the electrode. On the basis of this and previous work, more stable capacity could be achieved by using LiCl-rich LiCl-KCl electrolyte, a lithium content greater than 46 at.% in the negative electrode, and an operating temperature above 460°C. As a result of these changes, the capacity-loss rate of ANL's and contractors' cells was reduced significantly to less than 0.03% per cycle.

Post-test analyses had shown that swelling of the electrodes was one of the causes of cell failure on cycling. Studies were undertaken to determine the magnitude of the swelling and the forces involved. Measurements were made both with a small-scale special apparatus at Argonne and with a device specified by Argonne for tests of two full-scale multiplate cells at Eagle-Picher, one with boron nitride (BN) felt separators and the other with BN fabric separators. A number of factors were found to have an effect on swelling: (1) loading density of the electrodes, (2) percent utilization of the active materials, (3) compressibility of the separator, and (4) degree of mechanical restraint during cycling. Temperature had no significant effect. As additional cells were constructed and tested, electrode and current-collector hardware designs were improved to control swelling.

In the operation of a practical battery, situations could arise in which the system would have to be cooled to room temperature, and then reheated to the operating temperature. There was some concern about the effects of alternate freezing and thawing of the molten salt electrolyte. Tests showed, however, that as many as 60 freeze-thaw cycles had no serious effects on well-designed cells at 25, 50, and 75% state of charge.

In 1983, computer modeling was used to correlate cell designs with the performance of

Li-Al/FeS cells. The validity of the computer model was verified by experimental results, and the model was then extended to Li-Al/FeS_2 cells.

At this point, the Li-Al/FeS system had reached a stage of development where the cell designs had been established, and further work was directed toward the design, fabrication, and testing of battery modules to meet the schedule for the Mark II phase of the program. A comprehensive report, entitled "Li Alloy/FeS Cell Design and Analysis Report" (ANL-84-93), was compiled by Eddie Gay with the intention of providing the technical information that would be needed by any organization that might have a future interest in the technology.

Li-Al/FeS_2 Cells. The program goals for the Mark III battery cells were a specific power of 200 W/kg, a specific energy of 300 Wh/kg, and a lifetime of 1,000 charge-discharge cycles. Cells having iron disulfide (FeS_2) positive electrodes appeared to offer the best shot at achieving these goals. Iron disulfide, also called "pyrite," in its crystalline form has a yellow metallic luster similar to that of gold. Because it has often been mistaken for gold by panners, it has been named "fools' gold," a term that the cell developers preferred to avoid. During the battery program, Duane Barney displayed a very large crystal of the material on his desk.

For reasons mentioned earlier, cells having FeS_2 electrodes were operated only on the upper (first) voltage plateau, which is at about 1.65 V *vs.* the Li-Al negative electrode. Investigations of Li-Al, Li-Si, and Li-Al-Si electrodes showed that their capacity densities were generally similar. A Li-Al alloy of 53 at.%, rather than the usual 48 at.% lithium, was selected to increase the lithium activity when the cell was near the end of discharge. A new electrolyte composition, 25 LiCl-37 LiBr-38 KBr (mol%), with a eutectic melting temperature of 310°C, was selected because of its higher lithium content and lower melting temperature than the LiCl-KCl used previously. The lower operating temperature tended to slow the loss of sulfur from the FeS_2, which had been a source of capacity decline.

Figure 5-4 shows a comparison between a Li-Al/LiCl-KCl/FeS_2 cell operated on both voltage plateaus and a higher-performance Li-Al/LiCl-LiBr-KBr/FeS_2 cell of the same capacity (24 Ah) discharged only on the upper voltage plateau. The higher performance of the upper-plateau cell was attributed to two factors: (1) improved electronic conductivity of the electrode and (2) the increased liquidus range of the LiCl-LiBr-KBr electrolyte. Utilization of the active material was about 89% of the theoretical capacity, and the cell was operated for more than 300 cycles with no change of capacity. This, along with other results, led to a decision to use the upper-plateau cells in future work.

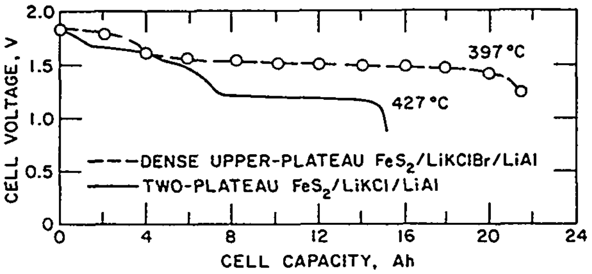


Fig. 5-4. Discharge Curves for Two-Plateau and Upper-Plateau-Only FeS_2 Cells

The cell design effort then continued, with the following activities:

1. Experiments to determine the influence of physical electrode parameters on cell performance.
2. Examinations of electrochemical electrode processes with candidate active materials that provide effective overcharge protection for lithium/metal sulfide cells.

3. Demonstration of long life and ultra-high pulse power capability for a Li-Al/FeS_2 cell.
4. Modeling studies of cylindrical electrodes, which are simpler and less costly than flat-plate designs.
5. Measurement of potential changes during different kinds of electrochemical testing by use of voltage sensors inserted at various locations within a Li-Si/FeS_2 cell.

High-intensity current-pulse techniques were used to relate performance to cell-design parameters. The self-cooling effect during high-power discharge of the FeS_2 electrode permits very compact packaging of the cells in a battery. At this point in the development work, a specific power of 150-300 kW/kg in 1- to 1000-ms pulses appeared feasible. The very high power-pulse capability of the system could lead to several special applications such as powering electromagnetic launchers.

Lifetime tests were performed on a 24-Ah Li-Al/LiCl-LiBr-KBr/FeS_2 bicell. Discharge and charge rates were 4 and 8 h, and cutoff voltages were 1.25 and 2.05 V, respectively, which kept the cell within the upper-plateau range, and the operating temperatures were between 388 and 427°C. The cell capacity remained essentially constant over 400 charge-discharge cycles and 5,400 h. The results of a post-test analysis of this cell indicated that the design had a potential for 1,000 cycles of high-performance operation.

A number of advances were made in the various components of the cells. The composition of the LiCl-LiBr-KBr electrolyte was changed from 25-37-38 mol% to 34-32.5-33.5 mol%, thereby increasing the conductivity about 25%. The possibility of replacing boron nitride (BN) felt separators flooded with the molten salt electrolyte by electrolyte-starved MgO powder separators was investigated. The powder separators are rigid bodies held together by capillary forces in the pores. The advantages are increased resistance to chemical attack, especially in overcharge-protected cells where metallic lithium is present, and the ease of confining a solid rather than a liquid material in the desired locations. A modification in the positive electrode composition to 50-50 mol% FeS_2-CoS_2 plus 5 mol% Li_2S was also studied.

In a battery configuration, many cells must be connected in series to achieve a useful voltage. Because the cell capacities are not exactly the same for various reasons, passing the correct amount of current through one cell to effect a full charge may overcharge the next one. An electronic charge-equalization device was developed to avoid the problem, but it was cumbersome in that it required an individual electrical lead to each cell. The ideal situation, which occurs in certain other battery systems, is to have a cyclic chemical process that begins to take place when a cell is fully charged, so additional current has no effect. A breakthrough for the Li-Al/FeS_2 system occurred in 1986 when it became evident that chemical overcharge protection was a possibility. This was done by limiting the capacity of a lithium electrode of a specific composition such that lithium metal was produced when the voltage rose at the end of charge. The lithium metal dissolved in the electrolyte and diffused to the positive electrode, where it was oxidized to the sulfide, thereby creating a "chemical short circuit." This so-called "lithium-shuttle" mechanism proved to be a practical method for avoiding overcharge damage to the cell. In the engineering development of overcharge-tolerant cells, a Li-Al_5-Fe_2 alloy, which has a potential of -260 mV *vs.* the usual Li-Al electrode, was used.

Up to about 1986, essentially all of the cell development work had been on cells having rectangular, flat-plate electrodes. In that year a model was developed for a design in which seven rod-shaped positive electrodes having an outer annulus of MgO powder separator material were contained in a cylindrical cell.

Although the anticipated electrical performance for that cell design was comparable to that of a flat-plate cell (a specific energy of 190 Wh/kg and specific power of 185 W/kg), the fabrication cost should be lower.

Electrochemical investigations were conducted in 1987 on thin-electrode primary Li-Si/FeS_2 cells under investigation at Sandia National Laboratories. The main objective was to determine the effect of compressive force on cell performance and the optimum ratio of electrolyte to active material. The work at Sandia, adapted from the earlier studies at Argonne, was aimed toward military applications, which is a classic case of research finding use in an area far afield from the original purpose. Cells were later produced commercially by the U.S. subsidiary of the French company, SAFT (Société des Accumulateurs Fixes et de Traction).

In 1988, a major emphasis was started on bipolar battery designs. In a bipolar battery, the cells were stacked in a pancake fashion so that the positive and negative electrodes had a common current collector, the bipolar plate (see Fig. 5-5). This type of arrangement greatly reduced the cell weight by eliminating much of the hardware and also resulted in a uniform current density, which improved the electrochemical performance. Calculations projected outstanding performance for a bipolar electric car battery—a 640-km range and acceleration similar to that achieved with a high-performance gasoline engine.

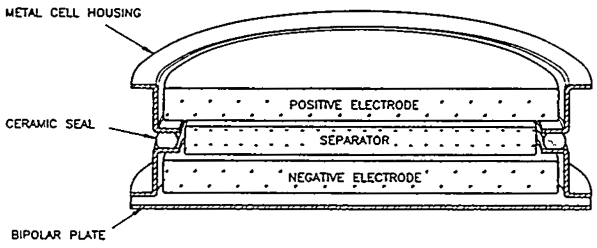


Fig. 5-5. Bipolar Li-Al/FeS_2 Cell Design

The major problem to be faced in the development of bipolar cells was the peripheral seal. This seal had to provide electrical insulation, form a gas-tight bond between the metal components (usually iron and molybdenum), have a coefficient of expansion compatible with those of the metal components, and be resistant to corrosion by the molten salt electrolyte and the active materials in the electrodes. Early attempts to use gaskets or other arrangements had not been satisfactory. Remarkably, Tom Kaun and the others in the group were successful in developing a seal that met all these requirements. Tests of the hermetic seal were conducted by constructing and operating a 3-cm-dia bipolar cell with a LiAl-10 mol% $Li_5Al_5Fe_2$ negative electrode and an upper-plateau FeS_2 positive electrode. The cell showed very good electrical performance, and a post-test analysis after 400 h of operation confirmed the integrity of the hermetic seal.

CELL TESTING

Eagle-Picher Industries, Gould Inc., and Argonne continued to build groups of state-of-the-art "status cells" and occasional modules consisting of several cells to measure progress toward the program goals. Sixty Li-Al/FeS bicells were tested in 1980. Capacity fading, which had been a concern at the time, was reduced to 0.02%, 0.03%, and 0.08% per cycle in the ANL, Eagle-Picher, and Gould cells, respectively, which was a significant improvement. Specific energies for the Eagle-Picher and Gould cells were 80 and 93 Wh/kg, respectively. The Gould cells had a short lifetime of about 80 cycles due to problems with the boron nitride felt separators in their particular design, so they decided at that time to switch to MgO powder separators. In 1981, Eagle-Picher and Gould each fabricated over 100 cells. The specific energies of these cells ranged from about 70 to 90 Wh/kg, and specific powers were between approximately 55 and 75 W/kg. It did not appear at this point that the Li-Al/FeS system was going to be able to meet the 1996 performance goals, despite the fact that a number of marginal design improvements looked feasible. The results for the last sets of status cells are listed in Table 5-4. The following year, the two contractors each built four "best effort" cells in which the specific power was increased markedly, to 102 and 132 W/kg, respectively.

Post-test examinations yielded valuable information on cell failure mechanisms, in-cell corrosion reactions, and electrode morphology (*i.e.*, microstructure, active material distribution and utilization, reaction uniformity, impurities, and cross-contamination of electrodes). The two major causes of cell failure were extrusion of material from the iron sulfide electrode and localized protrusions of Li-Al alloy through the separator. Almost all the other problems were short circuits caused by electrical feedthrough failure or metallic deposits in the separators. The results of post-test analyses of failed cells were an invaluable guide in the development of improved electrode beds and hardware components. The techniques that Jim Battles, John Smaga, and others developed for the post-test examinations have subsequently found much wider application than in this program alone.

MODULES, BATTERIES, AND AUXILIARY COMPONENTS

Table 5-5 lists the small batteries that were constructed and tested in 1980.

A detailed analysis was made of the heat generated in Li-Al/FeS cells during constant-current charge-discharge cycling. The heat-generation rate proved to be substantially higher during discharge than during charge, and it increased significantly at the end of charge and the end of discharge. Calculated internal temperatures of a five-cell module agreed well with experimental values. Work also continued on the development of charging equipment and on commercialization studies in which various market factors were assessed.

Efforts were continued on establishing working relationships with potential users of the Li-Al/FeS battery, in both institutional and private sectors. A joint program with Eagle-Picher Industries was under way to develop a 30-kWh fork-lift battery for the U.S. Army, an economic analysis for a bus battery was proposed to the U.S. Department of Transportation, and technical discussions were held with the Chrysler Motors Corp., General Motors, Inc., and the Ford Motor Co. In 1982, a study of battery-vehicle interactions was performed jointly by ANL and the Toyota Motor Co.

Table 5-4. Performance Data for Status Cells

Performance Characteristic	Eagle-Picher	Gould
Ave. Peak Capacity, Ah	157	340
Ave. Specific Energy, Wh/kg	80	90
Ave. Peak Specific Power, W/kg	70	80
Cycle Life	330	345
Capacity Loss per Cycle, %	0.06	0.02

Table 5-5. Small Batteries Tested in 1980

No. of Cells	Battery Voltage, V	Battery Capacity, kWh	Thermal Insulation	Cycle Life
9	10.6	3.0	Conventional	72
10	12	2.5	Vac-foil	71
10	12	2.5	Vac-foil	79
10	11.6	3.8	Conventional	270
10	11.8	4.0	Conventional	150

Also in 1982, the development and testing activities on Li-Al/FeS batteries were split off from the rest of the program and incorporated into the Industrial Electrochemical Projects programs under Mike Yao. In 1983, a study supported by DOE was directed toward a full-scale Li-Al/FeS battery design for a Chrysler T-115 van. An artist's conception of this 162-cell battery is shown in Fig. 5-6. A complementary program was funded by the Electric Power Research Institute (EPRI) for the development of a 10-cell Li-Al/FeS module to be built by Gould Inc. and tested at ANL.

By 1984, a wide interest had developed in the Li-Al/FeS battery system, both in the U.S. and internationally. Contractors to the U.S. Department of Defense were using the technology to build advanced, nonrechargeable, thermal batteries. The U.K. and Canada both had aggressive programs on potential commercial and defense applications. Varta, A.G., in Germany and SAFT in France were also involved. The foreign discussions included a visit from a Soviet delegation to ANL at Gould's request in the early 1980s. The ANL people attending the meeting were told that they were to limit their discussions to material that had been published.

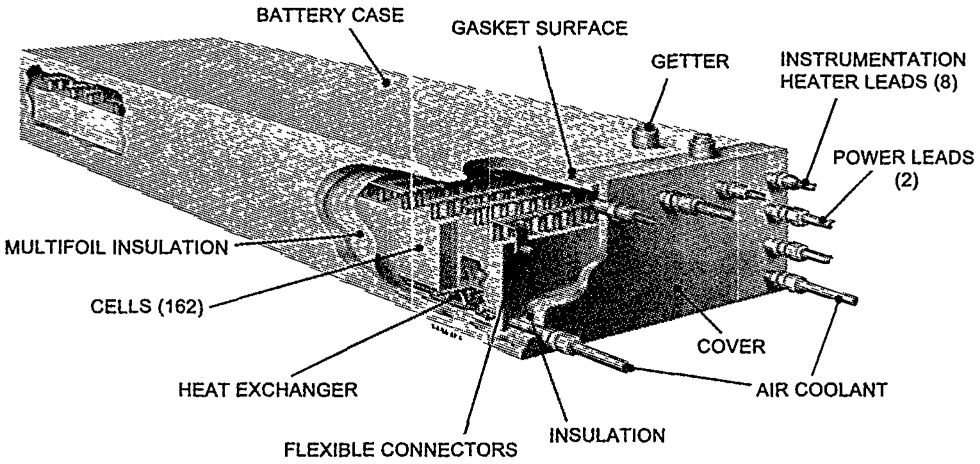


Fig. 5-6. Design for a Li-Alloy/FeS Van Battery

The Soviet group of about ten people included a female interpreter, and it was understood that they would speak only Russian. One member of the group very definitely had the appearance and demeanor of a policeman, and he said nothing during the technical discussions, leading to a suspicion that he was a KGB man. It was apparent that the Soviet scientists had read the ANL literature and were familiar with the names of the ANL staff people they were meeting. That evening Gould hosted a dinner at their headquarters in Rolling Meadows, and, after several of the traditional toasts, some of the Soviets became not only jovial, but also bilingual. The consensus of the ANL people after the meeting was that the Soviets were doing very little, if any research on lithium-alloy/metal sulfide batteries, although they claimed to have a program.

In 1985, Gould delivered two nine-cell, 12-V Li-Al/FeS modules to ANL for testing in a program funded jointly by EPRI, DOE, and the Tennessee Valley Authority. Under a power regime specified by the standard J-227a/D simulated driving profile, one of the modules delivered a specific energy of 104 Wh/kg (on a cell-weight basis), which was considered acceptable for electric van propulsion. Gould then constructed two 36-V batteries, which were tested in 1987. The first battery, designated Mark I, was based on the design used in the 12-V modules. Its power and its specific energy (49-110 Wh/kg of cell at a 40-A constant-current discharge and 77-112 Wh/kg of cell on a simulated driving profile) were considered satisfactory, but its lifetime was inadequate (113 cycles). The failure was caused by iron deposition in the separators. The thermal insulation and thermal control auxiliaries limited the specific energy of the Mark II battery.

An effort was made to improve thermal control of the battery by developing a high-efficiency, lightweight, low-cost insulated jacket in a collaborative program between ANL and the Westinghouse Oceanic Division (formerly Gould Ocean Systems Division) of Cleveland, Ohio. A part of this work was done jointly between ANL and Meyer Tool and Manufacturing Co. of Oak Lawn, Illinois. If developed successfully, this technology could also be useful in several other applications, *e.g.*, sodium/sulfur batteries, sodium/chloride batteries, monolithic fuel cells. Two full-scale insulated cases were fabricated and tested. The heat loss was 208 W, which was considerably higher than the 100-W goal, but it appeared that this figure could be decreased by using a chemical getter to lower the residual gas pressure and by optimizing the types and thicknesses of the insulation layers. One of the cases was used to house a Gould 36-V electric van battery module, which achieved a lifetime of about 103 cycles. The specific power for the module was 71 W/kg and the specific energy for a driving profile was 70 W/kg. The corresponding values for the cells themselves were >95 W/kg and >110 Wh/kg.

By the end of the 1980s, the basic technology of Li-Al/FeS cells and batteries had been developed, but additional work was still needed to improve their performance and lifetime before they could be considered ready for commercial application.

PERSONNEL

The lithium-alloy/iron sulfide program was hit hard by the budget cuts in the early 1980s. The effort dropped from about 35 full-time people in 1980 to approximately 10-12 by 1984 and to about 4 or 5 full-time people by the end of the decade. Different individuals were in charge of the overall program as it underwent the resulting organizational changes: Duane Barney, John Ackerman, Jim Battles, and Paul Nelson. Others who participated in the program at one time or another during the 1980s include Karl Anderson, Jack Arntzen, Lou Bartholme, Milt Blander, Ira Bloom, Alan Brown, Al Chilenskas, Clint Christianson, Bill DeLuca, Mike Duoba, Magdy Farahat, Al Fischer, Don Fredrickson, Eddie Gay, Kenneth Gillie, Ed Hayes, Roger Hogrefe, Tim Holifield, Fred Hornstra, Tom Kaun, John Kelley, Dennis Kilsdonk, Verne Kolba, Wally Kremsner, Gene Kucera, Dick Malecha, Jane Marr, Fred Martino, Bill Miller, Jim Miller, Bali Misra, Frank Mrazek, Mike Myles, Neil Otto, Sandy Preto, George Redding, Laszlo Redey, Mike Roche, Laury Ross, Paul Shimotake, John Smaga, Bob Steunenberg, Bob Swaroop, Ziggy Tomczuk, Tony Tummillo, Ravi Varma, Don Vissers, John Weber, and Carl Webster. The secretaries were Sue Bykowski, Marian (Gardner) Harkins, and Sherry Grisko.

Other High-Temperature Battery Research

SODIUM/SULFUR BATTERIES

Sodium/sulfur battery cells employ metallic sodium as the negative electrode and elemental sulfur as the positive electrode. The sodium and sulfur react electrochemically, at first forming polysulfides (Na_2S_5, Na_2S_4, Na_2S_3, Na_2S_2), and finally Na_2S if the reaction is carried to completion:

$$2\,Na + S \rightarrow Na_2S$$

The open-circuit voltage of the Na/S cell is about 2.0 V. The cell design usually consists of a ceramic tube containing the sodium, which is surrounded by the sulfur. The ceramic separator between the reactants is made of "beta alumina," which is capable of sodium ion conduction. A minimum operating temperature around 300°C is required to maintain liquid phases in the electrodes and to assure adequate ionic conductivity of the beta alumina.

The term "beta alumina" is actually a misnomer because it implies a phase of pure aluminum oxide, which is not the case, but it has come into general use. The material actually consists of Na_2O-Al_2O_3, Na_2O-MgO-Al_2O_3 and similar compositions, in which aluminum and oxygen atoms form spinel-like blocks that make up hexagonal layers spaced apart by Al-O-Al columns. Sodium ions occupy the spaces between the planes and are relatively free to move about in directions perpendicular to the c-axis. For use in cells, the tubes are fabricated by pressing and sintering the powder, which provides lower, but isotropic conductivity (the same in all directions). In most of the work at ANL on Na/S cells, the solid electrolyte was β''-alumina, which has the approximate composition $Na_2O{\cdot}MgO{\cdot}5Al_2O_3$. The addition of MgO was shown to improve the sodium ion conductivity of the material.

Joe Kummer and Neil Weber of the Ford Motor Co. had reported work on the Na/S system, and interest in the system developed rapidly. By the mid-1970s significant research efforts were in progress at the Ford Motor Co., Dow Chemical Co., General Electric Co., General Motors Corp., and TRW in the United States. Foreign programs included the British Rail Technical Centre, Chloride Silent Power, Ltd., as well as UKAE, Harwell in Great Britain, Brown Boveri & Cie and VARTA Batterie AG in Germany, Laboratoires de Marcoussis in France, and Yuasa Battery Co., Ltd., in Japan.

Sodium/sulfur and lithium-alloy/iron sulfide batteries had a lot in common in that they were both novel electrochemical systems, they evolved at about the same time, they both involved high-temperature operation, and they were being considered for the same practical applications—electric vehicles and load leveling on utility systems. In the development work, they tended to have the same general types of problems, such as corrosion, internal stresses, cell leakage, heat management, and capacity matching of cells during charging. The two systems were definitely competitors with respect to anticipated performance, cost, and lifetime.

The battery groups at Argonne were not deeply involved in Na/S cell and battery development, but they were able to make useful contributions to the technology due to the facilities and expertise available at ANL for extensive performance testing and post-test diagnostics.

In 1983, post-test examinations were started on Na/S cells from the Ford Aerospace and Communications Corp. to identify life-limiting mechanisms, long-term degradation of critical components, and characterization of the sulfur-electrode morphology. Detailed examinations showed that the morphology of the sulfur electrode was complex and involved the phases Na_2S_2, Na_2S_4, Na_2S_5, and sulfur. Phases resulting from corrosion of metallic components were $NaCrS_2$ and $NaAlS_2$. When the cells were cooled down from the operating temperature, the composition gradients persisted, so it was possible to observe the reaction fronts. It appeared that several metastable phases were formed in the sulfur electrode. There was still concern about the integrity of the β''-Al_2O_3 electrolyte in spite of advances in the cell design, and freeze-thaw cycling produced fractures. In at least one case, fracture was caused by inadvertent cooling during electrical testing. In 1986, work was completed on testing of four load-leveling cells, five electric-vehicle cells, and one cell for a satellite application from Ford. Department of Energy support for Na/S cell work at ANL was terminated at that time.

Tests were then initiated on Na/S cells from Chloride Silent Power, Ltd., in Great Britain. Test results from four 20-Wh cells translated into a vehicle range of 218 km and a peak power of 108 Wh/kg. One failed at the 388th cycle; the others ran for 524-807 cycles. Several other cells and small modules were tested and examined. One of the modules was a one-third size electric vehicle battery containing 960 cells (300 Ah at 64 V), which came complete with charging and thermal management systems. Although one cell failed after 155 cycles, the module was still delivering 80% of its capacity after 225 cycles.

By the end of the decade, the Na/S and Li-alloy/iron sulfide batteries were in similar positions. Tests had shown that performance and lifetime goals could be met on occasion, but not consistently. It was also becoming more difficult to justify large development programs in an era of tight budgets and a general lack of enthusiasm on the part of the public for electric cars and energy conservation.

GLASS ELECTROLYTE SYSTEMS

Although nearly all the work on sodium/sulfur cells was done with the β''-alumina solid electrolyte, an interest developed in glasses capable of sodium-ion conduction as a possible alternative. Glass electrolyte had several properties that could be advantageous: (1) ease of fabrication into different shapes, (2) high strength in thin sections, (3) an absence of grain boundaries, and (4) isotropic ionic conductivity. The Dow Chemical Company had developed a sodium borate glass for use in sodium/sulfur cells, and a joint effort between the Materials Science and Technology and CMT Divisions at Argonne had produced a sodium-ion conducting glass called NASICON, which was composed of sodium, zirconium, and silicon oxides. The Dow glass had a high resistivity of 24,000 ohm-cm at 300°C, while the values for NASICON and the β''-alumina were about 500 and 5 ohm-cm, respectively. The resistivity of the Dow glass was too high for use in practical cells and that of NASICON was at best marginal. A value of about 200 ohm-cm was considered to be the maximum for cells using thin NASICON electrolytes.

In 1982, a systematic study of NASICON-type glasses was undertaken to determine optimum compositions in the Na_2O-Al_2O_3-ZrO_2-SiO_2 system for glass electrolytes to be used in Na/S cells. Many factors had to be considered, including the composition regions that form glasses, the temperatures required, ionic conductivity, glass transition temperatures, coefficients of thermal expansion, and chemical stability toward sodium and mixtures of sulfur and sodium sulfides. A large number of glass compositions were prepared and characterized with respect to physical properties and corrosion resistance. The composition, $42Na_2O$-$8Al_2O_3$-$5ZrO_2$-$45SiO_2$, was selected and given the name "ANL glass." The resistivity of the material was 221 ohm-cm at 300°C, and its corrosion resistance in the Na/S cell environment proved similar to that of the β''-Al_2O_3.

During the development work on the glass electrolyte, various design studies were conducted on cells. The most promising design concept appeared to be one in which the sodium was contained in many small (1.5-mm OD) glass electrolyte tubes that were immersed in the sulfur. One specific conceptual design was a 150-Ah cell consisting of 4,000 such tubes, which had a projected specific power of 2,000 W/kg and specific energy of 200 Wh/kg.

A great deal of effort was put into techniques for fabricating glass electrolyte tubes having small diameters and thin walls. Production of uniform 500- to 1,000-g glass billets from the high-purity reagents was straightforward, but drawing the tubes was not so easy. Several small-scale Na/S cells were tested and achieved 36-40 cycles at 4-h charge and 8-h discharge rates, and the cell failures were not necessarily related to the electrolyte. These and other small-scale experiments revealed no inherent problems with the glass electrolyte, although it was still a long way from practical application in full-size batteries.

Because of its ability to conduct sodium ions, the glass electrolyte can be used in a reference electrode in which the reference material is completely isolated from the rest of the system. A miniature reference electrode was developed and used to characterize the sodium-sulfur system. This characterization was done by means of emf measurements and techniques such as coulometric titrations.

COMPOSITE SOLID ELECTROLYTE SYSTEMS

On the basis of some preliminary work reported earlier by Hitachi, Ltd., and the Electric Power Research Institute (EPRI), a small program was started in the late 1980s on composite solid electrolytes consisting of about 50 vol% each of sodium beta alumina and glass. The ANL glass appeared to be ideal for this purpose. The beta-alumina is expensive and difficult to fabricate into shapes such as flat plates for use in high-performance cells, but it is an excellent conductor of sodium ions. The glass is more amenable to fabrication in various configurations, but its conductivity is mediocre. The thought was that it might be possible to capitalize on the better features of both by forming them into a glass-ceramic mixture. Preliminary attempts to prepare a composite electrolyte resulted in a material having a resistivity of 1700 ohm-cm. The initial results were encouraging, but it was clear that more work would be required to develop a viable composite electrolyte. After a significant additional effort, which included a change in the glass composition to Na_2O-Al_2O_3-SiO_2, composites with excellent resistivity values (about 30 ohm-cm at 250°C) were obtained.

ALTERNATIVE CELL SYSTEMS

One can easily think of many combinations of elements and/or compounds that have the thermodynamic properties to generate a voltage when placed in an electrochemical cell. Very few make the grade as useful systems, however, because of a multitude of other conditions that must be satisfied, such as kinetic factors, electrochemical reversibility, compatibility with materials, and the availability of a suitable electrolyte, to name a few. The following systems were selected for exploration largely on the basis of information that had been developed in the existing battery programs.

Calcium/Metal Sulfide Cells. This work was predicated on the use of calcium as a low-cost substitute for lithium in the lithium-alloy/metal sulfide cells. The cell components were negative electrodes of $CaAl_{1.2}Si_{0.4}$, positive electrodes of $Fe_{0.93}Co_{0.07}S_2$, boron nitride felt separators, iron (negative) and molybdenum (positive) current collectors, and LiCl-NaCl-$CaCl_2$-$BaCl_2$ electrolyte (m.p., 383°C). A 154-Ah bicell of this type, which was operated for 102 cycles (3500 h), had a specific energy of 47 Wh/kg and a specific power of 50 W/kg. (The theoretical specific energy of this cell was 610 Wh/kg.) Multiplate cells were projected to have higher specific energy and power (>120 Wh/kg and 170 W/kg, respectively). A problem was encountered with declining coulombic efficiency, however, which limited the cell life to about 300 cycles. The cell life was limited by contamination of the felt separator by finely divided particles from the electrodes.

Sodium/Alkali Nitrate Cells. The sodium/alkali nitrate cells consisted of a molten sodium negative electrode, β"-alumina solid electrolyte, and a molten alkali nitrate positive electrode. The overall cell reaction is

$$2\,Na + MNO_3 \rightarrow Na_2O + MNO_2$$

where MNO_3 is the alkali nitrate, and MNO_2 is the corresponding nitrite. Three alkali nitrates were used: $NaNO_3$, $LiNO_3$, and $NaNO_3$-$LiNO_3$ eutectic. A 1.62-V cell with the eutectic electrode was operated at 206°C for 14 cycles. Potentiometric titrations and X-ray data showed the following reactions of $NaNO_3$ at 345°C and $LiNO_3$ at 275°C:

$$2\,Na + NaNO_3 \leftrightarrow Na_3NO_3$$
$$4\,Na + 2\,LiNO_3 \rightarrow Li_2O + Na_3NO_3 + NaNO_2$$

Additional cell tests were conducted reasonably successfully, but it appeared that an operating temperature of 330-350°C would be required, giving them no significant advantage over the existing sodium/sulfur cells, which operate at about 330°C.

Sodium/Metal Chloride Cells. Investigations were conducted on Na/MCl_x cells in which a metal chloride was substituted for the sulfur electrode in sodium/sulfur cells. Nickel dichloride ($NiCl_2$) was used for the positive electrode, and a secondary electrolyte of liquid $NaAlCl_4$ was required. Thus, the basic cell was

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

Variations of this system included the use of a composite electrolyte instead of beta alumina, iron chloride instead of nickel chloride, and additions of sulfur to the positive electrode. Conceptual cell-design studies for this system, using high-surface-area cells, yielded specific-power and specific-energy projections of about 300-500 W/kg and 200 Wh/kg, respectively.

The experimental studies were focused on means of increasing the performance of the $NiCl_2$ electrode. In the initial investigations, an 18 vol% nickel electrode had an area-specific impedance of 1.2 ohm-cm^2 at 300°C. By fabricating the electrode with larger and more uniform porosity, the area-specific impedance was reduced to 0.80 ohm-cm at 260°C. These impedance values were better than those for state-of-the-art cells, and these results pointed the way for further studies in the 1990s.

Aqueous Battery Research and Development

DEVELOPMENT OF ELECTRIC-VEHICLE BATTERIES BY CONTRACTORS

The program on aqueous-electrolyte batteries continued with the major effort consisting of research and development by industrial contractors on three types of batteries:

Lead-Acid:

Eltra Corp., Plymouth Meeting, PA
Exide Management and Technology Co., Yardley, PA
Globe Battery Division of Johnson Controls, Inc., Milwaukee, WI

Nickel/Iron:

Eagle-Picher Industries, Inc., Joplin, MO
Westinghouse Electric Corp., Pittsburgh, PA

Nickel/Zinc:

Energy Research Corp., Danbury, CT
Exide Management and Technology Co., Yardley, PA
Gould Inc., Rolling Meadows, IL

A milestone in 1981, which called for recommendations to DOE on a reduction in the number of contracts, resulted in three remaining contracts: lead-acid by Globe and nickel/iron by Eagle-Picher and Westinghouse. Work on the nickel/zinc system was discontinued in 1982 because of cycle-life problems caused by the zinc electrode, which is notorious for its poor behavior. (Joe Consiglio, who served as a consultant to CMT, once observed wryly that research on shape changes and dendrite formation in zinc electrodes has provided lifetime employment for a lot of electrochemists over the years.) In about 1985, the Globe name was shortened to "Johnson Controls." From 1984 to the end of the decade, essentially all of the contract work on aqueous batteries consisted of the Johnson Controls effort on lead-acid batteries and the Eagle-Picher effort on nickel/iron batteries. Significant progress was made on both systems.

Lead-Acid Batteries. This technology had been around for a long time, so the principal research activities dealt mostly with reducing the weight, increasing the power and energy, and extending lifetime during deep-discharge cycling. Eltra worked on lightweight, expanded-mesh electrode grids. Exide investigated electrode separator materials, changes in sulfuric acid electrolyte concentration, and cell design variations, including tubular positive plates. Johnson Controls was concerned mostly with an innovative design in which the electrolyte was pumped through porous electrodes. This approach increased the utilization of active material from about 30% to 55%. In 1983, Johnson Controls delivered full-size (108-V) electric-vehicle batteries to the National Battery Test Laboratory (NBTL) at Argonne for verification tests and to the Jet Propulsion Laboratory, Tennessee Valley Authority, and Detroit Edison for in-vehicle testing. This was considered to be intermediate state-of-the-art (ISOA) technology. Johnson Controls continued to provide cell modules and small batteries for NBTL and in-vehicle testing throughout the 1980s.

Nickel/Iron Batteries. Like lead-acid batteries, nickel/iron batteries (invented by Thomas Edison) were a well-developed technology that had been used in various industrial applications, but not for electric-vehicle propulsion, which demands high specific power and energy together with long cycle life and low cost. Experience had shown that most of the problems associated with the nickel/iron cell were at the nickel oxide (positive) electrode. Westinghouse, in an effort to reduce weight and cost, came up with a sintered steel wool electrode plated with nickel. They also investigated electrolyte and gas-management systems. Although reasonably good progress was made in achieving higher specific energy and power, and an extended lifetime of >900 cycles, the Westinghouse contract was concluded in 1983.

Eagle-Picher took the approach of thick, sintered electrodes in the nickel/iron cell. In 1982, the Northrup Corp. purchased and placed in operation 12 electric vehicles with Eagle-Picher batteries. Full-size batteries were delivered to the Jet Propulsion Laboratory, the Tennessee Valley Authority, and the U.S. Postal Service in 1984. In 1985, a multicell module achieved an equivalent of >55,000 miles of simulated electric car driving in NBTL, and long lifetime (>30,000 miles) was obtained in tests at the Tennessee Valley Authority. Although specific power and energy were still marginal for electric-vehicle use, the nickel/iron system appeared to have a potential for commercialization, and Eagle-Picher focused their effort on cost reduction.

NATIONAL BATTERY TEST LABORATORY (NBTL)

Electrical Performance Testing. Entering the 1980s, NBTL continued its function of testing contractors' and other cells, modules, and batteries (Fig. 5-7). In 1981, the testing capability was increased to 50 test stations (45 for cells and modules and 5 for full-size batteries). The following year, three high-current modules and two battery cyclers were added, and the environmental testing annex was commissioned. In this facility, three chambers were provided in which batteries could be tested at temperatures from -30 to +50°C, and safety measures, including special ventilation, were taken to permit testing of zinc/chlorine batteries.

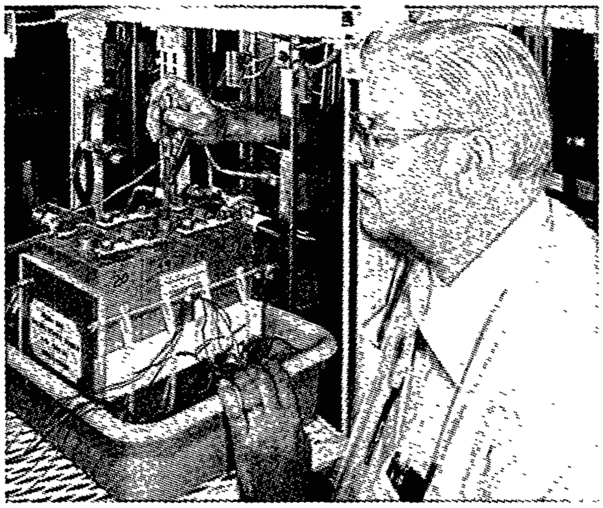


Fig. 5-7. Nickel-Zinc Module Being Prepared for Testing in National Battery Test Laboratory

Computer hardware and software were expanded, improved, and modified to handle many specialized tasks such as a library of driving cycles, data acquisition from individual cells in a 256-cell battery, pulsed-current charging and discharging, and thermal testing.

By 1985, over 1700 cells had been tested since 1978, and a capability had been added for testing high-temperature Li-FeS and Na/S cells. At that time the laboratory had assumed a somewhat different role with less emphasis on ANL contractors' cells and batteries and increased activity in general-purpose testing of a wide variety of cells and batteries. Ragone plots were developed for a variety of battery types. These are logarithmic plots of specific energy *vs.* specific power (see Fig. 5-8). Ragone plots are a convenient way of displaying data to be used in estimating battery discharge times for almost any load profile.

Post-Test Analysis and Diagnosis Laboratory (ADL). When electrical performance testing was completed, the cells, modules, or batteries were subjected to

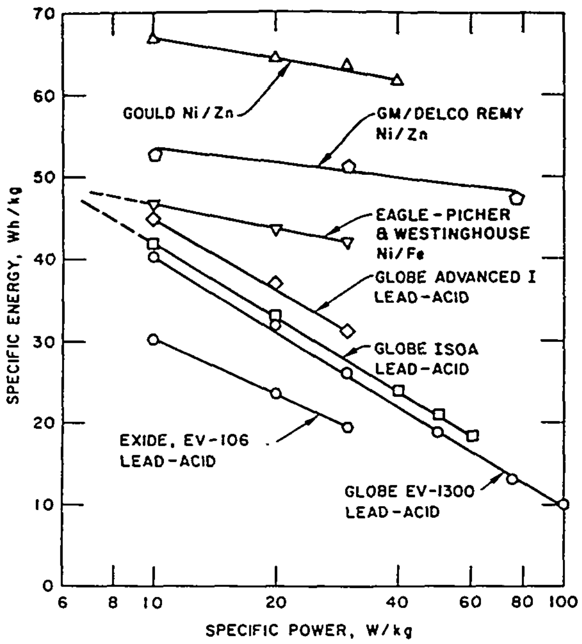


Fig. 5-8. Ragone Plot for Various Batteries Tested at NBTL

post-test examinations, which usually showed the cause of failure or performance loss. Other valuable information was obtained, such as corrosion, chemical phases in the electrodes, distortion of cell hardware, and many other effects.

The analysis normally proceeded through three stages: (1) evaluation of NBTL test results, non-destructive testing, dissection, and visual examination, (2) detailed analyses of component materials, individual electrode cycling, examinations by scanning electron microscopy (SEM), X-ray fluorescence, and other appropriate instrumental methods, and (3) identification of cell-failure mechanisms.

Failures of lead-acid cells usually occurred in the positive (PbO_2) electrode due to deterioration and/or shedding of active material from the electrode, or to current-collector corrosion. In the nickel/iron cells, failures were most often a result of contamination of the nickel oxide (positive) electrode by iron or mechanical failures of the cell hardware. As mentioned earlier, the nickel/zinc cells were plagued by shape changes and dendrite formation in the zinc (negative) electrode. Although these effects could be ameliorated somewhat by resorting to measures such as vibrating electrodes, further development work on this system was halted.

When a post-test examination was completed, the contractor was provided with a report of the findings and recommendations for corrective action. On many occasions, contractors' representatives observed the examinations as they were being performed.

SUPPORTING BATTERY RESEARCH

An in-house program was conducted by CMT to provide supporting research backing up the more applied work being done by the contractors and ANL. Much of the work under this task involved mathematical modeling of cell and battery behavior and heat effects produced by battery operation. The modeling effort also included studies of battery-vehicle integration in electric vehicles, and an analysis was made in 1980 of all the battery performance and vehicle data available at the time. Models were generated for the thermal effects in batteries (heat-generation rates, heat removal by convection and radiation, and temperature distribution). Models were developed for the equivalent electrical circuit of a battery to determine how it would behave as a component in an integrated system such as an electric vehicle. A mathematical model was constructed for vibrating electrodes (of particular interest to the Ni/Zn battery). Up until about 1983, mathematical models were based largely on statistical experimental data. A new approach was taken at that time, in which fundamental electrochemical principles, and engineering considerations, were integrated into a physical-mathematical model applicable to any battery system with minor modifications. Results from this model and those from experimental data were in excellent agreement both for lead-acid and nickel/iron batteries.

Several supporting research studies were conducted on lead-acid cells. Overcharging can result in the production of arsine (AsH_3) and stibine (SbH_3), which come from arsenic and antimony present as alloying elements or impurities and are highly toxic. The production rates of these gases under different conditions were quantified by experimental measurements and used to make recommendations for ventilation in charging facilities. Laser-Raman and neutron-scattering techniques, in cooperation with the Solid State Science (SSS) Division, were used to study the structures of electrodes in lead-acid cells, and these were followed by an in-depth, neutron-diffraction study of PbO_2 on Pb, Pb-Sb, and Pb-Ca-Sn grids. These studies revealed important information on the behavior of PbO_2 electrodes in lead-acid cells.

Current distributions in zinc electrodes and ionic conductivities of zincate-potassium hydroxide electrolytes were investigated. Zinc is transported between the electrodes of a Ni/Zn cell in the form of zincate (ZnO_2^{2-}) ions. Laser-Raman and nuclear magnetic resonance techniques were used to investigate the structure of the zincate ions. Only one dominant Zn^{2+} species with tetrahedral coordination was found. Resistance factors in the separators and the effects of electrolyte agitation in Ni/Zn cells were evaluated. Penetration of the separator material by growth of zinc deposits was a continuing problem in these cells. In the case of nickel/iron cells, about the only problem unique to that system was iron contamination of nickel electrodes, which was examined in some detail.

Most of the other supporting work was of a general nature, such as thermal management, charging and discharging regimes, self-discharge rates, overcharge effects (gas evolution and water loss), and effects of temperature.

OTHER BATTERY APPLICATIONS

Although the primary emphasis of the aqueous battery program was on electric-vehicle propulsion, two other applications were given some attention: (1) load leveling on utility networks and (2) hybrid fuel-cell/battery vehicles.

Load Leveling. The requirements for load-leveling batteries differ considerably from those for vehicle propulsion in that the major consideration is low cost, rather than low weight. Implicit in the cost are manufacturing cost, cycle life, and volumetric energy density (kWh/m^3). A cost and design study of lead-acid batteries in 1980 indicated that they might be marginally acceptable for bulk electrical energy storage, and goals were set for an acceptable system: a lifetime >4,000 cycles, a maximum initial cost of $50-75/kWh, and a minimum energy density of 75 kWh/m^3.

Contracts were awarded to C&D Batteries, Inc., and Exide for three tasks: (1) research and development on advanced lead-acid cells and modules, (2) demonstration of pilot-line production of advanced modules, and (3) construction of a 5-MWh battery for testing in the Battery Energy Storage Test (BEST) facility. The C&D contract was dropped for lack of funding. Exide, in 1982, exceeded 6,000 cycles with 1,800-Ah cells and 15,000 shallow cycles with 200-Ah cells. In 1983, three modules delivered to ANL for parametric cycle-life tests exceeded the design goals.

Hybrid Vehicle. Studies were performed for DOE on a hybrid vehicle concept that combined a methane-fueled phosphoric-acid fuel cell with a battery for an electric bus. The idea was to operate the vehicle primarily on the fuel cell with a small amount of surplus power to charge the battery. When extra power was needed for acceleration or hill climbing, the additional energy would be retrieved from the battery. This application would require a smaller, but higher-power battery than the all-electric vehicle.

INDUSTRIAL ELECTROCHEMICAL TECHNOLOGY

In the early 1980s, the Chemical Technology Division undertook a program aimed at reducing the amount of energy consumed nationally in electrolytic processes for the production of various materials. Although this work was not battery-oriented, it is mentioned here because it was done as an adjunct to the aqueous battery program. Preliminary surveys indicated potential process improvements for the commercial production of chlorate, hydrogen peroxide, ozone, chlorine and sodium hydroxide (chloralkali process), aluminum, and zinc. Most of the ANL in-house work was performed on processes for the conversion of Al_2O_3 to Al_2S_3, followed by electrolysis of the Al_2S_3 in a molten salt solvent, *e.g.*, $NaCl\text{-}KCl\text{-}MgCl_2$. The proposed process ran into several difficulties, including an inability to convert the aluminum oxide completely to sulfide and incomplete electrolytic reduction of the Al_2S_3, so the effort was terminated.

Studies of the chloralkali process indicated that the NaOH concentration in the cells could be increased from the usual 29% to about 50% without serious polarization problems in membrane cells. The conclusion was that the membrane, rather than polarization or conductivity effects, was the limiting factor on energy savings and technical feasibility in the production of 50% NaOH in membrane cells.

In 1983, the Electrochemical Industrial Associates (IEA) program was proposed. This program, sponsored by ANL, was intended to provide consulting and some experimental support to dues-paying industrial members in the technology of batteries, fuel cells, and industrial processes. The program was unsuccessful; the industries preferred to work through special research and development contracts. As DOE funding of the electrochemical programs had decreased steadily through the 1980s, the Division did pick up some "work for others," but the overall program continued to diminish in scope.

PERSONNEL

In 1980, this was the largest program in the Division, and it was organized as the Office of Electrochemical Program Management under the direction of Mike Yao. Group Leaders were Clint Christianson, Fred Hornstra, Glenn Cook, and Ralph Loutfy. Financial support both for contract work and for in-house research diminished throughout the decade, causing certain reorganizations. The engineering development work on lithium-alloy/metal sulfide batteries was moved into this organization in the mid-1980s, and all the battery work had been consolidated into one entity by 1990. Paul Nelson, who had become the Deputy Division Director in 1982, had jurisdiction over the electrochemical programs. After Mike Yao's departure in 1985, John Ackerman was placed in charge of the battery and fuel-cell work, and Clint Christianson became a Section Head responsible for the aqueous battery program. In 1989, Mike Myles was given overall responsibility for the electrochemical programs. The following is an attempt to list those associated with this program in the 1980s:

John Ackerman, John Barghusen, Joe Becker, Ed Berrill, Dick Biwer, Ira Bloom, Alan Brown, Louis Burkel (MST), Earl Carothers, Al Chilenskas, Clint Christianson, Glenn Cook, Dave Corp, E. Creamer, Bill DeLuca, Eva Folke, Don Fredrickson, Eddie Gay, Mike Genge, Mark Hash, Ed Hayes, Roger Hogrefe, Fred Hornstra, Chen-Chao Hsu, Tom Kaun, Jiri Klinger, Dick Kmiec, Marvin Kronenberg, Johnsee Lee, Tien Lee, Ralph Loutfy, Jane Marr, Janet Meisenhelder, John Miller, Nguyen Mingh, Frank Mrazek, Tom Mulcahey, Mike Myles, Ron Paul, Dave Poa, John Rajan, Laszlo Redey, Lewis Ruppert, Paul Shimotake, Merril Singleterry, John Smaga, Greg Smith, Carl Swoboda, Tony Tummillo, Ravi Varma, George Vasilopulos, Don Vissers, John Weber, Carl Weber, and Mike Yao. Secretaries included Marlene Bukowski, Wendy Strle, Elaine Estand, Sherry Grisko, Kerry Kilian, Wendy Lamb, Dawn Landis, and Charlotte LeGrand, who was the head secretary until she left the Division in 1985.

Fuel Cells

The Division's fuel-cell program had become well established by 1980, and, like several other DOE programs, consisted of two responsibilities: (1) technical management of DOE's programs on advanced fuel-cell development and (2) supporting research and development on molten carbonate fuel cells (MCFCs). This responsibility was expanded in 1981 to include solid oxide fuel cells, which were being developed at the Westinghouse Electric Corp. In 1982, DOE management of its fuel-cell programs was shifted from Washington Headquarters to the Morgantown Energy Technology Center in Morgantown, West Virginia.

In the mid-1980s, workers at ANL came up with a novel concept known as the monolithic solid oxide fuel cell, which had a potential for very high performance and a capability to run on hydrocarbons, as well as the hydrogen, carbon monoxide, natural gas, or alcohol fuels normally used in fuel cells. Initial funding for this work was provided by the Defense Advanced Research Project Agency (DARPA) of the Department of Defense (DOD). The CMT fuel-cell programs experienced the same budget squeeze as the battery programs and others, but managed to survive through the 1980s.

MOLTEN CARBONATE FUEL CELLS

The molten carbonate fuel cell (MCFC), as outlined in the previous chapter, consisted of a lithiated nickel oxide cathode and a porous nickel anode separated by a rigid electrolyte tile composed of molten Li_2CO_3-K_2CO_3 in a solid $LiAlO_2$ matrix. The operating temperature was about 1000°C, and each cell generated about 0.8 V. The fuel of greatest interest was "synthesis gas" (hydrogen and carbon monoxide) produced from coal in a fuel processor. Advantages claimed for this system were (1) use of coal, (2) very low pollution, and (3) high efficiency (50% from coal to bus bar).

Two major contractors were involved in the MCFC program, the General Electric Co. and United Technologies Corp. Their objective was to develop and fabricate full-size (0.5- to 1.0-MW) cell stacks and provide DOE with information needed to proceed with stack development. Supporting work was performed by the Energy Research Corp., mainly on possible incorporation of a reforming catalyst into the fuel cell, and by the Institute of Gas Technology on methods of handling sulfur impurities in the fuel.

Electrolyte Studies. Work continued, in cooperation with members of the Materials Science Division (MSD), on the preparation of tile electrolytes from $LiAlO_2$ powder and Li_2CO_3-K_2CO_3 salt by pressing and sintering. The sintered electrolytes needed to be thin and porous (about 60%). Information from the literature suggested that tape casting might be an alternative to pressing and sintering for electrolyte preparation. The tape-casting procedure involves preparation of a thick slurry (slip) of the powders in a mixture of plasticizer, binder, deflocculating agent, and solvent. The mixture is distributed on a plate in a specified thickness, dried to form a pliable sheet, and fired to form a thin ceramic. Tape casting did not prove to be suitable for molten carbonate fuel cells, but experience with the technology became very useful in later work on monolithic solid oxide fuel cells. Work continued on the pressed and sintered tiles to optimize conditions for their preparation and to determine their behavior (swelling and other effects) during in-cell tests.

Cathode Development. Efforts were also continued on the preparation of cathodes, which were basically nickel oxide (NiO) doped with lithium oxide (Li_2O) to impart electrical conductivity. The cathodes were made initially by in-cell oxidation and lithiation of a porous, sintered nickel plate in the molten carbonate electrolyte under an air-carbon dioxide atmosphere. A more controlled procedure was developed in which electrode plates of the composition $Li_{0.05}Ni_{0.95}O$ were prepared for later assembly into the cells.

Although the lithiated nickel oxide cathode performed reasonably well, it underwent a very slow dissolution process that limited its lifetime to about 4,000 hours, which was far short of the 40,000-hour goal. This was something of a setback in the program, which resulted in work on alternative cathode compositions. Certain oxides such as Li_2MnO_3, $LiFeO_2$, and ZnO were expected to be chemically stable and to exhibit electronic conductivity when doped with appropriate additives. Detailed studies were conducted on Li_2MnO_3 and $LiFeO_2$ doped with Ca^{2+}, Fe^{3+}, Al^{3+}, and Nb^{5+} with some encouraging results. As of 1989, NiO continued to be the cathode of choice, but the alternatives were still of interest as possible replacements.

Anode Development. The anodes in MCFCs were a porous nickel alloy. The idea of using electrically conductive oxides was explored. Potential candidates for this purpose were oxides that might have dual valence states, *i.e.*, $LiFeO_2$, Li_2TiO_3, Li_3TaO_4, Li_3VO_4, Li_3NbO_4, Li_2ZrO_3, MnO, and CeO_2. Good conductivity requires electronic defects, which means that the material must be non-stoichiometric. Detailed studies of these compounds showed undoped $LiFeO_2$ to be a promising possibility, and an investigation was started on MnO. As of 1989, however, this work had not progressed to the stage where these materials were ready to replace porous nickel as the anode.

Methods were investigated for introducing controlled porosity into oxide electrodes during their fabrication. Pore-size distribution, shape, and degree of interconnection are all factors in achieving a successful electrode. A technique that proved particularly successful was to incorporate small ceramic fibers produced by a spray process into the electrode mix. The procedure worked well both for pressed and sintered and tape-cast electrodes.

Contract Work and Commercialization. Argonne's role as technical manager of the DOE Fuel Cell Program prohibited any design or development work at the Laboratory; its activities were limited to basic research and technical support. Stated briefly, the goals set in 1981 for the contract work on MCFCs were as follows.

1. Demonstration of 20- to 100-cell stacks of full-size cells.
2. Design of facilities for testing full-scale stacks.
3. Operation of single cells under a variety of conditions.
4. A reference design for a coal-fueled fuel-cell plant.
5. Experimental operation using the product of a coal gasifier.

In 1982, DOE decided to place most of the development work on MCFCs at United Technologies Corp., but General Electric, Energy Research Corp., the Institute of Gas Technology, and ANL remained in the program. The DOE plan was to develop a pilot plant on a schedule consistent with an expectation that commercialization would begin to accelerate after 1987.

Three system-design studies were made. These studies employed an MCFC model from Physical Sciences, Inc. (PSI) on reforming methane into CO and H_2, based on the premise that natural gas would be the best fuel for entering the market. The study included three cases: (1) a conventional external reformer, (2) a reformer heated by the sensible heat in recycled fuel, and (3) a reformer integral with the anode of the fuel cell (internal reforming). Energy-conversion efficiencies were estimated to be 50-60%. One conclusion was that operation at pressures of 6-10 atm would be economically advantageous.

The problem mentioned earlier about limited lifetime of MCFCs came to light in 1982, and the original goal of building and operating a full-scale stack by the mid-1980s was delayed by 3-4 years. In 1983, a small plant analysis was made for phosphoric acid fuel cells operating on natural gas fuel, and this was followed by a wider market application analysis conducted by the ANL Energy and Environmental Sciences Division (EES) with participation by the CMT and Engineering (ENG) Divisions.

In 1984, the United Technologies work was transferred to an organization called International Fuel Cells (IFC), which had previously been a part of United Technologies. At about the same time, the DOE set a goal of a full-scale stack of cells having a lifetime of 40,000 hours (roughly five years) in the 1990s. By 1985, IFC had operated 20-cell stacks that gave excellent performance at first, but then developed problems with the NiO cathodes. At that time, several other ANL divisions were participating in the fuel-cell program, namely, Materials and Components Technology (MCT), Engineering (ENG), Energy and Environmental Sciences (EES), and Materials Science and Technology (MST). With the increasing competition for the diminishing funding and the proliferation of divisions at ANL, there was a general tendency toward fragmentation of the larger applied programs into specialized groups in different divisions.

Development of MCFCs by contractors continued in the 1980s. International Fuel Cells continued operation of a 20-cell, full-area (0.7 m^2), 25-kW stack for 1,700 hours, and ERC ran a four-cell, 0.4-kWh stack with internal reforming of the fuel.

SOLID OXIDE FUEL CELLS

Tubular Cell Design. The development of solid oxide fuel cells (SOFCs) began several years later than that on other advanced fuel cells. The principal difference between SOFCs and the previous types was the use of a solid, rather than liquid electrolyte to transport ions between the electrodes. In the early 1980s, the Westinghouse Electric Corp. was working on a solid oxide cell that consisted of a metal oxide (lanthanum manganite) cathode, a cermet (Ni or Co in ZrO_2) anode, and a Y_2O_3-stabilized ZrO_2 solid electrolyte capable of transporting oxygen ions. Electrical connectors between the cells were lanthanum chromite, which is electronically conductive and served the same function as the metallic bipolar intercell connectors in the MCFCs.

The Westinghouse cells had a tubular configuration and operated at about 1000°C. At the anode, hydrogen and carbon monoxide in the fuel gas react with O^{2-} ions from the electrolyte, giving up electrons to an external circuit and forming water and carbon dioxide as the products. At the cathode, oxygen accepts electrons from the external circuit, forming O^{2-} ions in the electrolyte. The electrodes were very thin, typically about 25 μm, while the electrolyte and interconnectors had thicknesses of several hundred micrometers. In a power-plant application, 100 or so cells would be connected electrically in series with parallel gas flows to form a module. The SOFCs were of a simpler design than the MCFCs, but the thermodynamic efficiency was 10-20% lower. The thought was that the SOFCs would be used in smaller, lower-cost plants with a pressurized gas and steam turbine bottoming cycle. An overall efficiency of at least 60% was anticipated for this type of system.

The program goals for 1985 were to demonstrate (1) acceptable cell lifetime and performance, (2) a thermal management system in a submodule of 15-25 cells, and (3) a 5-kW generator. Argonne had the same role as in the other programs, that is, to provide technical management and support. The support work included independent cell testing to assess the technology, modeling to gain insight into the cell behavior, and other general technical support.

By 1984, Westinghouse had obtained stable cell performance for more than a year and had operated a 300-W unit. The following year, over 9,000 h of stable performance was achieved, and plans were made to scale up the system to 5 kW in 1986. Argonne management of the Westinghouse program was terminated because of a possible conflict of interest with Argonne's development work on their monolithic solid oxide fuel cell (MSOFC).

Monolithic Solid Oxide Fuel Cell. In 1981, workers in CMT came up with a novel design for a solid oxide fuel cell capable of outstanding performance. Because the cell components were all thin solids, it appeared that they could be fabricated into a compact, monolithic structure that would achieve a power-to-volume ratio about 100 times that for molten carbonate cells. Development work on MSOFCs began at ANL in 1983 as a joint effort of the CMT and MST Divisions supported by DOE and the Defense Advanced Research Projects Agency (DARPA). The DARPA support derived from the fact that a compact, very high-power fuel cell could have a number of military uses.

A monolithic fuel cell stack, along with the chemical reactions and current-flow pattern, is shown in Fig. 5-9. The electrode materials and chemical reactions are basically the same as those in conventional tubular SOFCs. The two electrodes and intervening electrolyte, each having a thickness of about 0.025 to 1.0 mm, were fabricated in one piece as a thin, three-layer sheet formed into a honeycomb-like cell with a structure much like corrugated paperboard. The cells were stacked with sheets of electrically conductive material between them to provide a current path from cell to cell, similar to the bipolar plates used in MCFCs. Fuel and air were passed through the cells in alternating passages through the honeycomb. At the operating temperature of about 800-1000°C, hydrocarbon fuels were reformed within the cell, so the cells could be operated with hydrocarbon, as well as hydrogen or other fuels. The cells could be arranged for parallel flow of the reactants, or stacked with

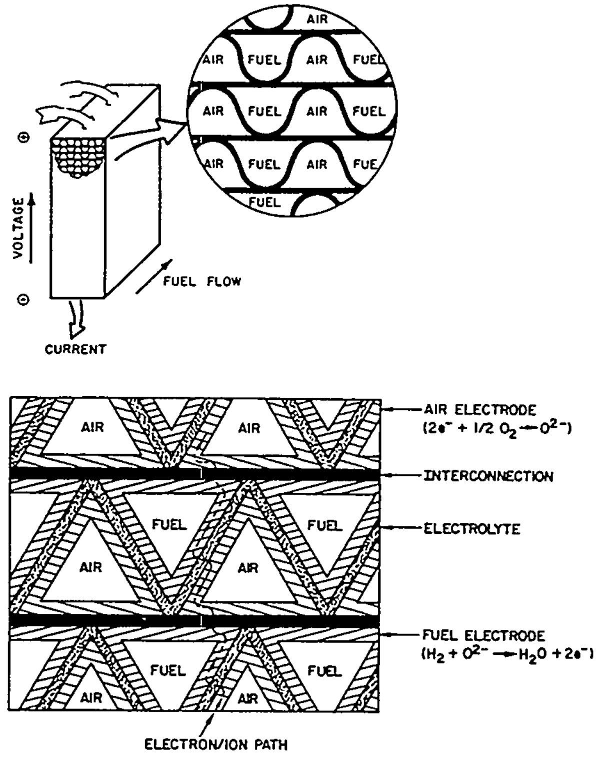


Fig. 5-9. Monolithic Solid Oxide Fuel Cell

each cell oriented 90° from the adjacent ones to establish a cross-flow pattern. One of the advantages of the monolithic design was that manifolding of the gaseous reactants and products was relatively simple. The cross-sectional areas of the gas passages in the honeycomb were equivalent to a diameter of 1-2 mm.

The cathodes (on the air side) consisted of strontium-doped lanthanum manganite ($LaMnO_3$), and the anodes (on the fuel side) were a nickel-yttria (Y_2O_3)-stabilized zirconia (YSZ) cermet. The solid electrolyte was Y_2O_3-stabilized zirconia ZrO_2, which conducted oxygen ions between the electrodes. The material connecting the cells in a stack was strontium-doped lanthanum manganite. It is interesting to note here that the research leading to the selection, synthesis, and testing of these materials was highly dependent on advances in solid-state science that were occurring very rapidly at that time.

Development of the electrodes was tricky. The cathode needed sufficient porosity to permit a reasonable rate of oxygen diffusion to the cathode/electrolyte interface where the oxygen molecules react. The electrolyte had to be very thin so its electrical resistivity (for oxygen ions) would not limit the current density (and power) too much, while at the same time it had to be leak-tight with no cracks or open porosity. In the anode, the electrical conductivity depended on particle-to-particle contact, which was lost if the nickel content was too low. If it was too high, however, thermal expansion of the electrode was too great to match it with the other layers.

Fabrication of the three-layer composites was an equally challenging task. Sequential tape casting, coextrusion, and other procedures were investigated with some success. A critical factor during fabrication was to match not only the coefficients of thermal expansion of the finished components, but also their shrinkage patterns during firing in the fabrication process. Any gas leakage between the electrodes would cause a loss of efficiency, and a great deal of effort went into the elimination of cracks or open porosity. By 1986, this effort was largely successful, and two cells were operated for more than 700 hours at a temperature of 1000°C and a current density of 50 mA/cm^2, using hydrogen fuel and air. Successful operation was also achieved with hydrocarbon fuels (methane, ethane, propane, octane), ethanol, and natural gas containing 5 ppm sulfur. By 1987, essentially all the defects had been eliminated, and the cell performance was approaching the theoretical level.

Although the basic technology had been demonstrated on a small scale, much work was going to be needed in scaling the system up to practical power level of at least a few kilowatts. A decision was made that a team consisting of ANL, Allied Signal Aerospace/AiResearch, and Combustion Engineering should do this development work. Allied Signal was to be the prime contractor and ceramic fabricator, Argonne was to develop and improve materials technology, and Combustion Engineering was to develop and test fuel-cell systems. Table 5-6 gives fuel-cell performance projections for different types of cells powering electric vehicles.

Table 5-6. Fuel Cell Performance Projections for Electric Vehicles

Fuel Cell Types	Power Density, W/L
Conventional Phosphoric Acid	302
Proton Exchange Membrane	1,575
Molten Carbonate	700
Monolithic Solid Oxide	2,779

PERSONNEL

The MCFC program continued into the 1980s, and work on the MSOFCs began in 1983. The funding agencies at the time felt very strongly that Argonne's role in the programs had to be limited to program management and technical assistance to the agency, with only a limited experimental effort supporting the technology development. In both fuel-cell programs, the basic technological concepts had been demonstrated at ANL by the mid-1980s, and remaining development, scale-up, and demonstration efforts were relegated to industry. In the Division, the result was that the sizable research effort in the early 1980s dwindled down to a small group of four or five people by the end of the decade. Up until about 1987, Dean Pierce and Darrell Fee were the group leaders for the molten carbonate and solid oxide programs, respectively, both of them reporting to John Ackerman, who was also the technical manager for all DOE fuel-cell programs. In 1987, Dean and Darrell both left the fuel-cell program, and Mike Myles became responsible for all the CMT electrochemical programs. Jim Smith assumed responsibility for the molten carbonate work, and Chuck McPheeters was given the solid oxide program. Later on, Mike Krumpelt took on the solid oxide work, and became particularly recognized for his assessments of potential fuel-cell applications.

Other individuals who worked on fuel cells in the 1980s include Paul Blackburn, Alan Brown, Terry Claar (MST), Glenn Cook, Dennis Dees, Tony Fraioli, John Heiberger, Hann-Sheng Huang, Tom Kaun, Kim Kinoshita, Verne Kolba, Ted Kraft, Gene Kucera, Frank Mrazek, Roger Poeppel (MST), John Rajan, Jim Sim, Joe Stapay, Bob Steunenberg, John Young, and Stan Zwick. Judy Popik was the principal secretary for these groups; Marlene Bukowski and Alice Birmingham also provided secretarial services.

Coal Utilization

Fluidized bed combustion of coal in a limestone bed continued to be the Division's major coal technology program in 1980.

ARGONNE PREMIUM COAL SAMPLE PROGRAM

In 1984, Argonne was awarded the Premium Coal Sample Program, the objective of which was to provide the coal research community with well characterized and stabilized samples of coal for research purposes, *e.g.*, development of a general understanding of the basic structures and the fundamental reaction processes of coal. The program was a joint effort between the Chemistry and Chemical Technology Divisions. The responsibility of CMT was design, construction, and operation of the coal-processing facility. The Chemistry Division was responsible for characterizing and administering the coal sample bank.

Two separate, sealed enclosures were constructed in Building 211 (formerly the cyclotron building) between Buildings 200 and 205. Each enclosure had a volume of approximately 1,500 cubic feet. A nitrogen atmosphere containing less than 100 ppm by volume of oxygen was maintained in each enclosure. In the first enclosure, about 3/4 metric ton of coal could be crushed and ground to the desired particle size. The crushed material was blended in a large blender located between the two sealed enclosures and then transferred to the second enclosure, where it was apportioned by means of a spinning riffler either to 5-gallon glass carboys or to a filler-sealer machine. This automatic machine metered the coal in either 5- or 20-g amounts into amber borosilicate glass ampoules, which were then flame sealed. About 5,000 of the 20-g ampoules and 10,000 of the 5-g ampoules were produced in each coal-sample run. The balance was stored in the 5-gallon carboys for packaging later and distribution to the research community. A variety of coals were processed in the mid-1980s.

SEPARATION OF COAL MACERALS

An outgrowth of the Premium Coal Sampling Program was a research program in the Chemistry Division on coal macerals. Macerals are microscopically distinguishable organic remains, which are present in all coals. The separation of coal macerals from the mineral matter and sulfur content of coal could make possible the tailoring of feedstocks for optimum utilization of coal and for more efficient coal-conversion technologies.

The Chemistry Division used density-gradient centrifugation for separation of macerals. By this procedure, only milligram to gram amounts of macerals could be separated in a single run. Therefore, the CMT Division was asked to develop a continuous process for production of large quantities of macerals. Two process concepts were investigated, both based on the fact that when a paramagnetic fluid in placed in a magnetic field gradient, the apparent density of the fluid increases. The magnetic field could, in theory, be "tuned" to produce a density at which the coal macerals could be separated. The first concept was a simple flow system in which separations were attempted at the very high magnetic fields produced by a superconducting quadrupole magnet, using manganese chloride as the paramagnetic fluid. In the second concept, centrifugation was carried out using a colloidal suspension of magnetite, which has a magnetic susceptibility 1,000 times that of manganese chloride. This allowed use of a simple electromagnet. Unfortunately, neither system worked very well, so the program was terminated.

FLUIDIZED-BED COMBUSTION OF COAL

At the end of the 1970s, the DOE concluded that atmospheric fluidized-bed combustion (AFBC) of coal was ready for commercialization. The two major applications of this technology were generation of steam for industrial purposes (boiler sizes of 50,000 to 200,000 lb of steam per hour), and for generation of electricity in large utility boilers. An AFBC steam boiler at Georgetown University had been operated without major problems, and its builder offered an entire series of AFBC boilers for commercial use. The Tennessee Valley Authority (TVA) was proceeding with construction of a 20-MW AFBC pilot plant and design of a 200-MW power plant.

In 1980, programmatic control of CMT's fossil energy program was transferred from DOE Headquarters to the Morgantown Energy Technology Center (METC) in Morgantown, West Virginia. Additional refinements of AFBC technology by CMT were authorized. The CMT program was aimed at solving problems, filling information gaps, improving process operability and economics, and reducing environmental impacts. In the early 1980s, work was concentrated in two areas: (1) development of a methodology for predicting the amount of a given limestone or dolomite sorbent required to retain effectively the SO_2 produced during combustion of coal, and (2) development of a hydration process for enhancing the extent to which a sorbent could be sulfated.

Prediction Methodology for Sorbent Utilization. A key to the widespread use of the AFBC technology was the ability to predict accurately the sorbent feed rate required for different limestones and dolomites that keep SO_2 emissions within environmental standards. To provide a prediction methodology, Darrell Fee undertook the development of two models, one to predict in-bed sulfation and the other to predict particle attrition within the fluidized bed. The background information for development of these models was published in a sourcebook on the utilization of limestones and dolomites (ANL/CEN-80-10). This sourcebook contained the chemical, physical, and morphological properties of 29 limestones and dolomites, as well as their distribution in the United States.

A CMT in-bed sulfation model was developed, for which knowledge of sorbent-specific sulfation behavior was required. This was best obtained by thermogravimetric analysis (TGA). For this purpose a standard TGA was defined. Comparison of model predictions with actual combustor experience showed that the model underpredicted the sulfur retention for a given Ca/S molar ratio by 20 to 30%. Two reasons were advanced for this discrepancy: (1) the extent of sulfation in the freeboard region above the bed was not taken into account, and (2) the standard TGA did not adequately show the in-bed sulfation behavior of a sorbent. In a large Babcock and Wilcox boiler, the amount of sulfur captured in the freeboard region was 9 to 10% of the total, which is a significant amount. Experiments also showed that the maximum amount of sulfation found by the TGA was generally slightly lower than that in an actual AFBC. The reasons for this were not pinned down.

In 1982, the model was revised to include sulfation in the freeboard area and to take into account the variation in sorbent particle size in the fluidized bed. (Equations for the model appear in ANL-83-55, pp. 64-65.) Better agreement with operating experience was achieved with this model. The model was something of a *tour de force*, but it was never fully perfected. (Darrell Fee, who had been the leader of this effort, became group leader of the SOFC group at that time.) Other people who contributed to development of the model were Liang-Shih Fan, Irv Johnson, John Lenc, Mike Myles, John Shearer, Greg Smith, Ira Wilson, and S. Wong.

A stochastic model was developed to predict the change in the size distribution of sorbent particles as a result of attrition. Pneumatic-transport attrition data were used to verify the model. The model predicted the experimentally measured particle-size distribution to within half an order of magnitude.

Hydration-Enhanced Limestone Utilization. In a search to increase the sulfation of limestone, hydration and subsequent in-bed dehydration of partially spent sorbents greatly enhanced their sulfur-retention capacity. Sulfation of limestone is impeded by buildup of a surface layer of $CaSO_4$. Treatment with water hydrates residual CaO to form $Ca(OH)_2$, with a resultant expansion that cracks open the surface layer. Subsequent dehydration of the $Ca(OH)_2$ yields a highly reactive form of CaO for reaction with additional SO_2.

A demonstration of the hydration process in CMT showed that nearly 90% of the CaO could be utilized by employing five hydration-sulfation cycles conducted alternately in the same fluidized-bed unit. Similar results were obtained at the Grand Forks Energy Technology Center. However, elutriation losses of fine particles were high because of decrepitation of the sorbent particles caused by the hydration-dehydration cycles. Make-up of the sorbent losses resulted in a high sorbent-to-coal ratio for achievement of high calcium utilization (see Fig. 5-10).

Sorbent hydration in a fluidized-bed unit was also investigated. With residence times of only 10 to 20 minutes, the fluidized-bed hydrator would be only 2.5 to 5% of the size of the fluidized-bed combustor. Economic assessments projected operational savings of $214,000 per year for an industrial boiler producing 100,000 lb of steam per hour. The projected period for payback of the additional

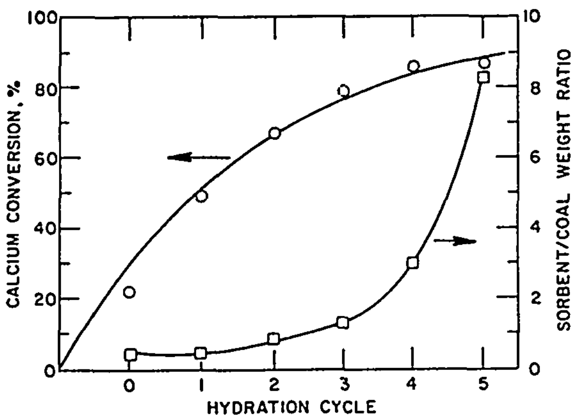


Fig. 5-10. Results of Limestone Hydration Experiments

capital costs required to install the hydration process was 1.5 yr for sulfation and hydration in the same fluidized-bed unit and 1.1 yr for separate sulfation and hydration units. The DOE terminated financial support of the hydration process despite industrial interest in it because of the increase in sorbent utilization.

Because atmospheric fluidized-bed combustion was considered ready for commercial use, emphasis in CMT was shifted to development of pressurized fluidized-bed combustors (PFBCs) for utilities and to advanced fluidized-bed concepts such as multistage combustion and circulating beds.

CLEANUP OF HOT GASES FROM PRESSURIZED FLUIDIZED-BED COMBUSTORS

Work continued in the 1980s on hot gas cleanup technology for PFBCs. The high-temperature, high-pressure off-gas generated from a PFBC is expanded through a gas turbine to recover energy. Alkali metal sulfates are formed by chemical reactions of alkali metal chlorides in the off-gas by the reaction

$$2\,NaCl + H_2O + SO_2 + 1/2\,O_2 \\ \rightarrow Na_2SO_4 + 2\,HCl$$

Atmospheric-pressure studies in the late 1970s showed that the alkali metal chlorides could be removed effectively by beds of diatomaceous earth and activated bauxite. In the early 1980s, an experimental apparatus that allowed tests to be made at 10 atm pressure was fabricated and placed in operation (see Fig. 5-11). The hot flue gas was first passed through a primary (hot) cyclone to remove the bulk of the particulate matter. A small fraction of the gas was then diverted through the bauxite sorber unit to test its effectiveness for removal of the alkali compounds. The main flow of the flue gas continued through a cold cyclone, after which both gas streams were combined and filtered through a metallic filter for final knockdown of the fine particulate material. This system removed essentially all the particulate matter from the flue gas. The activated bauxite was regenerated by water leaching. The capture efficiency of the activated bauxite for alkali metal compounds was not decreased with repeated regeneration.

Tests were conducted to determine the extent to which activated bauxite and diatomaceous earth were themselves sources of alkali. Under conditions closely resembling those of actual PFBC operation, the amount of sodium and potassium evolved from activated bauxite was very small. On the other hand, evolution of alkali metal compounds from a diatomaceous earth (Emathlite) continued at a

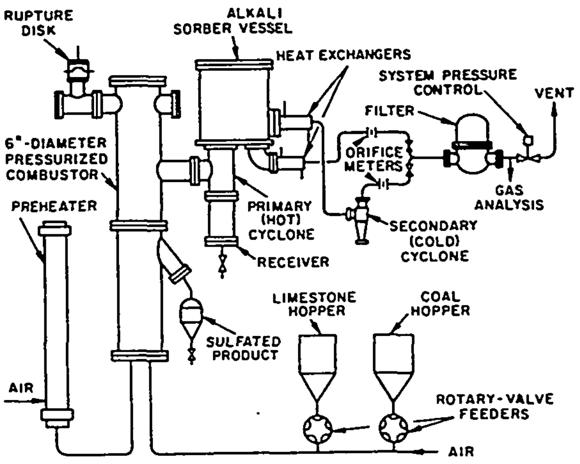


Fig. 5-11. Pressurized Fluidized Bed Facility

very high rate over the 50-hour duration of the experiment. Diatomaceous earth was therefore dropped from further consideration as an adsorbent.

The concentration of alkalis entering the absorber bed was analyzed by a computer-controlled, flame-emission spectrometer supplied by Ames Laboratory. A batch-type alkali and particulate sampling train (APST) was also installed as a backup for analysis of alkali metal content of the off-gases. Results obtained with the Ames emission spectrometer were often one or two orders of magnitude lower than those obtained with the APST. This difference was traced to capture or absorption of both NaCl and KCl vapors on the walls of the Type 304 stainless steel sampler to the Ames analyzer. As a satisfactory substitute for the Type 304 stainless steel was not readily available, use of the Ames sampler was abandoned. To obtain the alkali content of the PFBC off-gas, small alkali absorbers were installed in the off-gas stream exiting from the PFBC. (No stainless steel sampling line was used.) After a given time for absorption of alkali metal compounds, analyses of the analytical beds gave a time-averaged alkali metal concentration. Excellent results were obtained by this analytical method. The sodium vapor concentration resulting from combustion of a high-sodium lignite was 1.42 and 1.50 ppm as measured by two activated bauxite beds and 1.30 ppm by a diatomaceous earth bed. Since more than 99.8% of the NaCl was removed in a bauxite sorber unit, the alkali metal specification for an industrial gas turbine of 0.024 ppm was concluded to be readily achievable.

In about 1988, the PFBC was fitted with silicon carbide candle filters. All of the off-gas from the PFBC was passed through these candle filters. These, in conjunction with a hot cyclone through which the exiting flue gas was passed, removed over 99.8% of the particulates from the flue gas, which is adequate removal of particulate from gas to be expanded through a turbine.

The hot off-gases from fluidized-bed combustion contain organic matter that consists partly of carcinogenic or mutagenic polycyclic aromatic hydrocarbons (PAHs). The only analytical method then available for analyzing these gases for those organic compounds was gas chromatography (GC) combined with a mass spectrometer (MS) and a computer spectra-reduction system. The CG separates the complex mixture of components, and the MS identifies the mass of each compound. Before analysis by this procedure, the PAHs had to be concentrated by a factor of a million. This was done by adsorbing them on a resin and then desorbing them by volatilization or by solvent extraction. Nonuniform behavior of the PAHs in stack gas cast doubt on the veracity of the analyses.

On-line monitoring systems were then investigated because they would eliminate the problems of sampling and sample concentration and also provide real-time data. Double (or triple) mass spectrometry, multiphoton laser ionization mass spectrometry, and induced fluorescence in a molecular beam were evaluated as possible analytical methods, but proved inadequate for in-line monitoring of PAHs in stack gas, and the program was discontinued.

MANAGEMENT ACTIVITIES

A variety of management activities were performed for the Morgantown Energy Technology Center. They comprised the following:

1. A PFBC technology assessment.
2. An evaluation of cyclone performance in PFBC applications.
3. An assessment of methods for the discharge and handling of solids from PFBC combustors.

4. A study of heat-exchanger design and operation for PFBCs.
5. A study of the technology status of particulate removal from high-temperature, high-pressure combustion gases.
6. A survey of instrument and measurement needs for FBCs.
7. A review of the hot gas cleanup system proposed for the Curtis-Wright 13-MWe pilot plant.
8. An assessment of international fossil energy programs based on reviews of the literature, foreign-travel trip reports, and interviews of foreign visitors and U.S. travelers.
9. Development of a Materials-Process-Product-Model computer code to obtain cost and process information for various energy technologies.
10. A conceptual design for an AFBC for installation in the Argonne power plant.
11. An up-to-date assessment of fluidized-bed technology, both in the U.S. and elsewhere.
12. Design of advanced fossil energy systems as a partial update of a 1976 Energy Conversion Alternatives Study performed by NASA (NASA TM-73871).
13. Technical assessments for environmental control for coal utilization. These were directed mainly to NO_x from various coal-related energy technologies.
14. Management of the Atmospheric Fluidized-Bed Cogeneration Air Heater Experiment for DOE, the objective of which was to assess materials and process performance of in-bed air heaters for co-generation of electricity and process steam in an AFBC.

Walt Podolski and several other individuals associated with the coal program contributed to these various efforts.

PERSONNEL

Irv Johnson remained in charge of the coal program until 1981, when Al Jonke returned to the Division and assumed that responsibility. Other CMT personnel associated with the program in one way or another in the 1980s were: Rajiv Agrawal, Roy Benson, Milt Blander, Amrit Boparai, Alan Brown, Erv Carls, Martin Clemens, Gary Dyrkacz, Tony Engelkemeier, Magdy Farahat, Darrell Fee, Jack Fischer, Bob Heinrich, Jim Helt, Richard Henry, Hann-Sheng Huang, Terry Johnson, Sheldon Lee, John Lenc, Peter Lindahl, Shelby Miller, Russell Mowry, Mike Myles, Robert Nelson, Frank Nuñes, Arthur Pelton, Walt Podolski, Leo Raphaelian, Carmen Sabau, Satish Saxena (Consultant), John Schneider, Charlie Schoffstall, John Shearer, Gregory Smith, Sherman Smith, John Stockbar, Bob Swaroop, Bill Swift, Gale Teats, George Vandegrift, Ravi Varma, Don Vissers, John Vogel, John Weber, Florence Williams, Ira Wilson, John Young, and Tony Ziegler.

Magnetohydrodynamic Heat and Seed Recovery Technology

Throughout the 1980s, the CMT Division continued as the lead division in a multi-divisional effort called the MHD Heat and Seed Recovery Project. This project, headed up by Terry Johnson, was organized to develop components downstream from the MHD generator (also called the "channel-diffuser"). These components comprise the MHD bottoming cycle, which is described in Chapter 4. This work was done in cooperation with other DOE contractors, including Babcock and Wilcox, the University of Tennessee Space Institute, and Mississippi State University. The work performed by CMT was directed to (1) control of NO_x, and SO_x, (2) measurements of the fouling of convective steam-generating tubes in the radiant boiler, (3) thermodynamic support studies, (4) recovery of the K_2CO_3 seed material, and (5) evaluation of candidate materials of construction.

The Fossil Energy Users Laboratory (FEUL), initially called Argonne Magnetohydrodynamics Process Engineering Laboratory (AMPEL), was constructed to accommodate a wide range of experiments under conditions simulating those in the radiant heat boiler where steam is produced from hot gases flowing from the MHD generator. Shown in Fig. 5-12, the facility had two test legs. One leg had an oil combustor capable of burning liquid fuel in various types of oil-solid mixtures and coal slurries; the other leg had a two-stage cyclone coal combustor. These combustion units were housed in two metal buildings (approximately 25 ft wide by 55 ft long by 30 ft high) erected near the Argonne power plant. Instrumentation and facility-control systems were located in an adjacent trailer.

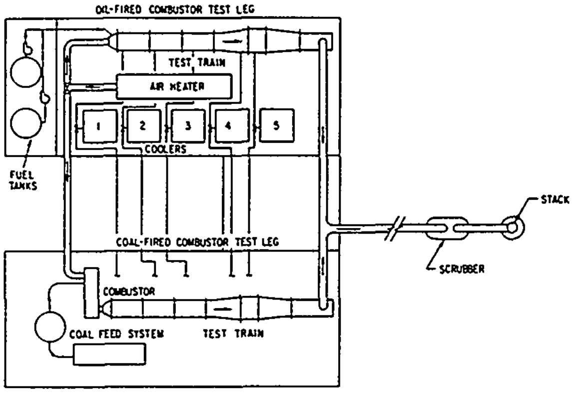


Fig. 5-12. Major Components of Fossil Energy Users Laboratory (FEUL)

CONTROL OF NO_x AND SO_x EMISSIONS

Most of the work in this area was on reducing the concentration of nitric oxide (NO) in the gas entering the radiant boiler, which contained NO at a concentration of 3,000 to 10,000 ppm, to below the emission standard of about 500 ppm in the gas exiting the boiler. Tests were run in FEUL to verify a chemical kinetics model that was based on reaction-rate constants for 29 reactions involving oxygen, carbon, hydrogen, and nitrogen. The model showed that the required NO concentration in the exit gas could be achieved by cooling the gas from its entrance temperature of 2000°C to the exit temperature of 1500°C at a rate no higher than 200 to 300 degrees per second. The tests showed that the model could be used to predict reliably the behavior of NO in an MHD power plant.

The SO_x was efficiently removed from the combustion gas by reaction with the K_2CO_3 seed material to produce K_2SO_4.

FOULING OF STEAM GENERATOR TUBES IN THE RADIANT BOILER

The work conducted in FEUL consisted mainly of fouling tests designed to investigate the nature and thickness of deposits formed on the steam tubes in the radiant boiler. Such information was needed for the design of the radiant heat boiler. The fouling conditions in this boiler were especially severe because the gas coming from the MHD generator contained about 2 wt% K_2SO_4 and 0.2 wt% coal ash. In fouling tests conducted through 1987, tube banks were exposed to combustion gas at temperatures up to 1500°C. The test train for the fouling tests is shown in Fig. 5-13. These tests demonstrated that the character of the tube deposits depended primarily on whether the gas temperature was above or below 1063°C, the melting point of K_2SO_4. At gas temperatures below 1063°C, entrained seed and ash formed a low-density, loosely adhering deposit that was readily removed by soot blowing. At gas temperatures above about 1300°C, the outer surface of the growing deposit reached the melting temperature, and the depositing seed and ash material flowed off the tubes, resulting in a stable deposit thickness and a steady-state heat-transfer