amounted to about 35,000 fuel elements. This corresponds to about five reactor-core replacements with new fuel. The FCF demonstration was discontinued in 1969, and outside sources were used to supply the new fuel; the spent fuel was reprocessed at ICPP.

The CEN Division continued to function as a support organization for designing special equipment and procedures, conducting tests, and troubleshooting, with special responsibility for melt refining and cell operations. This work included measurement of the air in-leakage to the argon cell, development of special lighting equipment, design of shutters for the shielding windows to protect them from radiation damage, testing of materials (electrical insulators, for example), development of continuous purification systems for support glove boxes located outside the cell, and development of auxiliary process equipment.

The major pieces of equipment that were developed by CEN were the Interbuilding Transfer Coffin and skull oxidation equipment. The transfer coffin was needed to transport discharged fuel assemblies from the reactor to the Fuel Cycle Facility—a distance of about 100 feet. The coffin, as it finally evolved, was a heavy (20-ton) lead-shielded cask with provisions for continuous removal of fission-product decay heat during storage and transit. It also served as a chemical reaction vessel in which provisions were made to convert sodium adhering to the fuel elements and subassembly surfaces to sodium hydroxide, which was subsequently removed by flushing with water. The sodium was converted to its hydroxide by adding humidified air to the circulating argon coolant until the reaction was completed. This procedure was necessary because direct addition of water to the metallic sodium could have resulted in small fires and explosions.

The skull oxidation technique was used to recover the heel and uranium that coated the wetted surfaces of the zirconia crucible (skull) after the purified metal had been poured into the mold. Conditions were developed for controlled oxidation of the skull at a temperature of 700-750°C by slow addition of oxygen to the argon atmosphere of the melt refining furnace. The oxide powder formed by this operation was then dumped from the crucible and sent to the ICPP for processing.

This ongoing support effort for the Fuel Cycle Facility was directed by Milt Levenson, Les Coleman, and John Schraidt. Many people were involved, including George Bernstein, Al Chilenskas, Tom Eckels, Johan Graae, John Ludlow, Bill Miller, Mike Slawecki, and Howard Stethers.

In 1969, EBR-II's role was changed from that of a fast breeder reactor demonstration to one of an irradiation facility for the national fast breeder program. Argonne had proposed a reactor named "FARET" for that purpose, but a potentially more advanced facility, the Fast Flux Test Facility (FFTF), was approved for construction at the Hanford Engineering Development Laboratory (HEDL) near Richland, Washington. A decision was made that EBR-II would serve this function until FFTF was ready. The emphasis had begun to shift to oxide fuels in the fast breeder program on the basis of safety and achievable burnup. More recent developments of metal fuels, however, have eliminated the burnup advantage of oxide fuels, and the same is true for safety because of the inherent nuclear stability of sodium-cooled, metal-fueled reactors under abnormal conditions.

In 1970, the FCF was redesignated FEF (Fuel Examination Facility), and almost all the fuel processing equipment was removed. Since then, a new, larger fuel examination facility, called HFEF (Hot Fuel Examination Facility) was built. It is now known as HFEF/N(north) and the original FCF is HFEF/S (south).

Pyrochemical Process Development

Development of the skull reclamation and blanket processes for metallic fast breeder reactor fuels continued at CEN for several years into the 1960s. A large glove-box facility was constructed in Bldg. 205 for demonstration of an integrated Skull Reclamation Process. This was followed by construction of a Skull Reclamation Process pilot plant in a large inert atmosphere enclosure in Bldg. 310. A similar sequence had been planned for the Blanket Process, but work proceeded only through construction and operation of a small engineering-scale unit in Bldg. 205. All work on these processes ceased at the end of September 1965, when the AEC stopped development of metal fuels and concentrated the funding on mixed UO_2-PuO_2 fuels. The shift to mixed oxide fuels was made to take advantage of the technology and commercial base that was in place for the fabrication of oxide fuels for light water reactors.

The Division then turned its attention to development of processes for mixed oxide (UO_2-PuO_2) fuels, using liquid metal and salt solvents and taking advantage of the separation concepts that had evolved in development of the EBR-II Skull Reclamation and Blanket Processes. These concepts were based on differences in the solubilities of the fuel constituents in liquid metal solvents and in their partition behavior between liquid metal and salt solvents.

Under the direction of Bob Steunenberg and Les Burris, several process flowsheets applicable to mixed oxide and also to mixed carbide (UC-PuC) fuels were developed. A central feature of these processes was a separation of plutonium from uranium and noble metal fission products by salt transport of the plutonium. A molten salt is cycled continuously between a donor metal alloy, in this case copper-33 wt% magnesium, and a receptor alloy, zinc-5 wt% magnesium. When the system reaches equilibrium, the activity of plutonium is the same in the two liquid metals.

The plutonium activity, a_{Pu}, is related to the concentration and activity coefficient by the relationship:

$$a_{Pu} = x_{Pu} \gamma_{Pu}$$

where x_{Pu} and γ_{Pu} are, respectively, the concentration and activity coefficient of the plutonium. Because the activity coefficient of plutonium in the zinc-magnesium solution is about 1/10,000th of that in the copper-magnesium solution, its concentration in the receptor alloy is about 10,000 times that in the donor alloy at equilibrium. Therefore, essentially all the plutonium transfers to the receptor·alloy.

As shown schematically in Fig. 3-3, a salt-transport separation involves two vessels containing liquid metal solvents which are connected by means of a molten salt that circulates between them. Both liquid metals contain magnesium, and $MgCl_2$ is a constituent of the salt phase. Uranium and the noble metal fission products are essentially insoluble in the Zn-Mg alloy and remain in

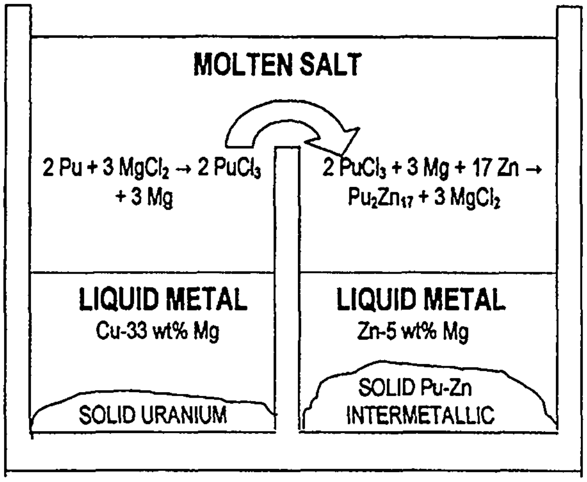
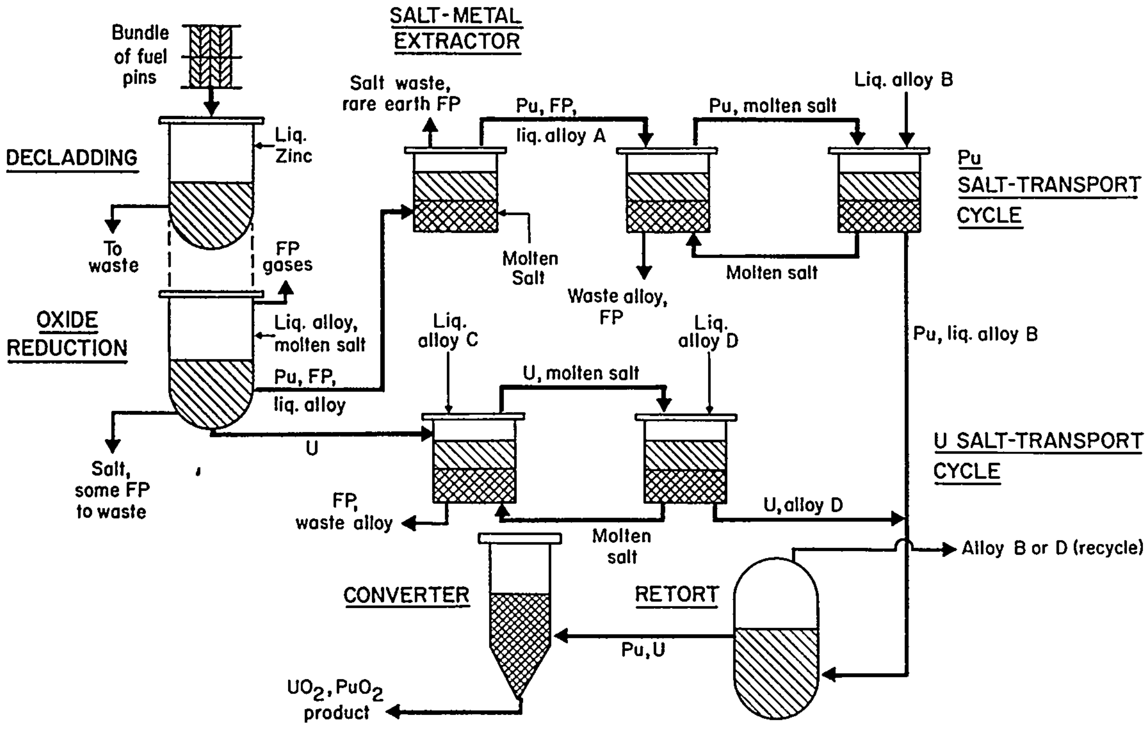


Fig. 3-3. Salt Transport Separation

that vessel as precipitated solids. The plutonium, because of its much higher activity coefficient in the Cu-Mg alloy than in the Zn-Mg alloy, reacts with the salt and is transported as $PuCl_3$ to the Zn-Mg alloy, where it is reduced back to the metal by the magnesium. The alkaline earth and rare earth fission products mostly remain in the salt. Uranium (with the noble metals) is recovered by decanting the supernatant Cu-Mg alloy, washing with magnesium to remove residual copper, and retorted to remove the adhering magnesium. Plutonium is recovered by vaporizing the zinc and magnesium.

A conceptual process based on salt-transport separations is shown in Fig. 3-4 to illustrate a potential application. Numerous variations could be made in this flowsheet, depending on the requirements for a particular fuel. For example, the liquid zinc decladding step might be replaced by mechanical or oxidative decladding methods.

At this stage of the program, Irv Johnson and his colleagues had generated a very extensive body of phase relationship and thermodynamic data on liquid metal solutions. This information, coupled with a large collection of data on the partitioning of



The fuel is first declad by dissolving the cladding in liquid zinc as shown here, or by mechanical or oxidative decladding methods. The mixed oxide fuel is then reduced by a liquid Cu-Mg-Ca alloy with a molten salt flux. Most of the alkaline earth and rare earth fission products stay in the salt flux. The liquid metal solution containing the plutonium becomes the donor alloy for a salt transport separation in which the plutonium is recovered in a Zn-Mg solution and the uranium, along with the noble metal fission products, is recovered from the Cu-Mg alloy. The product solutions are then retorted to remove the solvent metals, leaving metallic uranium and plutonium as the products. The uranium and plutonium are combined in the desired proportions and oxidized to form a mixed oxide powder for fabrication of new fuel.

Fig. 3-4. Pyrochemical Process for Fast Breeder Reactor Oxide Fuels various elements between liquid metal and molten salt solutions, generated mostly by Jim Knighton and co-workers, provided a wide variety of possibilities for the development of new processes. Several variations of the Salt Transport Process were developed. For example, a countercurrent liquid metal-molten salt extraction battery was developed to make the process more efficient. An alternative decladding step was oxidative decladding (also under consideration for the fluoride volatility processes). In this step, the stainless steel cladding was punctured or slit, after which the UO_2 was oxidized to U_3O_8, which expanded the cladding and pulverized the oxides, allowing their separation from the cladding. The U_3O_8 was then reduced to UO_2 by hydrogen to provide the feed material for the subsequent reduction to the metal. Mixed carbide fuels could be accommodated by first converting them to the oxides. The process would then be the same as that for the oxide fuels.

Construction of a glove-box facility to demonstrate the Salt Transport Process was terminated by the AEC (as were many other programs in other AEC laboratories) so the AEC could concentrate its funding resources on development, design, and construction of the Fast Flux Test Facility (FFTF) at Hanford.

The Group Leader for engineering development of the Salt Transport Process was Dean Pierce. Other participants in the program were Jack Arntzen, George Bennett, Tom Cannon, Terry Johnson, Jim Knighton, Paul Mack, Martin Kyle, Kazuo Nishio, Tony Rashinskas, John Schilb, Gale Teats, Ken Tobias, Bill Walsh, Don Wenz, Irv Winsch, and Ray Wolson.

Chemistry of Liquid Metals

The Division emerged from the 1950s with a strong program in place on the chemistry of liquid metals under the leadership of Hal Feder and Irv Johnson, which was initially directed primarily toward liquid metal solvents for nuclear fuel reprocessing. Starting in the early 1960s, the research expanded into two other major areas, the use of liquid sodium as a reactor coolant and liquid lithium as an electrode material in regenerative galvanic cells and secondary (rechargeable) batteries. Both of these blossomed into major programs in the 1970s.

The continuing work on liquid metal solvents for pyrometallurgical fuel reprocessing was concerned mostly with liquid zinc, cadmium, magnesium, and copper as solvent metals for the skull reclamation and blanket processes being developed for EBR-II. Extensive data were obtained on the solubilities of the actinide and fission-product elements in zinc, cadmium, and to a lesser extent, binary solvent systems such as zinc-magnesium. Most of the data were obtained by taking filtered samples. In some cases partial or complete phase diagrams were obtained by sampling, thermal analysis, and emf measurements. Equilibrium solid phases were characterized by X-ray diffraction and metallography. Solubility data, together with emf and effusion measurements, provided information on the thermodynamic characteristics of the systems. In many cases, the equilibrium solid phases were intermetallic compounds.

An important example of this from a process standpoint is illustrated in Fig. 3-5, where the solubility of uranium in liquid cadmium is shown as a function of temperature. At temperatures up to 471.5°C, the uranium solubility increases with temperature and the equilibrium solid phase is UCd_{11}; above that temperature (the peritectic point), the solid phase is uranium metal with a retrograde solubility.

Other interesting observations were made with these liquid metal solvents. One is that tracer levels of solutes exhibited much the same coprecipitation behavior that is observed

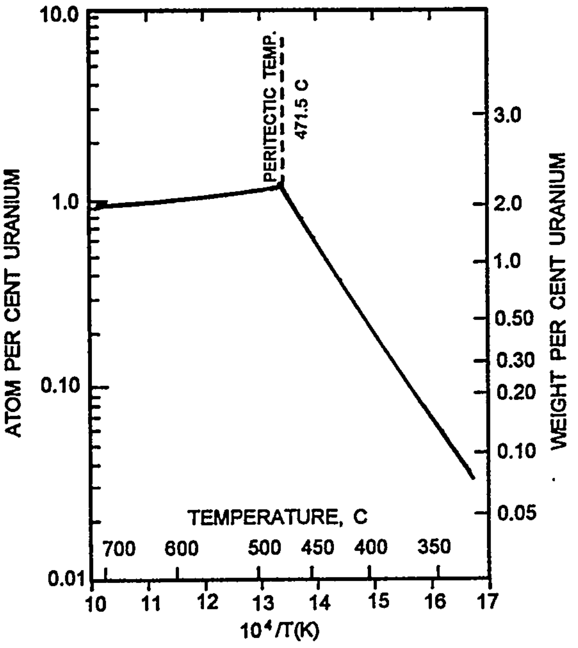


Fig. 3-5. Solubility of Uranium in Liquid Cadmium

in aqueous solutions, *i.e.*, they obeyed the Doerner-Hoskins Law:

$$\log [(\text{tracer in sol'n.})/(\text{total tracer})] \\ = \lambda \log [(\text{carrier in sol'n.})/(\text{total carrier})]$$

In general, the values of λ were near unity when the solid phases of the carrier and the coprecipitated material had similar crystal structures. Another interesting observation was that the solubilities of metallic elements in liquid zinc and in liquid cadmium showed a periodicity similar to that of the periodic table when they were plotted against their atomic numbers. The theoretical reason for this is not fully understood, but plots of this type were sometimes useful in gaining some idea of how a fission-product element might behave in a process when no other information was available.

Studies were conducted on the partitioning of uranium and other elements of interest between immiscible liquid metal phases such as aluminum-cadmium, lead-zinc, and bismuth-zinc. During the latter 1960s, the pyrochemical research work shifted largely to separations involving differences in the distribution behavior of fuel constituents between liquid metal and molten chloride solvents. The information from the above studies, together with distribution-coefficient measurements, provided the engineers with an excellent data base for process design work; it was also one of the most systematic, comprehensive programs ever to have been done on the basic chemistry and thermodynamics of liquid metal solutions. A major effort was also devoted to determinations of the distribution behavior of many elements between liquid metal solutions and molten salt phases. The distribution coefficient depends upon a chemical equilibrium when two elements are present in an oxidized form (such as a chloride) in the salt solution and a reduced form (the metal) in the liquid metal solution. For example, the distribution of uranium between liquid Mg-Zn and a salt containing $MgCl_2$ depends upon the equilibrium reaction:

$$\text{U(Zn-Mg)} + 3/2\ \text{MgCl}_2\text{(salt)} \leftrightarrow \\ \text{UCl}_3\text{(salt)} + 3/2\ \text{Mg(Zn-Mg)}$$

The thermodynamics of reactions of this type have been reported extensively by Irv Johnson. Jim Knighton and his co-workers obtained experimental data for a large number of systems in which the liquid metal phases were zinc, cadmium, magnesium, and aluminum, alone or in mixtures, and the molten salt phases were mixtures of alkali metal and alkaline earth chlorides. Figure 3-6 shows the large differences in distribution coefficients of rare earth elements and some actinide elements (uranium, plutonium and curium) between molten $MgCl_2$ and liquid Mg-Zn mixtures. The solute-element distributions are changed markedly by altering the composition of the liquid metal phase, this figure being an example of one of the many systems that were studied. Perhaps the most

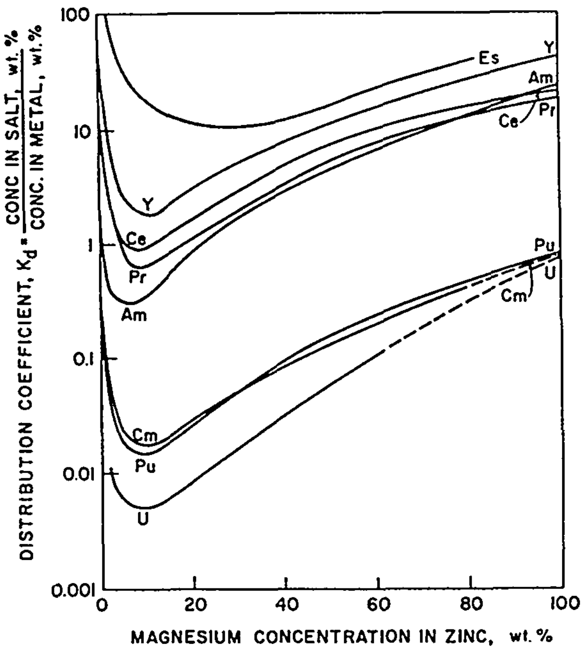


Fig. 3-6. Separation of Rare Earths from Actinides

"far-out" example of this type of separation is represented by a patent Jim Knighton and Bob Steunenberg obtained for the separation of californium from einsteinium. Although the separation worked like a charm, it is an excellent candidate for the patent least likely to ever succeed for commercial application. This work did, however, attract the interest of Glenn Seaborg because of its thermochemical implications.

Many individuals were involved in the foregoing work—Irv Johnson, Karl Anderson, Martin Chasanov, Pete Hunt, Jim Knighton, Al Martin, Ken Tobias, and Bob Yonco. Ewald Veleckis and Erv Van Deventer conducted the effusion studies. Bob Schablaske and Ben Tani played a crucial role in the phase identifications.

One person who livened things up quite a bit in the liquid metal research program was Gideon Hirsch, who came from Israel to spend a year or so at ANL. He was a very bright individual with an overwhelming personality that was basically incompatible with a structured organization. Upon his arrival, he displayed a rubber stamp with his name, identifying him as a physical chemist, educator, philosopher, political scientist, and several other qualifications. He claimed that he essentially had a Ph.D. with only some thesis work to complete, but the exact status of it seemed to be a moot point. During most of his assignment, he worked in Irv Johnson's group on the effects of attractive forces within liquid metal solvents. During his stay at ANL, he was given to doing things such as going on unauthorized travel and submitting the bill to ANL after the fact. He seemed to range all over the Chicago area, became acquainted with Studs Terkel, and visited Eric Hoffer on the West Coast. He requested an audience with Linus Pauling, but no one knows whether it took place. He kept trying to make appointments with the Lab Director Dr. Crewe, who, being an English gentleman, put up with two or three of them. Gideon finally left ANL, much to the relief of Everett Proud, went to work for a couple of companies, and eventually surfaced as a Wall Street broker. This memo, which he wrote just before leaving ANL, was typical:

March 16, 1967

TO: A. Crewe — Laboratory Director
FROM: G. Hirsch — Chemical Engineering

I would like the idea of giving a farewell seminar to the Laboratory on "Applied Philosophy."

If the subject is mine, I will choose, "Physical Chemistry, Society, Entropy, God, Computers, and Human Beings."

G. Hirsch

It might have been an interesting seminar, but apparently Dr. Crewe was not receptive to the idea.

The second area of liquid metal chemistry research, which began about 1963, led by Fred Cafasso in Irv Johnson's group, was concerned with metallic sodium. The main interest in sodium was its role as a coolant for EBR-II and other liquid metal cooled reactors, where impurities in the sodium such as oxygen, carbon, hydrogen, and nitrogen might result in corrosion or buildup of solid phases in the primary and secondary coolant systems. The initial studies were on carburization, purification, and analysis of liquid sodium. Thermodynamic studies were made on potential sodium reactions and on binary alkali metal systems. Analytical methods were worked out for oxygen and carbon in sodium, and potential purification schemes were investigated. During this period, some basic research was performed on the thermodynamics of liquid binary alkali metal systems, and ultrasonic methods were used to investigate possible complex species in liquid binary alkali metal systems. Another piece of work that deserves mention in this connection is a study in which Ira Dillon determined the critical properties of several alkali metals.

In 1968, an applied sodium technology program was initiated to develop methods and processes to handle, analyze, treat, and maintain a purity of sodium suitable for a reactor coolant. This expanded effort included the following chemistry studies:

1. Development of methods for handling and studying liquid sodium from its melting point to approximately 800°C under conditions that preserve the integrity of the liquid metal.
2. Development and refinement of analytical methods for the determination of carbon, oxygen, nitrogen, hydrogen, and tritium in liquid sodium.
3. Development for in-line monitoring of these impurities in liquid sodium.
4. Investigations of carbon behavior—reactions with other elements, characterization of compounds formed, and transport of carbon through liquid sodium systems (decarburization of ferritic steels, and carburization of austenitic steels) that would change the physical properties of the steels.

Some of the chemical studies involved the decarburization of steels through the formation of disodium acetylide (Na_2C_2). Exposure of Fe-0.11 wt% C alloy to sodium at 400 and 650°C resulted in formation of the acetylide. The solubility of helium in liquid sodium was measured, and the role of surface diffusivity in its mass transfer in sodium was studied by immersing samples of α-iron in liquid sodium at 800°C and examining the surfaces of the specimens.

The individuals participating in the sodium chemistry program were Hal Feder, Fred Cafasso, Jim Althoetmar, Karl Anderson, Sanat Dhar, Jim Eberhart, Pete Hunt, Loretta Jones, V. Khanna, Wally Kremsner, Charles Luner, Dick Murray, George Redding, Ewald Veleckis, Don Vissers, and Bob Yonco.

In the energy-conversion program, liquid sodium-lead, sodium-bismuth, lithium-bismuth, and lithium-tin alloys were used as positive electrode materials in thermally regenerative galvanic cells, which are described in the section on energy conversion. Liquid lithium was also being considered as a blanket/coolant material for fusion reactors, which became a subject of interest to CEN in the 1970s. From a theoretical standpoint, liquid lithium metal, because of its highly electropositive character and lightweight, would be an excellent positive electrode material for a storage battery. Attempts to use it, however, were largely thwarted because of its aggressiveness toward insulating materials and its solubility in LiCl-based molten salt electrolytes, which led to high self-discharge rates. These problems were solved by alloying the lithium with aluminum to reduce its activity, but at the expense of somewhat lower performance.

The basic research program on lithium included the following:

1. Extensive studies were made of the thermodynamic properties, including phase relationships, solubilities, and free energy functions of the systems Li-Se, Li-Te, Li-Sn, Li-H, Li-T (tritium), Li-C, Li-O, and Li-Al.
2. Experimental studies were conducted on the handling of liquid lithium from its melting point (179°C) to approximately 1000°C under conditions that preserved the integrity of the metal.
3. Analytical methods were developed or refined for the determination of H, O, N, and C in liquid lithium. Most of the facilities for these methods became an established part of the Analytical Chemistry Laboratory.
4. The compatibility of liquid lithium with molten halide salt systems of various compositions was investigated to select the salts that could be used as electrolytes with lithium electrodes.

The liquid lithium work, headed up by Art Tevebaugh and Carl Crouthamel, was performed by Elton Cairns, Kathleen Davis, Al Fischer, Mel Foster, Ellen Hathaway, Bob Heinrich, Stan Johnson, Gene Kucera, Vic Maroni, Jim Peck, and Bob Shablaske.

Fluoride Volatility Processes

In 1960, the development of fluoride volatility processes consisted of three activities:

1. The Direct Fluorination Process for the recovery of uranium and plutonium from Zircaloy-clad uranium oxide fuel elements of the type used in the Dresden power plant.
2. The Aqueous-Dissolution-Fluorination (ADF) Process for enriched uranium-zirconium alloy fuels, which involved aqueous dissolution of the fuel, fluidized-bed drying of the solution to a dry powder, and fluorination to recover the uranium as UF_6.
3. The Fused Fluoride Volatility Process in which zirconium-uranium fuel elements were dissolved in molten $NaF-ZrF_4$ by passing a mixture of HF and fluorine through the system to recover the uranium as UF_6.

Although the technical feasibility of the latter two processes had been fairly well demonstrated, further work indicated that the most promising approach was to use gaseous reagents on the solid fuel materials in fluidized beds. Such beds offer many advantages, including control of the reagent concentrations and addition rates, excellent heat-transfer characteristics, and ease of remote materials handling. Therefore, work on the direct fluorination process for oxide fuels was expanded and development studies were started on fluidized-bed processes for the alloy fuels as well. During the 1960s Al Jonke was responsible for the engineering development; Jack Fischer was the Group Leader of the laboratory program until about 1964, when Martin Steindler was assigned to that position.

LABORATORY INVESTIGATIONS

The two largest efforts in the laboratory studies were directed toward the fluorination of oxide fuels and the chemistry of PuF_6. Some early experiments were conducted on the possibility of using sulfur tetrafluoride (SF_4) as a fluorinating agent for UF_4, PuO_2, PuF_4, UO_3, U_3O_8, UO_2, and UO_2F_2. The conclusion was that SF_4 acted as a fluorinating agent, but not as an oxidizing agent with these materials. Uranium hexafluoride was produced only when the uranium was present initially in the hexavalent state, *e.g.*, UO_3 or UO_2F_2, and the by-product of the reaction was thionyl fluoride (SOF_2). Additional studies showed that SF_4 reduced PuF_6, but not UF_6, to the tetrafluoride:

$$SF_4 + PuF_6 \rightarrow SF_6 + PuF_4$$

This reaction offered the possibility of using SF_4 as a chemical trap for removing PuF_6 from a gaseous mixture of UF_6 and PuF_6 by converting the PuF_6 to solid PuF_4.

The principal laboratory investigations on the direct fluorination process were directed toward the initial fluorination step. Direct fluorination of UO_2 to UF_6 had been demonstrated, and it was found that PuO_2 undergoes the same reaction with fluorine at 400°C. Various materials, including MgF_2, ZrF_4, CaF_2, and alundum (a refractory form of Al_2O_3), were tested as fluidized bed media for the fluorination reactions. The best results were obtained with an alundum bed in which the uranium was first removed to a satisfactory level, followed by a 10-hour fluorination at 350-550°C to remove 95-99% of the plutonium. A two-zone fluorinator was devised in which the lower bed contained the UO_2 fuel pellets and alumina and the upper bed contained only alumina. Oxidation with an oxygen-nitrogen mixture converted the UO_2 to U_3O_8 fines, which were transported into the upper bed where they were fluorinated. Systematic studies were made of the effects of bed height and temperature from 450 to 500°C, and 99.5-99.9% fluorination of the uranium was achieved. These studies were done with a 1.5-in.-dia fluidized bed reactor. The experiments used mixtures of fluorine, nitrogen, and oxygen as the fluidizing gas. The nitrogen served as an inert diluent to control the rate of the reaction, and the oxygen enhanced the fluorination by decreasing the particle size of the uranium oxides, thereby increasing their surface area. When the fluorinations were performed, the uranium tended to be fluorinated first, followed by the plutonium. Some degree of separation of the two was accomplished by this effect and could be enhanced by manipulating the composition of the gas stream.

The marginal stability of PuF_6 presented both difficulties and opportunities in the development of a process flowsheet. The vapor pressures of UF_6 and PuF_6 are roughly the same, so they can be volatilized together to separate them from most fission products, and then be separated by selective decomposition of the PuF_6 to form non-volatile PuF_4. The objective was to remove all the plutonium from the original fuel, separate it from the uranium and fission products, and then recover it as a purified product stream for reuse. The studies that were conducted on the chemistry of PuF_6 were far too extensive to describe here in detail, but some of the highlights are as follows:

1. Equilibrium constants for the reaction $PuF_4 + F_2 \leftrightarrow PuF_6$ were determined.
2. The selective reduction of PuF_6 by SF_4 and by bromine was evaluated.
3. Selective thermal decomposition by the reaction $PuF_6 \rightarrow PuF_4 + F_2$ was also investigated as a means of recovering plutonium from UF_6-PuF_6 mixtures. A detailed study was made of the kinetics and mechanism of the thermal decomposition of PuF_6 over a temperature range of 140 to 173°C. The experiments were conducted in packed and unpacked vessels to determine the effect of surface area.
4. Methods were developed for quantitative transfers of PuF_6. In experiments with 10-100 g of PuF_6, 98% transfers

from trap to trap were achieved. Fluorine had little effect in suppressing losses.

5. Extensive data were obtained on the self-decomposition rate of PuF_6 caused by the alpha activity of the plutonium.
6. Studies were conducted on the decomposition of PuF_6 by gamma radiation both in the absence and presence of other gases. The G values (molecules decomposed per 100 MeV absorbed) for PuF_6 was 7.5. This value was not affected significantly by the presence of helium, but krypton, oxygen, or nitrogen increased it.
7. X-ray diffraction results showed that the lattice constants for UF_6, NpF_6, and PuF_6 decreased in that order.
8. The absorption spectrum of PuF_6 was determined.
9. Solid-liquid and liquid-vapor equilibria for the system UF_6-PuF_6 were measured.
10. Various solid fluoride compounds were evaluated for use in chemical traps to separate UF_6, PuF_6, NpF_6, and volatile fission-product fluorides from one another. Beds of solid NaF, LiF, and MgF_2 were found to be the most useful for this purpose.

Some laboratory work was done in support of the process development effort on zirconium-enriched uranium alloy fuels containing 5 and 30 wt% uranium. The optimum recovery of uranium was obtained by treating the alloy with HCl gas in a fluidized bed of alundum to convert the zirconium to $ZrCl_4$ (sublimation point 331°C at one atmosphere) and the uranium to nonvolatile lower chlorides. Uranium recoveries as UF_6 of 99.5% were achieved when using either fluorine at 350°C or chlorine monofluoride (ClF) at 200°C as a fluorinating agent. It was also shown that HF gas would convert the $ZrCl_4$ to ZrF_4 to decrease the amount of fluorine required to convert the uranium to UF_6.

A number of other smaller research areas such as the kinetics of the reaction of fluorine with nickel and the confinement and treatment of PuF_6 in process off-gases were also explored in the laboratory program. The individuals involved in the fluoride volatility laboratory work included Peter Alfredson, Tom Baker, Tom Gerding, Bill Gunther, A. Hariharan, Roger Jarry, Carl Johnson, Bob Kessie, George Manevy, Howard Porte, George Redding, Jim Riha, Jim Savage, Bob Shablaske, Bill Shinn, Roberta Shor, Dave Steidl, Martin Steindler, John Stockbar, and Verne Trevorrow. Alfredson was on assignment from Australia, and Manevy was from the French Atomic Commission (CEA).

As an interesting sidelight, John Stockbar was moonlighting as a local police magistrate in Lockport at about this time.

PROCESS DEVELOPMENT

Aqueous Dissolution Fluorination and Fused Salt Processes. Both of these approaches were under consideration for the processing of fuels consisting of a small amount of highly enriched uranium alloyed and clad with metals such as zirconium and aluminum. Because of the high enrichment and small amount of the uranium, the plutonium levels were too low to warrant its recovery.

The Aqueous Dissolution Fluorination (ADF) process involved (1) aqueous dissolution of the fuel, (2) fluidized-bed drying of the solution to a dry powder, and (3) fluorination to recover uranium as the hexafluoride. These basic steps were demonstrated with about 95% recovery of the uranium. This scheme appeared to be technically feasible, but other process concepts without the aqueous dissolution appeared more attractive, and this program was discontinued.

The fused salt process, also for enriched uranium alloy fuels, consisted of immersing the fuel elements in a molten NaF-ZrF_4 molten salt and sparging the system with hydrogen fluoride gas at temperatures of 600-700°C, which converted the fuel constituents to the fluorides. The resulting UF_4 was then converted to volatile UF_6, which could be recovered in a cold trap. Due to the highly corrosive nature of the system, a graphite dissolver was required, and a frozen wall technique was developed. This technique consisted of heating the molten salt internally while the vessel wall was kept at a temperature such that a layer of solid salt was maintained on its inner surface. This process concept also seemed to be feasible in principle, but there were concerns about its operation and maintenance in a fully remote facility, and the effort was discontinued.

At this stage of development of fluoride volatility processes, it appeared that the greatest promise lay in all-volatility schemes using fluidized beds and gaseous reactants.

Direct Fluorination Process for Alloy Fuels. Both Brookhaven (BNL) and ANL were involved in this development, and it was aimed primarily at alloy fuels that contained low levels of highly enriched uranium in zirconium, although some additional work was done with aluminum and stainless steel systems. The basic steps of this process were as follows:

1. Decladding and conversion of the zirconium and uranium to their tetrachlorides by reaction with gaseous HCl in a fluidized bed of alundum at 350-450°C.
2. Conversion of the tetrachlorides to the tetrafluorides by passing gaseous HF through the bed at 270-350°C.
3. Volatilizing the uranium with fluorine gas at 200-500°C to produce UF_6.

In the early work on this process, many scoping studies were made on decladding reagents and conditions, development of suitable fluidization equipment, and optimization of operating conditions.

A pilot plant with a 6-in.-dia fluidized bed unit and a 30-kg capacity was constructed, in which the direct fluorinations were conducted. Eighteen runs were made, during which 24 fuel elements containing either natural uranium-zirconium or uranium-aluminum alloy were tested. Performance of the equipment was generally trouble-free. The throughput rate was 3 kg/hr for both fuel alloys, and uranium recoveries were greater than 99%.

This work was followed by high-activity-level experiments with irradiated fuels conducted by Al Chilenskas and co-workers in the Senior Cave facility. These fuels included high-enrichment uranium-Zircaloy and uranium-aluminum alloys, low-enrichment uranium oxide, and mixed uranium-plutonium oxide. The objective was to obtain information on (1) the distribution of fission products, (2) decontamination factors that might be realized, and (3) the effects, if any, of irradiation and fission products on uranium recovery.

For the alloy fuels, a simple two-step procedure was used in which the fuel was treated with HCl in a 1.5-in.-dia fluidized bed to form volatile chlorides of zirconium or aluminum, which were vaporized. The non-volatile uranium chlorides (UCl_3, UCl_4) were collected in a packed bed filter and then treated with a nitrogen-fluorine mixture to form UF_6, which was collected on sodium fluoride (NaF) pellets. Further purification of the UF_6 could be achieved by subsequent desorption and collection in cold traps. The zirconium or aluminum chloride in the HCl off-gas was collected as a solid in a condenser, and the HCl was removed by a filter-scrubber arrangement. Fluorine was removed from the nitrogen-fluorine off-gas by a bed of activated alumina (Al_2O_3).

The removal of uranium from the reactor and filter beds was similar to that found in the pilot-plant operation, which suggested that the pilot-plant data could be used for irradiated fuels. Fission-product iodine and krypton were both volatilized completely during the hydrochlorination step. Fission-product cerium, cesium, and strontium were essentially non-volatile and remained in the reactor and filter beds. The ruthenium was basically non-volatile—less than 1% volatilized and that was collected in a magnesium fluoride (MgF_2) fission-product trap. The fission products that were predominantly volatile were molybdenum, technetium, and tellurium. About 21% of the neptunium was found with the uranium. The NaF trap removed most of the remaining activity, giving high overall decontamination factors in the range of 10^6 to 10^7. The results of this work, together with the pilot-plant experience, indicated that the direct fluorination process for alloy fuels was a viable candidate for plant-scale application.

Direct Fluorination Process for Oxide Fuels. Work had started in the late 1950s on direct fluorination schemes for processing uranium oxide fuel of the type used in commercial power reactors. This is low-enrichment (3% or so) uranium dioxide, which is in the form of pellets typically one-half inch in diameter and length. The pellets are clad with Zircaloy or stainless steel tubing to form fuel elements. Plutonium is bred in the fuel during irradiation and is present in low concentrations along with fission products.

The early engineering experiments were conducted with UO_2 pellets in beds of fluidized MgF_2 that were 3, 6, and 9 in. in diameter. The fluorination reaction is highly exothermic, so provisions had to be made both for control of the reaction rate and for heat removal from the bed. Fortunately, the fluidized bed was very effective in conducting heat to the vessel wall, which was air-cooled. (The excellent thermal conductivity of fluidized beds was well known, but little information was available as to how effective they would be in a bed packed with fuel pellets, so a large effort was put into basic studies of this type of situation.) The investigators also found that the reaction rate could be regulated easily by controlling the rate of fluorine addition, and development was initiated on an automatic temperature-control system, using this concept. Although the reaction rate was proportional to fluorine concentration, the efficiency of fluorine utilization was essentially independent of it. Several materials, including MgF_2, ZrF_4, CaF_2 and Al_2O_3 (alundum), were tested as the granular materials in the fluidized bed experiments. Alundum showed the best overall performance, and it was used throughout the remainder of the program with good results.

The fluorination of UO_2 in a fluidized bed, because of its heterogeneous nature, introduced a large number of variables that had to be addressed in the engineering work. For this reason, many experimental studies had to be conducted on a meaningful scale during process optimization. One such variable was the composition of the fluorine-bearing gas used in the process. The early runs were made with nitrogen as the diluent. In this case, the fluorination reactions were:

$$UO_2 + F_2 \rightarrow UO_2F_2$$
$$UO_2F_2 + 2\,F_2 \rightarrow UF_6 + O_2$$

The two reactions occurred simultaneously, and the UO_2F_2 spalled off the pellet as it was formed. The use of oxygen as a diluent converted UO_2 to U_3O_8, which also spalled off the pellet, and some of this effect may have occurred due to the oxygen produced by the fluorination reaction. To take advantage of these reactions, a two-zone bed design was adopted, in which the UO_2 pellets underwent the primary fluorination as a packed bed in the lower zone, and the finely divided intermediate products rose to the upper zone. Both zones contained fluidized alundum. This arrangement eliminated caking and channeling problems that had been encountered in the single-stage beds. The beds were equipped with blowback filters to return fines to the fluidized region.

Several methods of fuel decladding were evaluated. In some of the early work, Zircaloy cladding was removed chemically by a gas mixture of 10% HCl-90% HF at 500°C, which converted the zirconium to the tetrafluoride. An $HF-O_2$ mixture was used to remove the stainless steel cladding. Another approach was oxidative decladding, in which the cladding was punctured or slit to admit oxygen, which converted the UO_2 to U_3O_8 (a method also tried in the pyrometallurgical processes). The resulting powder in the ruptured fuel segments was then fluorinated to recover the uranium as UF_6. To achieve complete recovery, measures such as gas pulsing, reduction, and reoxidation of the material, and mechanical vibration were investigated. It appeared that several decladding options were feasible, depending on the nature of the fuel.

Some work was done on the use of BrF_5 as a fluorinating agent. This compound converted U_3O_8 to UF_6, and the PuO_2 to PuF_4. This offered the possibility of separating the uranium and plutonium by a two-stage fluorination in which BrF_5 was added first to fluorinate the uranium, followed by fluorine addition to volatilize the plutonium. The BrF_3 by-product in this case could easily be refluorinated to BrF_5 in a separate step.

Engineering-Scale Alpha Facility. A particularly impressive achievement of the fluoride volatility program was the design, construction, and operation of an alpha facility where work with plutonium could be done on a pilot-plant scale. John Vogel had the primary responsibility for this job, and he used the Critical Path Method (CPM), a project management procedure that was relatively new at the time, in planning the design and construction of the facility. A simplified diagram of the facility is shown in Fig. 3-7. The major components were two alpha-containment boxes to house the process equipment. The larger box was 17.5 ft high, 27 ft long, and 3.5 ft wide; the other was 10 ft high, 13 ft long, and 3.5 ft wide. Although the process was to be operated remotely, the boxes, which were based on the standard CENHAM glove-box design, were equipped with windows and gloves, and platform elevators were provided for the workers. The boxes were equipped with bagout ports, electrical service, air line inlets, filters, and sphincter openings. The larger box, which was to house the main process equipment, had two large bagout ports under an overhead crane, and it was located inside a negative pressure cell as a further safety precaution. In addition to the two boxes, the facility also included a large control panel.

The major equipment items in the larger box were a fluidized-bed fluorinator (3-in. dia and 6-ft long); two series-connected 4-in.-dia,

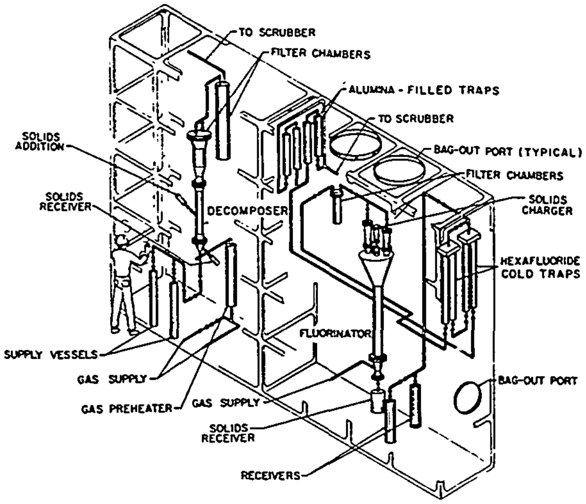


Fig. 3-7. Engineering-Scale Alpha Facility

10-ft-long condensers chilled by trichloroethylene; and 4-in.-dia Al_2O_3 traps. The smaller box contained metering equipment for the fluorine, oxygen, and nitrogen streams. A particular concern with the fluoride volatility processes was the hazard associated with PuF_6, which is chemically and radiologically toxic, is extremely reactive chemically, and exists in a gaseous form. Any possibility of its release to the outside had to be eliminated. Bob Kessie conducted extensive tests and studies on this problem and found that a combination of hydrolysis by humidified air and filtration was effective in removing PuF_6 from exit gas streams. This work involved an in-depth study of the mechanisms involved in the hydrolysis reaction and filtration.

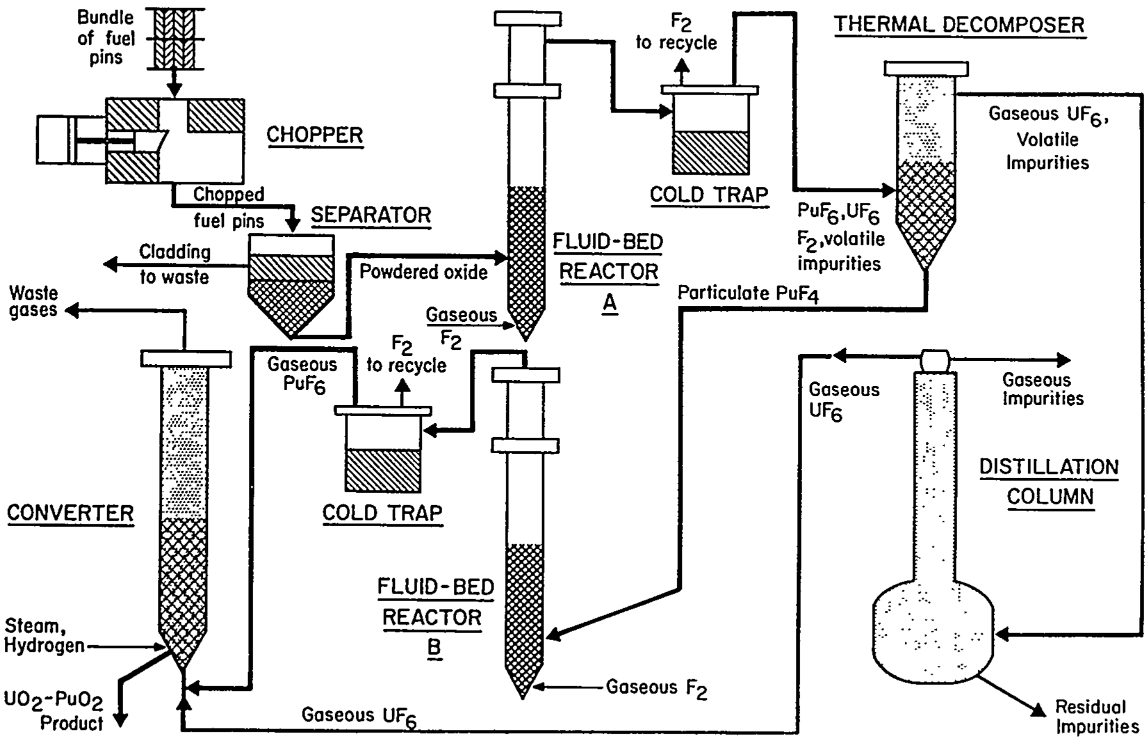
Work on the alpha facility began in 1962, and it was ready in 1965 for shakedown runs, which were conducted with 9-kg batches of UO_2. One impressive achievement was the production of PuF_6 from PuF_4 on a kilogram scale. A 2.3-kg batch was fluorinated in the fluidized bed with product recoveries of 79, 101, and 99% and rates of 2-6 lb PuF_6/hr per square foot. In 1965, the AEC had decreed that development of the fluidized-bed fluoride volatility process was to become a cooperative effort by four AEC labs: Argonne, Brookhaven, Oak Ridge National Laboratory, and the Oak Ridge Diffusion Plant. There was also a great deal of industrial interest in the process at the time. In 1968, ANL was directed to change the emphasis from light water reactor fuels, which contain about 0.5-1.0% plutonium, to fast breeder fuels, where the plutonium content is about 20% in the core and 4-5% in the blanket. Conceptual flowsheets were devised for this application (Fig. 3-8). In 1969, the fluoride volatility processes were included in the national policy decision to discontinue essentially all of the nuclear fuel reprocessing work in the U.S.

Conversion of Uranium Hexafluoride to Uranium Dioxide. The final product of fluoride volatility processes is uranium hexafluoride (UF_6), which may also contain plutonium hexafluoride (PuF_6), depending on the type of fuel being processed. In the 1960s, the fuel of choice for most reactors was uranium dioxide, so there was a potential need for a process to convert the uranium hexafluoride to the dioxide in a ceramic-grade form that was suitable for the refabrication of new fuel. The method that was selected for development work was a combination of steam pyrohydrolysis and hydrogen reduction in fluidized-bed reactors. The basic reactions are

$$UF_6 + 2\,H_2O \rightarrow UO_2F_2 + 4\,HF$$
$$UO_2F_2 + H_2 \rightarrow UO_2 + 2\,HF$$

It was discovered early in the program that these reactions could be conducted simultaneously with a mixture of steam and hydrogen, or sequentially as shown. Fluidized beds were particularly well suited for this application because of their capabilities for good heat removal, rapid reactions resulting from the large solid-gas surface area, and their flexibility in controlling the conditions to achieve the desired particle-size distribution of the product.

Both the simultaneous and sequential approaches were investigated using 3-in.-dia fluidized bed reactors and static bed depths up to about 21 in. Most of the work was done first on the two-step sequential approach because of its greater flexibility, the main point being that it could be run at two different temperatures. A great deal of effort was required to solve problems such as bed caking and to determine optimum temperatures, bed depths, and the velocities and compositions of the fluidizing gas. The best results were obtained when the first step was operated at 230°C with a superficial gas velocity of 0.75 ft/sec, a static bed depth of



The UO_2-PuO_2 fast breeder reactor fuel pins are first chopped into short lengths, and the oxide fuel in the form of powder is separated from the metallic cladding material. The oxide fuel is charged into a fluidized bed of alumina (Al_2O_3) powder where the uranium and plutonium oxides are converted to their volatile hexafluorides by a gas stream containing elemental fluorine. The uranium is volatilized first, followed by the plutonium hexafluoride. Both are collected in condensers where the gaseous fission products, krypton and xenon, and the volatile fission-product fluorides (those of niobium and ruthenium), are removed. The uranium and plutonium hexafluorides enter a thermal decomposition step, where the plutonium hexafluoride is reduced to the non-volatile tetrafluoride. The uranium from this step is purified by a distillation-sorption procedure, and the plutonium is recovered by fluorinating the tetrafluoride back to the hexafluoride. The purified uranium and plutonium hexafluorides are then subjected to a hydrolysis reaction with steam and hydrogen to form a $(U,Pu)O_2$ powder suitable for refabrication of new fuel pellets.

Fig. 3-8. Fluoride Volatility Process for Fast Breeder Reactor Oxide Fuels

15 in., 245% excess steam over the stoichiometric requirement, 15% recycle of solids, and an average bed particle size of about 350 µm. Favorable conditions for the second step were a temperature of 650°C, a 50-50 mixture of steam and hydrogen, and a static bed depth of 21 in. The fluoride content of the product was less than 200 ppm, which is well below the acceptable maximum of 300 ppm.

The group then turned its attention to the one-step process. The effects of various operating variables were determined, with special attention being given to the particle-size distributions and densities of the products. Sintering in hydrogen was studied as a means of increasing particle density. The results indicated that either the one-step or the two-step process could be used to convert UF_6 to UO_2.

This work, which was performed by M. Jones, Irv Knudsen, Norm Levitz, Don Raue, and Takeo Tamura, is summarized in ANL-6902.

Calcination Studies. The calcination work, although it did not involve a fluoride volatility process, is included in this section because the fluoride volatility programs and other programs using fluidized-bed technology were closely connected and coordinated under Al Jonke's leadership. The following calcination studies, performed by John Loeding, Norm Levitz, Charlie Schoffstall and John Kincinas, were unusual in that a major objective in most process development programs is to scale up the operations for application in a large plant. In this case, the objective was to calcine plutonium or highly enriched uranium solutions in small columns to avoid criticality problems. The small units also reduced the quantity of off-gases to be handled.

The fluidized bed calciner was a 2.25-in.-dia column with a conical bottom in which nozzles were mounted vertically in the apex of the cone to spray the atomized solution upward. The spray nozzles and decomposition of the feed material provided most of the fluidizing gas. A dual blowback bayonet filter system was used at the top of the column. After some initial optimization work, 20 consecutive startups were made successfully with runs longer than seven hours. After some minor equipment modifications, runs of 5-14 hr were made at temperatures of 425-450°C, with frequent blowback every 3 or 4 min. The bed depths were 10-15 in. with residence times of 5.2 and 7.8 hr, respectively. This work had to be suspended due to manpower needs elsewhere, but the results showed that fluidized bed calcination was possible in small, criticality-safe equipment.

Basic Fluidization Studies. A large body of information on the care and feeding of fluidized beds had been and was continuing to be generated in the applied programs, and CEN was developing a reputation for its expertise in this technology. It was appropriate to devote some systematic investigations of more general applicability and greater theoretical depth. In 1960, Ken Williamson, a Ph.D. student from Pennsylvania State University, began a study of the downward transport of solids in a multistage fluidized bed without downcomers, using external vibration. The bed was contained in a three-stage, 6-in.-dia Pyrex and metal column. Individual external vibrators were arranged so that the vibrational energy was transmitted independently to each of the three bed support plates in the column by a metal rod. Glass beads served as the bed material. The throughput rate was controlled by the percentage of "on time" of the vibrators. A correlation was obtained for throughput rate as a function of feed particle density, shape, and size; column cross-sectional area; density and superficial velocity of the fluidizing gas; and depth and size of beads used on the bed support plates.

The second phase of Williamson's work was a study of the effects of operating variables on the adsorption of water by silica gel. Murphree stage efficiencies (ratio of actual change to that if the vapor composition reached equilibrium in the stage) were near 100%. These data permitted calculations of mass-transfer coefficients.

In 1963, John Gabor and John Savage began basic studies on the mixing of fluidized particles in beds packed with larger solid bodies. An example of this situation is the fluorination of uranium dioxide fuel pellets mentioned earlier, where the fuel pellets were too heavy to be fluidized and, therefore, constituted a packed bed in the column, while the fluidized material in the void parts of the bed was granular alumina. A major function of the alumina was to remove the heat of reaction from the bed by transferring it to the walls of the column. In the basic studies, copper and nickel shot were used as the particles. (This permitted the use of a magnetic technique for separating the two metals as an analytical method.) The rate of mixing was proportional to the size of the packing, which is consistent with a random-walk model for eddy diffusion in flowthrough packed beds. Mixing rates were higher in the absence of the fixed packing, and they increased with increased height of the fluidized bed. With fixed packing, baffling resulted in more uniform fluidization, and mixing was independent of bed height. An empirical correlation was developed for beds containing spherical packing, which relates the diffusivity of the fluidized solids to the packing size, the fluidized particle size, and the gas-flow rate.

An investigation was then started on heat conduction in the lateral direction in fluidized-packed beds and on longitudinal transport of particles. The thermal conductivities were correlated by an equation involving the density and heat capacity of the fluidized particle, the diameter of the fixed packing, and the fluidizing gas velocity and minimum fluidizing gas velocity, both corrected for packing void fraction.

A basic study was undertaken by Manfred Baerns and Devabhaktuni Ramaswami on the fluidization of fine particles of a size less than 50 μm. In this size range, frictional and interparticle attractive forces become significant and tend to cause channeling in the bed.

John Gabor and Ramaswami conducted a theoretical study of fluidized particle motion caused by a rising bubble and developed a computer program to simulate the eruption of a bubble at the bed's surface. John Holmes and Lowell Koppel, a faculty member from Purdue University, developed models to predict heat-transfer coefficients at the wall of a fluidized bed and conducted experiments on particle mixing and the relationship between particle residence time and heat transfer.

Ramaswami, Masaru Kobayashi, Bill Brazelton, and Charlie Schoffstall undertook a study to compare the behaviors of pulsed-flow and straight-flow fluidized beds and to determine the best design for the feed-gas distributor. Better mixing was obtained with the pulsed-flow beds, and a simple cone gas distributor proved superior to a sintered metal distributor for the pulsed beds.

Physical and Thermodynamic Properties of High Temperature Materials

In 1963 a systematic effort was begun to determine the thermodynamic properties of high temperature nuclear reactor fuels and materials under the direction of Russ Edwards in Hal Feder's section. Russ, a wiry, muscular individual, enjoyed outdoor athletic activities and, as a result, chose to live in the Indiana Dunes area, which meant about a 60-mile daily commute each way in his Volkswagen "beetle." On one occasion, he was seriously injured in an auto accident that few people would have survived, but apparently due to his excellent physical condition he recovered completely. A somewhat professorial type, he was exacting about his experimental work and liked to interpret his results in terms of theoretical principles.

For the first few years, this program was concerned almost exclusively with the phase relationships and thermodynamics of uranium dioxide, which was the fuel of choice for most reactors under consideration at that time. These studies were aimed primarily at the U-UO_2 region of the uranium-oxygen system.

The initial work consisted of five activities:

1. Effusion vapor pressure measurements by Malleseety Chandrasekharaiah and Phil Danielson, using a Knudsen effusion apparatus.
2. Mass spectrometric effusion studies by John Reishus and Phil Danielson, using a Bendix time-of-flight mass spectrometer to measure species in the gas phase.

3. Transpiration studies by Marv Tetenbaum and Carol Clifton, in which an inert gas was passed over a heated sample to determine the identity and composition of species in the gas phase.
4. Phase-diagram investigations by Al Martin, Leo Yannopoulos, and Frank Mrazek, using conventional thermal analysis and metallographic techniques.
5. Interdiffusional studies by those same individuals to evaluate the compatibility of refractory metals such as tungsten, rhenium, and molybdenum as containment and support materials for the fuel materials under investigation.

Some of this work was done as a collaborative effort with Ray Ackerman and Bob Thorn of the Chemistry Division, who made certain equipment available for the purpose. This integrated approach to the uranium dioxide studies gave the work a wide scope and permitted cross-checking of results obtained by different methods.

A U-UO_2 phase diagram that evolved from these studies is shown in Fig. 3-9.

An outstanding characteristic of this system is a wide liquid miscibility gap above the monotectic temperature of 2470°C. At the monotectic temperature, the O/U ratio units for the three condensed phases in mutual equilibrium are liquid uranium, 0.05; monotectic liquid, 1.30; and hypostoichiometric UO_2, 1.61. Through a combination of the effusion studies, transpiration experiments, and mass-spectrometric measurements, the vapor pressures and compositions for the system shown in Fig. 3-9 were characterized in detail. This information was used to develop a thorough thermodynamic description of the system, which was valuable both as a basic scientific contribution and as a guide in interpreting phenomena observed during examinations of irradiated reactor fuels.

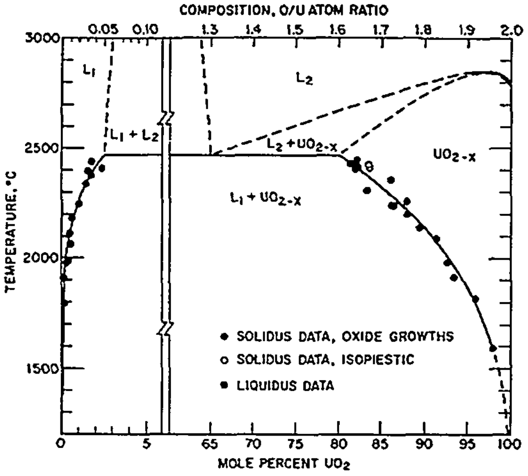


Fig. 3-9. Uranium-UO_2 Phase Diagram

After his arrival at ANL in 1964, Jim Battles joined Russ Edwards in a study of the vapor deposition of tungsten claddings on complex W-UO_2 cermets. This was a part of the ROVER project for nuclear-powered space vehicles, which was a highly classified program at that time. Other studies were undertaken on systems involving refractory metal oxides. A study of the system U-W-UO_2 showed that the miscibility gap on the U-UO_2 side extended into the interior of the ternary phase diagram. Paul Blackburn came to CEN in 1967, and replaced Russ Edwards as the Group Leader in 1968. The program was expanded to include plutonium to provide information on potential oxide fuels for LMFBR applications. This effort included phase-diagram studies of U-Pu-O by Al Martin and Frank Mrazek; mass-spectrometric vaporization investigations by Jim Battles, Gordon Gunderson, John Reishus, and Bill Shinn; effusion measurements by Phil Danielson, and transpiration studies by Paul Blackburn and Steve Banaszek.

For the mass-spectrometry work with plutonium, a glove box was designed and constructed to house the source end of a time-of-flight mass spectrometer, which included a high-temperature Knudsen cell as the inlet system. The initial phase of this study, by Jim Battles, John Reishus, and Gordon

Gunderson, was to find a material for the Knudsen effusion cells that was completely compatible with the uranium and plutonium oxides at high temperatures (>2000°C). The compatibility studies showed that tungsten and molybdenum react with $UO_{2.08}$ at relatively low temperatures, as evidenced by vapor species such as W_3O_9 and Mo_3O_9. A study of the Re-O system showed that an unusual vapor species, Re_2O_7, was the predominant species at 800°C. Vapor pressures of Re_2O_7 over the two systems Re-ReO_2 and ReO_2-ReO_3 were determined. Further compatibility studies identified iridium as being completely compatible with the uranium and plutonium oxides, and it was used in all the subsequent mass-spectrometry work. Based on this work, iridium was also selected as the cladding material for $^{238}PuO_2$ power sources in space applications. Reishus left ANL in 1967 to obtain a doctor of divinity degree, and Gunderson left for other opportunities. About that same time, Bill Shinn returned to the group.

During the period 1967-70, the mass spectrometric-Knudsen diffusion studies were completed on the systems Pu-O, U-Pu-O, and Na-U-O. Jim Battles and Bill Shinn determined the partial pressures of plutonium oxide vapor species, and enthalpy data were derived from the results. These were all first-of-a-kind studies. Complementary investigations of the U-Pu-O system included phase-diagram studies by Al Martin and Frank Mrazek, who established the metal-rich boundary of the U-Pu-O fluorite phase, using equilibration and metallographic methods, effusion measurements by Phil Danielson, and transpiration experiments by Paul Blackburn and Steve Banaszek. Paul Blackburn and Hong Yih Chen investigated possible reactions between cesium oxide and iodine that might occur in irradiated fuel. Their initial results suggested a possible Cs-U-O ternary compound.

Although the primary emphasis at the time was on oxide fuels, both for light water and fast breeder reactors, there was also some interest in the carbides, sulfides, and phosphides of uranium and plutonium, all of which are highly stable ceramic materials. Reishus, before leaving ANL, had conducted some studies on UN and UP. Mass-spectrometric Knudsen effusion studies were planned for the systems Pu-C, U-Pu-C, PuP, and PuS. Jim Battles, Russ Edwards, and Bill Shinn measured the pressures of plutonium gas over the two-phase regions of Pu_2C_3-C, Pu_2C_3-PuC_2, and PuC_2-C and determined the enthalpies of the formation reactions. Marv Tetenbaum and Pete Hunt used transpiration methods to measure the carbon activity and the total pressures of binary carbon species in the vapor phase as a function of temperature and composition. These data provided information on the locations of phase boundaries in the U-C system at high temperatures and estimates of the free energies and heats of formation of UC. Further work on these systems was terminated in 1970 as a consequence of priorities established for the LMFBR programs.

Reactor Safety

Through the mid-1960s, the Chemical Engineering Division continued a large reactor safety program to determine the nature and extent of chemical reactions that could occur during a reactor accident. The purpose of these studies was to provide information that would aid in minimizing the hazards of such accidents. The main areas of research were (1) metal oxidation and ignition kinetics, (2) metal-water (steam) reactions, and (3) studies related to fast reactor safety.

METAL OXIDATION AND IGNITION KINETICS

Work in this area was focused on the kinetics of air oxidation of metallic uranium and plutonium up to temperatures approaching their melting points. Oxidation rates for both metals were determined as a function of temperature and characterized (parabolic or linear), and the protective effects of oxide films were assessed. An interesting phenomenon in the case of plutonium, which undergoes six phase changes between room temperature and 600°C, was a change in the plutonium oxidation rate when a change of phase occurred.

METAL-WATER REACTIONS

In water-cooled reactors, coolant failure or a severe nuclear excursion could cause the reactor core metals to melt and disperse rapidly in water. Chemical reactions between the dispersed metal particles and the water could release an amount of energy approaching or exceeding that released by the fission process during a nuclear excursion. Realistic estimates were needed of the rate and extent of chemical reactions during hypothetical reactor accidents.

Among the metal-water reactions that were studied were stainless steel-steam at 1400°C, steam at 1500°C with UO_2 fuel elements clad with stainless steel or Zircaloy-2, and UO_2-steam at 1500°C. Small autoclave experiments were conducted in the Transient Reactor Test Facility (TREAT) facility, a pulsed thermal reactor used for safety studies. This reactor, located at the National Reactor Test Station (NRTS), went critical in 1958. The purpose of these experiments was to determine the reaction between fuel and water during reactor excursions. Several fuels were studied, the two principal ones being UO_2 fuel-pin clusters having Type 304 stainless steel and Zircaloy-2 cladding. The resulting data were used to make predictions of the extent of metal-water reactions that would occur during a loss-of-coolant accident in a water-cooled reactor.

FAST REACTOR SAFETY STUDIES

The purpose of these studies was to determine the consequences of core melting and rapid dispersion of reactor materials in the liquid sodium coolant due to coolant failure or a rapid reactor excursion. In one set of experiments, small samples of metals heated to temperatures between 1500 and 2400°C were dropped into liquid sodium, which was at 250°C. The list of metals comprised zirconium, vanadium, nickel, Type 304 stainless steel, molybdenum, tantalum, and uranium. None of them reacted with the sodium, but the sudden quenching in sodium produced severe fragmentation, especially with the stainless steel. Similar behavior was observed with UO_2. Autoclave experiments were also conducted in TREAT to measure the expulsion of sodium during sharp reactor transients and to determine the extent of fuel fragmentation. Such information was used to estimate the migration of fuel particles in a fast reactor during and following an excursion. Studies were also made of sodium-air and sodium-water reactions using sodium spray-injected into a reaction vessel to simulate the violent expulsion of sodium from a reactor core.

At the end of Fiscal Year 1968 (September 30, 1968), the Reactor Safety program was transferred to the newly formed Reactor Analysis and Safety Division (RAS).

Lou Baker headed up the Reactor Safety program. Art Tevebaugh and Dick Ivins were also involved in management of the program. Other participants were Don Armstrong, John Barghusen, Charles Barnes, Jim Bingle, Jim Boland, John Cassulo, Martin Chasanov, Dae Cho, Marshall Deerwester, Don Fischer, Bill Gunther, Larry Harrison, Jim Hesson, Len Leibowitz, Bob Liimatainen, Larry Mishler, Kazou Nishio, John Pavlik, Jim Peck, Chester Rogers, Martin Silverman, Carl Stretch, Dave Swift, Frank Testa, Kegham Varteressian, and Bob Wilson.

Chemistry of Irradiated Fuels

A program was initiated, primarily by Carl Crouthamel, with the objective of obtaining fundamental chemical data on irradiated fast reactor fuels to gain an understanding of the chemical processes that occur within the fuel during the irradiation. The initial studies were directed to carbide and oxide fuels. This work required a number of specialized facilities and equipment, and an inert atmosphere enclosure was installed in one cell of the Chemistry Division cave facility in Bldg. 200.

An impressive array of new instruments was assembled, including a Leitz remote metallograph, a spark-source mass spectrometer, a 4096-channel analyzer with two solid-state detectors for γ-ray spectroscopy, a surface ion-emission spectrometer, and a shielded electron microprobe. The first studies, made by Norm Chellew, Max Adams, and Chuck Honesty, were on pressed-and-sintered and arc-melted uranium monocarbide and on irradiated uranium dioxide. Microdrilling and laser sampling were used to obtain concentration profiles of the fuel constituents. The electron microprobe proved to be an excellent tool for the fuel examinations. Results from a stainless-steel-clad UO_2-20% PuO_2 fuel pin irradiated to 3.7 at.% burnup in EBR-II showed a fuel-cladding interaction, fission-product iodine at the fuel-cladding interface, and iron from the cladding in the fuel matrix. Somewhat similar effects were observed with a UC-20% PuC fuel pin.

The microprobe operators developed a procedure by which "maps" of the sample were made in which each element was represented by a particular color. This feature was useful in visualizing the migration of elements that had occurred during irradiation of the sample. These rather spectacular colored pictures of the sample surface were also very useful for public-relations purposes.

Some work was also done with tagging methods to identify positions of fuel failures in a reactor. One method involved spiking each fuel element in a subassembly with a unique ratio of two sodium-soluble radioactive isotopes that could be detected in the coolant sodium in the event of a leak. The other method involved the use of two xenon isotopes, again in unique ratios, which could be detected in the cover gas over the sodium coolant.

In 1969, the group, still under the direction of Carl Crouthamel, had expanded to include Harry Edwards, Ping-Kay Hon, Laury Ross, and Gus Staahl. Carl Johnson, Norb Stalica, Chuck Seils, and Karl Anderson did the electron microprobe work; Bob Meyer and Carl Johnson handled the sodium-soluble tagging studies; the xenon tagging was a joint effort between George Bernstein and Les Coleman at CEN and the EBR-II staff at the Idaho site.

Preparation of Fast Reactor Fuels

The preparation of metallic and oxide fuels for fast breeders was mentioned in the previous discussions of pyrometallurgical and fluoride volatility processes, respectively. Work was also done on several other more exotic materials that were under consideration as potential fuels. In 1960, Carl Crouthamel and Bill Knapp terminated a study they had been doing on a "Slurrex" process for making a ThO_2-10% UO_2 ceramic fuel, which involved a gel precipitation step and firing the resulting material to 1000°C.

Carbide fuels were being considered both for high temperature gas-cooled reactors (HTGRs) and certain other types of reactors. As an outgrowth of the pyrometallurgical program, work was initiated on schemes for producing mixed uranium-plutonium carbide fuel material by precipitation from liquid metal solutions. The first experiments used hydrocarbon gases (methane, ethane, propane, acetylene) as the carbon source; these gases were bubbled through a solution of uranium in molten zinc-magnesium. In later work, activated charcoal and graphite were added directly to the solution. The procedure consisted of adding the carbon to a Zn-12 wt% Mg-15 wt% U solution and agitating the system for several hours at 800°C. The product was recovered by pouring off most of the supernatant liquid metal and removing the remainder by vacuum retorting. These studies were done in cooperation with George White of MET (the Metallurgy Division, now Materials Science), who evaluated the fabricability of the products. The material sintered readily and made excellent fired pellets with densities greater than 90% of theoretical value. The procedure was scaled up to produce 0.5-1.0-kg batches of material for the fabrication tests by MET.

A fluidized-bed process for the preparation of uranium monocarbide (UC) was also investigated. In this process, 300- to 600-g batches of (U-15 wt% Pu) fuel pins were hydrided at 250°C by a hydrogen-2 vol% methane mixture to form a fluidizable powder. The material was then dehydrided by continuing the operation at a temperature of 500°C with the same gas mixture. The product from this step was fluidized with a hydrogen-6 vol% methane mixture at 800°C and 2 atm pressure. The hydrogen/methane ratio was critical in avoiding the formation of plutonium sesquicarbide (Pu_2C_3), but, if necessary, this compound could be reduced back to the monocarbide by treating the product with hydrogen. Several batches of (U-20% Pu)C were prepared and fabricated into pellets by pressing and sintering.

A second method of preparing carbide fuels from the oxides entailed the reaction of UO_2 with graphite at 1500-1800°C in a bed fluidized by an inert gas. There were some problems with sintering of the UO_2, but a projection was made that a 30-kg/day plant-scale operation could be achieved with a 12-in.-dia fluidized bed. Preliminary work was also done on the use of a plasma torch to conduct this reaction, but the program was terminated due to a fading interest in carbide fast reactor fuels.

A small program was directed to the conversion of uranium metal to the dioxide to prepare oxide fuel for a breeder reactor from the metallic uranium product of a pyrometallurgical process. The uranium was first hydrided-dehydrided in a fluidized bed, and then treated with a CO_2-inert gas mixture for 4-9 hr with the temperature increasing from 400 to 825°C. When the carbon content of the product was found to be too high, a partial nitriding reaction prior to the CO_2 addition resulted in a stoichiometric product with an acceptable carbon content (<100 ppm).

Some work was done on the preparation of uranium monosulfide, another refractory material that was in contention as a fast reactor fuel. This preparation involved: (1) hydriding-dehydriding of uranium to form a fine powder, (2) heating the powder with the stoichiometric amount of hydrogen sulfide (H_2S) at 400-500°C, and (3) heating the resulting mixture to 1900°C to convert any unreacted uranium and higher uranium sulfides to the monosulfide. About 2 kg of this product was prepared in 100- to 300-g batches to provide the MET Division with material for fabrication and irradiation tests.

Finally, research was conducted on a paste of uranium nitride (UN) in liquid sodium, which had been proposed as a semi-fluid blanket for fast breeder reactors. The idea was that this material could be circulated through tubes, which would serve as heat exchangers and would have some advantages over solid blankets: (1) ease of fission-product gas removal, (2) the possibility of frequent or continuous processing, and (3) reduction of thermal gradients in the blanket. The UN was prepared by exposing uranium shot to nitrogen first at 900-1050°C, followed by several hours at 1350°C. When mixed with sodium, this material formed a paste that had the degree of fluidity needed for the purpose.

Terry Johnson took the lead on the initial carbide studies, assisted by John Trischan. Dean Pierce, John Lenc, John Pavlik, and Marion Bowden worked on the precipitation studies, and Irv Winsch, Tom Cannon, and John Schilb handled the plutonium experiments. Don Armstrong, G. Gorth, Dave Grosvenor, John Holmes, Paul Krause, Paul Nelson, John Pavlik, Charles Payne, Ed Petkus, Nick Quattropani, D. Ramaswami, and Sy Vogler did the fluidized-bed and plasma-torch studies. Sy Vogler and John Trischan carried out the sulfide studies, and Paul Nelson, Martin Chasanov, and Clarence Lehmann did the work on paste blankets.

Preparation of High-Purity Plutonium-238 Metal

The Division was requested to investigate the potential use of pyrochemical methods for the recovery and purification of plutonium-238 in various materials. This isotope, which was used as a power source in the space program, has about 300 times the alpha activity of the plutonium-239 associated with fuel reprocessing and therefore required special handling procedures. The major hazard was neutrons produced by (α,n) reactions with impurities such as fluorine, oxygen, and other common light elements. Paul Nelson, Jack Fischer, Jim Haley, John Lenc, and John Schilb conducted these studies.

A special glove-box facility was adapted for the work by using water as shielding for protection against the neutron emissions. Jack Fischer solved a problem that had plagued many people doing glove box work. Every time a researcher weighed something, read a pressure, or observed something significant, he or she had to disengage from the gloves, check their hands, make an entry in the notebook, and then reinsert their hands back into the gloves. Jack installed a voice-activated tape recorder to record the data orally.

Two laboratory-scale runs were made to demonstrate the recovery of metallic plutonium-238 by the reduction of $^{238}PuO_2$ in liquid zinc-magnesium or zinc-calcium, followed by vacuum distillation of the solvent metals. Most of the undesirable elements that cause (α,n) reactions were removed by this procedure. Two other experiments were conducted with $^{239}PuO_2$ microspheres (a stand-in for $^{238}PuO_2$) by the above procedure, except that the plutonium was subjected to a salt-transport separation and recovered by retorting. A satisfactory recovery of plutonium and a good separation from the light elements was achieved in both experiments.

In two further runs, an attempt was made to recover high-purity plutonium metal from a $^{239}PuO_2$-molybdenum cermet fuel. The cermet was disintegrated successfully, but the plutonium product contained excessive copper from the $CuCl_2$ used in the salt-transport separation. Work on this project was discontinued June 30, 1969.

Determination of Nuclear Constants

With the prospect of EBR-II coming on line soon, there was a need to have detailed, accurate information on pertinent cross sections for reactor physics calculations involving fast neutrons. Much of this information was available, but there were gaps that needed to be filled and questionable values that needed be checked. To perform these calculations, one needs to know (1) the neutron energy spectrum of the reactor as a function of age and location in the core, (2) capture and fission cross sections as a function of neutron energy, and (3) the production rate of nuclides from other nuclides. Cross-section data are required both for the fuel constituents and the other components such as control and structural materials.

Most of the early studies in the 1960s made use of Van de Graaff generators in the Reactor Engineering (RE) and Physics (PHY) Divisions, which could produce monoenergetic protons at a prescribed energy level. The proton beam was then directed to a lithium target to produce monoenergetic neutrons through the reaction $Li^7(p,n)Be^7$. The range of neutron energy levels was 0.4 to 1.7 MeV. The capture cross sections were derived by counting the decay rate of the activation product. This count was done with an alpha pulse-height analyzer in conjunction with a 256-channel analyzer. The detector was a thallium-activated NaI crystal.

The Mark III version of EBR-I was used to determine neutron capture/fission cross sections of U-233, U-235, U-236, Pu-239, and Pu-240. The samples were irradiated for 800,000 kWh. The fission cross sections were obtained by analysis of fission-product Cs-137, which is produced at a rate essentially independent of neutron energy. Technetium-99 was shown to share this characteristic and to be an alternative isotope for monitoring fission. This observation was of interest because cesium was removed during the melt refining process for EBR-II fuel, whereas technetium remained with the uranium and plutonium. The capture cross sections were established from mass spectrometric analyses of the products. Capture/fission cross-section ratios were measured for specimens from various locations in the EBR-I reactor, and they varied significantly. For example, the values for U-233 ranged from 0.06 in the core to 0.13 in the outer blanket. A computer program was developed to reduce the EBR-I data to monoenergetic neutron cross sections. Following the EBR-I irradiations, arrangements were made to insert samples of U-233, U-235, U-238, Pu-239, and Pu-240 into EBR-II for similar measurements.

The rare earth elements were of interest as possible control materials. Neutron capture cross sections were determined for Eu-170, Gd-158, Pr-141, Lu-175, La-139, Y-84, Y-89, Yb-176, Ti-50, Rb-85, Rb-87, Sr-84, Sr-86, and Sr-87, using the Van de Graaff machines. Radiative capture and scattering of neutrons by structural materials such as molybdenum and niobium were also determined.

Integral capture cross sections were determined by irradiating specimens of stainless steel and other structural metals in EBR-II and examining the reactor neutron energy spectrum. Further capture-to-fission ratios were determined by irradiations of various uranium and plutonium isotopes, and experiments were conducted to measure the fast fission yields of tritium, hydrogen, and helium as a function of neutron energy.

During the course of this work, an ongoing effort was maintained on the development of new counting techniques. A liquid scintillation system employing a photoelectric tube and amplifiers was developed for 4π beta counting, and in 1967 a lithium-drifted germanium detector was installed.

Carl Crouthamel was the principal investigator during most of this work, but Don Stupegia and Ed Dewell handled this responsibility during the two years that Carl was absent from ANL. Norm Dudey, Bob Heinrich, Al Madson, Chris Gatrousis, Jackie Williams, and Gene Kucera also made major contributions to this program.

Calorimetry

The calorimetry program continued with the objective of determining the thermodynamic properties of substances of interest in high temperature chemistry and nuclear technology. This was a major part of the Division's overall effort on the physical chemistry and thermodynamics of high-temperature materials, which also included phase studies, property measurements, and other activities. The specific mission of the calorimetry group was to determine the room-temperature and high-temperature enthalpies (heats) of formation.

In using combustion calorimetry to determine the enthalpy of formation of compounds, accurate data must be available on the enthalpies of formation of the reaction products. For example, a determination of the enthalpy of formation of US (uranium monosulfide), using fluorine combustion calorimetry, involves the reaction

$$US + 6\,F_2 \rightarrow UF_6 + SF_6$$

The value for the enthalpy of formation of US can be no more accurate than the values available for UF_6 and SF_6. For this reason, much of the effort in the calorimetry program was aimed toward the enthalpies of formation of fluorides of the individual elements. Although literature data were available on most of these fluorides, many of the values had been obtained by indirect methods or were questionable for some other reason and were therefore redetermined experimentally by the fluorine combustion method. These elements included Al, B, C, Cd, Gd, Ge, H, Hf, Ho, I, La, Mg, Mo, Nb, Ni, P, Ru, S, Se, Si, Ta, Th, Ti, U, W, Y, Zn, and Zr.

Calorimetric measurements are inherently difficult not only because they require very careful, precise techniques and equipment, but for many other reasons as well. The starting material must be of high, or at least exactly known purity. Some substances are difficult to ignite. In most cases, a thin wire was used to start the reaction, which then proceeded to a foil and then to a more substantial sample such as a pin. In other situations, some other readily ignitable material was used as a fuse. A jet of fluorine produced the best ignitions in certain cases. With many materials, the reaction did not go to completion, so the unreacted portion had to be separated, characterized, and measured by weighing or other means. There were also problems with reactions of substances such as uranium, which have multiple oxidation states. A large amount of effort was required to obtain good data for UF_6 due to the formation of UF_3, UF_4, and ill-defined compounds between UF_4 and UF_6, but it was finally done successfully.

In the early fluorine-combustion work, the fluorine that was commercially available had significant impurity levels (1.14% O_2, N_2, CF_4, C_2F_6). Larry Stein of the Chemistry Division purified fluorine by fractional distillation and obtained a purity of 99.96%, which was considered satisfactory. The General Chemical Division of the Allied Chemical Co. built a similar still that produced 99.9% fluorine for commercial sale.

Some of the information on compounds was obtained by oxygen combustion methods. Enthalpies of formation were measured for UN, WS_2, ZrH_2, ZrD_2 (D is deuterium), MoS_2, SiC, Pu, PuC, Pu_2C_3, PuO_2, PuN, and as information on fluorides of the elements began to emerge, the fluorine combustion method was used to determine enthalpies of formation for BN, B_2O_3, HfB_2, NbB_2, SiC, SiO_2, TaB_2, UP, US, UB_2, ZrB_2, and Na_2C_2.

The combustion calorimetry work produced data for a standard temperature of 298 K (25°C). In practical applications such as process calculations, it is necessary to have enthalpy data over a wide temperature range. Ideally, if entropy values are available or can be calculated and the thermodynamics of pertinent phase transitions are known, free energies of formation can be obtained. This information would yield a complete set of thermochemical data for a compound, similar to those published in the widely used JANAF (Joint Army, Navy, Air Force) tables.

To provide the higher-temperature enthalpy data, a drop calorimeter capable of temperatures up to 1500°C was constructed (Fig. 3-10). This device consisted basically of a furnace in which a sample suspended by a wire was heated to a precisely known temperature and then dropped through a gate mechanism into a calorimeter where the heat evolution was measured as the sample cooled.

Although simple in principle, this equipment was highly complex in its design, construction, and operation, and several years of effort were required to work out all the problems and place it in operation in 1966. A second drop calorimeter of the same basic design, but with numerous modifications, was built to extend the temperature capability up to 2500°C. In the higher temperature calorimeter an electron-gun heater and a pyrometer for temperature measurement were used instead of the resistance furnace and thermocouple used in the 1500°C calorimeter. Later on, a third drop calorimeter having a temperature capability of about 3300°C was constructed. Induction heating was used to heat the specimen in that unit.

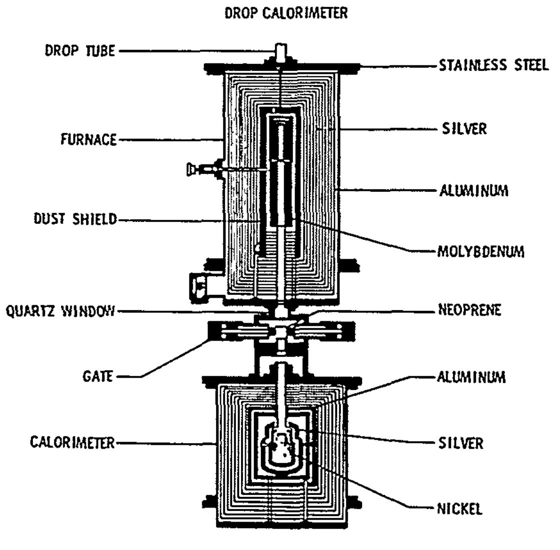


Fig. 3-10. Schematic of Drop Calorimeter

Ward Hubbard was the individual in charge of this work; others who participated include Milt Ader, Don Fredrickson, Elliott Greenberg, Jerry Johnson, Ralph Nuttall, Pat O'Hare, Howard Porte, Ed Rudzitis, Jack Settle, Rosemary Terry, Erv Van Deventer, Steve Wise, and Bob Kleb from Central Shops.

Energy Conversion and Storage

THERMOELECTRIC RESEARCH

In 1961, Hal Feder and Russ Edwards started a fundamental research program on thermoelectricity to contribute to the technological development of systems in which the thermoelectric effect is used to convert nuclear reactor heat directly into electrical power. Both liquid and refractory solid thermocouple materials were investigated. The criterion for evaluating such materials was a "figure of merit," Z, which was defined as follows:

$$Z = S^2\sigma/k$$

where S is the Seebeck coefficient, σ is the electrical conductivity, and k is the thermal conductivity. (The Seebeck coefficient is a measure of the effect of temperature difference between the two junctions of a thermocouple on the electrical potential that is generated.)

The work on liquid materials was directed mainly toward the indium-antimony (In-Sb) system. Seebeck coefficients were measured at compositions over the entire liquid range of the system at various temperatures from about 630 to 750°C. Temperature differences of 10 to 15°C were used for the two legs of the thermocouple. An addition of 20 at.% bismuth raised the Seebeck coefficient of indium by approximately a factor of two, and the values were of the order of 1 μV/°C.

Results were generally similar for the systems In-Bi and Sb-Bi.

The studies of solid materials were concerned primarily with uranium monosulfide (US), a compound known to be stable up to high temperatures. Uranium and thorium monosulfides were selected on the basis of their stabilities up to high temperatures and their electronic similarity to cerium sulfide, which was known to have a large Seebeck coefficient. Over the temperature range from 150 to 1200°C, Seebeck coefficients for the US were -40 to -90 μV/°C, which are somewhat lower than those for cerium sulfide. When converted to a figure of merit, the Z values for US were considered to be about a factor of ten too low to be useful for practical applications, and the program was discontinued in 1963.

During the course of these studies, a great deal of information was generated on the thermodynamic and physical properties of these systems in addition to their thermoelectric characteristics. Some of the individuals who contributed to this work were Russ Edwards, Phil Danielson, Clyde Metz, Frank Mrazek, and Marv Tetenbaum.

THERMALLY REGENERATIVE GALVANIC CELLS

At about the same time that the work on thermoelectric systems ended, a research study on thermally regenerative galvanic cells was initiated, largely through the efforts of Carl Crouthamel. The eventual goal of this effort, like that of the thermoelectric program, was to couple a nuclear reactor with a device that would convert the thermal energy directly into electricity. The idea was to dissociate a chemical compound by the reactor heat and then recombine the dissociation products to form that same compound in an electrochemical cell to produce the electricity. This was not a new concept created at ANL; work was already in progress at various laboratories, but it was felt that CEN's experience and capabilities for handling liquid metals and molten salts would be a major asset in mounting such a program.

Argonne researchers recognized that the efficiency of a thermally regenerative electrochemical system would be unlikely to exceed that of a steam turbine because it, too, would be subject to the Carnot cycle limitation. It might, however, have other advantages: (1) few, if any, moving parts, (2) adaptability to a wide range of plant sizes, (3) compactness and lower weight, and (4) ability to isolate the system rigorously through its useful life.

The first system to be investigated was the lithium/hydrogen cell, which consisted of a liquid lithium electrode, a hydrogen electrode in which the hydrogen was admitted by permeation through an iron diaphragm, and a molten LiCl-KCl electrolyte (m.p. 352°C). The overall cell reaction is

$$2\,Li + H_2 \rightarrow 2\,LiH$$

The lithium hydride product dissolved in the electrolyte. Because little was known about the phase relationships of LiH with the alkali metal halides, a considerable experimental effort was devoted to this subject. Some of the results are given in Table 3-2.

Table 3-2. Lithium Hydride Salt Systems

System	Minimum Melt. Pt., °C	Eutectic Comp., mol% LiH
LiH-LiCl	495.6	34.0
LiH-LiBr	453.3	29.7
LiH-LiI	390.8	23.5
LiH-LiF	684	Solid Solution

Information was also obtained on the systems LiH-KCl, LiH-NaCl, and LiH-LiCl-KCl. From the standpoint of phase relations, LiH behaved much like an alkali metal halide.

Initial electrical measurements on the Li/H_2 cell showed a high efficiency, but the current was limited by slow diffusion of the hydrogen through the Armco iron diffusion barrier. Other barrier designs and materials were tested, and some work was done on the regeneration of Li/H_2 cells. The final conclusion was that the overall efficiency that could be expected from the Li/H_2 cell was in the range of 8 to 12%, which is about the same as that for existing mercury-vapor-cycle and thermoelectric devices.

Work was also started on bimetallic concentration cells with liquid metal electrodes:

M_A / Electrolyte + M_A Salt / M_A in M_B

where M_A is a volatile metal, and M_B is non-volatile. As the cell is discharged, M_A is transported through the electrolyte as ions, and its concentration increases in the M_B electrode. The cell is regenerated thermally by vaporizing M_A selectively from the M_A-M_B electrode and returning it to the pure M_A electrode. After an evaluation of the alkali metals, lithium was selected as the volatile metal, and the LiCl-KCl eutectic was chosen as the electrolyte. Polarization curves were measured for lithium electrodes in combination with other liquid metal electrodes, which included Te, Bi, Sn, Pb, Zn, and Cd. The potentials ranged from 1.93 V for the Li/Te couple down to 0.66 V for Li/Cd. On the basis of the potentials, vapor pressures, solubilities, and other factors, Li/Sn and Li/Bi were selected for further initial studies. Solid intermetallic compounds exist in both systems: Li_5Sn_2 and Li_2Sn in Li-Sn and Li_3Bi in Li-Bi. Thermodynamic functions of these systems were determined, and preliminary regeneration studies were started on Li-Bi, Li-Sn, and Na-Sn. The system Na-Bi was investigated by mass spectrometric and effusion measurements. Attention was turned to various other electrolyte compositions, including LiF-LiCl, LiF-LiCl-LiI, NaF-NaCl-NaI, LiF-LiI, and LiBr-LiI. The compound Li_3Bi was found to be soluble in molten LiF-LiCl. This discovery led to a series of solubility and absorption spectrum studies of lithium and sodium intermetallic compounds in molten salts. The solutions were of various colors.

Table 3-3 is a summary of the more promising regenerative galvanic cell systems that were operated. The only one that was run in a regenerative mode was the Na/Pb cell, with a regeneration temperature of 825-875°C. The cells all operated reversibly with no significant overvoltages.

Table 3-3. Regenerative Galvanic Cell Systems

System	Open-Circuit Potential, V	Current Density, A/cm^2	Temp., °C
Na/NaF-NaCl-NaI/Na in Pb	0.4	0.2	575
Na/NaF-NaCl-NaI/Na on Bi	0.6	1.1	530-615
Li/LiF-LiCl-LiI/Li in Bi	0.9	2.2	500
Li/LiF-LiCl-LiI/Li in Sn	0.6	1.0	500
Li/LiF-LiCl-LiH/H_2	0.3	0.2-1.0	525-570

Additional regeneration studies were conducted on a few of the candidate systems. In the Li-Bi system, the vapor pressures of the two components did not differ sufficiently for a practical operation. Engineering investigations were made on the regeneration of Na-Bi and Na-Pb cells. A cell operated at 543-600°C with regeneration temperatures of 775-875°C produced 7 A at 850°C. With the cell operating at 575°C, its open-circuit potential was 0.41 V. Vapor-liquid equilibrium measurements were made on the Na-Bi system, and the thermodynamics and phase equilibria for the system were characterized by emf measurements and thermal analysis studies, respectively. Other supporting information was obtained on the densities, viscosities, and surface tensions of various electrolyte salts and liquid metal solutions. Corrosion studies were also performed to determine the compatibilities of the liquid salts and metals with a number of metallic and ceramic materials that might be used as materials of construction.

During the operation of Na/Bi cells, the system proved to be electrochemically reversible (capable of both charging and discharging by an electric current) with high efficiencies, which suggested its possible use as a secondary (rechargeable) battery. A much higher voltage could be obtained, however, from the Li/Te system, which had been tested earlier. The Li/Te system was not suitable for a thermally regenerative cell because the high stability (large negative free energy of formation) of Li_2Te made thermal regeneration impossible, but that would be of no concern for a rechargeable storage battery. In a test of a Li/LiF-LiCl-LiI/Te cell, at 480°C, high current densities up to 5 A/cm^2 were achieved. By this time it was recognized that thermally regenerative cells could be made to work, but the low voltages and difficult engineering and materials problems in the regeneration cycle made it hard to justify further development work. The use of cells of this type in rechargeable batteries, however, seemed to show great promise, and the work began to head in that direction. This, of course, changed the potential practical application from the direct conversion of heat to electricity to one of electrical energy storage on utility systems and electric cars. For CEN, it was also a step away from nuclear work to a more politically acceptable area.

Numerous people were involved in the different phases of this program. The initial studies were done by Carl Crouthamel, Mel Foster, and Dave Anthers, who were soon joined by Dick Eppley, Bob Heinrich, Carl Johnson, Steve Banacek, John Allen, Al Fischer, and Stan Johnson. In 1964 Jim Hesson and Paul Shimotake joined the group and began looking at the engineering aspects. Elton Cairns appeared on the scene in 1967, and Jim Bingle, Ellen Hathaway, Gene Kucera, and Jim Peck joined the effort. Leadership in this work was provided mainly by Carl Crouthamel, Art Tevebaugh, and Elton Cairns.

LITHIUM-CHALCOGEN BATTERIES

The lithium/tellurium couple was the first to be investigated in the research and development program on rechargeable batteries. Several fundamental studies were made to gain a better understanding of the chemical and electrochemical characteristics of the system. Mel Foster and Gene Kucera made emf measurements to determine the effect of the changing cathode composition on the cell as it was discharged. Mel Foster, Carl Johnson, Kathleen Davis, Jim Peck, and Bob Schablaske established a phase diagram for the lithium-tellurium system, using thermal analysis and X-ray diffraction techniques. Carl Johnson and Mel Foster determined the phase diagram, which was of particular interest because it has a ternary eutectic at the unusually low temperature of

265°C. (In the case of the battery systems, the minimum operating temperature was usually the melting point of the electrolyte.) Vic Maroni and Ellen Hathaway conducted a series of Raman spectroscopic studies on the systems Li_2Se-LiF-LiCl, Li_2Te-LiF-LiCl, KCl-$MgCl_2$, $MgBr_2$-MgBr, and UO_2Cl_2 in NaCl-KCl-$MgCl_2$.

On the more applied side, Paul Shimotake, G. Rogers, and Jim Peck began operating cells of the type Li/LiF-LiCl-LiI/Se, in which the lithium and selenium were both liquids. These cells had an open-circuit potential of about 2.4 V and could produce short-circuit current densities of 11-13 A/cm^2. Work began on paste electrolytes, which served as mechanical spacers and electronic insulators between the electrodes while permitting the transport of lithium ions. These separators were formed by pressing a mixture of an inert powder such as $LiAlO_2$ with the molten salt electrolyte to form a structure that remained solid at the operating temperature of the cell. Porous metal structures were used in the liquid lithium and selenium electrodes to provide physical support and also to serve as current collectors. Paul Shimotake, Ramamritham Sridhar, and John Cassulo put a substantial effort into the development of these current collectors. Some additional initial investigations were conducted on the Li/S and Li/P couples as potentially useful battery cells.

Preliminary engineering design studies of batteries using cells of this type showed their potential for very high performance, both in energy capacity and power. In one progress report, the following practical applications were listed in order of what was considered to be higher-probability ones first: (1) spacecraft, (2) military communications, (3) materials-handling vehicles, (4) military vehicles, (5) boats and submarines, (6) remote locations, (7) buses and trucks, (8) urban automobiles, and (9) off-peak energy storage for central stations. The way things actually played out, the first funding was provided by the AEC for items (8) and (9) and by the U.S. Army for item (4). A rather surprising development was funding from the National Heart and Lung Institute to develop an implantable battery for an artificial heart, which produced some bad jokes about heartburn, but the idea appeared to be more feasible than one would think at first glance. The lithium/selenium system was selected for the heart battery; lithium/selenium and lithium/sulfur were both in contention for the other applications.

Elton Cairns, who came to ANL from the General Motors Research Lab, was in charge of this work in 1968-69. He was a widely recognized authority in the electrochemical field, which was a significant asset in obtaining funding from various organizations. He was highly competent both in the theoretical and experimental aspects of the work and a good leader. One quirk that bothered the staff at times was his proclivity to change the settings such as voltage or current on someone's experiment in their absence. He always had a good reason for making the change, but it was not always consistent with the experiment the investigator had in mind. Elton had another unusual practice; at personnel evaluation time, he would collect all the laboratory notebooks and read them in detail as a part of the evaluation. Probably not a bad idea; it was an objective measure and it encouraged good record keeping. One time Elton was asked what he would like to do eventually in his career, and he indicated that he would like to be on the faculty at the University of California with a few graduate students. That is what he is doing now.

FLUIDIZED BED COMBUSTION OF COAL

In 1969, the Division, as a part of the movement toward environmental research, began a program on the combustion of coal in a fluidized bed to which limestone was added as a means of reducing the emission of sulfur dioxide (SO_2) during combustion. A literature survey and preliminary laboratory experiments with fixed beds had shown that limestone (natural $CaCO_3$) was the most promising material for this purpose. An empirical model based on laboratory kinetic data was developed to determine the fluidized bed operating parameters such as bed height, superficial gas velocity, and optimum bed particle size.

Bench-scale experiments were conducted in a 6-in.-dia fluidized bed combustor to determine the SO_2 emissions under conditions prevailing in coal-fired power plants and industrial steam boilers. With a combustion temperature of 1600°F and a superficial gas velocity of 3 ft/sec, the following effects were observed:

1. The SO_2 concentration in the flue gas was reduced by 29 to 87% of that without the limestone additive.
2. The most favorable result was obtained with a calcitic limestone of 25-μm average particle size at 2.2 times the stoichiometric requirement.
3. For any particular limestone, the SO_2 removal increased with decreasing particle size.
4. The maximum utilization of CaO during the experiments was 38%.
5. The combustion efficiencies of carbon burned in two experiments were 96.7 and 97.1%.
6. Virtually all the ash from the coal was elutriated.
7. Bench-scale experiments at 1600°F showed that the source of NO_x compounds in the flue gas came from nitrogen compounds in the coal. In other words, little or no NO_x had been formed by fixation of atmospheric nitrogen in the combustion process.
8. The limestone addition produced a 30-40% reduction of nitric oxide in the flue gas.

Al Jonke led these initial studies, which were performed by Erv Carls, Roger Jarry, and Milt Haas.

Analytical Chemistry

By 1960, the scope of the Division's activities had expanded from the original work on solvent-extraction processes into a larger and much more diversified group of programs, including pyrometallurgical and fluoride volatility fuel reprocessing, reactor safety, calorimetry, and several other areas. Each of these depended heavily upon the Analytical Laboratory, which had to expand its range of capabilities to meet this need. The group then consisted of a large section for elemental analysis, plus other sections for the development of new analytical methods, X-ray diffraction and spectroscopy, gas chromatography, and radiochemistry. In 1963, a new section was formed to conduct studies with a newly acquired electron-probe microanalyzer. (The term "section" here refers only to the various organizations within the Analytical Laboratory and has no connection with the term used elsewhere for a major part of CEN as a whole.)

During the 1950s and 1960s, manufacturers of scientific instruments were capitalizing on advances in electronic technology to come out with a variety of new applications. One of these was the electron microprobe. During that period, the Division also acquired an atomic absorption spectrometer and a new 75-kV X-ray spectrometer. As these advances continued to be made, new designs of more mundane instruments such as analytical balances made the analytical work faster, easier, and more accurate.

The volume of work being handled by the Analytical Laboratory during the 1960s was extraordinary. In a typical year the elemental analysis section alone used over 100 methods to perform more than 13,000 analyses. The X-ray section determined several hundred diffraction patterns and made many spectrographic assays, identifications, and structural studies. The gas chromatography section analyzed numerous gas samples from glove boxes, furnaces, and calorimeters.

The analytical research was, for the most part, an outgrowth of the service work. As the Division's programs changed, existing analytical methods had to be modified or new methods had to be developed. In the majority of the samples, the element of interest was only a minor constituent, and the analytical method had to either tolerate or separate the matrix material from the element of interest. The matrix materials, which were often present in amounts as much as a million times greater than that of the element to be analyzed, were typically zinc, magnesium, salt fluxes, and aluminum oxide. Typical research problems included a method for dissolving PuO_2 and spectrophotometric determinations of Pu(IV) and ruthenium.

Mention was made earlier that the startup of EBR-II, which burned uranium-235 in a fast neutron flux, had a somewhat different spectrum of fission-product yields than those for thermal reactors. The burnup of spent fuel from a reactor can be determined from the concentration of a fission-product nuclide in the fuel if its fission yield is known. None of the 85 or so fission-product nuclides had all the nuclear and physical characteristics to be ideal for this purpose, but the Analytical Chemistry research group investigated a number of the most promising candidates for this purpose and obtained fission-yield data for them. Among these were Tc-99; La-139; Cs-133 and -137; Pr-141; Mo-95, -97, -98, and -100; Ru-101, -102, and -104; and total rare earths.

There was some concern as to whether the burnup monitors for the metallic EBR-II fuel would be applicable to oxide and carbide fuels. Tests that were conducted on irradiated uranium dioxide fuel showed that molybdenum and technetium were not suitable burnup monitors because of their tendency to migrate during irradiation, but that the rare earths were excellent candidates for this purpose. An X-ray spectrometric method for assaying the quantities of fission-product lanthanum, cerium, praseodymium, and neodymium was developed to measure the burnup of oxide fuels.

Bob Larsen, Carl Crouthamel, and Bob Meyer were in charge of various aspects of the analytical chemistry programs. Other members of the group included:

Murray Barsky
Maureen Binelli
William Bloom
Eugene Bozisch
Vera Drabek
Florence Ferry
Ruth Hanna
Bob Heinrich
Myron Homa
Ruth Juvinal
Carol Kosner
Gene Kucera
Verne Lemke
Russ Malewicki
Fred Martino
Bob Oldham
Al Panek
Ray Popek
Laury Ross
Dino Santelli
Bob Schablaske
Chuck Seils
Gregory Smith
Stan Siegel
Nora Stalica
Ben Tani
Ziggy Tomczuk
Florence Williams (Smith)
Jackie Williams

Waste Processing and Gamma-Irradiation Facility

As of the end of 1962, routine disposal of liquid and solid radioactive wastes by CEN was discontinued, and the operation was transferred to the Plant Services Department. During the last year of operation, about 50,000 gallons of liquid waste was processed. The high-level gamma irradiation facility was also shut down after seven years of operation. Irradiations were conducted on 5,432 samples in 1961 and 2,443 in 1962, not counting the dosimetry samples used to measure the radiation fluxes.

Studies and Evaluations

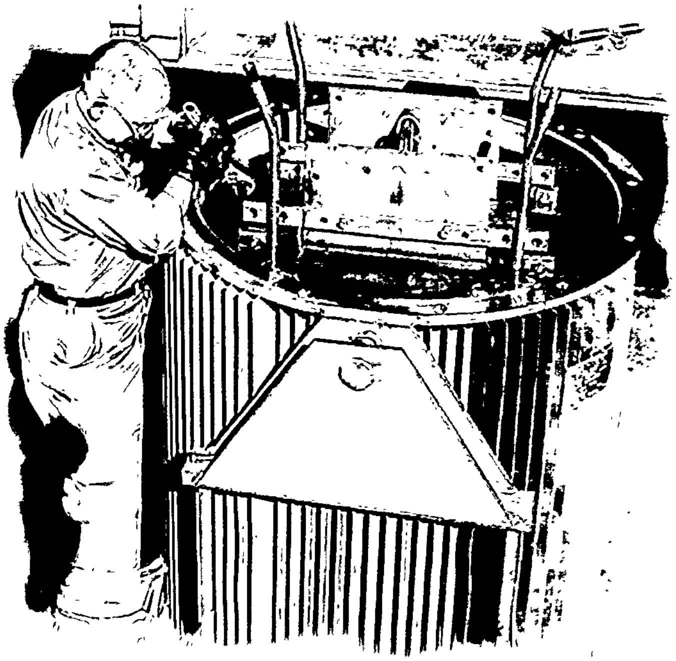
Studies and evaluations were done from time to time on the feasibility and costs of projected applications of research and development programs of the Chemical Engineering Division. These might be best described as looking at the forest rather than the trees.

In 1964, Bill Mecham, Wally Seefeldt, Virgil Trice, and Milt Levenson reported on an interdivisional study that was being conducted for the AEC on the estimated costs of power generation by metal fueled reactors, based on a 1000 MW(e) plant. The following topics were covered.

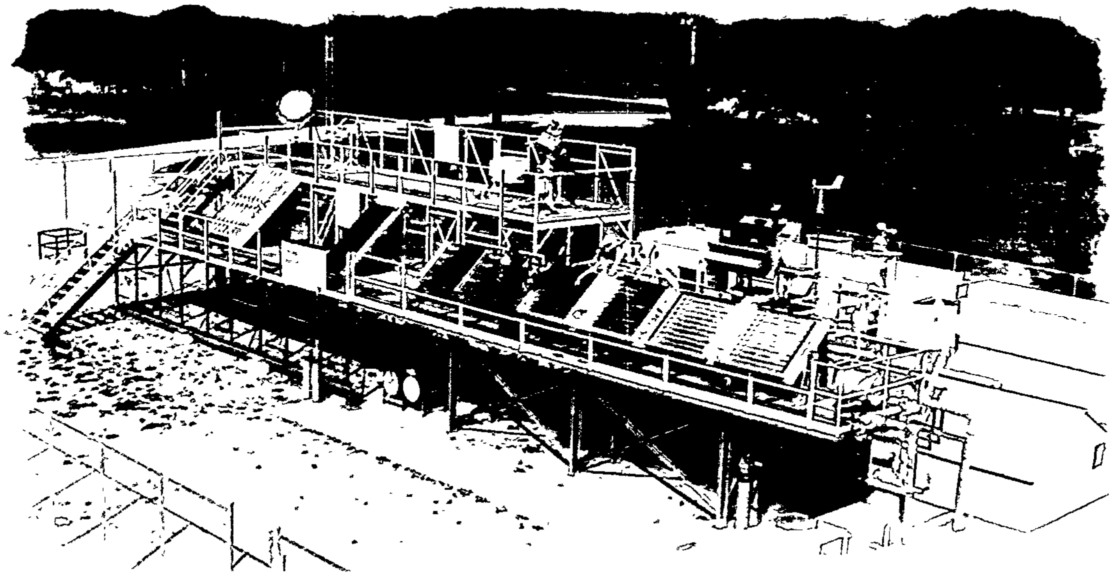
1. A reference pyrochemical process
2. Preparation of fuel for processing
3. Removal of fission products
4. Separation of uranium and plutonium and their recovery as ingots
5. Composition of the product ingots
6. Estimated costs for the reactor fuel cycle

A second study was undertaken by this same group to compare the costs of reprocessing plutonium metal and oxide and carbide fuels by aqueous, fluoride volatility, and pyrochemical processes.

Bill Mecham, in 1967, conducted a study on the problems of tritium in power reactor fuel cycles. This study considered the sources of tritium in discharged fuel, its behavior both in aqueous and nonaqueous processes, and methods for its disposal. Because tritium cannot be separated economically from the large volumes of water used in aqueous processing, its disposal would have to be accomplished by dilution and release to the environment. In the case of fluoride volatility and pyrometallurgical processes, the tritium can be recovered in a small volume of gas, which can be stored or immobilized by further treatment.



1970-1980: TRANSITIONS



1970-1980

(top, left) Calorimeter for determining basic thermochemical properties of a wide variety of materials.

(top, right) National Battery Test Laboratory used for standardized testing of cells, multicell modules, and batteries built by industrial firms.

(bottom) Solar energy testing facility in which arrays of different types of solar energy collectors were tested.

4

1970-1980: Transitions

The 1970s was a difficult period for the United States in that it seemed to present a continuous series of new problems. At the beginning of the decade, the foremost U.S. concern was to extricate itself from the extended Vietnam War. That was finally accomplished in 1975, but with little feeling of success. Richard Nixon defeated George McGovern by a landslide in the 1972 presidential election, but was forced to resign in favor of Vice President Gerald Ford in 1974 as a result of the Watergate incident. Meanwhile, in 1973, the Organization of Petroleum Exporting Countries (OPEC) suddenly stopped oil shipments to the U.S., causing a severe fuel shortage and an eightfold rise in the cost of crude oil, which, in turn, set off an inflationary spiral with interest rates rising to 15% or more. Jimmy Carter, by defeating Ford in the 1976 presidential election, inherited the problems of the continuing oil shortage, inflation, and hostility of some Mideastern nations. His last year in office became particularly difficult when Iranian militants seized 52 American embassy personnel as hostages.

In spite of increasing opposition by antinuclear and environmental groups, many commercial nuclear power plants were built and started up in the 1970s and construction of others extended into the 1980s. In 1975, the AEC was abolished. Its regulatory function was taken over by the Nuclear Regulatory Commission (NRC), and its other responsibilities were given to the Energy Research and Development Administration (ERDA). The ERDA was short-lived; in 1977 it was absorbed into a new cabinet-level Department of Energy (DOE). During this ten-year period, ANL had two new Laboratory Directors, Robert G. Sachs in 1973 and Walter E. Massey in 1979. In 1973, Leslie Burris replaced Richard Vogel as Director of the Chemical Engineering Division. Y-Wing, an office complex with an auditorium, and the National Battery Test Laboratory facility were added to Bldg. 205.

The large pyrometallurgical and fluoride volatility fuel reprocessing and reactor safety programs had all but disappeared by about 1970, and were supplanted largely by expanded programs on sodium technology, fluidized-bed combustion of coal, and high-temperature battery development. Work continued on materials chemistry and thermodynamics, analytical and reactor chemistry, and technologies employing liquid metal and molten salt solvents. These programmatic changes resulted in some layoffs and transfers to other divisions. Many of the staff members had to become familiar with new areas of work, and several people were hired to provide special expertise for the new programs. The work became more interdisciplinary and required increased capabilities in areas such as computer applications, materials science, electrochemistry, and electrical engineering. The Division's funding also shifted somewhat, with a larger proportion of the support coming in from non-nuclear branches of the DOE and from other federal agencies. In the mid-1970s, the DOE adopted a management policy of placing programmatic management "in the field," and CEN was given overall management responsibilities as the "lead laboratory" for the aqueous battery, advanced battery, and fuel-cell programs.

THE NATIONAL SCENE

In the early 1970s, the war in Vietnam was beginning to wind down, and, after a brief incursion into Cambodia, much of the American force in Vietnam was withdrawn. Peace talks were held in Paris in 1973, and the remaining U.S. troops were brought back home. Full-scale war erupted again in 1975 with a Communist victory; Marine guards and civilians had to be rescued from the U.S. Embassy and evacuated along with about 140,000 Vietnamese refugees. Many felt that the Vietnam War had ended in a U.S. defeat, and it was a bitter experience both for the veterans and the civilian population.

In 1972, President Nixon ran for a second term, defeating his Democratic opponent, George McGovern, by a large margin. At one point in the election campaign, the police nabbed five men who were attempting to break into the Democratic National Headquarters. The break-in, of itself, was of minor consequence and received little public attention until well after the election, but when the attempted cover-up that followed it was revealed some time later, several of President Nixon's advisors landed in jail, and Nixon finally resigned on August 8, 1974. Gerald R. Ford, the Vice President, assumed the presidency, and one of his first acts was to grant Nixon a full pardon. (The previous year, the Vice President, Spiro T. Agnew, had been convicted of income tax evasion and replaced by Ford.)

Jimmy Carter, a Democrat and former Governor of Georgia, defeated Ford in a race for the presidency in 1976. Carter, who had served in the nuclear navy as a submarine officer under Admiral Rickover, adopted a strong anti-nuclear stance, and played a major role in negotiating a nuclear non-proliferation pact, signed by 15 countries in 1977. A deeply religious man, devoted to peace, and perhaps idealistic, he was generally opposed to the idea of nuclear power because of its potential for nuclear proliferation. He called nuclear power "the option of last resort," withdrew funding for plutonium processing, and opposed the Clinch River Breeder Reactor proposed by Oak Ridge. In 1978, the U.S. signed a treaty to turn control of the Panama Canal over to the Panamanians by 2000, and the "Framework for Peace" in the Middle East was signed by Egypt's Anwar Sadat and Israel's Premier Menachem Begin after a 13-day conference at Camp David arranged by President Carter.

The decade ended on two particularly sour notes. The Soviets invaded Afghanistan, and Iranian militants seized the U.S. Embassy in Teheran, taking 52 American embassy personnel as hostages. They were held for 444 days.

NUCLEAR POWER

The nuclear power industry entered the 1970s with a highly optimistic view of its future. At the same time, the U.S. Navy was adopting nuclear power plants for its newer and larger vessels. Numerous contracts for the construction of civilian nuclear power plants were negotiated, and many were started up by the end of the decade. Other plants did not become operational until the 1980s and 1990s, due to the long construction times. The reactors that started producing power on a commercial scale in the 1970s are listed in Tables 4-1 and 4-2.

In 1973, the Arab oil-producing cartel, OPEC, suddenly slapped an embargo on their oil shipments, mainly in retaliation for U.S. shipments of arms to Israel during the Yom Kippur war. The price of crude jumped from $2 to $16/barrel. A gasoline and fuel oil shortage developed quickly in the United States. President Carter donned a sweater, admonished the public that they should do likewise and turn down their thermostats, and declared "the moral equivalent of war" on oil usage. Unnecessary use of automobiles was discouraged, and long lines

Table 4-1. U.S. Power Reactors in the 1970s

		Type	MW(e)	Start
Dresden 1 (Morris, IL) *	Commonwealth Edison	BWR	200	7/60
Indian Point 1 (Buchanan, NY)*	Consolidated Edison	PWR	257	1/63
Hanford N (Richland, WA)*		LGR	860	7/66
Haddam Neck (Haddam Neck, CT)	Conn. Yankee Atomic Power	PWR	590	1/68
San Onofre 1 (San Clemente, CA)*	So. Cal. Ed., San Diego G & E	PWR	436	1/68
Nine Mile Point 1 (Scriba, NY)	Niagara Mohawk Power	BWR	610	12/69
Oyster Creek (Forked River, NJ)	GPU Nuclear	BWR	619	12/69
Dresden 2 (Morris, IL)	Commonwealth Edison	BWR	794	6/70
R. E. Ginna (Ontario, NY)	Rochester Gas & Electric	PWR	470	7/70
Point Beach 1 (Two Rivers, WI)	Wisconsin Electric Power	PWR	485	12/70
Millstone 1 (Waterford, CT)	Northeast Utilities	BWR	660	3/71
Robinson 2 (Hartsville, SC)	Carolina Power & Light	PWR	683	3/71
Monticello (Monticello, MN)	Northern States Power	BWR	536	6/71
Dresden 3 (Morris, IL)	Commonwealth Edison	BWR	794	11/71
Palisades (South Haven, MI)	Consumers Power	PWR	780	12/71
Point Beach 2 (Two Rivers, WI)	Wisconsin Electric Power	PWR	445	10/72
Vermont Yankee (Vernon, VT)	Vermont Yankee Nucl. Power	BWR	504	11/72
Maine Yankee (Wiscasset, ME)	Maine Yankee Atomic Power	PWR	860	12/72
Pilgrim (Plymouth, MA)	Boston Edison	BWR	670	12/72
Turkey Point 3 (Florida City, FL)	Florida Power & Light	PWR	666	12/72
Surry 1 (Gravel Neck, VA)	Virginia Power	PWR	801	12/72
Quad Cities 1 (Cordova, IL)	Commonwealth Edison	BWR	789	2/73
Quad Cities 2 (Cordova, IL)	Commonwealth Edison	BWR	789	3/73
Surry 2 (Gravel Neck, VA)	Virginia Power	PWR	801	5/73
Oconee 1 (Seneca, SC)	Duke Power	PWR	846	7/73
Browns Ferry 1 (Decatur, AL)	Tennessee Valley Authority	BWR	1,065	8/74
Fort Calhoun (Fort Calhoun, NB)	Northern States Power	PWR	478	9/73
Turkey Point 4 (Florida City, FL)	Florida Power & Light	PWR	666	9/73
Prairie Island 1 (Red Wing, MN)	Northern States Power	PWR	503	12/73
Zion 1 (Zion, IL)	Commonwealth Edison	PWR	1,040	12/73
Kewaunee (Carlton, WI)	Wisconsin Public Service	PWR	503	6/74
Cooper (Brownville, NB)	Nebraska Public Power	BWR	764	7/74
Peach Bottom 2 (Delta, PA)	PECO Energy Co.	BWR	1,159	7/74
Indian Point 2 (Buchanan, NY)	Consolidated Edison	PWR	975	8/74
Oconee 2 (Seneca, SC)	Duke Power	PWR	846	9/74
3- Mile Island 1 (Londonderry Twp., PA)	GPU Nuclear	PWR	786	9/74
Zion 2 (Zion, IL)	Commonwealth Edison	PWR	1,040	9/74
Oconee 3 (Seneca, SC)	Duke Power	PWR	846	12/74
Arkansas Nuclear One (Russellville, AR)	Energy Operations Inc.	PWR	836	12/74
Peach Bottom 3 (Delta, PA)	PECO Energy Co.	BWR	1,035	12/74
Prairie Island 2 (Red Wing, MN)	Northern States Power	PWR	500	12/74
Duane Arnold (Palo, IA)	IES Utilities	BWR	538	2/75
Browns Ferry 2 (Decatur, AL)	Tennessee Valley Authority	BWR	1,065	3/75
Rancho Seco (Clay Station, CA)*		PWR	913	4/75
Calvert Cliffs 1 (Lusby, MD)	Baltimore G & E	PWR	825	5/75
James A. FitzPatrick (Scriba, NY)	New York Power Authority	BWR	780	7/75
Donald C. Cook 1 (Bridgman, MI)	Indiana/Michigan Power	PWR	1,020	8/75
Brunswick 2 (Southport, NC)	Carolina Power & Light	BWR	754	11/75
Edwin I. Hatch 1 (Baxley, GA)	Georgia Power	BWR	810	12/75
Trojan (Prescott, OR)*		PWR	1,095	

Indian Point 3 (Buchanan, NY)	New York Power Authority	PWR	965	8/76
Beaver Valley (Shippingport, PA)	Duquesne Light	PWR	810	10/76
St. Lucie 1 (Hutchinson Island, FL)	Florida Power & Light	PWR	839	12/76
Browns Ferry 3 (Decatur, AL)	Tennessee Valley Authority	BWR	1,065	3/77
Brunswick 1 (Southport, NC)	Carolina Power & Light	PWR	767	3/77
Crystal River 3 (Red Level, FL)	Florida Power Corp.	PWR	825	3/77
Calvert Cliffs 2 (Lusby, MD)	Baltimore G & E	PWR	825	4/77
Salem 1 (Salem, NJ)	Public Service Elec. & Gas	PWR	1,106	6/77
Joseph M. Farley 1 (Dothan, AL)	Southern Nuclear Operating	PWR	860	12/77
North Anna 1 (Mineral, VA)	Virginia Power	PWR	893	6/78
Davis-Besse (Oak Harbor, OH)	Toledo Edison	PWR	877	7/78
Donald C. Cook 2 (Bridgman, MI)	Indiana/Michigan Power	PWR	1,090	7/78
3 Mile Island 2 (Londonderry Twp., PA)	GPU Nuclear	PWR	792	12/78
Fort. St. Vrain (Platteville, CO)*		HTGR	330	1/79
Edwin I. Hatch 2 (Baxley, GA)	Georgia Power	BWR	820	9/79

* No longer in operation as of 1995.

Table 4-2. Foreign Power Reactors in 1970s

Country	No. of Reactors	Total Power, MW(e)
Armenia	1	400
Belgium	3	1,647
Bulgaria	2	800
Canada	8	5,136
Finland	2	1,155
France	5	4,693
Germany	8	7,358
India	3	390
Japan	21	14,288
Korea	1	556
Pakistan	1	125
Russia	8	5,292
Slovakia	1	408
Spain	1	438
Sweden	5	3,115
Switzerland	4	2,020
Taiwan	2	1,208
Ukraine	1	925
United Kingdom	22	5,434

developed at the filling stations, where the operators adopted various stratagems to deal with the situation, such as shorter hours or alternating days for odd and even license numbers. Christmas lights were frowned upon—there were some somber winter nights in those years. Many Argonne employees were glad that they had formed car pools. The oil shortage persisted through the 1970s, and then began to wane by about 1980 because of several factors, including conservation efforts, increasing availability of oil from other sources, and OPEC members' propensity to cheat on one another.

For the nuclear industry, the oil shortage was a double-edged sword. It made the American public aware of the nation's dependency on foreign energy sources and the need for alternatives to petroleum. At the same time, the steep increase in fuel prices threw the U.S. economy into an inflationary spiral with interest rates rising well into double-digit figures. As a result, the capital costs for nuclear plants rose sharply, and the price of yellowcake (uranium ore concentrate) rose from $7 to $35/pound. The Westinghouse Electric Corp. had to renege on its commitments to customers for uranium oxide at the agreed price. The AEC seemed to be losing its credibility, and the antinuclear forces began publicizing a variety of safety concerns. Permits for reactor construction slowed to a snail's pace due to intervenors in the licensing process and other roadblocks. The cost of capital during these delays was a major problem. In the 1950s, some had thought that nuclear power would be too cheap to meter; in the 1960s, the projected costs were mills per kilowatt-hour; and by the end of the 1970s they were in cents per kilowatt-hour. On top of all this, the projected use of electricity in the U.S. was revised significantly downward. The net effect of all these negative factors was to cast a dark shadow over the earlier optimistic outlook on the future of commercial nuclear power, and no construction of new power reactors has been undertaken in the U.S. since about 1979. There was talk of replacing existing reactors at the end of their lifetimes with a second generation of more fuel-efficient breeder reactors, but this, too, became a doubtful prospect in view of the ban on fuel reprocessing and concerns about safety, waste disposal, and potential proliferation of nuclear weapons.

The General Electric Co. and the Westinghouse Electric Corp. supplied most of the reactors for the nuclear power plants in the U.S. In most, but not all cases, the boiling water reactors were built by General Electric and the pressurized water reactors by Westinghouse. The Babcock and Wilcox Co. and Combustion Engineering Inc. also produced several reactors. Among the more prominent architect-engineering firms were the Bechtel Corp., Ebasco Dorsch Consultants, Sargent & Lundy Engineers, Stone & Webster Engineering Corp., Fluor Corp., and Gilbert Associates, Inc.

Two power reactor incidents of note occurred in the 1970s. The first was in 1975, when a fire broke out in the electrical cable systems of two 1,100-MW(e) Browns Ferry reactors operated by the Tennessee Valley Authority and located in Decatur, Alabama. The fire propagated through the entire cable system, shutting down both reactors and disabling the emergency core cooling system of one. The nuclear components of the plant were not affected, and there was no hazard to the public, but the antinuclear activists used the opportunity to further their cause.

A much more serious failure occurred on March 28, 1979, at Three Mile Island Reactor 2 near Harrisburg, Pennsylvania. The accident began as a small break in the loss-of-coolant system in which a valve stuck open, allowing coolant to escape from the vessel. The emergency core cooling system kicked in as designed, providing makeup water for the core. The operators, confused by the signals in the control room, shut off the emergency cooling system for several hours, whereupon the decay heat of the core vaporized the remaining cooling water in the vessel. Before the operators resumed the flow of emergency coolant, about one-third to one-half of the core melted down. The molten fuel and cladding dropped into the bottom of the vessel, where the molten metal from the cladding reacted with the water, forming a hydrogen "bubble." This situation prevailed for some time, giving the news media a field day with hour-by-hour reports, including much speculation about a possible explosion of the hydrogen. A small amount of radioactivity was released, but the situation was brought under control. The radioactive fallout from the incident was minimal, but the political fallout was enormous. People who claim to have been injured by fallout from Three Mile Island are still filing lawsuits. (One of the current programs in the Division includes an evaluation of the feasibility of using electrometallurgical methods to process the damaged core material and debris from the Three Mile Island reactor.)

The research and development work on nuclear fuel reprocessing by the Chemical Engineering Division at ANL, and at the other AEC laboratories as well, had become nearly dormant as of 1970. This change was in conformance with the AEC directives that the work at ANL should be shifted from nuclear to environmental programs. Although the research and development work on reprocessing had languished, there was some commercial activity in the 1970s. The first commercial plant, which was built by Nuclear Fuel Services, Inc., in West Valley, New York, and had a capacity of 1 ton/day, was started up in 1966. In 1972, it was shut down for retrofitting to meet increasingly stringent licensing requirements. Because of the high cost of retrofitting and the small capacity of the plant, further operation was deemed impractical, and the plant was shut down in 1976. A 1 ton/day plant for processing low-enrichment uranium oxide fuel was built by General Electric in Morris, Illinois. This process employed an aqueous Purex and ion-exchange first cycle to produce nearly fully decontaminated uranium oxide. The solid product was then to have been purified in a second cycle using fluoride volatility-fluidized bed technology to produce fully decontaminated UF_6. The process was never operated successfully, the main reason being that insufficient surge capacity had been inserted between the process steps to provide the necessary operational flexibility. Another problem was that the fluoride volatility portion of the plant was designed for "hands on" (non-remote) maintenance, which turned out to be impractical due to the radiation levels. This plant, however, is serving as a useful but expensive storage facility for discharged fuel subassemblies from commercial light water power reactors. Construction was begun on a larger (5-ton/day) central processing plant at Barnwell, South Carolina. Construction of this plant, which employed solvent-extraction technology, was completed in the late 1970s, but the ban on fuel reprocessing blocked its operation.

Public skepticism about reactor safety and concern regarding the potential proliferation of nuclear weapons had been growing, which was not surprising in view of the reactor accidents and the efforts of antinuclear and environmental groups. President Gerald Ford, feeling this pressure, suspended commercial processing, his main concern being the large amount of high-purity plutonium that might be diverted to nuclear weapons. President Jimmy Carter continued the ban on fuel reprocessing. Although the Unites States was attempting to set a good example, it was not taken very seriously by the rest of the world. Reprocessing continued to be pursued vigorously by several foreign countries, notably France, England, Japan, India, and Russia. France constructed a large 5-ton/day commercial plant at LaHague, where both

French fuel and that from other countries are processed. England, which has continued to recover fuel from its own nuclear power reactors, has recently built a 5-ton/day plant known as THORP (Thermal Oxide Reprocessing Plant), which replaced a former plant. When THORP was started in 1993, England began to sell its processing services to other countries. Japan has built a fuel reprocessing plant, which is scheduled to go into operation in 1998, and India has been using the Purex process since 1982 at the Tarapur Fuel Processing Plant, which has a 1/2-ton/day capacity. Fuel reprocessing is also suspected to be taking place in Russia, China, and possibly North Korea.

The AEC entered the decade of the 1970s with Milton Shaw continuing as the director of Reactor Development and Technology. Until 1973, Congress had supported the nuclear research programs with lump-sum funding covering both safety and breeder development, the allocation between the two being decided by the AEC. Shaw's general approach was to push the breeder development, thereby diverting funding away from research and safety programs such as the Loss of Fluid Test (LOFT). Safety became a contentious issue involving the AEC, Shaw, the reactor vendors, and the Advisory Committee on Reactor Safeguards. The friction increased to a point where the AEC prohibited its safety staff from communication with the regulatory staff on safety matters. This confusion contributed to a public loss of confidence in the nuclear regulatory process. The situation was not improved by the publicity attending the Karen Silkwood incident at Kerr-McGee in 1974. Hollywood did its part, too, by coming out with nuclear scare films such as *The China Syndrome*.

In 1973, Congress passed legislation abolishing the AEC, replacing it with the Nuclear Regulatory Commission (NRC) to perform the regulatory functions, and the Energy Research and Development Administration (ERDA) to handle the non-regulatory and promotional functions. In 1977, ERDA was absorbed by a new Cabinet-level entity, the Department of Energy (DOE), with James Schlessinger as the Secretary of Energy. Congress eliminated the Joint Committee on Atomic Energy (JCAE) in 1977. It is worthy of note here that, particularly in the earlier years, several senators and congressmen on this committee became quite knowledgeable about nuclear science and technology and played an important role both in promoting and guiding the programs. One effect of the demise of this committee was to put more policy-making power in the hands of the DOE managers.

When the DOE was created, its mission was quite different from that of its predecessors in that the nuclear component had been downplayed sharply in favor of energy-conservation measures, environmental concerns, and alternative (preferably renewable) energy sources. It does, however, continue to have the responsibility for U.S. nuclear weapons programs.

THE LABORATORY

Argonne had two new laboratory directors in the 1970s. On April 6, 1973, Robert G. Sachs replaced Dr. Duffield, thereby becoming ANL's fifth director. Dr. Sachs, a physicist with a Ph.D. from Johns Hopkins, had taught at Purdue and the University of Wisconsin. He had also been at Argonne in 1946-47 and served as Associate Laboratory Director for High Energy Physics from 1964 to 1968. Dr. Sachs had the appearance and demeanor of a quiet, scholarly sort of person.

On July 2, 1979, Dr. Sachs was succeeded by Dr. Walter E. Massey. Dr. Massey had earned a Ph.D. in physics at Washington University and been on the faculties at the University of Illinois and Brown University. He gave the impression of being an energetic, ambitious, career-oriented individual. While serving as the Laboratory Director of Argonne, he also continued as professor of physics and in other activities at the University of Chicago. The Laboratory had two Deputy Directors at the time, Robert N. Laney, in charge of research and development, and Michael V. Nevitt, who was responsible for physical research. At the next lower level were several Associate Laboratory Directors, who had jurisdiction over general areas of related research and development work that encompassed parts or all of various divisions. Those concerned with CEN activities at the time were Jack Kyger (Engineering Research and Development), Gale Pewitt (Energy and Environment), and Mike Nevitt (Physical Research).

THE DIVISION

General Information

The management structure of CEN as of January 1970 is given in Table 4-3. At that time, Dr. Richard Vogel was the Director, Donald Webster was the Deputy Director and also Associate Director along with Les Burris and Arthur Tevebaugh. Everett Proud was the Assistant Director. Paul Nelson and Duane Barney became Associate Division Directors in the 1970s, and Paul then became the Deputy Director.

Dr. Vogel, in 1973, left Argonne to accept a position with the Exxon Corp. in Washington State. He subsequently moved on to the Electric Power Research Institute (EPRI) in California in 1983 and continued to keep in touch with his former colleagues at CEN through various technical contacts, including some contract work that the Division did for EPRI on post-irradiation fuel examinations. During his career, Dr. Vogel garnered numerous honors, including the AIChE Robert Wilson Award, and fellowships in the ANS and AIChE.

Leslie Burris was appointed to replace Vogel as CEN Division Director in 1973. As ANL entered the 1970s, many significant changes were coming about, not only in CEN, but also in the entire nuclear community. On the national scene, nuclear power was having problems both with economics and public acceptability. The antinuclear and environmental groups had gained enough support to have a major effect on the political decisions that were being made in Washington. These manifested themselves in the types of programs the AEC would support in the national laboratories, and it was clear that there would have to be a transition from nuclear to environmental research. There was still interest in the breeder reactors as a long-range energy source, and support continued in the areas of sodium chemistry and technology, reactor safety, and nuclear waste disposal. Nuclear fuel reprocessing as such was out. The Division explored new program areas, including cleaner methods of burning coal in power plants, solar collectors, fusion power, high-performance batteries for electric

Fig. 4-1. Leslie Burris

Table 4-3. CEN Organization as of January 1970

Division Director:	
Richard C. Vogel	
Deputy Division Director	
Donald S. Webster	
Associate Division Directors:	
Leslie Burris	Program Manager, Sodium Technology
Arthur D. Tevebaugh	Energy Conversion, High Temperature Materials, Calorimetry
Donald S. Webster	Coal Combustion, Fuel Reprocessing
Assistant Division Director:	
Everett R. Proud	
Section Heads:	
Elton J. Cairns	Energy Conversion & Physical Chemistry
Fred A. Cafasso	Sodium Chemistry
Carl E. Crouthamel	Analytical Chemistry, Neutron Cross Sections, Chemistry of Irradiated Fuels
Albert A. Jonke	Process Development, Fluidization Processes
Paul A. Nelson	Sodium Engineering
Group Leaders:	
Paul E. Blackburn	High Temperature Materials
Lester F. Coleman	Safety, Criticality & Special Studies
Norman E. Dudey	Nuclear Cross Section Measurements
John T. Holmes	Sodium Engineering
Ward N. Hubbard	Calorimetry
Carl E. Johnson	Chemistry of Irradiated Fuels
Robert P. Larsen	Analytical Chemistry & Burnup Analysis
Norman M. Levitz	Engineering Process Development
Robert J. Meyer	Sodium Analytical Methods
William E. Miller	Sodium Engineering
R. Dean Pierce	Pyrochemical Engineering
Joseph Royal	Publications Review Group
Martin J. Steindler	Chemical Process Development
Robert K. Steunenberg	Energy Conversion & Physical Chemistry

Harold M. Feder, Joseph E. Draley, and Charles E. Stevenson are listed as Senior Chemists or Engineers in a January 1970 description of the CEN staff.

vehicles and off-peak electrical energy storage, and fuel cells that were not limited to hydrogen as the fuel. The coal, battery, and fuel-cell programs developed into sizeable efforts in the 1970s.

When the AEC was disbanded into ERDA and NRC, and then DOE was formed, the interfaces between CEN and the funding offices became more fragmented. Each office wanted its own separate progress reports rather than the previous reports issued by the Division as a whole. The consequence was that well over 400 topical and progress reports were issued by CEN during the period 1970-1979. Because the funding and reporting functions were so diverse, much of the Division operated in a matrix-management type of structure in which the Division upper management remained cognizant of technical programs and maintained administrative control of the people and programs. However, many of the negotiations with the funding agencies as to the work to be done, and scheduling and funding requirements, were conducted at a lower (usually section-head) level under the general direction of upper management. Some of the CEN people involved in this arrangement were given the title "Program Manager." The individuals in these positions spent a lot of time and effort traveling to Washington, Germantown, or Morgantown visiting DOE managers in order to keep their programs healthy. There were jokes about taking along "groveling pads" to wear on their knees while begging for funding.

Matrix management had become a popular idea, and it was well suited to the Division's needs at the time, given its wide variety of programs and funding sources. Manpower and facilities could be organized into team efforts that often involved a variety of disciplines. This kind of flexibility tended to stabilize the Division as the individual programs waxed and waned.

One significant organizational change in CEN came about on July 1, 1971, when the analytical support groups from the Chemical Engineering and Chemistry Divisions were consolidated into a single cost center. This combined group was given the official name "Analytical Chemistry Laboratory" (ACL), a separate entity that would provide analytical services to the entire Laboratory, but would still remain a component of the Chemical Engineering Division. This organization was to be self-supporting by doing the work on a fee-for-service basis, at a cost of $25.50/ hour. During the initial stages of operation, Bob Larsen supervised the group in Bldg. 205, and Ralph Bane was responsible for the groups in Bldgs. 200 and 212. Norman Dudey was the first full-time manager of ACL until he left the Laboratory for another position after a year or so. Norm was replaced by Eugene Voiland, who had come to ANL from KAPL. After about three years, Voiland left for a position with General Electric at the Morris plant. Paul Cunningham, who was a Ph.D. chemist from the University of California at Berkeley and had been involved in CEN research programs for several years, became the manager of ACL in 1975. During his tenure in that position, he also served as Section Head for Analytical and Environmental Research in CEN. Since its inception, ACL has had to face a number of challenging problems, the foremost one being whether the new programs in the division would continue to generate a sufficient demand for analytical work to provide the necessary financial support. Analytical charges were highly visible on the cost reports, and in some instances the research groups felt they could save money by doing some of their own analyses. There were also instances in which a research group would have to purchase a specialized analytical instrument to obtain the data they needed and a question arose as to whether the research group or the ACL should have jurisdiction over that equipment. A means of funding some supporting development work on analytical methods also needed to be arranged. These problems were resolved eventually, and the ACL became well established in its present form.

When Cunningham left ANL in 1982 for a somewhat similar position at Los Alamos, David W. Green became the manager of the ACL and still is. Green is also a Ph.D. from Berkeley, who came to CEN from the Chemistry Division. He had worked previously as a Research Associate at the University of Chicago and taught at Albion College. In 1996, the ACL celebrated the 25th anniversary of its formation. Because of internal transfers among programs and other factors, it is difficult to establish exactly who the charter members of the ACL are, but they are believed to include those listed in Table 4-4.

The women who worked in CEN as secretaries, clerks, and other such positions were essential to the success of the Division's operations. Although their work was very much appreciated by the technical and administrative staff, it was usually not visible beyond initials on memos or internal reports. Many staff people probably don't realize how often the secretaries saved them from embarrassment or worse by correcting their spelling and grammar, retrieving some obscure piece of information from a file, handling phone calls adroitly, or working overtime to have material ready for the Review Committee or a trip. Many of them were instrumental in organizing the various parties, luncheons, and other social functions. A Secretaries' Day once a year falls far short of giving them the credit they deserve.

In the early 1970s, Alice Graczyk operated the Division Office under Dr. Vogel and then Les Burris. Anne Melton, Everett Proud's secretary, handled many of the administrative details of that office. Doreen Prucha was the principal secretary in Herb Brown's operation and Evelyn Rafacz continued to serve as Dr. Lawroski's secretary. Marie Driskell and Joy Swoboda were handling attendance records, purchase requisitions, equipment records, and a number of other miscellaneous items. Maria (Scaropoulos) Contos began working in the Technical Editing office. Some of the other secretaries and clerks in CEN at the time are listed in Table 4-5.

By the mid-1970s, the Division had once more outgrown the available space in Bldg. 205. A particularly pressing need was for an auditorium. Room A-059 was satisfactory for group meetings, but too small and not well laid out for Review Committee meetings, large program reviews, seminars, and other such functions. Office space was

Table 4-4. Analytical Chemistry Laboratory Personnel in the 1970s

Murray Barsky
Maureen Binelli
William Bloom
Eugene Bogusch
Vera Drabek
Florence Ferry
Irene Fox
Ruth Hanna
Robert Heinrich
Ben Holt
Myron Homa
Kenneth Jensen
Ruth Juvinall
John Kartunnen
Gwendolyn Kesser
Eugene Kucera
Robert Larsen
Vernon Lemke
Russell Malewicki
Fredrick Martino
Robert Meyer
Robert Oldham
Allen Panek
Ray Popek
Laurids Ross
Dino Santelli
Robert Schablaske
Charles Seils
Stanley Siegel
Norbert Stalica
Benjamin Tani
Ralph Telford
Zygmunt Tomczuk
Florence Williams (Smith)
Jacqueline Williams

Table 4-5. Secretaries, Clerks, and Others in the 1970s

Karen Beres
Alice Birmingham
Susan Butz
Patricia (Wood) Canaday
Ann Chaplin
Di Ann Fager
Carol Gehrke
Sherry Grisko
Paula Hataburda
Carol (Richie) Hendricks
Barbara Jivery
Mary Keigher
Judith King
Jackie Lehmann
Sally Leonard
Sheila Madson
Sharon Matlak
Debra McCann
Marcella Moore
Kathy Mueller
Sofia (Gawenda) Napora
Bonnie Nolan
Marge (Swanson) Panek
Julitta Pyle
Darcell Richards
Susan Rodighiero
Susan (Cathimer) Roessler
Vita Shiffer
Maureen Sobczak
Jackie Stakkowski
Janet Steinquist
Renee St. Germain
Katherine Wall
Candace Weiler
Melania Wilson

also in short supply again, due in part to the many industrial participants and other temporary people who were there at the time. Y-Wing was constructed in 1975-76 to fulfill these needs. Covering a total ground area of about 4,300 sq. ft, Y-Wing is a two-story structure consisting of an auditorium with a lobby area, 25 offices, a conference room, an open office area for secretaries and their equipment, and an exterior lobby, which also connects to the main part of Bldg. 205 on both levels. The auditorium and its lobby are attractively decorated and serve the purpose well, although there were a few start-up problems. There seemed to be a problem in finding projector lenses that were compatible with the distance and size of the screen. The other problem was more serious. For a time, the ventilation system was either inadequate or not functioning properly. On one hot day in August, during a major program review, the room became hot and essentially unventilated during a morning session. With the large crowd, the odor became unbearable and the meeting finally had to repair to the auditorium in Bldg. 200. That problem has long since been corrected, but it was an embarrassing experience for the people in the program who were trying to make a good impression on their reviewers and visitors.

Another addition was made to Bldg. 205 in 1978 to accommodate the growing need for laboratory space by the National Battery Test Laboratory. A particular concern was to have a separate facility where zinc/chlorine and other such batteries could be tested safely. The addition, designated J-156 and located at the end of J-Wing, has an area of about 1,550 sq. ft, and consists mostly of open laboratory space. It is currently used for battery and environmental work.

Although not a new addition, Room C-201, located upstairs at the north end of C-Wing, was used for a purpose some people were not aware of. When Dr. Vogel was faced with a task that required deep concentration, such as writing a journal article, he used that room as a hideaway with strict orders that he not be disturbed. If he "invited" you up into that room, you knew you were in for some very hard work.

The most serious accident in the history of the Division occurred late in the afternoon of October 17, 1972, when an accumulation of hydrogen and air exploded in a glove box located in Laboratory G-102. Two interconnected glove boxes (Nos. 6 and 7) were being used to investigate a process for the preparation of uranium-plutonium oxide fuel pellets. The process involved the reduction of

UO_3 and PuO_2 powders to a UO_2-PuO_2 mixture by heating them to about 600°C in a stream of cracked ammonia (75% hydrogen-25% nitrogen) in equipment simulating a fluidized-bed reactor. The powder was then pressed and fired at 1650°C to form the ceramic pellets.

The explosion was more in the nature of a rapid deflagration than a detonation, but it made a loud noise that could be heard throughout the building. It had sufficient force to blow out the safety glass panels in the two glove boxes and the glass panels in doors and walls between the laboratory and the connecting corridor. The concrete block walls of the laboratory showed slight structural damage. Two employees who were in the laboratory suffered lacerations and bruises from the explosion and a third employee cut his hand on debris while evacuating the corridor. The laboratory had to be decontaminated to remove the plutonium activity. Several factors appeared to have been involved in the incident. Large quantities of hydrogen had apparently leaked into the box from a hydrogen exit line during an experiment three weeks earlier. A hydrogen-monitoring instrument gave no warning of a high level because it had been cross-connected after a calibration, and a high concentration of air resulted from inadequate ventilation of the glove boxes. The hydrogen-air mixture was most likely ignited by an electrostatic spark.

Division Administration

In CEN, responsibilities for management of the research and development programs pass from the Division Director down through the Associate Directors, and then to the various Section Heads, Group Leaders, and Program Managers. Management of the Division's administrative functions is the responsibility of the Assistant Division Director. Everett Proud had become the Assistant Division Director in 1966 and his secretary, Anne Melton, handled much of the routine work. A job description for the Assistant Division Director written by Everett at the time describes it as "being responsible for management of the Division to the level delegated to him by the Division Director. The responsibility falls into five categories: (1) personnel, (2) procurement, (3) budget management, (4) building facilities, and (5) the instrument shop." When Lee Mead departed from ANL in 1963, Ron Breyne had been given responsibility for the procurement function, and his role expanded while he served as an Administrative Assistant under Proud. In 1967, the Division was shocked by the premature death of John Schraidt, who had been handling the facilities and services operations plus a number of other responsibilities such as Division Safety Officer and had been intensely involved with the EBR-II Fuel Cycle Facility. He also performed some of the Associate Division Director's functions during the transition between Frank Masten and Everett Proud. Alice Graczyk had begun her career in CEN as Schraidt's secretary. John Natale was another major player in that area who handled many other projects. He was one of the original designers of the ubiquitous CENHAM glove boxes mentioned earlier.

In 1965, Herb Brown was placed in charge of the building facilities and services such as the machine shop, installation crews, reclamation crews, graphic arts, service requests and work projects. He also reported to Proud. Herb was assisted by Les Dorsey, Ernie Johnston, and Pleasant Kelsheimer. Doreen Prucha was the secretary. "Big Ernie" was particularly noted for his ability to install heavy safety-glass glove-box windows because of his size and strength. Les Dorsey, among other things, was given the job of tracking equipment inventories, which required checking the ANL serial number tag on every "sensitive" item in the Division, a job that required a lot of tact. Somehow, he always remained good-natured during the process.

After Schraidt's death, Les Coleman became the Division Safety Officer and handled the job with the same rigorous, no-nonsense manner that Schraidt had employed. Les also assumed responsibility for the instrument shop.

In 1974, Ron Breyne transferred to BIM (Biology and Medicine Division), where he served as Assistant Division Director, and Leo Morrissey took over the financial management and budgeting work. Later on, Paul Eident also joined in that effort. In 1978, Everett left CEN to work for Betsy Anker-Johnson, who had been appointed Associate Laboratory Director for Basic Energy Sciences. At that time, Ron Breyne and Herb Brown began to serve as joint Assistant Division Directors, with Ron in charge of the personnel, procurement, and budgeting operations and Herb handling the building and facility responsibilities.

Personnel

By 1970, the composition of the staff of CEN had changed significantly from that in the early days of the Division, when most of the people were in their 20s and 30s. Those individuals were now in their 40s and 50s, and they accounted for a peak in the age distribution curve, which has diminished gradually as new, younger people have joined the Division, and is currently disappearing due to retirements. Many of those retirees now work on a limited part-time basis as STAs (Special Term Appointees).

From the time the Division was formed until about 1990, the basic categories of full-time employees were as shown in Table 4-6. There were also functional titles, such as Group Leader, Section Head, Assistant Division Director, and Division Director. The technician/operator and secretary/clerk categories were paid hourly. The higher-level technical personnel were paid monthly, and the higher administrative levels were on a biweekly salary schedule. The claim is sometimes made that the qualifications of ANL engineers and scientists at the assistant, associate, and senior levels are equivalent to those of assistant, associate, and full professors at a major university. That is probably true in many cases, as evidenced by the fact that ANL staff people often teach courses, serve as thesis advisors, or conduct cooperative research with university professors, but whether it is a valid generalization is a moot point.

Table 4-6. Personnel Categories

Technician/Operator I Technician/Operator II Technician/Operator III Senior Technician/Operator Engineering/Scientific Assistant Engineering/Scientific Associate Assistant Engineer/Scientist Associate Engineer/Scientist Senior Engineer/Scientist	Secretary/Clerk I Secretary/ Clerk II Secretary/Clerk III Senior Secretary/Clerk Administrative Assistant

The Laboratory has always encouraged employees to avail themselves of educational opportunities, some in-house, and others on college and university campuses. In the 1970s, the MBA degree was beginning to be favored strongly in business organizations nationwide, and the University of Chicago offered an "Executive Program" to Argonne staff members. The purpose of this program, which resulted in an MBA degree, was to strengthen the managerial capabilities of individuals in positions of leadership. Several CEN people completed this training in the 1970s: Erv Carls, Eddie Gay, Dave Green, Martin Kyle, Paul Nelson, and Mike Yao. In addition to the regular staff, the Division has always had a large number of temporary personnel, including visiting scientists, consultants, industrial participants, trainees of various kinds, faculty appointments, graduate and post-doctoral students, co-op students, STAs, and others.

All personnel matters of the Division were administered by the Assistant Division Director. These included the recruiting and hiring of weekly-rated, salary, and engineering and scientific assistants. Final decisions in personnel selection were normally made with the concurrence of appropriate Group Leaders or Section Heads. Applications of more senior personnel were screened by the Assistant Division Director, who also administered the Division's Equal Opportunity Employment Program. Salary reviews and performance appraisal programs were also his responsibility. Other personnel matters included security clearances, travel, promotions, education and training, consulting and training contracts, and numerous other functions. He also served as the Division's representative on the ANL Personnel Committee B. Sofia (Gawenda) Napora was designated to maintain the CEN personnel records, and has continued in that capacity for years. She has an excellent memory for names of people who have been in the Division.

Personnel activities such as recruiting and hiring, salary increases, and promotion of the more senior staff members were handled by the Division Director and other upper management people. Applicants for employment were usually subjected to a schedule of interviews and asked to make a presentation on their thesis or whatever other research they had been doing. Promotion cases for those in this category were presented to ANL Personnel Committee A.

Procurement

In addition to office supplies and other such items that are purchased routinely by most business organizations, CEN had such a diversity of programs that procurement was often anything but routine. Frequently, the desired item did not exist and had to be fabricated, often from exotic metals or special ceramics. Many common items could be obtained from the CEN stockroom, but budgetary restraints had resulted in a marked decrease in the inventory by the 1970s, necessitating greater use of the Laboratory's central facilities. The Division maintained an extensive file of industrial catalogs that were very useful in tracking down some item that would fill the need. One intriguing catalog in that file was a listing of railroad locomotives with various options, including the desired color scheme. The reason for that catalog being in the file is uncertain, but it may have had something to do with the facilities at EBR-II.

The Assistant Division Director was responsible for all Divisional procurement. That covered all purchases, including equipment for the technical programs. Other items in this area were the establishment of work projects, outside contracts and consulting agreements, property-control records, equipment library, and equipment utilization program.

Budget Management

The Assistant Division Director's duties included all the financial management and budgeting activities in the Division. Funding for the technical programs required the preparation of 189a forms, which were basically program proposals to the funding agencies that outlined the work to be done, the schedule, and the costs. Technical personnel prepared the texts of the proposals, but manpower levels, costs, and cost codes were worked out with the budget people, who then tracked the expenditures to ensure that they remained within the budget. Materials and services and Division overhead had to be included in the costs. Taxes on programs were imposed in some cases to cover administrative costs of Program Directors and Associate Laboratory Directors. Manpower was also charged to programs for purposes such as quality assurance, technical editing, computer assistance, and other items. Budget management was not an easy task during the unstable funding conditions in the 1970s. Oftentimes a program would be part of the way through the fiscal year and suddenly hear from the sponsor that they could provide only a fraction of the funding level in the original projection at the beginning of that year. This created a big problem because of the multiplying effect. As a somewhat extreme example, if word was received midway through the fiscal year that the funding was 50% of the original amount, it meant the work had to stop immediately. The confusion was compounded in 1976, when Congress, unable to pass the budget legislation on time, changed the beginning of the fiscal year from July 1 to October 1. A separate set of program plans and 189s had to be prepared for this so-called "Transition Quarter."

In addition to budget management, the Assistant Division Director was responsible for handling time cards, staff attendance records, absentee reports, cost code assignments, special materials requests, and a number of other items, including arrangements for fund drives and Division social activities such as the annual picnic.

Building Facilities and Services

This aspect of the Assistant Division Director's responsibilities was handled by Herb Brown, who reported to Everett Proud and was assisted by Artie Freeman, Pleasant Kelsheimer, and Les Dorsey. Doreen Prucha was Herb's secretary and she was assisted by other secretaries or clerks as necessary. The primary responsibility of this office was the operation and maintenance of Bldg. 205 and any other areas under the jurisdiction of CEN. Installation work involved the Plant Service people, electricians, pipefitters, carpenters, laborers, and others. Some Plant Service personnel worked regularly in Bldg. 205. This office prepared service and work project requests and monitored performance of the work. A visitors' register was maintained in that office, and it held the keys to all storage spaces. Physical arrangements were made for special events such as program reviews, seminars, and open houses. Work in special facilities, including the caves and plutonium glove boxes, was overseen to ensure that all the safety equipment was functioning properly.

In addition to the multitude of complex systems that must be maintained to operate the building, the courtyard and nearby exterior areas were of concern. Ever since Bldg. 205 was built, it seems as if the "front yard" has been torn up at least 50% of the time for one reason or another. Jan Muller once quipped that "They should put a zipper in it."

The design of engineering and much of the laboratory equipment has always been an important aspect of the Division's activities. Schraidt's group did most of this work, although many engineers and a few chemists also did detailed design work. In some cases, design engineers, including Jim Kotora and

Israel Pollack, were brought in from other divisions for special projects. Johan Graae was involved in many different design efforts. Dick Malecha, although not a member of CEN originally, has been involved with the Division in various capacities for many years. Dick has a special expertise in the area of quality assurance and was involved in Laboratory-wide QA work for several years. Largely as a result of his influence, CEN was one of the first divisions to incorporate detailed QA-related specifications in shop drawings. It is difficult to make a sharp distinction between designing and drafting, the way it is done in CEN, but some of those who did the work were Harry Smith, Ernie Singleton, Bob Frank, Ray Stimak, Tony Keledus, and Norm Schoij. These people were assigned from Central Shops, but functioned as a part of CEN.

The machine shop was staffed by Central Shops personnel, but, like the designers and draftsmen, they were usually assigned to CEN for extended periods of time so they became acquainted with the CEN people whose work they were doing. Some of the longer-term machinists were Bill Voss, Tom Denst, Ed Lewandowski, Phil Brown, and Ted Wist.

There were others who worked in Bldg. 205 on a rather regular basis. Everybody from that period remembers the electrician, Pat Doolin, with his impish (and Irish) sense of humor. At one time two painters, both named “Wally,” were working in the building, which sometimes caused a bit of confusion.

For many years, Bill Olsen operated the instrument shop. This facility had the capability to provide equipment design service, construction, maintenance, and repair of most of the instruments used by the Division. The principal function of the shop was to repair instruments being used in the research and development programs. Over the years enough equipment had accumulated from former programs to provide an inventory of items that could sometimes be used in new programs without the cost and lost time involved in ordering new ones. This office also maintained supplies of spare parts and chart paper.

Computers

By 1970, impressive progress had been made in the manufacture of miniaturized integrated circuits containing tens of millions of components on a single microchip, and it was inevitable that someone would soon exploit the technology in the form of a practical computer microprocessor. That occurred in 1971 when an American engineer, Marcian E. Hoff, combined the basic elements of a computer on a single silicon chip. That microprocessor was known as the Intel 4004, and it was followed immediately by frenetic development programs at many research laboratories to come out with their own versions. The first affordable desktop produced for personal use was the Altair 8800 and it was marketed by Micro Instrumentation Telemetry Systems in 1974. The Tandy Corporation, in 1977, was the first major electronics company to produce a personal computer by adding a keyboard and CRT monitor along with a cassette recorder to store programs. Soon thereafter, Stephen Wozniak and Steven Jobs formed Apple Computer Inc., and produced excellent machines that found wide acceptance. Apple became one of the outstanding success stories in the American business world. In the area of personal computers, International Business Machines, Inc. (IBM) was a sleeping giant; it didn’t introduce a PC until 1981. It is amusing to recall at this point that *Popular Mechanics* magazine had predicted in 1949 that in the future a practical computer may weigh as little as 1.5 tons.

Mel Foster was coordinating the computer applications within CEN. At that time, essentially all of the computations were made on the large machines in the Applied Mathematics Division (AMD), which were connected to a station in CEN consisting of a card reader, paper tape reader, cardpunch, and printer. In 1974, Mel joined Dr. Vogel and Carl Crouthamel in their move to Exxon in Washington State and his job at CEN was taken over by Steve Gabelnick, who had been doing work on matrix-isolation spectroscopy and other studies that led to a familiarity with the ANL computer facilities.

In addition to the main-line computer facilities at AMD, the people in CEN began branching out into all sorts of applications to take advantage of the rapid advances in the technology that were occurring in the 1970s. To assist in the implementation of these applications, computer specialists were brought in from AMD and commercial organizations to contribute their expertise. Some of these people, including Glen Chapman, John Osudar, and Bob Land, became permanent members of the Division. Bob Kessie, a chemical engineer who had been involved in several earlier research and development programs and had been a long-time hobbyist in electronics, took to these new developments like a fish to water and did a lot of work with a Varian minicomputer on data acquisition and control. Some of the earliest programs to make extensive use of dedicated computer facilities were proof of breeding, calorimetry, examination of irradiated fuels, battery development and the National Battery Test Laboratory, physical properties research, and coal combustion.

Another important development in the mid-1970s was the introduction of the small hand-held calculators. When Bill Schertz arrived from Texas Instruments to join CEN he had one of those calculators, and also a digital watch, both of which were novel and attracted great interest. Irv Johnson purchased a Texas Instruments Model SR-51 in July 1975 and used it for many years. The hand-held calculators were a real time saver for those individuals who made many simple day-to-day calculations that did not justify the use of the large computers. These hand-held devices were in much demand by the staff, but ANL management was reluctant to provide them because of their cost (a few hundred dollars) and "volatility" (susceptibility to theft). Those who had them had to follow security procedures nearly as stringent as those for plutonium.

There were varied reactions, as one might expect, to the explosion of computer technology in the 1970s. A few would have preferred to stick with their slide rules and have as little as possible to do with it. Most realized that it was inevitable and began to take courses, read manuals, and learn to type. (This was the period when owner's manuals written by computer specialists were unintelligible to the average person—a practice that has not yet disappeared completely.) It was easy to be intimidated by the language. In those days most people had never heard of bits, bytes and baud, RAM and ROM, machine language, assembly language, floppy disks, hard disks, Fortran, Pascal, Cobol, Basic, hexadecimals, parity, and hundreds of other terms, many of which almost any 12-year-old could explain today. And then there were those for whom computers had become a compelling interest. Some people spent much of their time during evenings and weekends writing programs, which can become an obsessive activity. Home desktop computers as we know them were not available until the late 1970s, but a few hobbyists managed to assemble workable systems. Irv Johnson recalls his experience in developing a home computer capability: "My first step was to buy a KIM-1, a single-board basic computer. Input and output were by means of a keypad and four segmented video displays. A very primitive operating system was located in ROM on the board, and I had 1 KB of memory. Programming was by machine language. Later I added 4 KB of memory and was able to obtain a Tiny Basic that could be used. The addition of a homemade video terminal and keyboard resulted in a complete usable computer. Programs were saved on a regular small tape recorder. With this system, I learned a lot about programming, but could not do the complicated calculations I needed. I then built a Heathkit H11, a PC version of the Digital Equipment Corp. LSI-11. At first, input and output were by Teletype™ and storage was on paper tape. I then added a dual floppy disk (8 in.) and video terminal, giving me a real home computer for which I could write Basic, Fortran, or assembly language. By including a modem, I could then transfer programs between ANL and home. Later on, I went by stages to a 'PC,' an XT, an AT and finally a 486DX."

Application of computers in the technical programs has already been mentioned here and there. In 1978, the computer group started placing summaries of their activities in the Division reports. Their activities in 1978 and 1979 consisted of (1) computer modeling and simulation, (2) laboratory automation, (3) database development, and (4) general support (consulting, equipment specifications, *etc.*).

In the modeling area, a program was developed to calculate potential surfaces, equipotential contours, and current-density distributions for collector plates in lithium/metal sulfide battery cells. A model was constructed to calculate tritium concentrations during release and cleanup after a hypothetical accident in a fusion reactor. A NASA code was modified to calculate complex chemical equilibria (up to 12 components) in the formation of a non-ideal solution from condensed species.

Laboratory automation activities were supported in the National Battery Test Laboratory (NBTL), the ambient-temperature and lithium/metal sulfide battery programs, and the ion-microprobe facility. Three systems based on a Digital Equipment Corporation (DEC) PDP-11 family of processors were installed to perform the following functions:

1. Acquire data from the 50-cell lithium/metal sulfide cell lifetime testing facility and to acquire data and control cell tests for the development and engineering work, including the Mark 1A battery.
2. Automate experiments, including viscosity, calorimetry, density, and thermal diffusivity measurements of materials in the reactor-safety program.
3. Collect and process data from the ACL's new gas-chromatograph, mass-spectrometer system.
4. Calculate the results of coal-char combustion with sulfur retention by limestone in a fluidized bed (coal program).
5. Calculate the total flow of all fissile and fertile materials through a large number of nuclear reactors of three generic types (Pu-producing, Pu-consuming, and U-233-consuming).

Databases were assembled to assist CEN staff in reviewing DOE proposals, to centralize information collection, and to generate reports and statistical data. Databases were also set up to assist CEN administrative personnel in various activities, and general support was provided to Division members in the form of consulting, data-management services, a computer documentation library, CEN's time-sharing and batch-entry facilities, and audiovisual minicomputer course materials. In 1979, work was started on a database file for CEN publications.

The secretarial staff also saw a major change in the 1970s when the electric typewriters began to be replaced by "word processors." The word processor was a stand-alone system with a keyboard, video screen, floppy disk storage, and captive printer. This system had some of the features of the current computer word-processing programs in terms of editing, moving text, *etc.* Unlike most of the technical staff who were starting to use computers, the secretaries didn't have to learn to type to use these new devices, and they seemed to appreciate the versatility and capability to store their work on disks.

Miscellany

By the 1970s, the 20 years of the Division's existence was sufficient time for some traditions and lore to have developed. As mentioned before, the average age of the staff had increased. In the earlier days, many of the people were single, and there was a lively social life among the CEN members. One consequence of this, especially in the 1950s and 1960s, was a number of intradivisional marriages. Building 205 isn't exactly the Club Med type of atmosphere that one would expect to engender romantic relationships, but they did develop. By the 1970s, the following marriages had taken place between CEN members or between Division members and people closely associated with CEN:

Milt Blander - Marie-Louise Saboungi
Herb Brown - Norma Pinches
Carl Cushing - Beatrice Hjelte
Phil Danielson - Doris Andersen
Len Hanna - Ruth Peterson
Phil Fineman - Olga Giacchetti
Peter Kafalas - Eleanor Juco
Eugene Kucera - Gene McCloud
Ted Olszanski - Ruth Voiland
Ron Paul - Nola Joy Tasharski
Ed Peterson - Betty Reilly
Chuck Seils - Laureen Peterson
Jack Settle - Leila Buckner
Art Shor - Roberta Wagner
Carl Swoboda - Joy Holloway
Ronald Wingender - Doris Michalek

Three major social occasions are sponsored periodically by the Division: (1) a picnic, (2) a Thanksgiving season Turkey Raffle, and (3) an in-house buffet just prior to the Christmas-New Year's Day holiday break. One other affair that might also be mentioned is the Review Committee dinner, where the Division staff socializes with the Review Committee members and among themselves. The picnics, with food, drinks, games, and other activities, take place at Argonne Park and present an opportunity for the spouses and children of Division employees to become acquainted with one another. The Turkey Raffle usually involves some form of entertainment when the drawings are held in the Bldg. 205 auditorium. The annual Christmas parties, which were held originally in the large L-Wing lunchroom, were moved off-site for several years, and now take place in the A-059 Conference Room and adjoining tornado shelter under X-Wing. Secretaries' Day is generally observed off-site by small groups, as is Bosses' Day if the secretaries think they deserve it. Birthdays are sometimes observed by serving cake and coffee during the day. Program groups go out to lunch occasionally, sometimes to celebrate some special event, and individuals occasionally host group parties at their homes. At present, the age curve for the Division's population has reached the stage that there are numerous retirement parties, usually at the Flame restaurant.

For several years, the Laboratory has operated an after-hours "Exchange Club" in Bldg. 617 to encourage more informal contact among the technical staff members, who tend to become compartmentalized by geographic and administrative factors. It did seem to accomplish that purpose, and its use was expanded to include essentially all ANL personnel. Some used it as a "singles bar" when that idea was popular, and at closing time some of the groups would proceed on to a commercial establishment such as Ripples to continue the party. In general, the employees at ANL were probably not as close knit socially as those at sites such as Oak Ridge or Los Alamos because they were widely scattered over the Chicago metropolitan area and their social life tended to be more oriented toward their own communities.

Given the hundreds of people who have been in the Division over the years, it would be impossible to recount the wide variety of personal interests and activities that were represented. In general, they were probably rather typical of any Chicago suburban community. Possibly the longest standing group is the Division's Golf League. Their first annual tournament was in 1952. According to the *Argonne News,* the participants in the 1958 tournament were Jack Fischer, John Loeding, Don Fischer, Jim Bingle, Les Burris, Al Chilenskas, Ira Dillon, and George Bennett, who made the arrangements. More recently, regular members of the golf league have included Dave Green, Bill Miller, Les Burris, Vic Maroni, and Bob McBeth (from the Chemistry Division). For several years there was a volleyball group consisting mostly of members from the pyrochemical program, which included Dean Pierce, Bill Walsh, Les Burris, and Bill Murphy. This group didn't seem to recognize that volleyball is not a contact sport, and sometimes showed up at work somewhat battered and bruised. A CEN softball team was organized by Ron Breyne, Ziggy Tomczuk, and others. Dean Pierce has been a physical fitness enthusiast all his life and is an excellent athlete who has participated in triathlons and other such events. Now an STA, he still rides a bicycle to Argonne from his home in Naperville on the days he works. Paul Nelson became interested in running in the 1970s and participated in the Chicago Marathon. There are many others in the Division who are involved in athletics and sports, including a large number who coach or officiate in organized youth athletics.

Several people in the Division are boaters, including Leo Morrissey who has participated for years in the prestigious Mackinaw sailboat races. Powerboat owners include Jim Battles, whose enthusiasm for fishing has become legendary in the Division. There are a number of private pilots, two of whom, Ward Hubbard and John Ackerman, moved on to the more demanding sport of competitive gliding.

Another interesting group is the chess team, of which Dave Green, Ziggy Tomczuk, Ewald Veleckis, and Bill Walsh have been members. A surprising outgrowth of this activity came from Bill's experience in playing chess with prisoners at the Stateville Penitentiary. At an ANL seminar, a Dr. Carl Pfeiffer discussed the effects of chemical imbalances in the body on human behavior. Bill procured hair samples from some of the prison inmates and others and found strong correlations between abnormal behavior and the levels of trace elements and compounds such as zinc, copper, and amino acids. On the basis of these findings, he eventually established a clinic aimed primarily at curing behavioral disorders in children, using dietary changes and supplements, but no prescription drugs. He was the founder and is now president of the Carl Pfeiffer Clinic in Naperville, which has become highly successful in treating tens of thousands of patients per year, with many referrals from psychiatrists and other physicians.

A few musicians have surfaced in CEN. John McKee, Chuck McPheeters, and Jim Eberhart formed a guitar trio and sang numbers typical of the Sons of the Pioneers at the Turkey Raffles. On one occasion, Sandy Preto joined them, making a quartet. Sandy, who did electrochemical research studies in the battery program, had another talent. She took up belly dancing and, for a short time, moonlighted occasionally at an Aurora night club. She also presented her "Sasha" routine at one of the Turkey Raffles. Another musician who contributed much to some of the CEN social affairs was Cindy Wesolowski, who plays the accordion and also has an excellent singing voice. Many other Division personnel sing or play instruments, but have not been heard at CEN.

Some other performers who deserve mention are Bob Larsen and Ed Berrill, who could always get a lot of laughs, and Johan Graae, who was nearly always called upon to give an impromptu speech at parties. Pat Doolin, mentioned earlier as the electrician who was assigned to Bldg. 205 for years, was a talented magician. One of his best tricks was to pass a cigarette (lighted or not) through a borrowed coin; you could watch it from a distance of a foot or two and still not understand how he did it. Pat also served many years as a scoutmaster, as did Herb Brown with Martin Steindler as his assistant.

TECHNICAL PROGRAMS

As stated earlier, CEN's technical programs in the 1970s underwent a major shift from nuclear reactor technology toward environmental research and alternative energy options. Impetus was added to this trend by the oil embargoes. Another trend that affected the Division strongly was a decision by the AEC, ERDA, and especially DOE to place more of their management activities "in the field." By 1979, the total funding for CEN was about $31 million, with about a third of the amount being contracted out to industries, universities, and other ANL divisions. The distribution by program areas was roughly as follows: electrochemical (batteries and fuel cells), 58%; fission-related work, 16%; coal technology, 13%; basic energy sciences, 8%; other, 5%. By the end of 1979, about 284 people were employed by CEN, 222 of whom were staff. The increased management effort for the funding agencies required a significant part of the staff effort.

Lithium/Metal Sulfide Batteries

INTRODUCTION

In 1970, the research and development work on high-temperature batteries was still in an exploratory stage. A decision had been made to discontinue the work on thermally regenerative galvanic cells in favor of rechargeable batteries, which seemed to have more promise for commercial application. Although a large amount of information had been generated on active materials for the electrodes and electrolytes and numerous experimental cells had been built and tested, many questions remained as to their potential performance and lifetime as well as their suitability for battery configurations. The principal candidates for the positive electrode material were the chalcogens (sulfur, selenium, and tellurium), and lithium was favored for the negative electrode. Early on in the program, it became evident that the terms "anode" and "cathode" were going to lead to confusion in the case of rechargeable cells. The chemical definitions are that oxidation occurs at the anode (negative electrode) and reduction at the cathode (positive electrode) when a cell is discharged. On recharge, however, the situation is reversed so the negative electrode becomes the cathode and the positive electrode the anode. To avoid confusion, a decision was made to avoid the terms anode and cathode and simply call them negative and positive electrodes, which is true during both charge and discharge.

There was some uncertainty about the optimum composition for the molten salt electrolyte, which had to be capable of transporting lithium ions between the electrodes, have a sufficiently high decomposition potential to be stable at the cell voltage, and have a low enough melting point to permit a reasonable operating temperature. In addition to the electrodes and the electrolyte, suitable materials had to be available for components such as electrode separators, current collectors, electrical feedthroughs, and cell insulators and housings. Another uncertainty in the program at the time was the practical application envisioned for high-temperature batteries. Several funding agencies were supporting the work with different applications in mind, including electric-vehicle propulsion and load-leveling on electric utility systems.

The result of the above situation was that a concentrated effort was made during the first two or three years to obtain the additional information needed to select the most suitable combination of cell components. The effort was then focused on the development of specific cell and battery designs for defined applications. During this period, the program expanded greatly and included the addition of industrial participants to the overall effort. This expansion, together with other factors, produced several management changes in the 1970s. The first year or two, Art Tevebaugh was the cognizant Associate Division Director, and then Don Webster assumed this responsibility until Paul Nelson became the director of all the electrochemical programs in 1973. Elton Cairns was the Section Head in charge of the high-temperature battery work until he returned to the General Motors Research Laboratory in 1974, and then went on to Lawrence Berkeley Laboratory and the University of California in 1978. Managers of the High Temperature Battery Program were Dick Ivins (1974-76), Bob Steunenberg (1976-78), and Duane Barney (1978-84). Al Chilenskas was Manager of Advanced Battery Development. Section Heads at various stages of the program were Elton Cairns, Bob Steunenberg, and Eddie Gay. Group leaders at one time or another included Al Chilenskas, Bob Steunenberg, Eddie Gay, Bill Walsh, Jim Battles, Paul Shimotake, Don Vissers, Bill Miller, and Mike Roche.

INDUSTRIAL PARTICIPANTS, CONSULTANTS, AND CONTRACTORS

A major goal of this program was to involve industrial organizations in the effort so the technology could be transferred to industry as it was being developed. In 1973, battery firms were solicited for an assignment of one or more of their scientists or engineers to assist in the development work and assess the likelihood of future commercial feasibility of the technology. Approximately 20 industrial participants worked on the program for periods of a few weeks to a year on a cost-shared basis. Some of these participants were Ray Hudson and Ken Gentry from Eagle-Picher Industries, Inc., Dick Rubischko from Gould Inc., Jim Birk from the Atomics International Division of Rockwell International, Robert Hamilton from the Carborundum Co., and Doug Stakem from Catalyst Research Corp.

In 1975, cell development and fabrication programs were initiated at Gould, Eagle-Picher, and Catalyst Research. At about the same time, management of a program supported by DOE at Atomics International was transferred to ANL. Ray Hudson headed up the operation at Eagle-Picher, Dick Rubischko and later Barry Askew the one at Gould, Sy Sudar the one at Atomics International, and Doug Stakem the one at Catalyst Research. (Catalyst Research dropped out of the program after a couple of years, and the General Motors Research Laboratory joined the effort later with Elton Cairns as the principal investigator.) Procurement contracts were negotiated with Carborundum to develop and supply boron nitride (BN) felt separator materials. Dick Malecha was given the responsibility for handling routine management of these subcontractors.

Many consultants were used in the high-temperature battery program. Scott Wood of the Illinois Institute of Technology and Bruce Wagner of Arizona State University assisted the chemistry and materials groups. John Newman from the University of California, Berkeley, did extensive work on the mathematical modeling of the processes occurring in Li(Al)/iron sulfide cells, and one of his students, Richard Pollard, did a Ph.D. thesis on that subject. Some of the other consultants included Richard Alkire, University of Illinois; Theodore Beck, Electrochemical Technology Group in Seattle; Douglas Bennion, University of Utah; John Dunning, General Motors Research Laboratory; Robert Huggins, Stanford University; George Janz, Rensselaer Polytechnic Institute; Rob Selman, Illinois Institute of Technology; Warren Towle and William Tiedemann, Johnson Controls (formerly Globe-Union); and Ernest Yaeger and Boris Cahan, Case Western Reserve University. Certain members of CEN or program review committees who had special expertise in the area, including Ed Buzzelli, Westinghouse Electric Corp., Terry Cole, Ford Motor Co., Charles Tobias, University of California, Berkeley, and Wayne Worrell, University of Pennsylvania, also provided helpful technical advice.

In 1976, ANL and the Chicago Section of the Electrochemical Society co-sponsored a Symposium and Workshop on Advanced Battery Research and Design, which was attended by many of the above individuals and organizations, as well as a number of foreign participants. The proceedings are reported in ANL-76-8.

EXPLORATORY STUDIES

A large body of information had already been accumulated at ANL on the chemistry and technology of molten halide salts in the nuclear fuel reprocessing and regenerative galvanic cell programs and in the basic studies of molten metals and salts. For cells having lithium negative electrodes, it was clear that a lithium halide salt system would be the most suitable, and the LiCl-KCl eutectic was selected on the basis of its relatively low melting point (352°C), high decomposition potential, compatibility with construction materials, and low cost.

From the standpoint of theoretical specific energy (W-hr/kg), the lithium/sulfur cell (Li/LiCl-KCl/S) was the best of the systems under consideration, and a concerted effort was made for about three years to build and operate cells of this type. One of the several problems associated with this cell was the lithium electrode. The liquid lithium in the negative electrode caused several problems: (1) It was sufficiently soluble in the electrolyte to impart some electronic conductivity, which led to current inefficiency and self-discharge of the cell. (2) Its chemical activity was sufficient to cause some reduction of the potassium in the LiCl-KCl electrolyte,

$$\mathrm{Li + KCl \rightarrow LiCl + K}\uparrow$$

which, over a period of time, resulted in metallic potassium deposits in the cell and a change in the LiCl:KCl ratio in the electrolyte. (3) The lithium metal, being a potent reducing agent, was not compatible with oxide ceramics such as magnesia (MgO) and alumina (Al_2O_3) used as electrical insulators. (4) At cell operating temperatures (generally 400-450°C), it was difficult to confine in the negative electrode structure. Confinement of lithium in the negative electrode was most likely related to two factors: competition between the lithium and the electrolyte to wet the electrode structure, and the fact that the cell housings were normally at the negative electrode potential, which meant the lithium could deposit on the housing wherever electrolyte was present. Many ingenious electrode designs using various metals in porous forms such as mesh, felts, and foams were designed and tested, but none was fully successful.