All of the above problems were finally resolved by going to lithium-aluminum alloy negative electrodes. The Li-Al phase diagram, which had been investigated earlier by Yao, Heredy, and Saunders [J. Electrochem. Soc. 115, 1039 (1971)] and was refined by Jack Settle and Mike Myles in Jim Battles's group, is shown in Fig. 4-2. At 450°C, there is a composition range between 10 and 47 at.% Li, where two solid phases $(\alpha + \beta)$ coexist in equilibrium and the electrical potential remains constant at 292 mV relative to elemental lithium. When cycled electrochemically, this material formed a porous, interconnected (skeletal) microstructure that is ideal for highrate, efficient electrodes, and it did not change appreciably over thousands of cycles in welldesigned electrodes. On recharge, the lithium all deposited in the electrode because of its decreased chemical activity in the Li-Al structure.

The price to be paid for these advantages was a significant, but acceptable decrease in the voltage and specific energy of the cells. The lithium-silicon system was also a



Fig. 4-2. Lithium-Aluminum Phase Diagram

candidate for the negative electrode. In this case, the electrode discharges through a series of voltage steps at 42, 150, 277, and 326 mV vs. elemental lithium, which correspond to the transitions

$$\begin{array}{l} \text{Li}_{3.90}\text{Si} \rightarrow \text{Li}_{3.25}\text{Si} \rightarrow \text{Li}_{2.33}\text{Si} \\ \rightarrow \text{Li}_{1.71}\text{Si} \rightarrow \text{Si} \end{array}$$

In practice, the Li-Si electrodes were generally operated between about 50 and 80 at.% lithium. A Li_{3,25}Si electrode in combination with an FeS or FeS₂ positive electrode has a specific energy approximately 10% higher than that for Li-Al in a similar cell. Lithium-aluminum negative electrodes were used in most of the cells that were built and tested, but the Li-Si electrodes were also used successfully, particularly in Li-Si/FeS₂ cells at General Motors and in Li-Si/FeS cells at Gould. In some cases, Gould used mixtures of Li-Al and Li-Si. Some exploratory work was done on calcium negative electrodes at ANL, but it was not continued into full-scale cells. Subsequent studies have shown that a ternary Li-Fe-Al system is an excellent negative electrode.

A somewhat similar situation developed in the case of positive electrodes. On the basis of previous work reported in the literature and preliminary studies at ANL, the chalcogens (sulfur, selenium, and tellurium) were selected for the initial investigations. Of these three elements, sulfur had the advantage in terms of voltage and specific energy, and a large amount of effort went into research on the behavior of sulfur in electrodes, both in its basic chemical and physical properties and in development of practical electrode the structures. The high oxidation potentials of chalcogens required the use of refractory metals such as molybdenum or niobium for current collectors and other components of the positive electrode, and many different experimental electrode designs were evaluated. Selenium and tellurium, with additives such as

thallium in some cases, were tested in many cell configurations, but were finally abandoned because of their lower voltages and specific energies and short cycle life caused by soluble species in the electrolyte. Much attention was given to sulfur electrodes, due in large part to the enthusiasm of Elton Cairns for lithium/sulfur cells because of their very high voltages and theoretical specific energies (W-hr/kg).

A major problem with sulfur was its nearzero electronic conductivity. Attempts to increase the conductivity by various additives such as carbon black and phosphorous sulfides were unsuccessful. Another serious problem was the tendency of sulfur to dissolve in the electrolyte, which caused a serious loss of capacity on extended charge-discharge cycling. It was clear at this point that a new approach had to be taken toward the positive electrode. Don Vissers, Ziggy Tomczuk, and Bob Steunenberg came up with the idea of using metal sulfides, which are solids and offer some degree of electronic conductivity. The iron sulfides (FeS and FeS₂) seemed to show the most promise, and they performed well in preliminary tests. Workers at the Atomics International Division of Rockwell International had the same idea at about the same time, but the ANL group managed to get a patent. The more promising metal sulfides for this application are given in Table 4-7.

From a technical standpoint, any of the above materials could be used successfully, but cobalt and nickel sulfides were deemed too expensive for large-scale practical application, which left FeS and FeS₂ as the materials of choice. (Later in the program, Laszlo Redey and Don Vissers developed a Ni₃S₂ reference electrode for use in molten salts that was highly successful and resulted in a patent and an IR-100 Award.) Titanium disulfide, TiS₂, undergoes a reversible reaction with lithium, and cells of this type were operated. The reaction differs from those of FeS and FeS₂, however, in that it involves a lithium insertion or intercalation mechanism that allows only one lithium atom to enter the TiS₂ lattice, which limits the specific energy.

As was the case with the Li-Al electrode, the iron sulfide electrodes produced lower voltages and specific energies than sulfur, but later testing showed that they performed very well electrochemically, with a long cycle life. At this time, the program became focused on the two systems:

Li(Al) (solid)/LiCl-KCl (liquid)/FeS (solid)

Li(Al) (solid)/LiCl-KCl (liquid)/FeS2 (solid)

These systems, with solid electrodes and a liquid electrolyte, were of a more conventional configuration for a storage battery.

Material	Potential vs. Li°, mV	Material	Potential vs. Li°, mV
FeS	1620	FeS ₂	2066, 1620
NiS	1830, 1656	CoS ₂	1997, 1900, 1663
Co ₉ S ₈	1663	NiS ₂	2034, 1830, 1656
Ni ₃ S ₂	1656		

Table 4-7. Promising Positive Electrode Materials

The overall discharge reactions for these cells are

 $2 \text{ Li} + \text{FeS}_2 \rightarrow \text{Li}_2\text{S} + \text{FeS} \qquad (1.67, \ 1.33 \text{ V})$ $2 \text{ Li} + \text{FeS} \rightarrow \text{Li}_2\text{S} + \text{Fe} \qquad (1.33 \text{ V})$

The theoretical specific energy for the Li/FeS cell is 460 Wh/kg, and that for the Li/FeS₂ cell, if both voltage plateaus are used fully, is 680 Wh/kg. Both are respectable values in spite of the compromises made in both electrodes. At first glance, these discharge reactions appear to be straightforward, but that turned out not to be the case, especially for the FeS electrode. The discharge process in the FeS electrode proved to be very complex, and a large effort was made by the materials and chemistry groups to identify the reactions and the intermediate phases that were formed. As many as six electrochemical and four chemical reactions appeared to be involved. A variety of techniques were used to identify the phases and reaction paths, including X-ray diffraction and metallographic studies of partially charged and discharged cells. Two compounds, LiK₆Fe₂₄S₂₆Cl (W-Phase) Li,FeS, and (J-Phase, formed by reaction with the KCl in electrolyte), were identified the as intermediates in the discharge reactions. The J-Phase was shown to inhibit the kinetics of the discharge reaction. Studies of the reactions showed that alternative paths existed for the discharge process, one of which did not involve J-Phase. As shown in Table 4-8, the

concentration of KCl in the electrolyte can be lowered to avoid the formation of J-Phase. The latter two salts improved the cell performance significantly, but at the price of higher operating temperatures.

Some cells were operated with FeS₂ positive electrodes, which produced two voltage plateaus, the first at about 1.6 V and the second at 1.33 V. Cells with FeS electrodes showed a single plateau at 1.33 V. Although the FeS₂ cells had a higher average voltage and specific energy, they had the disadvantages of a voltage change during discharge, corrosion of the metal cell parts, and long-term loss of capacity. Through the 1970s, most of the cells were of the Li(Al)/LiCl-KCl/FeS type, but at the end of the decade, the following options were still considered viable:

Negative Electrodes: Li-Al, Li-Al-Fe, Li-Si, Li-Al-Si Positive Electrodes: FeS, FeS₂ Electrolyte: LiCl-KCl, LiF-LiCl-LiBr

MATERIALS RESEARCH AND DEVELOPMENT

The high temperatures and corrosive materials used in the cells required an extensive effort on materials research and development. Martin Kyle handled much of this work until about 1973, when an expanded program was instituted with Jim Battles as Group Leader. John Smaga was a major contributor to the

	1	
System	Composition, mol%	Melting Point, °C
LiCl-KCl (eutectic)	58.8-41.2	352
LiCl-KCl	66.7-33.3	425
LiF-LiCl-LiBr	22-31-47	430

Table 4-8. Electrolyte Systems

materials work. A special laboratory facility was set up in J-101, where metallographic work could be done entirely within a controlled-atmosphere glove box. A unique feature of this facility was an arrangement in which samples inside the glove box could be observed from outside by a microscope mounted in the top of the box, either directly or by closed-circuit television. This arrangement was very useful in showing and explaining results to coworkers or visitors. This group also had a laboratory in Room A-141 that was used for corrosion testing and other purposes.

The materials program was far too broad to describe in detail. Extensive corrosion tests were conducted on all the metallic components of the cells. Fortunately, it turned out that lowcarbon steel and stainless steel, which are relatively inexpensive and easily fabricated, could be used for cell housings and supporting structures for the lithium-aluminum electrodes. Stainless steel was preferred, mainly because it was not subject to oxidation by the air atmosphere outside the cells. The positive electrodes presented more of a problem, particularly with sulfur or FeS₂ as the active material. Refractory metals such as molybdenum could be used as current collectors, but they are expensive, heavy, and difficult to fabricate. For the FeS electrodes, iron or low-carbon steel was used as current collectors, but some corrosion occurred during long-term charge-discharge cycling. Adding iron powder to the electrode mix largely solved this problem. Alumina (Al_2O_3) was used successfully as electrical insulators in certain parts of the cells, although long-term exposure resulted in the formation of some LiAlO₂. The separator had to meet a severe set of requirements. It had to be resistant to reduction by the lithium electrode and to oxidation by the positive electrode. At the same time, it had to serve both as an electrical insulator and as a porous medium for the liquid electrolyte to permit the transport of lithium ions between the electrodes. A great deal of development work

and testing resulted in two types of separators that gave excellent performance: boron nitride (BN) felt or woven cloth, and porous plaques pressed from magnesium oxide (MgO) and the electrolyte salt. The production of BN in these forms was a technical breakthrough by the Carborundum Co., which was making it for an undisclosed military application. It was formed by extruding boric oxide (B_2O_3) as fibers, which were converted to BN by treatment with ammonia, followed by a high-temperature exposure to nitrogen. Although Carborundum was most accommodating in developing and these materials, this producing effort demanded a great deal of guidance and attention from the Materials Group. Several options for electrode separators as of 1979 are listed in Table 4-9.

Another troublesome problem that was solved mainly by Mike Myles working with subcontractors was the development of a hermetic feedthrough from the positive electrode to an external cell terminal. (An extension of the cell housing served as the negative terminal.)

In addition to the traditional materials work, this group made very major contributions to two other areas of the program. One was in the identification of chemical phases and physical structures formed in the electrodes during different stages of charge and discharge. This work contributed to an understanding of the cell chemistry and provided guidance for future electrode designs. The other contribution was the identification of cell-failure mechanisms. The most common mode of cell failures was short-circuiting that developed over a period of time during charge-discharge cycling. This usually resulted from expansion of the negative electrode, which resulted in extrusion of the active material and breaching of the separator. Extensive studies of this phenomenon by the Materials and Chemistry Groups resulted in electrode design recommendations (loadings, geometry, etc.) that solved, or at least greatly alleviated this problem. Some of the other

Form	Material	Comments
Woven Fabrics	BN	Used in early cells; satisfactory, but expensive.
Felt	BN	Well developed, satisfactory, expensive, but reasonable cost projected for mass production.
Powder	MgO, AlN, Si ₃ N ₄	Pressed or vibratorily compacted; inexpensive, used satisfactorily in test cells.
Porous Plaque	MgO, Y ₂ O ₃	In the experimental stage.

 Table 4-9.
 Status of Electrode Separator Materials

failures were caused by loss of separator integrity, escape of material from the positive electrode, and hardware problems. Extensive post-test examinations of weak and failed cells that were conducted by this group were the principal source of information needed to improve the cell designs. The excellence of this type of work by the Materials Group became well recognized and resulted in programs supported by other organizations.

CELL DEVELOPMENT

In the exploratory stages of the program, many different cell designs were used, most of them being cylindrical (pancake) assemblies held together by bolted flanges and ranging from about one to six inches in diameter. In a few cases, cells were stacked together in series to form small batteries. As the program became more focused on specific energy and power requirements and on configurations better suited to practical applications, cells of the types shown in Figs. 4-3 and 4-4 were developed. This development depended heavily on results of work by the Materials Group on electrode separators, electrical feedthroughs, and other components. Tom Kaun played a particularly major role in the development of new electrode and cell designs and obtained a large number of patents. The cylindrical and prismatic cells had a central

positive electrode and two outer negative electrodes, which were grounded to the cell housing. Each of the negative electrodes normally had about one-half the capacity of the central positive electrode. These configurations were called "bicells" because they were, in effect, two cells connected in parallel with a common positive electrode. Although the earlier rectangular prismatic designs were also bicells, the more advanced designs, as shown in Fig. 4-4, had multiple negative and positive electrodes.

The electrodes were plaques of the active material that were usually made by pressing or pasting the active material into a metallic supporting structure, such as a mesh or foam. The function of the current collectors in the electrodes was to maintain a uniform current density and provide connections to a bus bar,



Fig. 4-3. Cylindrical Cell Design



Fig. 4-4. Rectangular Prismatic Cell

which was connected through an insulating feedthrough to the outer terminal. Retainer screens or cloths were used in some cases on the electrode surface to prevent the escape of particulate material. The function of the electrode separator was to insulate the electrodes electrically from one another while at the same time containing the liquid electrolyte necessary for the transport of lithium ions between the electrodes. Cylindrical cells of the type shown in Fig. 4-3 were about 5 in. in diameter, and the prismatic cells (Fig. 4-4) ranged from about $5 \times 7 \times 1.5$ in. up to $7 \times 7 \times 2$ in.

In the late 1970s, the rectangular prismatic cell design was selected for continuing development because it was better suited to cells with multiple negative and positive electrodes. For example, the cell shown in Fig. 4-4 has five Li-Al negative electrodes and four FeS positive electrodes. The two outer negative electrodes are half as thick as the others. The positive electrodes are interconnected by a bus bar that leads to the positive terminal of the cell. The negative electrodes are grounded to the cell walls, which conduct the current to the negative terminal attached to the cell housing. The

multiplate cell design permits the use of relatively thin electrodes with a high surfaceto-volume ratio, which results in high specific power at acceptably low current densities, and high utilization of the active materials in the electrodes, which increases the specific energy.

"STATUS CELLS"

The program was coming under increased pressure from DOE to provide assurance that demonstrable progress was being made in the cell performance and cycle life. The response was to initiate an effort in which Eagle-Picher, Gould, and ANL each designed and built groups of identical state-of-the-art cells for standardized statistical testing. In general these "status cells" were of the prismatic multiplate design, about 5 to 7 in. wide, 7 in. tall, and 1 in. thick. The principal difference in the cells produced by the three organizations was that BN separators were used in the Eagle-Picher and ANL cells, while Gould preferred MgO powder.

There were also differences in the designs and materials used in the cell electrodes and hardware. The cells were tested at ANL by charge/discharge cycling until the cell capacity had decreased to 80% of its initial value, which usually occurred after several hundred and, in some cases, up to 1000 or so cycles. A 50-cell test facility (Fig. 4-5) was constructed in which the cells were cycled continuously at the operating temperature of 400-450°C. A computer was used to monitor the results.

Tests were conducted on other cells to determine the effects of various duty cycles, for example, discharges typical of a driving profile for an electric automobile. Effects of overcharge and overdischarge were examined.

In addition to the electrical performance testing, Al Chilenskas and his coworkers conducted safety tests on cells, which were subjected to vibration and shock with little if



Fig. 4-5. Fifty-Cell Test Facility for Li/Metal Sulfide Cells

any effect. Cells were also crushed to evaluate hazards that might result from a vehicle crash in which the molten salt electrolyte could be released from the cells at operating temperatures. These, too, were uneventful; most of the salt remained in the cell, and what little did escape solidified quickly.

BATTERIES

Al Chilenskas was in charge of the battery work in the program. All the potential applications of high-temperature batteries that were under consideration required voltages much higher than those of the individual cells, so a large number of cells had to be connected in series to form a useful battery. The battery then had to be enclosed in a housing with high-efficiency thermal insulation to maintain its operating temperature while minimizing the loss of thermal energy, which reduces the overall energy efficiency. Internal electric heaters were installed with the cells to heat the battery during startup and any time that additional heating was needed to supplement the resistive heating produced by normal charging and discharging. The development of heat-management strategies and highefficiency thermal insulation was a major effort in the battery program. One quirk in the chemistry of the system that made the job a bit easier was an entropic effect in FeS cells that tended to level out the heating and cooling effects during the charge-discharge cycles.

Two basic types of high-efficiency thermal insulation were investigated: conventional and vacuum multifoil, with several different versions of each. The thermal conductivities of the better ones were in the range of $1-3 \times 10^{-3}$ W/m·K. Calculations for a small LiAl/FeS automobile battery with 1/2-in. pegfoil insulation produced by the Linde Division of Union Carbide would have a heat-loss rate of 66 W and energy densities of 87 W-hr/kg and 150 W-hr/L. Table 4-10 lists the three small experimental batteries were operated in the 1970s.

Another problem that had to be addressed was cell equalization during charging. Unlike nickel-cadmium and certain other batteries, lithium-alloy/iron sulfide cells have little tolerance for overcharging, so the individual cells had to be returned to the same state of charge. This required the development

Year	No. of Cells	Voltage, V	Capacity, kW-hr	Thermal Insulation	Cycle Life
1977	6	8.8	1.0	Vac-Foil	11
1979	10	5.9	3.7	Conventional	34
1979	5	5.6	1.6	Vac-Foil	70

Table 4-10. Experimental Batteries Operated in the 1970s

of a computer-controlled charge-equalization system, which was designed by Fred Hornstra and the Computer Applications Group. Once developed and placed in operation, the charge-equalization system performed well.

One of the "problems" with the battery development program was that the cells were beginning to exhibit long cycle life. The long cell life was desirable, but it resulted in tests that required months, or even up to a year, before a cell failed. Consequently, a great deal of time elapsed before the effect of a new design feature could be evaluated in a posttest examination. The DOE was becoming impatient with the rate of progress toward an in-vehicle battery demonstration, and, in 1978, mandated that one be done immediately. The CEN engineers and scientists felt that it was premature and so indicated, but the DOE insisted, so Eagle-Picher was given the job of assembling a battery (designated Mark IA). The Mark IA battery consisted of two modules, each containing 60 cells that were fabricated in the charged state, arranged in two rows of 30 each, and connected in series to provide the required voltage (see Fig. 4-6). Each module was enclosed in high-efficiency thermal insulation and had a capacity of 20 kW-hr.

During heatup, one of the modules developed a short circuit external to the cells, which propagated from cell to cell. The only external indications that something was awry



Fig. 4-6. Mark IA Battery

were fluctuations in the cell voltages and the internal temperature, which rose to over 1000°C. As is usually the case, the incident occurred in the middle of the night. A 24-hour watch had been set with Don Vissers and Sandy Preto on the night shift. They called the fire department as a precaution, but no action was required. The other module, which was alongside and connected in series, was unaffected by the failure.

Extensive examinations were conducted on the failed module, and electrolyte leakage was established as the primary cause of failure. The other module was not tested, but the cells were removed and used for other testing. A few days after the incident, Barry Askew, the Program Manager at Gould, concerned about the political aspects of the failure, asked a group of visitors from ANL, "Has there been much fallout over the Mark IA meltdown?" He was told that he could have found a better choice of words while talking to people recently involved in nuclear programs. The failure of the Mark IA battery was, in fact, a serious setback and may have been part of the reason for diminishing support of the program in the following years.

The program did continue, however, with plans for a Mark II battery in which Eagle-Picher and Gould would each produce a 10-cell module with emphasis on reliability.

By the mid-1970s, the potential applications being considered for high-temperature batteries had narrowed down to two: electric vehicles and load leveling. Al Chilenskas instigated design and cost studies on batteries for both of

these applications. The design criteria for load-leveling batteries were (1) 100 MW-hr of electrical energy stored in about 7 hr and discharged over peak-load periods of 5 hr for five days per week, (2) a plant lifetime of 20 years, and (3) a cost (in 1978 dollars) of \$45-55/kW-hr. Four conceptual designs were developed by ANL and outside contractors.

Throughout the high-temperature battery program, there were discussions concerning the most likely practical applications of electric vehicles. Delivery vans and commuters' cars seemed to be the best possibilities because they both involve relatively short, predictable routes that are compatible with daily, overnight recharging. In the early stages of battery development, at least, electric family cars capable of cross-country trips did not seem to be feasible. Electric vehicle design studies were conducted jointly by the Toyota Motor Company and ANL for a van and an automobile. The vehicle requirements and projected performance are shown in Table 4-11.

PERSONNEL

Because of the large scope of this program and the number of people involved in several aspects of the work, it is virtually impossible to give proper credit to each individual. The following is an attempt to list the contributors under the general areas into which they put most of their effort.

Chemical Research: John Ackerman, Milt Blander, Paul Cunningham, Jim Eberhart, Al Fischer, Ellen Hathaway, Myron Homa, Paul Hunt, Carl Johnson, Stan Johnson, Gene Kucera, Vic Maroni, Jane Marr, Al Martin, Carlos Melendres, Sandy Preto, Laszlo Redey, Mike Roche, Laury Ross, Marie-Louise Saboungi, Bob Schablaske, Stan Siegel, Ramamritham Rob Selman, Sridhar. Sim. Bob Steunenberg, Jim Condeocita (Cajigas) Sy, Ben Tani, Ziggy Tomczuk, Verne Trevorrow, Don Vissers, Bob Yonco.

Materials Research & Development: Jim Battles, Jim Bouquist, John Dusek (MSD), Martin Kyle, Jim Mathers, Frank Mrazek, Trent Latimer (MSD), John Mundy (MSD), Mike Myles, Ted Olszanski, Neil Otto, Jack Settle, John Smaga, Bob Swaroop, Wayne Tuohig (MSD), Dave Walker (MSD), Tim Wilson.

Cell Development & Testing: John Allen, Karl Anderson, Jack Arntzen, Lou Bartholme, Glen Chapman, Tom Cooper, Dennis DeNuccio, Ron Elliott, Bruce Feay, Bill Frost, Eddie Gay, Tom Kaun, Bob Kessie, Dennis Kilsdonk, John Kincinas, Nick Koura, Wally Kremsner, Fred Martino, Chuck McPheeters, Miller, John Osudar, Bill George Redding, Jim Riha, Bill Schertz, Paul Shimotake, Noel Vargo, Bill Walsh, Mike Yao.

Battery Development & Evaluations: George Bernstein, Ed Berrill, Steve Box, Al Chilenskas, Bill DeLuca, Johan Graae, Magdy Farahat, Ed Hayes, Fred Hornstra, Henry Kacinskas (ENG), Verne Kolba,

Vehicle	Van	Automobile
Curb Weight, lb	3150	2350
Battery Weight, lb	950	660
Payload, lb	795	330
Total Weight, lb	4900	3340
Acceleration Time (0-60 mph), sec	22	16
Maximum Speed, mph	95	85
Range (Overnight Charge), mi	100	100

Table 4-11. N	Vehicle Requirements	and Projected	Performance
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Israel Pollack (ENG), Al Zielen (EIS), Sam Zivi (ENG).

Other: Duane Barney, Dick Beatty (QA), Elton Cairns, Jay Geller (QA), Dick Ivins, Dick Malecha, Paul Nelson.

Development of Aqueous Batteries for Electric Vehicles

The Electric and Hybrid Vehicle Research and Development and Demonstration Act, passed in 1976, called for the development of improved batteries for electric-vehicle propulsion. This activity, which was part of the Department of Energy's Electric Vehicle Project, was intended to reduce national petroleum consumption by the transportation sector. The Office of Electrochemical Project Management (OEPM) was established at ANL to manage the development of improved batteries suitable for electric-vehicle applications by the late 1980s. Three types of batteries were identified by OEPM as suitable candidates for this application: lead-acid, nickel/iron, and nickel/zinc. These names for the three systems are used universally in the trade, but may be a bit misleading in that the

actual electrode materials are Pb/PbO₂, Fe/NiOOH, and Zn/NiOOH, respectively. The electrolyte in the lead-acid battery is sulfuric acid (H_2SO_4); an alkaline electrolyte such as a solution of potassium hydroxide (KOH) is used in the other two systems.

Neng-Ping (Mike) Yao, who had been instrumental in starting this program, was placed in charge as Program Manager and Director of OEPM. Mike had an interesting background, having been born into an aristocratic Chinese family and then receiving much of his education in Japan. He received his doctorate from the University of California at Los Angeles (UCLA), where he did his thesis work under Professor Douglas Bennion, a well-known electrochemist who later did some consulting work for the ANL battery program. Yao came to ANL from the Atomics International Division of Rockwell International, Inc., where he and Laszlo Heredy did the original work on the lithiumaluminum electrode. Mike was fluent in English, Chinese, and Japanese, a rather unusual combination. Prior to his assignment to OEPM, he worked a few years on the hightemperature battery program at ANL.

Specific managerial assignments in the OEPM program as of 1979 were as follows:

Mike Yao	Project Manager and
	Director, OEPM
Clint Christianson	Deputy Project Manager
Fred Hornstra	Manager, NBTL
Tien Lee	Technical Monitor, Lead/
	Acid Contracts
John Rajan	Technical Monitor,
-	Nickel/Iron Contracts
Jim Miller	Technical Monitor,
	Nickel/Zinc Contracts
Glenn Cook	Group Leader, Battery
	Support Research
Bill DeLuca	Group Leader, Battery
	Components
Frank Foster	Contract Administrator
Jay Geller	Quality Assurance
	Engineer

Other members of the team included Mike Genge, Jiri Klinger, Dave Poa, Jodean Waters, and John Barghusen.

Industrial contractors on a cost-sharing basis performed most of the battery research and development work in this program. The main function of ANL, in addition to managing the contract work, was to monitor their technical progress by standardized testing of their cells, modules, and batteries in the NBTL (National Battery Test Laboratory), located in Bldg. 205. The workers at ANL conducted some research of a more basic nature on these systems.

INDUSTRIAL CONTRACTORS' PROGRAMS

Eight major industrial contracts for the battery technology development were initiated early in 1978: (1) lead-acid (Eltra Corp., ESB, Inc., Globe-Union, Inc.), (2) nickel/iron (Eagle-Picher Industries, Inc., Westinghouse Electric Corp.), and (3) nickel zinc (Yardney Electric Co., Energy Research Corp., Gould Inc.). The 1980 performance goals for the three types of batteries are listed in Table 4-12.

The NBTL (Fig. 4-7) was established to conduct independent testing and evaluation of various battery systems as they were developed. (At the time, suspicions were aired occasionally that battery manufacturers sometimes were not entirely candid about the true performance and lifetime of their products. These suspicions were real enough that they surfaced occasionally as humorous slides at professional meetings of electrochemists.) Cells and batteries developed within the DOEsponsored programs and by private funding were tested in the NBTL (located in Laboratory H-102 of Bldg. 205 and expanded later into a new addition to the building, J-156). Those facilities as of 1980 were capable of the simultaneous testing of 27 cells or modules and one full-size (30-40-kW-hr) battery under simulated driving conditions as well as under normal cycling tests.

Graphical displays and tabulations of the results were directly available through a computer. The battery tests were normally in the following sequence:

- 1. Self-discharge (capacity loss in seven days).
- 2. Partial depth of discharge (to check "memory effects").
- 3. Energy density vs. power density (to provide performance and modeling data).
- 4. Simulated load profile tests (simulated electric-vehicle driving profile).
- 5. Peak power for sustained duration (30-sec at 80, 50, and 20% state of discharge).
- 6. Life-cycle tests (3-hr discharges until capacity declined to 75% of rated capacity).

In 1980, the capabilities of NBTL were expanded from 15 to 20 test stations, and work was started on further expansion to 40 test

Performance	Lead-Acid	Nickel/Iron	Nickel/Zinc
Specific Energy (W-hr/kg) at C/3 Rate ^a	42	54	64
Specific Power (W/kg), 30-sec avg at 50% Depth of Discharge	105	110	110
Cycle Life to 80% Depth of Discharge at C/3 Rate ^a	400	300	200

 Table 4-12.
 Performance Goals for Aqueous Batteries

^a The "C/3" rate corresponds to a full discharge in three hours.



Fig. 4-7. National Battery Test Laboratory (NBTL)

stations. A typical cell/module test station had current and voltage capabilities of ±500 A and 0-12 V. A full-size battery test station had +300 A, -1200 A, and 10-200 V capacity, which required a large power supply. A system was constructed to measure sustained peak power from a battery. Three walk-in chambers were built to permit testing under various conditions of temperature and humidity. Other items included a computercontrolled simulation of driving profiles, instrumentation to measure individual cell voltages during battery tests, and an interactive control console to provide support for the individual control console terminals.

Most of the research and development in this program was performed by the battery contractors. Argonne performed some supporting basic and applied research work to complement the contractors' efforts. The following is a brief summary of the ANL activities.

ANL SUPPORTING RESEARCH

Zinc Electrode Studies. The loss of capacity of zinc electrodes on cycling is a problem that has plagued battery manufacturers for years. Several experimental and modeling studies were focused on mass transport, reaction mechanisms, and current distribution in zinc electrodes. Galvanostatic polarization experiments, combined with known information from the literature, resulted in a new theory involving passivation of the electrode caused by precipitation of zinc oxide (ZnO) at the surface. The effect of zincate supersaturation on the conductivity of the electrolyte was also investigated. This study demonstrated the effect of reduced electrolyte conductance upon zinc electrode performance.

Thermal Modeling of Ni/Zn Cells. A study to model heat transfer within Ni/Zn cells was undertaken under a contract with the University of Illinois. An experimental cell was constructed to measure temperature distributions over full-size electrodes during charge-discharge cycling.

Nickel Electrode Capacity Loss. During tests and evaluations of near-term alkaline batteries, three adverse effects had been noted: (1) an inability to obtain a full charge from some batteries after several charge/discharge cycles, (2) a lower charge acceptance of nickel electrodes in Ni/Fe cells as compared to Ni/Zn cells, and (3) effect of temperature on recharge efficiency. To investigate these effects, NBTL test data were reviewed, measurements were made on individual cell electrodes, and benchscale experiments were performed. The first problem was quantified by NBTL data and individual tests, and some insight was gained into the problem, but the conclusion was that a detailed study would be required to reach an unambiguous understanding of the mechanisms involved. With regard to item (2), a small amount of soluble iron in the electrolyte resulted in more oxygen generation, which reduced the charge acceptance of the nickel electrode. Increasing temperature was shown to cause a marked capacity loss in the nickel electrodes.

Lead Positive Electrode Active Materials. In spite of the fact that the leadacid battery is a well-established technology, the electrochemistry of the system is still not well understood. As an example, the utilization of active material in the positive (PbO₂) electrode is limited to 30-50%. In-situ laser Raman spectroscopic studies were conducted on the electrodes to identify the reaction products, and the study was extended to evaluate the merits of using 4PbO·PbSO₄, tetrabasicleadsulfate (TBLS), as the active material in these electrodes. The results showed that a significant amount of PbSO₄ and minor amounts of $3PbO \cdot PbSO_4 \cdot H_2O$ and PbO·PbSO₄ were formed. The relative electrochemical oxidation rates were ranked tentatively as follows:

TBLS>PbO·PbSO₄>PbSO₄

Upon discharge of the fully charged electrodes, only $PbSO_4$ was observed as a product. Thus, the only value of using TBLS in the fabrication of electrodes would lie in morphological effects produced in the first discharge. Another study was undertaken on lead positive active material, using neutron-scattering methods. The results showed that hydrogen (or deuterium) was incorporated into the β -PbO₂ lattice and that the lattice was lead-deficient.

Arsine-Stibine Emissions. Small amounts of arsine (AsH_3) and stibine (SbH_3) can be evolved from lead-acid batteries during charging. Both are highly toxic gases. Air samples were taken during the charging of lead-acid batteries both in workplace situations and in laboratory tests and analyzed for arsine and stibine. The results served as a basis for an engineering analysis that resulted in recommendations on the ventilation of battery compartments in electric vehicles. *Post-test Battery Analysis.* Post-test analyses involving various analytical techniques and visual examinations were performed to determine causes of failure and to offer recommendations to the battery contractors that could be incorporated into their next generation of modules.

Battery Component Research and Devel-

opment. Charging regimes and parameters have an effect on battery performance and lifetime. By 1980, NBTL had in place computer-control and data-acquisition systems capable of handling up to 15 concurrent battery charge/discharge cycling tests. Extensive studies were performed on the effects of constant-current, constant-voltage charging; equalization charging; pulsed currents; and other charging strategies.

Battery/Vehicle System Integration. The oil embargoes of the 1970s and the air pollution in large cities both generated pressure on the DOE to accelerate the development of electric vehicles, and their natural response was to push strongly for early demonstrations of the technology. Integration of battery prototypes into vehicles was an essential part of this endeavor. Most of the in-vehicle battery testing was to be done by JPL (Jet Propulsion Laboratory), and the batteries were to be supplied by the commercial manufacturers. The NBTL had the responsibility for providing information on the batteries to be tested, evaluating battery configurations suitable for specific vehicles, and evaluating demonstration results. Computer modeling of battery behavior was undertaken to provide a better understanding of the electrode and cell behavior. An equivalent circuit model was developed to predict the response of the battery to driving cycles, regenerative braking, charge/discharge strategies, and other such factors. Finally, materials availability/cost analyses were performed to evaluate the effects of near-term market penetration by electric

vehicles on the cost and availability of key materials.

Fuel Cells

The major fuel-cell program in CEN, which began in about 1977, was directed toward cells that use molten carbonate as the electrolyte. Argonne became the lead laboratory with management responsibility for all the DOE work in that area, and CEN conducted an experimental research program of its own. Prior to that time, however, there were two small related programs that deserve mention. The first, which began in about 1971, did not involve fuel cells *per se* but was a close relative in that it employed an electrolytic cell with a molten carbonate electrolyte to replace CO_2 with oxygen in space capsules.

ELECTROLYTIC GENERATION OF OXYGEN FOR SPACE APPLICATIONS

The objective of this work, which was supported by the Ames Center of the National Aeronautics and Space Administration (NASA), was to recover oxygen from the CO_2 with high efficiency, and to recover an additional amount of oxygen from water to provide a total oxygen make-up stream of about 2.0 lb/astronaut-day. The carbon from the CO_2 was to be converted into a readily disposable or useful form. A particularly desirable reaction would be

 $4 \text{ CO}_2 + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ C}_2\text{H}_2 + 5 \text{ O}_2$

Although some progress was made, the research effort revealed several difficult technical problems, and it was terminated after about two years. Rob Selman did most of the work on that program. Sam Von Winbush, a visiting professor, also contributed to this work.

AQUEOUS ELECTROLYTES FOR HYDROCARBON FUEL CELLS

The second program, which began in about 1973 and was led by John Ackerman, was aimed at improved electrolytes for hydrocarbon/air fuel cells. The idea behind this work, which was supported by the U.S. Army Mobility Equipment Research and Development Command (MERDC), was to develop fuel cells that could use conventional fuels to propel military vehicles. Two potential advantages of such vehicles are that they would be quiet and that the fuel efficiency, in principle, could be high because fuel cells are not subject to the Carnot-cycle efficiency limitations of internal combustion engines. Conventional fuel cells with a phosphoric acid electrolyte had been used widely with hydrogen or alcohol as the fuel. The objective of this program was to use hydrocarbon fuels, and the effort was aimed mainly toward new electrolyte systems of much higher acidity. A number of organic and inorganic electrolyte with very high hydrogen-ion systems activities were investigated. John worked closely with the Army people at Ft. Belvoir during these investigations. This program was discontinued when funding was terminated.

MOLTEN CARBONATE FUEL CELLS

In 1977, CEN assumed its role as the lead laboratory for the DOE molten carbonate fuel cell programs with John Ackerman as the Program Manager. The overall objective of the DOE program was to develop fuel-cell power plants in which synthesis gas (hydrogen and CO) from a fuel processor such as a coal gasifier/clean-up system would be fed to fuel cells to generate electricity. The advantages of this type of plant are use of coal, very low pollutant emissions, and high efficiency (estimated at 60%, coal to bus bar). The increased use of coal, rather than oil, for power generation seemed like a particularly good idea in view of the oil embargo at the time.

The molten carbonate fuel cell program, like the battery programs, consisted of research and development work performed by a number of contractors under an ANL Program Office and supplemented by in-house work at ANL. The contractors included the Energy Research Corporation, Oak Ridge National Laboratory, the Institute of Gas Technology, and the General Electric Company. In addition to technical management, the CEN group assisted DOE with planning and evaluations. The molten carbonate fuel cell (see Fig. 4-8) consisted of a porous nickel alloy anode, a porous nickel oxide (NiO) cathode, an electrolyte structure that insulated the electrodes electronically but permitted passage of carbonate ions (CO_3^{2-}) , and metal cell housings, which, in the case of cell stacks, were cell separator plates. The housings (or plates) bore upon the electrolyte structure to form a "wet seal" that separated the cell from its surroundings. The electrolyte structure, commonly called a "tile," was a composite



Fig. 4-8. Molten Carbonate Fuel Cell. Dimensions: 11 × 11 cm. A = gas entrance slot; B = gas channels; C = gas exit slot; D = wet seal area.

of very small (<1 μ m) solid particles of lithium aluminate (LiAlO₂) and a mixture of lithium and potassium carbonates (Li₂CO₃ and K₂CO₃) that is liquid at the operating temperature of about 650°C.

Hydrogen and carbon monoxide in the fuel gas react at the anode with carbonate ion in the electrolyte to form carbon dioxide and water, giving up electrons to the external circuit. At the cathode, carbon dioxide and oxygen react and accept electrons from the external circuit to form carbonate ions, which are conducted through the electrolyte to the anode.

Anode:
$$H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^{-}$$

 $CO + CO_3^{2-} \rightarrow 2CO_2 + 2e^{-}$
Cathode: $2CO_2 + O_2 + 4e^{-} \rightarrow 2CO_3^{2-}$

The ANL in-house effort was directed first toward improving the wet seal and then mainly toward improvements in the electrolyte tiles. The people involved in this work, in addition to Ackerman, were Pat Finn, Kim Kinoshita, Gene Kucera, and Jim Sim. In 1978, Dean Pierce was brought in as a Group Leader. One of the first problems to be tackled was corrosion of the stainless steel housing in the area of the wet seal where the two halves of the housing pressed directly against the electrolyte structure. The corrosion was due primarily to gradients in the chemical potential in these areas. The problem was alleviated greatly by flame-spraying aluminum onto the wet seal area and then heating the housing to form a diffusion layer between the aluminum and the Type 316 stainless steel housing. On exposure to the cell environment, the aluminum was oxidized, producing a graded structure, presumably of lithium aluminate (LiAlO₂), alumina (Al₂O₃), aluminum, and stainless steel. The protective coating of lithium aluminate and alumina was non-porous and adherent.

Most of the ANL work concerned the development of electrolyte tiles of adequate

stability, strength, and performance. Above the liquidus temperature of the carbonate mixture (about 450°C), the tile was a very stiff plastic body held together by surface forces; below the liquidus temperature it was a hard, strong body resembling a ceramic. The carbonate content of the tile had to be high enough to transport carbonate ions at a rate sufficient for good cell performance without sacrificing the tile strength. The tiles typically had a carbonate content of about 65 wt%.

A key factor in the strength of the tile was the size and shape of the solid lithium aluminate particles. The compound exists in three different allotropic forms and can be prepared in various sizes and shapes (spherical "clumps," rods, bipyramids, and platelets). Methods were developed to prepare all three allotropic forms in high purity and to identify changes in the allotropic forms and particle morphology. The effects of these variables were evaluated in cell tests and post-test examinations. The initial tests were conducted with 7-cm-dia round cells, and in 1978 they were continued with 11-cm-square cells, which were more representative of a practical system.

The research and development work on electrolyte tiles continued in 1979, with more detailed studies of synthetic methods and the use of additional diagnostic techniques, including dilatometry to determine expansion, slumping and creep. New tile compositions were explored and some work was done on sintered electrolytes. By the end of 1979, the tile quality had improved significantly, and studies were started on long-term aging and degradation effects.

Coal Combustion

INTRODUCTION

In 1970, about 20% of the energy consumed in the United States was generated from coal. The rest was from oil (43%), natural gas (33%),

and hydroelectric and nuclear (4%). Most of the oil was imported because domestic sources had been depleted to the point that their recovery costs were too high to compete with foreign supplies. The use of natural gas was increasing rapidly as pipelines were built, thereby displacing coal and oil for many applications, including the generation of electrical power. Estimates of U.S. gas reserves at the 1970 rate of consumption ranged from about 50 to 100 years. In contrast, U.S. coal reserves, if they could be used, would sustain the rate of energy consumption at that time for several hundred years. S. David Freeman, Director of the Ford Foundation Energy Policy Project in the early 1970s, described the situation very succinctly: "There are two things wrong with coal today. We can't mine it and we can't burn it."

The environmental and safety problems associated with the use of coal as an energy source had become a matter of considerable public concern. Underground mining was dangerous, and news report of numerous fatalities, injuries, and chronic illnesses were Environmental common. impacts from underground mining included acid mine drainage, erosion, leaching of pollutants from wastes, fires in mines and waste piles, silting of streams, and destabilization of land over the mines. Deep mining, which produced most of the higher-grade anthracite and bituminous coal, was giving way to strip mining, which is much safer and more benign environmentally, but has its own problems. The areas where strip mining is feasible tend to have lowergrade deposits such as high-sulfur bituminous coal, sub-bituminous coal, and lignite. The environmental effects consist mainly of piles of earth from the mantle over the deposits and the excavated areas where the coal was removed. Reclamation of strip-mined land is usually possible, but expensive. In Northern Illinois, old strip mines, which become filled with clear water, are common, and are sometimes used

for recreational purposes such as swimming and fishing.

Once the coal is mined, burning it creates another set of environmental problems. The off-gases contain particulate matter, sulfur dioxide, nitrogen oxides, and carbon dioxide. Nearly all of the particulate matter can be removed by filters, which collect fly ash as a solid waste. The solid wastes from coal combustion contain a number of toxic substances that complicate their disposal. Liquid scrubbers can be used to treat the offgases, but they are expensive and create liquid waste, which requires further processing.

The many problems associated with power generation from coal resulted in extensive environmental legislation to set standards and regulate that aspect of the industry. At the same time, there was an awareness that energy from coal was needed in the long run to conserve oil and gas. It was clear that new technologies were the only way to reconcile these two requirements, and the oil embargo of 1973 emphasized the need for timely development of these technologies.

In 1969, the Chemical Engineering Division had started a program on the combustion of coal in a fluidized bed to which particulate limestone (CaCO₃) was added to reduce the emission of sulfur dioxide (SO₂) during the combustion process. This program was funded initially by the National Air Pollution Control Administration (NAPCA) of the U.S. Department of Health, Education and Welfare. Spurred by the 1973 oil embargo, President Nixon, in 1974, recommended a expenditure for \$35 million the direct (fluidized-bed) combustion of coal. Programs were sponsored by the Office of Coal Research of the U.S. Department of the Interior and the U.S. Environmental Protection Agency (EPA). There was pressure to move into the demonstration stage, and a 10-ton/day plant was being constructed by Pope, Evans and Robbins, Inc. Consideration was being given

both to atmospheric-pressure fluidized-bed combustion (AFBC) and to pressurized fluidized-bed combustion (PFBC). An advanced high-pressure concept was pursued jointly by Argonne, Exxon Research and Engineering, and Westinghouse Electric Corporation. The equipment had progressed to a scale of about 500 lb of coal/hr and a conceptual design was in the works for a 3-MWe plant. The level of effort on the coal program in the Chemical Engineering Division was increased markedly in the 1970s. Extensive bench-scale engineering studies conducted throughout the decade were supported by more basic investigations that provided an understanding of the chemical and physical principles involved in the process. By the end of the 1970s, CEN, in addition to the in-house work, was providing administrative support in a number of areas to the Morgantown, WV, Energy Research Center in the form of program planning, project management, and program reviews. A substantial amount of the manpower in CEN was committed to these activities.

Al Jonke was in charge of the coal program until 1978, when Irv Johnson assumed that responsibility. Individual parts of the program at various times were headed up by Erv Carls, Irv Johnson, Mike Myles, Bill Swift, John (G. J.) Vogel, and John Young.

CLASSES OF COAL

Ideally, a fluidized-bed combustion unit should be able to accommodate coal from any source. Four different classes of coal, as shown in Table 4-13, are found in the United States. The values in this table, adapted from Bureau of Mines information (Bulletin 650), should be regarded only as typical, rather than specific data, for the purpose of illustration. Anthracite, although an excellent fuel, is very limited in supply, constituting only about 2% of the United States coal reserves. Bituminous coal is plentiful and of good quality, except for the fact that much of it has a high sulfur content. This was the major reason for investigating new combustion techniques with a capability for *in situ* sulfur removal. It is interesting to note that Illinois has the largest bituminous coal reserves of any state in the nation, but Illinois coal is plagued with a high sulfur content (most of it 3 wt% or more) and, therefore, is useless for power generation without some means of sulfur control.

FLUIDIZED BED COMBUSTION OF COAL

Bench-Scale Engineering Experiments. The work that had been started in 1969 using a 6-in.-dia fluidized-bed combustion unit atmospheric pressure operating at was continued in 1970. The general features of this unit are shown in Fig. 4-9. The fluidized-bed combustor was 6 ft long, positioned vertically, and was equipped with a gas preheater for the fluidizing air and vibratory screw feeders for the coal and limestone. The flue gases passed through primary and secondary cyclone separators followed by a glass fiber filter. Infrared spectroscopy and other instrumental methods were used to monitor the composition of the flue gas. The principal variables in the operation were (1) Ca/S mole ratio in the feed, (2) type of limestone, (3) gas velocity, and (4) combustion temperature. Initial tests were conducted with pulverized limestone (25 µm), a superficial gas velocity of 3 ft/min, temperatures of about 800 to 900°C, and Ca/S ratios of 1.5-2.5. The temperature and gas velocity over these ranges had little effect, but raising the Ca/S ratio from 1.5 to 2.5 increased the SO₂ removal from 57% to 83%. Recycled limestone from the fly ash gave about the same results, and dolomite performed better than limestone (90 vs. 83%). The results from these runs produced sufficient information to develop a mathematical model from the data.

Class	Anthracite	Bituminous	Sub-bituminous	Lignite
Quality	Excellent	Good	Fair	Poor
Availability	Poor	Excellent	Good	Fair
Fixed Carbon, wt%	86-98	50-86	40-60	<40
Moisture, wt%	<2	2-6	20-30	40
Ash, wt%	3-9	4-12	5-10	5
Sulfur, wt%	0-1	0-3 or more	0-1	0-1
Heating Value, Btu/lb	13,000	13,000	10,000	7,000

Table 4-13. Classes of Coal



Fig. 4-9. Bench-Scale Fluidized-Bed Combustor

Work was then started on pressurized fluidized-bed combustion, using the 6-in.-dia bench-scale unit. This system was operated at 10 atm pressure with a compressed air feed, an air preheater, and an off-gas system made up of cyclone separators, filters, gas samplers, and pressure let-down valves. The unit was instrumented with a data-logging system. The principal coal used in the operation was a highly caking, high-volatile, bituminous type, but some work was also done with subbituminous coal and lignite. The coal feed was ground to a particle size of -14 mesh and dolomite was used as the sorbent for SO₂.

In the experiments with bituminous coal, the temperatures were about 800-900°C, the Ca/S mole ratios 1-3, and the gas velocities 2-5 ft/sec. The runs were all at 8 atm pressure with 3% oxygen in the flue gas and a bed height of 3 ft. Again, the effect of temperature was nil, and the sulfur retention increased with higher Ca/S ratios. The effluent gas met the EPA standard of 1.2 lb $SO_2/10^6$ Btu of energy produced. The NO_x levels were also low, well below the EPA standard of 0.70 lb NO/ 10^6 Btu.

Experiments were conducted with the 6-in.dia pressurized combustor to determine whether any difficulties would be encountered in processing lower-grade coals. One of these was a sub-bituminous coal with a high ash content of 17%, and the other was a lignite with a low heating value of 7,625 Btu/lb. The operating performance was excellent in both cases, which demonstrated the versatility of fluidized-bed combustion for processing coals of widely varying types and quality.

Some special tests were directed toward the effects of operating conditions on the concentrations of SO_2 and NO and other components in the flue gas. Sulfated dolomite was used in the bed. Changes in the temperature had no significant effect on the SO_2 and NO concentrations. A reduction of the operating pressure from 8 to 1 atm did not affect the SO_2 concentration, but did increase the NO level from about 200 ppm to approximately 400 ppm.

The continuing bench-scale work with the 6-in.-dia fluidized bed showed that dolomite was superior to limestone in experiments conducted at 950°C and 8 atm pressure with respect to sulfur retention, but NO concentrations in the flue gas were in about the same range (85-150 ppm, compared to the EPA standard of 500 ppm). The effects of excess combustion air were also investigated. This was of interest because combustion heat could be removed from the bed by generating steam in tubes immersed in the bed, by passing excess air through the bed, or both. With excess combustion air in the range of 17-50%, and with different Ca/S ratios, no consistent effect on sulfur retention by a dolomite bed was observed. The NO level in the flue gas, however. increased with the oxygen concentration, as expected (160, 200, and 220 ppm NO with 3, 6, and 9% oxygen, respectively). The combustion efficiency

increased linearly from 86 to 98% when the excess air was increased from 17 to 75%. Studies of particle-size effects showed that the particle sizes of coal and dolomite had no effect on the NO level in the flue gas or the combustion efficiency. The sulfur retention, however, increased with decreasing particle size of the dolomite.

Scale-Up Studies. In 1975, the ANL program on fluidized-bed combustion of coal underwent a major expansion supported primarily by ERDA. In addition to continuing research on fluidized-bed combustion and regeneration of the limestone or dolomite, a proposal was made to construct at ANL a Components Test and Integration Facility (CTIF). This facility was a 3-MW (electric equivalent) coal-combustion unit with a pressurized fluidized bed. This unit was to be tied into ANL's steam plant to utilize its coalhandling and water-treatment equipment. The idea behind the CTIF was to provide support for a full-scale pilot plant about ten times that size.

In 1976 a conceptual design study was initiated on the Component and Test Integration Unit (CTIU). The objectives were to provide technical support for a pilot-plantscale PFBC project; to provide a facility for materials evaluation, equipment-component testing, and instrument evaluation; and ultimately to investigate alternative and advanced concepts of PFBC systems. The CEN staff people put a great deal of thought and design effort into the CTIU project. The reference operating conditions for the combustor design are given in Table 4-14. The fluidized-bed combustor was contained inside a 12-ft-ID steel vessel with a pressure rating of 18 atm. The combustor itself was made up of a stack of flange-connected, refractory-lined modules. The modules were round, but the refractory liners in some cases were square. The hot gas removal system comprised three stages of particulate removal-two cyclone

Operating Pressure, atm	10	Excess Combustion Air, %	20
Bed Operating Temperature, °C	900	Superficial Gas Velocity, ft/sec	7
Bed Height, ft	8.4	Ca/S Mole Ratio	2
Freeboard Height, ft	23	Target Sulfur Removal, %	90
Fluidized Air, Dry, lb/sec	10	Combustion Efficiency, %	94

Table 4-14. Operating Conditions for CTIU Combustor

separators and a granular bed filter. Hot gases from the third stage cleanup flowed into a stationary turbine-test cascade. The system was thoroughly instrumented, including graphic displays, with overall control from a central module for process management and data acquisition and processing.

In August 1978, DOE decided to defer construction of the CTIU indefinitely and to use the existing facilities with comparable operating conditions and performance characteristics to achieve the program objectives.

Toward the end of the 1970s, DOE concluded that the industrial application of atmospheric-pressure, fluidized-bed combustion (AFBC) was ready for commercialization and was one of the technologies that could make a major impact quickly on the national energy problem. Four industries (chemical, petroleum, paper, and primary metals) accounted for about 70% of all fossil fuels used in boilers. The DOE recommended building one large (200,000 lb steam/hr) prototype AFBC for each of these industries. Also, several industrial AFBCs were being built, as were PFBC units. One of these was a 20-MWe PFBC test unit of the International Energy Agency (IEA) at Grimethorpe, England. After the design and engineering activities associated with the CTIU project had been brought to an orderly conclusion in late 1978, Erv Carls, who had been Technical Manager of that project, was appointed Experimental Program Manager of the Grimethorpe operation and

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spent two years in England in that position. During that time, he continued as an ANL employee on special assignment.

Limestone Studies. The term "limestone," which is calcium carbonate (CaCO₃), has sometimes been used generically in this program to include dolomite, a double compound consisting of calcium and magnesium carbonates (CaCO₃·MgCO₃). Limestone and dolomite occur naturally in large quantities, and both were investigated as sorbents for sulfur removal in the fluidized-bed combustion work. At the maximum operating temperature of 900°C normally used in these studies, calcium carbonate was stable, but magnesium carbonate in the dolomite decomposed (calcined) to the oxide, producing a CaCO3-MgO combination. At 950°C, however, the CaCO₃ also decomposed to form CaO. This process apparently produced larger interstitial openings in the particles, and the SO₂ retention was better than values predicted by a mathematical model from the lower-temperature data. At a Ca/S ratio of 1.5, the sulfur retention was 96%, compared to a predicted value of 89%. The NO levels in the flue gas were very low in the two experiments-135 and 120 ppm. Tests at 950°C also showed that dolomite was more effective than limestone in retaining sulfur.

Studies were conducted on the kinetics of sulfation and regeneration reactions of dolomite, using thermogravimetric techniques. The rate of the sulfation reaction

 $(CaCO_3 + MgO) + SO_2 + 1/2 O_2$ $\rightarrow (CaSO_4 + MgO) + CO_2$

was enhanced by the presence of water in the reactive gas stream, and the reaction was either first or three-quarters order in SO_2 concentration, depending, respectively, on the presence or absence of water vapor. The reaction was zero order with respect to water-vapor concentration, and it was one-fourth order in oxygen concentration with water vapor present. The apparent activation energy was 7.6 kcal/mol.

A rudimentary model for the sulfation reaction was developed on the following assumptions:

- 1. Diffusion through the macropores of the dolomite particles could be ignored as a rate-determining step.
- 2. The CaCO₃ crystallites were platelets.
- 3. Diffusion through the reaction layer was rapid relative to the movement of the reaction interface.
- 4. The effective diffusion coefficient was a function of the extent of the reaction.

The model fit the data and led to detailed structural studies of the material, using optical microscopy, X-ray diffraction, and scanning electron microscopy.

For economic reasons, the widespread use of limestone in fluidized-bed combustion of coal would require that sufficient quantities of suitable limestone be available at various locations across the country to avoid excessive shipping costs. Tests were therefore conducted to evaluate the effectiveness of representative limestones from different parts of the country for FBC use. Reaction rates of the limestone samples with a $SO_2/O_2/N_2$ mixture were determined by thermogravimetric analysis. The predicted values for the quantity of limestone required for a given quantity of coal, based on the test data, gave a range of 0.37 to 2.4 kg/kg coal. Sixty percent of the limestones were below 0.5 kg/kg coal. These results indicated that highly reactive limestones required to meet EPA sulfur emission standards are widely available in the U.S.

In the fluidized-bed combustion of coal, approximately one ton of limestone or dolomite would be sulfated for each 5 tons of coal (3 wt% S) combusted. The large volume of spent sorbent material would be a major wastedisposal problem unless some means were available for its recycle. A limestone regeneration process in which the sulfur could be recovered in a commercially useful form such as elemental sulfur, H_2S , or SO_2 might offset some of the processing cost. Various methods for regenerating limestone or dolomite were considered: (1) reductive decomposition of $CaSO_4$ by CO or hydrogen, (2) a two-step process in which CaSO₄ was reduced at 900°C to CaS, which was then converted to CaCO₃ and H₂S by reaction with a CO₂-H₂O mixture at about 600°C, and (3) a solid-solid reaction of CaS with CaSO₄ at about 1100°C to form CaO and SO_2 . The reductive decomposition was believed to be the most promising of the three methods, and partial combustion of the coal was a potential in situ method for generating the reducing gases. Dolomite that had been sulfated in coal-combustion experiments was regenerated by using methane in a 3-in.-dia reactor. The effects of temperature, fluidizing velocity, fluidized-bed height, solid-bed residence time, and total reducing gas concentration in the flue gas on the regeneration of CaO were examined. The results, in brief, were as follows:

- 1. Deeper beds resulted in poorer regeneration.
- 2. Increased fluidizing gas velocity affected regeneration adversely.

- 3. Higher regeneration temperatures (>1040°C) increased the extent and rate of regeneration.
- 4. Establishment of two reaction zones in the reactor was very effective in preventing CaS buildup.
- 5. Decrepitation of the particles in the bed occurred during regeneration.

Additional components were installed in the bench-scale equipment, and the combustion and regeneration systems were separated. Also, the inside diameter of the regenerator was increased from 3 in. to 4 in., and a coalfeeding system was added. Other supporting regeneration studies continued in CEN, one of which involved the use of carbon to regenerate sulfated limestone in an externally fired rotary kiln. This approach was discontinued due to a lack of durable construction materials and the high cost of clean fuel required to heat the kiln.

Inorganic Salt Additives. The use of inorganic salts as additives to enhance the effectiveness of limestone beds was investigated. Initial studies were made with sodium chloride (Nalco), using synthetic flue gas at 850°C. Changes in the surfaces of the particles were determined by porosimetry and electron microscopy. Trace amounts (1 mol % or so) of the added salt apparently caused structural rearrangements and migration of pores to form larger pores, which increased permeation of the gases into the particles. A similar effect was noted with calcium chloride (CaCl₂) additions to limestone and dolomite. Additions of larger amounts of CaCl₂ caused the formation of a liquid capable of dissolving CaO. This effect could lead to complete sulfation of the material.

The success of this general approach suggested the possibility of using other salts such as sodium carbonate (Na₂CO₃) or sodium hydroxide (NaOH), which do not contain corrosive chloride ions. Because of concerns about the corrosion that might result from these

salts, a laboratory-scale fluidized bed made of quartz was assembled to test various alloys in a simulated flue-gas environment at 850°C and 20-500 ppm SO₂ with NaCl or CaCl₂ added to the bed material. The alloy test specimens were located in and above the bed. Stainless steel and high nickel-alloy specimens in the bed showed higher corrosion rates with the salt additives, and specimens at 650 and 550°C above the bed exhibited extensive corrosive attack. In view of these results, a new, automated AFBC unit with a 6-in.-dia combustor was built with provisions for seven corrosion probes, each containing seven metal specimens (see Fig. 4-10). Several 100-hour tests were conducted, using coupons of nickel-, iron-, and cobalt-base alloys.

After the exposure, the coupons were examined by scanning electron microscopy and energy dispersive X-ray analyses. Additions of $0.3 \mod \% \operatorname{CaCl}_2$ to the sorbent had little effect on the corrosion rates, but additions of 0.5 mol % NaCl or 1.9 mol % Na₂CO₃ accelerated corrosion of most of the coupons. Samples near the top of the bed were attacked more severely than those near the fluidizing gas distributor. In general, most of the specimens were penetrated less than about 15 µm. The uncertainties in long-term corrosion rates calculated from these data were felt to be such that much longer test times would be required.

Experience from operation of gas turbines with hot flue gases from liquid fuel combustion units had indicated that alkali metal compounds such as chlorides and sulfates of sodium and potassium cause "hot corrosion" of gas-turbine hardware. This could also be a problem with PFBC combined-cycle power plants, where the flue gas is used to drive a turbine. Granular bed filters were being developed to remove these compounds, as well as particulate material. Diatomaceous earths and activated bauxites proved to be the best sorbents for these beds. Removals of 95-98% of the NaCl from the gas were readily achieved with these materials. Tests indicated that



Fig. 4-10. Corrosion Test Equipment

bauxite could be regenerated by washing with water. Particulate matter also had to be removed to prevent erosion of the turbine blades. A granular bed filter using sulfated limestone was investigated and found to remove 91 to 99% of the particulates from the gas. To reduce the loading of the bed, however, the use of a high-efficiency Donaldson TAN-JET[®] cyclone separator upstream from the bed was examined. The cyclone, by itself, was able to decrease the particulate concentration to about three times the acceptable level for use in a gas turbine.

Synthetic Sorbents. The possibility of developing synthetic sorbent materials as an alternative to limestone or dolomite was investigated. The thought was that it might be possible to synthesize a material having physical and chemical properties tailored to meet the specific needs of a fluidized-bed combustor.

Alkali or alkaline earth oxides deposited on a support such as α -alumina pellets were tested. Cylindrical α -Al₂O₃ pellets (1/8 × 1/8 in.) were impregnated with CaO, and their rates of sulfation were measured, using a synthetic combustion gas and a thermogravimetric analysis apparatus. The rate was 0.7 order with respect to SO₂ concentration and first order in the CaO concentration. The rate of sulfation was independent of water vapor content of the gas and increased with temperature from 750 to 900°C, above which it became independent of temperature. The sulfated additive (CaSO₄ in α -Al₂O₃) was regenerated with various reducing gases (H₂, CH₄, or CO), and the rate was 0.8 order in the reducing gas concentration. The rate was the same for CH₄ and H₂, but lower with CO. Other metal oxides (Na₂O, K₂O, SrO, and BaO) were also tested. The general conclusion was that the synthetic additives offered no significant advantages over limestone or dolomite.

Behavior of Trace Elements. Coal contains a large number of trace elements, which appear in the fly ash or the fluidized bed after the combustion process. Some of these elements, for example, mercury, lead, beryllium, and fluorine, are of particular environmental concern because of their toxicity. For this reason, studies were conducted to determine differences in the way trace elements behave in fluidized-bed combustors and in conventional coal-fired power plants. Preliminary data had indicated that the fluidized-bed system would reduce trace-element emissions.

Further studies of trace-element behavior in ten-cycle combustion-regeneration tests showed that nine elements (Cr, Tl, V, Mo, Zn, Ba, Fe, In, and Sr) were enriched in the sorbent as a result of coal-ash buildup on the surfaces of the dolomite particles. Eight elements that tend to be volatile in conventional coal-fired units were either enriched (Cr, Tl, and Zn) or remained stable (As, Cd, Pb, Ni, and Se) in the dolomite.

FOSSIL FUEL UTILIZATION AND CONVERSION

This program began with the title "Coal Conversion Technology Program" and was later renamed "Fossil Fuel Conversion and Utilization." Largely as a response to the oil crisis of the 1970s, a large national program on the conversion of coal into clean fuels was being sponsored by the U.S. Department of the Interior and other federal agencies, with support by the U.S. Bureau of Mines, private research organizations, and universities. The initial work at CEN was authorized by the AEC Division of Applied Technology in September 1974 and was aimed at problems related to an in situ (underground) coalgasification process being developed at Lawrence Livermore National Laboratory (LLL).

When ERDA was formed, the work continued as part of the *in situ* gasification program under ERDA's Division of Petroleum, Gas, and *In Situ* Technology. In 1975, CEN was authorized to begin an additional project in support of coal liquefaction development called "Physical Parameters in Synthoil Process." This work was done in cooperation with the ERDA

Pittsburgh Energy Research Center. With the advent of DOE, these programs were placed under its organization, and CEN began to provide technical support to DOE for its management of the overall alternative fuels development programs. This management support consisted of developing program plans, establishing objectives, reviewing contractors' proposals, providing contract placement documents for DOE, and presenting program reviews at contractors' annual meetings. This was much the same strategy that DOE was using in the battery, fuel-cell, and coal-combustion programs in CEN in the late 1970s, i.e., the primary function of ANL was to assist DOE in program management, although a small in-house research and development effort was also allowed.

Char is produced as a by-product during the *in situ* gasification of coal. Two possible uses of the char were under consideration: (1) production of hydrogen by a steam-char reaction, primarily for use in the coal-conversion processes, and (2) combustion to generate heat or electricity. The gasification reactions to be studied were

 $\begin{array}{l} \mathrm{CO} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2} \\ \mathrm{H_2O} + \mathrm{C} \leftrightarrow \mathrm{CO} + \mathrm{H_2} \\ \mathrm{CO_2} + \mathrm{C} \leftrightarrow \mathrm{2} \ \mathrm{CO} \end{array}$

A laboratory-scale unit to study the reaction of steam and oxygen with coal and char was originally designed to simulate in situ gasification conditions at a temperature of 800°C and a pressure of 40 atm, and it was later modified to operate at 1000°C and 136 atm. The variables to be studied were steam pressure, coal devolatilization rate, reaction temperature, and total pressure. During the construction of this unit, preliminary studies were conducted on char reactivity with oxygen and steam at atmospheric pressure and on the catalytic activity of coal ash. Chars were prepared from a number of coals and their reactivities with

1.7

steam and oxygen at atmospheric pressure were measured, by using a thermobalance. The activation energy proved to be about one-half of that reported in the literature, which suggested that catalysis by inorganic matter had occurred or that the reactions had taken place inside small pores having a high lengthto-diameter ratio.

Ashes of several coals were prepared, both by high-temperature oxidation and by lowtemperature ashing techniques, and the surface areas and surface acidities were measured. Surface acidity is used in the petroleum industry as a measure of the activity of cracking catalysts. On a unit area basis, the coal ash had a higher concentration of surface acid sites than a commercial cracking catalyst. which indicated potential cracking activity by the coal ash. Studies were conducted on the reaction kinetics of the processes occurring in the gasification zone of the coal-gasification process, i.e., steam-char, CO₂-char, hydrogen-char, water-gas shift, and methanation reactions. The coal samples were representative of coals where field tests were either in progress or were planned, and the type of coal was shown to have a significant impact on the steam-char reaction. The data from this work were intended for use by others in mathematical modeling of coal-gasification processes. In 1979, the experimental work on coal gasification was phased out due to budget constraints.

During 1976-77, CEN had a short-term experimental program on the Synthoil Process, a method for converting coal to a liquid fuel of low sulfur content that would be suitable for use in power production. The process consisted of liquefaction and hydrodesulfurization of the coal in a turbulent-flow, catalytic, packed-bed reactor. A slurry of the coal in recycled oil was treated with hydrogen at 450° C and 135-270 atm pressure in the presence of a Co-Mo/SiO₂-Al₂O₃ catalyst. The gross liquid products were centrifuged to remove the unreacted solids. The chemical reaction is exothermic, and a batch calorimeter was devised to measure the amount of heat evolved by the reaction. Plans were also made to determine heat-transfer characteristics to be used in engineering-design calculations, to develop improved methods for separating solids from the liquid product, and to test catalysts. Some preliminary work was done in these areas, but it was halted as a result of budget decreases and a shift of manpower to DOE management responsibilities. Several years later, after the immediate oil crisis was over, the national Synthoil effort in the 1970s was criticized severely by some politicians and the media as a "government boondoggle."

MAGNETOHYDRODYNAMICS

In the mid-1970s, a small CEN effort was initiated in support of the ANL program on magnetohydrodynamics (MHD). An MHD generator is basically an expansion engine that converts heat from combustion gases directly into electric power by passing the hot, partially ionized gases through a duct (or "channel") lined with electrodes and surrounded by magnetic coils that create a magnetic field across the duct. Movement of the electrically charged gas through the duct generates a current that is collected at the electrodes. The expanding high-pressure gas propels itself through the duct. Very high temperatures are required to ionize combustion gases, but an addition of small amounts of potassium or another alkali metal (seed particles) enhances ionization sufficiently to permit operation at temperatures of 2000-2500°C. Proposals for using MHD in generating plants usually involve passing the exhaust gases from a highpressure combustion unit first through an MHD generator and then into a boiler to produce steam for a conventional steam-turbine generator. Plant efficiencies for this type of system are projected to be as high as 60%.

The downside of this technology lies mainly in the corrosive gases and particulate

material, which, together with the high temperatures, present serious corrosion, erosion, and solids-deposition problems.

The coupling of high-pressure coalcombustion technology and high-efficiency (e.g., superconducting) magnets was a natural for Argonne, which had been working in both areas. A small CEN effort to provide chemical and engineering support for the MHD program at ANL was started in about 1975. This became a sizeable program at ANL, in which CEN was responsible for the development of technology associated with the components downstream from the MHD channel-diffuser, and for processes to recover and recycle the potassium carbonate (K₂CO₃) seed material. The major focus was on interactions between the slags and seed materials in the gaseous and the solid or liquid phases, and development of a process for removing sulfur from the spent seed material. In 1979, the Division assumed an additional task of conducting tests of MHD steam-generating components in a 2-MW facility constructed at ANL. One of several possible arrangements for these downstream components in an MHD plant is shown in Fig. 4-11.

The overall objective of the MHD Heat and Seed Recovery Project at ANL was to provide technical data for designing and operating the downstream gas system and the seed-recycle process. An immediate project goal was to support a 20-MW unit of this type that was being built at the time by the University of Tennessee Space Institute. The longer-range goal was to provide the technical data needed for a 500-MW Engineering Test Facility (ETF) to demonstrate the feasibility of a coal-fired MHD power plant. The Argonne MHD Process Engineering Laboratory (AMPEL) was a facility constructed by the ANL Engineering Division to test MHD steamgenerator components under prototypical MHD conditions. This facility could supply a mixture of combustion gas, potassium compounds, and coal ash at a rate of 1 kg/sec by burning a slurry of fuel oil, coal ash, and K_2SO_4 with air preheated to about 800°C. The Division was given the lead role in the experimental work with this unit. The equipment was operated in three different temperature regimes: 2000-1500°C, 1500-1200°C, and below 1200°C. Instrumented, temperature-controlled tubes were inserted in the system to measure heattransfer characteristics and to obtain samples of condensates and other deposits. Preliminary experiments showed that entrained solids in the gas tended to block radiant heat transfer to the wall, and deposits of K_2SO_4 and a potassiumrich slag phase were found on the tube walls. These effects were not "show-stoppers," but they had to be taken into account in the equipment designs.

A computer model, called "MHDGAS," was developed to predict the equilibrium partial pressures of gaseous species and compositions of condensed solids and liquids in the various regions of the system. Later, the model was extended to include diffusion rates within the condensed phases, and to incorporate several other elements present at low concentrations in the coal ash (iron, sodium, chlorine, lead, phosphorus, and zinc) to predict their behavior in the process. This computer model proved to be highly effective, and it was used extensively in the engineering-design work.

Recovery of the potassium seed material and its desulfurization became an important part of this program because of environmental and economic factors. Two types of processes for removing sulfur from the K_2SO_4 were: (1) those that recover the sulfur in a commercially usable form (elemental S, H_2S , SO_2 , and H_2SO_4), and (2) those that recover it in a disposable form (CaSO₄·2H₂O and MgSO₄). Both approaches were being explored as of the end of 1979.

PERSONNEL

In addition to those mentioned earlier, the following people worked in the coal



The combustion gas leaves the MHD channel-diffuser at a temperature of about 2000°C, a pressure of 1 atm, and a velocity of 100-200 m/sec. At this point, the gas contains liquid slag particles, many smaller than 1 µm in size, and about 1 wt% potassium vapor. In the first component, the radiant boiler, slag is separated from the combustion gas, while it is still at a high temperature, to minimize reactions with vaporized potassium species that occur at lower temperatures. The high concentration of NO_x produced in the combustor is allowed time to equilibrate to acceptably low levels by providing a relatively modest cooling rate of 200°/sec down to about 1600°C. At 1500°C or lower, additional air is injected into the fuelrich gas to complete the oxidation of CO to CO₂. The oxidizing conditions also cause the potassium seed material to condense primarily as K₂SO₄, which is an efficient way of removing sulfur from the flue gas. The K₂SO₄ and small amounts of solid slag deposit as a liquid or solid on the tubes of the steam and air heaters. A gas-cleaning system is then needed to remove the remaining slag-seed particles before the flue gas is exhausted to the atmosphere.

Fig. 4-11. Downstream Gas System for an MHD Power Plant

combustion programs: John Ackerman, Lou Anastasia, Dale Bowyer, Ronald Brock, Tom Bump, L. Burnett, Tom Cannon, Stanley Che, Tsewei Chen, John Falkenburg, Don Fredrickson, Darrell Fee, Ray Green, Milt Haas, J. Hepperly, Chen-Chao Hsu, Huang, Bill Hann-Sheng Hubble. Roger Jarry, K. Javdani, Irv Johnson, Lowell Koppel (consultant), Sheldon Lee, John Lenc, Alain Lescarret, John Montagna. Dave Moulton, Russell Mowry, Tom Mulcahey, Bill Murphy, Satyendra Nandi, Frank Nuñes, John Pavlik. Walt Podolski, Devabhaktuni Ramaswami, Jim Riha. Satish Saxena (consultant), Charlie Schoffstall, John Shearer, Atul Sheth, Stan Siegel, Gregory Smith, Sherman Smith, Eugene Smyk. Bob Snyder, John Stockbar, Gale Teats, Clarence Turner, Noel Vargo, Elmo West, and Ira Wilson. Some of these individuals were from other ANL divisions.

The overall MHD Program at ANL was under the direction of Mike Petrick of the Engineering Division. The CEN work was led Terry Johnson. bv who, along with Atul Sheth, did the computer modeling studies, which were a major part of the program. Others who were involved in various aspects of the MHD work in CEN were Paul Blackburn, Al Fischer, Carl Johnson, Sheldon Lee, and Bill Swift.

Sodium Technology

The basic chemistry program that had been started by Irv Johnson and Fred Cafasso in the early 1960s bore fruit in 1969 when Argonne was designated as the center for AEC's sodium analytical chemistry program. The major components of this program were development and standardization of improved analytical methods for impurity elements in sodium, and development of on-line meters for continuously monitoring the concentrations of impurity elements in flowing sodium. The objective of this program was to develop an advanced chemical-analysis and impuritymonitoring technology for the Fast Flux Test Facility (FFTF), a sodium-cooled fast reactor planned for construction at Hanford in the 1970s.

The impurity elements of greatest concern were oxygen, carbon, and hydrogen. In the core region of the reactor, cobalt-60 and manganese-54, which are intense gamma ray emitters, are produced by neutron activation of stainless steel. Oxygen reacts with stainless steel in the hot core regions to produce iron oxides. These, along with the Co-60 and Mn-54, are deposited in cooler regions outside the core (piping and the intermediate heat exchanger where heat is transferred to the secondary sodium system). The resulting high radiation levels that would prevail if oxygen corrosion of the stainless steel were extensive would make maintenance operations difficult. Carbon is transported from stainless steel components in the hot core region to cooler regions of the primary sodium system. The result is loss of strength of the stainless steel. A capability to monitor carbon concentrations in the sodium was needed to facilitate research on the kinetics of carbon transport. Monitoring of the hydrogen concentration in the secondary sodium system was needed for rapid detection of water-to-sodium leaks in the steam generator.

The basic research program was continued to provide a sound scientific foundation for understanding the behavior of impurity elements in sodium, especially their role in corrosion of stainless steel. Tom Kassner of the Materials Science Division headed up a Materials Performance Group that studied the roles of impurity elements in corrosion and loss of strength of stainless steel in the core region.

Because much of the sodium technology work at ANL was in CEN, we were assigned the responsibility of coordinating sodium chemistry programs among all the ANL divisions that were involved: besides CEN, Chemistry (CHM), Materials Science and Technology (MST), and EBR-II. Les Burris, assisted by Joe Draley, was the Sodium Technology Program Coordinator. Particularly important to this program was EBR-II because impurity meters could be tested under reactor operating conditions on the Radioactive Chemistry Loop, through which a small fraction of the primary sodium coolant could be circulated.

In the early 1970s, the Sodium Technology Program grew to an effort level of about 35 staff members. Fred Cafasso headed up the Sodium Chemistry and Analytical Standards programs. Paul Nelson was in charge of developing on-line impurity meters and administering a National Meter Program, which involved other national laboratories and commercial organizations.

ANALYTICAL STANDARDS PROGRAM

The objective of this program was to establish reference and standard methods for sodium analysis and to certify them for national use. Development of sampling methods and equipment was a considerable part of this effort. To help carry out these responsibilities, CEN organized, under Bob Meyer, a National Standards Working Group which involved representatives from several other laboratories in the United States. With the help of this group, a manual of analytical procedures was prepared for analyses of sodium and the reactor cover gas. The analytical methods were evaluated by a series of round-robin analyses by the various laboratories. After some difficulties with the procedures were resolved, an approved manual of sodium analytical methods was published. Researchers in the Standards Analytical Laboratory were Max Adams, Murray Barsky, Harry Edwards, Bob Haglund (MST), Al Panek, Mike Roche, Laury Ross, and Stan Skladzien.

One of the major advances in this program was the development of an improved method for determining the chemical activity of oxygen in sodium. Developed by Dale Smith of MST and Murray Barsky, the method involved equilibration of thin wires of vanadium with the liquid sodium at 750°C. The oxygen activity in the sodium could be derived from the oxygen content of the vanadium wire and data on the distribution coefficient of oxygen between vanadium and sodium.

NATIONAL METER PROGRAM

This program consisted of coordinating, as well as participating in, a national program to develop, test, and establish commercial availability for impurity meters to be used in FFTF and other sodium-cooled fast reactors. Meters were developed for oxygen, carbon, and hydrogen, as well as a detector of water leakage into sodium in a steam generator by monitoring the hydrogen concentration in the secondary sodium as it exited the steam generator.

Oxygen Meter. The oxygen meter chosen for testing and further development was an electrochemical device developed by the United Nuclear Corporation (UNC). It was a galvanic cell having a thorium oxide-yttrium oxide $(ThO_2-Y_2O_3)$ solid electrolyte and a coppercopper oxide (Cu-CuO₂) reference electrode. The cell developed a voltage that was dependent on the oxygen activity in the sodium. The electrolyte was in the form of a thin-walled tube of about 3/4-in. diameter, which was produced by isostatic pressing. The reference electrode material was contained in the tube around which the sodium flowed. Several other reference electrode materials were tested, namely, Na-Na₂O, Sn-SnO₂ and oxygen gas. The oxygen-gas electrode was selected. Most of the development work on the

oxygen meter was done by Lou Bartholme, Verne Kolba, Larry Marek, John McKee, Dick Schlueter (MST), and Don Vissers. Fred Cafasso and George Stavropoulos conducted some basic electrochemical studies of oxygen in sodium.

Twenty oxygen meters were tested to give a statistical measure of their performance, ten in CEN in a specially built loop, the Oxygen Meter Rig, and ten in Westinghouse Electric Corporation's Advanced Reactor Division at Hanford. Argonne people in this effort included John McKee, Paul Nelson, and Don Vissers. The meters were calibrated over an oxygen concentration range of 1 to 15 ppm, vanadium-wire equilibration using the procedure. The meters performed very well. Equipment used for oxygen meter calibrations is shown in Fig. 4-12.



Fig. 4-12. Oxygen Meter Calibration Equipment

Carbon Meter. A carbon meter had also been developed by UNC. A diffusion-type meter operated at 750°C, it was based on the principle that the rate of carbon diffusion through an iron membrane, at constant sodium flow rate, depends on the concentration of carbon in the sodium. The carbon reaching the other side of the membrane reacted with a flowing moist hydrogen-oxygen mixture to form CO, which was catalytically converted to CH_4 (methane), whose concentration was measured in a flame-ionization detector. A meter was calibrated by equilibrating sodium of known carbon activity with a metal specimen (*e.g.*, Fe-8 wt% Ni). Figure 4-13 shows the equipment module that was used for the equilibration.

The response time of the carbon meter to a step change in carbon concentration was about five minutes—somewhat slow, but adequate for reactor use where rapid changes of the carbon concentration in sodium would not be expected. John Allen, Charles Luner, Paul Mack, Don Raue, Mike Roche, Westly Ruther (MST), and Stan Skladzien were involved in the development of the carbon meter.

Hydrogen Meter. The hydrogen meter was developed for rapid detection of minute leaks in a steam generator of a sodium-cooled fast breeder reactor. The meter was patterned after one used successfully by Électricité de France, which was based on the rapid diffusion of hydrogen through a nickel membrane and subsequent measurement of the hydrogen concentration with a mass spectrometer. A vacuum drawn on the back side of the membrane provided an activity gradient that caused the hydrogen to diffuse.

Two versions of the hydrogen meter were developed in CEN under the leadership of Don Vissers. Lou Bartholme and John Holmes were also involved in this work. One version was the equilibrium hydrogen meter. It measured the hydrogen pressure above the sodium, which could be related to the hydrogen pressure in the sodium by Sievert's Law:

$$\mathbf{S} = \mathrm{KP}^{1/2}$$

where S is the concentration of sodium in hydrogen, ppm; K is Sievert's constant, ppm-torr^{1/2}; and P is hydrogen pressure, torr. Figure 4-14 shows an in-line arrangement of a hydrogen detector. The remarkably precise



Fig. 4-13. Module for Specimen Equilibration Carbon Meter



Fig. 4-14. Hydrogen Activity Meter

results from this meter are illustrated by the calibration curve in Fig. 4-15. The other version, the leak detector, was operated in the dynamic mode. The flux of hydrogen through the membrane was determined by monitoring the current to the ion pump, which maintained a vacuum on the back side of the membrane. When operated in the dynamic mode, the hydrogen meter was a highly effective leak detector. It satisfied very well the requirements for such a meter of high sensitivity, rapid response, reliability, and ruggedness. A 4% change from an initial hydrogen concentration

of 0.1 ppm could be detected within ten seconds.

Impurity Meter Modules. Two modules containing impurity meters and provisions for equilibration and temperature and flow control of metal specimens were designed and built for testing by Don Cissel on the Radioactive



Activity Meter

Sodium Chemistry Loop at EBR-II (see Fig. 4-16). Such modules were slated for installation at FFTF.

Similar meter modules were also tested at CEN on a small pumped-sodium loop called the Apparatus for Monitoring and Purifying Sodium (AMPS). This apparatus was built to characterize impurity levels in cold-trapped sodium as a function of several operating variables. Cold trapping (precipitation of impurities on a cold finger) is the normal method of maintaining sodium purity in sodium-cooled fast breeder reactors. The modules performed very well, both at EBR-II and on AMPS. Both types of hydrogen meters were installed on the EBR-II secondary cooling system, where they proved to be very reliable. The principal CEN personnel in this project were Lou Bartholme, John Holmes, Verne Kolba, John McKee, Paul Mack, Chuck McPheeters, Paul Nelson, Don Raue, Stan Skladzien, Mike Slawecki, and Don Vissers.

At EBR-II, the oxygen concentration in the primary sodium was only 1 ppm, much lower than had been found by the previously used chemical distillation procedure. The hydrogen concentration obtained by the equilibrium hydrogen meter was only 60 ppb. The



Fig. 4-16. Oxygen-Hydrogen Meter Module

concentrations remained essentially constant during the long time over which they were followed. This observation removed much of the concern about the level of impurities in cold-trapped sodium and on concentration fluctuations caused by system upsets. As a consequence, interest in installing impurity meters on the FFTF primary system waned. (FFTF has no secondary sodium system, the heat being exhausted to the atmosphere.) Installation, operation, and maintenance of the meters were eventually judged not to be cost effective, so the impurity meter program was phased out.

STEAM GENERATOR LEAK DETECTION

As part of the General Electric Company's program on steam generator systems development for a liquid metal fast breeder reactor (LMFBR), the Division was given responsibility for technical direction of work to evaluate leak-detection systems. Most of this work was conducted at the Sodium Components Test Installation (SCTI) at the Liquid Metal Engineering Center in Canoga Park, CA, where a large 30-MW steam generator was under test. The leak-detection system that was evaluated consisted of two ANL hydrogen detectors and two Westinghouse oxygen meters in the sodium, along with a gas chromatograph and a hydrogen meter in the cover gas. The covergas hydrogen meter consisted of a nickel diffusion tube surrounded by a heater that induced cover gas to flow past the diffusion tube by natural convection. The diffusion tube had to be heated to about 540-650°C to obtain performance comparable with that of insodium meters at 485-510°. Steady-state hydrogen and oxygen concentrations in the sodium were 60-80 ppb and 0.6 ppm, respectively. Steam-generator leaks were simulated by injecting hydrogen or water into the flowing sodium at rates ranging from 1×10^{-6} to 2×10^{-4} lb H₂O/sec.

Many tests were performed on the SCTI. At low sodium temperatures (about 200-300°C), the rate of solution of hydrogen in sodium is low, so bubbles of hydrogen entrained in the sodium reached the cover gas before dissolving. Under these conditions, a cover-gas hydrogen meter provided better sensitivity and better response than in-sodium hydrogen detectors. At temperatures above 370°C, the cover-gas monitor was unaffected by hydrogen injections that were easily detected by the in-sodium monitors. The oxygen meters also showed promise of good sensitivity, but alarm circuitry for them had not yet been developed when the program was terminated. From the information obtained, it was determined that water inleakage rates of as low as 2×10^{-5} lb H₂O/sec could be detected in less than one minute in the secondary loop of an LMFBR, well below leak rates that could cause significant damage in five minutes (approximately 10^{-3} lb/sec). The work at SCTI was terminated in October 1973. Chuck McPheeters and Don Vissers were involved in this work.

POST-1974 SODIUM TECHNOLOGY PROGRAM

The CEN sodium technology program underwent some significant changes in 1973 and 1974 as a result of budget cuts and shifting priorities by the AEC. During the 1974-1980 time span, the program consisted of three major areas of study: (1) tritium behavior and control, including development of in-sodium tritium monitors, (2) design and regeneration of cold traps used in LMFBRs for removal of impurities from sodium, and (3) processing of bulk sodium for use in LMFBRs or for disposal.

Tritium Behavior, Monitoring, and Control. A tritium monitor was developed to facilitate studies of tritium behavior in LMFBR systems. The tritium monitor, illustrated in Fig. 4-17, operated on the same principle as the that of the sodium meter, namely, the rapid diffusion of hydrogen isotopes through nickel membrane. Sodium-containing а tritium flowed on one side of the membrane while a sweep gas of argon-1% hydrogen flowed on the other. Tritium diffusing through the membrane was carried by the sweep gas into a proportional counter where the disintegration rate was monitored. The probe was designed to fit into an oxygen-meter housing such as the one that had been installed on many sodium systems and on the EBR-II primary and secondary sodium systems. Because the tritium count rate is affected by many variables, e.g., membrane area and thickness, gas flow rate, counting tube volume, and counting efficiency, each meter had to be calibrated by analyzing sodium samples for tritium.

Tritium Removal by Cold Trapping. Tritium is generated in an LMFBR by three-particle fission and by activation of boron in the control rods and impurities in the core region. It migrates readily through the LMFBR system and, without effective control, would be released to the environment. Cold trapping



Fig. 4-17. Tritium Meter Probe

has been found to be an effective way of removing it from sodium and assuring minimum environmental release.

Hydrogen, one of the major impurities in sodium, is removed as its hydride (NaH) by cold trapping. A study of tritium removal showed that, of the two possible mechanisms, coprecipitation with sodium hydride and isotopic exchange with hydrogen in precipitated sodium hydride, coprecipitation was dominant (see Fig. 4-18).



Fig. 4-18. Cold Trap Efficiency for Tritium Removal from Sodium

Tritium Behavior in EBR-II. Two tritium monitors were installed on the primary and secondary sodium systems at EBR-II and were used to study the behavior of tritium. In these studies, the cold traps on the primary and secondary sodium systems were bypassed to allow the tritium concentrations in these systems to build up. A computer model was developed to predict the changes in tritium and hydrogen concentrations. The measured and predicted concentrations, shown in Fig. 4-19, are in excellent agreement.

The development of the computer model required measurement of the permeation coefficient through the steam generator material (Croloy[®]: Fe-2.25 wt% Cr-1 wt% Mo). The



PHTS = Primary heat-transfer system IHTS = Intermediate heat-transfer system Symbols: Measured values Solid lines: Computer-generated values



formation of iron oxide layers on the steam side of the Croloy reduced the tritium permeation coefficient by a factor of approximately 160 compared to that of unoxidized Croloy.

From this study and the study of tritium removal by cold trapping, it was concluded that, in a 1000 MW(e) fast breeder reactor, more than 99.8% of the tritium generated would be removed by the cold traps. Tritium release to the environment would be well below the limits set by Federal regulations.

Chuck McPheeters, Don Raue, and Tom Renner performed most of the work on tritium in the sodium program.

DESIGN AND REGENERATION OF COLD TRAPS

The major impurities in sodium, hydrogen and oxygen, are removed by precipitation in a cold trap where, at the low temperatures of the trap (about 125°C), the solubilities of sodium hydride (NaH) and sodium oxide (Na₂O) are very low.

×.

Optimization of Cold Trap Design. Because of the reliance on cold traps to control impurities, particularly hydrogen and oxygen, optimization of the cold-trap design was studied in AMPS. Specially designed sacrificial cold traps were used to determine the distribution of deposits within the traps. A one-dimensional computer model was developed to predict the distribution of the precipitates. The deposition of sodium hydride was in excellent agreement with model predictions, but the agreement was not as good for sodium oxide. This was attributed to poor adherence of sodium oxide particles and to an inaccurate or drifting oxygen meter. Most of the precipitated material in an LMFBR cold trap is expected to be sodium hydride.

Cold Trap Regeneration. Cold-trap regeneration was investigated because of the likelihood that a secondary cold trap would plug in about one year as a result of diffusion, into the sodium, of hydrogen generated by water-side corrosion in steam generators. Replacement of a cold trap would be difficult and costly. A study was made of cold-trap regeneration by thermal decomposition of the sodium hydride under vacuum. The released hydrogen (and tritium) would be converted to water for subsequent disposal. Rapid release of hydrogen at temperatures between 300 and 400°C showed this to be a feasible procedure, but the program was terminated when the Clinch River Breeder Reactor (CRBR) was cancelled in 1983.

BULK SODIUM PROCESSING

This program consisted of two major activities: (1) reclaiming or upgrading sodium from various sources for use in the CRBR and (2) disposal of contaminated sodium. Sources of sodium for the CRBR included the two decommissioned reactors, Hallam and Fermi, which amounted to about one million pounds of the metal, and commercial-grade sodium, which contains too much calcium but is onequarter as expensive as reactor-grade sodium. A simple, inexpensive method for calcium removal was therefore sought.

Reuse of Sodium from the Fermi Reactor. In experiments conducted by Don Raue and Art Youngdahl (MST), analysis of Fermi sodium showed that it was suitable for direct use provided that it was passed through a 20-µm filter to remove carbon-bearing particulates. The program was ended before Hallam sodium could be sampled and analyzed.

Removal of Calcium from Commercial-Grade Sodium. Sought in this program was a calcium-removal procedure that could be used at the reactor site so that tank-car quantities of commercial-grade sodium could be processed by passing it through a calcium-removal procedure and into sodium storage tanks. Several selective calciumoxidation procedures were conceived, but the effort died when the CRBR was cancelled. These studies were made by Ralph Leonard, Chuck McPheeters, Don Raue, Tom Renner, Stan Skladzien, Ray Wolson, and Art Youngdahl (MST).

Recovery of Contaminated Sodium. A distillation process was developed for recovering sodium drained from used cold traps and other equipment components. Fission-product decontamination factors greater than 100 were achieved in a small (10.2-cm-dia) distillation column. The principal contaminant in the product was cesium. If desired, additional removal of cesium could be achieved by passing the recovered sodium through a reticulated vitreous carbon trap. Such a trap had been used successfully at EBR-II to remove cesium-137 from the primary sodium.

Disposal of Contaminated Sodium. A considerable quantity of contaminated sodium had accumulated in the U.S. as a result of LMFBR operations and reactor-development programs. In the CEN Division, Chuck McPheeters, Ray Wolson, Bali Misra, and Stan Skladzien investigated possible processes to convert the contaminated sodium and sodium-bearing waste to a disposable form.

A calcining process proved to be effective for converting sodium to sodium oxide, which could then be converted to a silicate glass for disposal. In the process, sodium was introduced into the upper end of a slanted rotary-drum reactor which had been preloaded with sodium oxide and was operated at a temperature of 200°C. Oxygen slowly introduced into the exit end of the reactor smoothly converted the sodium to sodium oxide. The process was also demonstrated, using a 55-gal drum as the reactor.

PERSONNEL

The following individuals were involved in the sodium technology program in the 1970s: Max Adams, John Allen, Murray Barsky, Lou Bartholme, Bob Blomquist, Les Burris, Fred Cafasso, Norm Chellew, Sanat Dhar, Joe Draley, Jim Eberhart, Harry Edwards, Magdy Farahat, Hal Feder, Erwin Filewicz (EBR), Joanne Fink, Al Fischer, Don Fischer, Sherman Greenberg (MST), Bob Haglund (MST), Dave Hebditch, John Heiberger, John Holmes, Honesty, Jimmy Chuck Humphrey, Les Jardine, Tom Kassner, Bob Kessie, Verne Kolba, Wally Kremsner, Romesh Kumar, Len Leibowitz, Ralph Leonard, Charles Luner, Paul Mack, Larry Marek, John McKee, Chuck McPheeters, Bill Mecham, Bob Meyer, Bill Miller, Bali Misra, Paul Nelson, Al Panek, John Pavlik, Don Raue, Tom Renner, Mike Roche, Laury Ross, Westly Ruther (MST), Atul Sheth, Slawecki, Stan Skladzien, George Mike Tetenbaum, Ewald Stavropoulos, Marv

Veleckis, Pete Vilinskas, Don Vissers, Ray Wolson, and Art Youngdahl (MST).

Fuel Element Failure Detection

Considerable effort, mainly by Norm Chellew, Les Coleman, Bob Kessie, and Bill Miller, was devoted to developing methods for detecting fuel-element failures for application in FFTF. The methods under consideration were based on cover-gas analyses of one kind or another, for example, detection of xenon and krypton isotopes in the cover gas by gamma-ray spectrometry. Out of this work evolved a very effective gas-tagging technique in which different ratios of Xe-133 and Xe-135 were added to the plenums of the fuel elements. If a fuel element failed, not only could the failure be detected, but the particular subassembly could be identified by the isotopic ratio. This tagging technique was used with great success until EBR-II was shut down in 1995.

Solar Energy

Solar energy, at first glance, would seem to be an ideal way to meet many of the nation's energy needs-it is renewable, non-polluting, and available in large quantities. In practical application, however, it poses a number of difficult problems. One is its intermittent availability both on a daily and seasonal basis, and during long periods of overcast weather in many parts of the country. Various means of energy storage, including pumped hydroelectric systems, flywheels, storage batteries, and conversion to hydrogen have been proposed to solve this problem, but have not come to commercial fruition. The other major problem is that the low intensity of sunlight requires that its energy be concentrated in some way to provide the high-grade energy needed for most applications. For example, solar airconditioning using the ammonia-water cycle needs a minimum temperature of about 120°C,

and large central power plants require temperatures of at least 300-600°C. In the case of photovoltaic cells, each cell typically produces about 0.5 V, so many cells are needed to obtain a useful voltage, and a large area is required to achieve the necessary power. In the early 1970s, all of these problems were being addressed in projects at various research organizations.

In August 1975, the Solar Energy Project at ANL was transferred from the ANL Accelerator Research Facilities (ARF) Division to the Chemical Engineering Division. The program was aimed toward the development of advanced solar collectors based on a concept used originally by Roland Winston of the University of Chicago to collect Cherenkov radiation in research studies. This concept, known the Compound Parabolic as Concentrator (CPC), used two parabolic surfaces to reflect and concentrate solar radiation onto an absorbing medium. The parabolic surfaces were in the form of a trough oriented in an east-west direction, with the opening of the trough aimed south. To increase the effective area, multiple troughs were placed side-by-side to form an array.

The geometry of the collectors was designed to concentrate the radiation without focusing the light, which permitted the collectors to accept the radiation over a relatively wide angle. This feature eliminated the need for expensive sun-tracking equipment. Some CPC collectors with low concentration capability (2X) could be stationary throughout the year, but higherperformance units required periodic readjustments. The solar program was oriented initially toward high-temperature (150-250°C) collectors suitable for solar thermal power generation or for industrial process heat. For successful practical application, the life-cycle cost of delivered energy from solar systems would have to compete with that from fossilfuel systems, so a major program objective was to develop low-cost solar collectors.

Flat-plate (non-concentrating) solar collectors were limited by heat losses to a maximum operating temperature of about 100°C, which is insufficient for absorption-cycle air conditioning. The required temperatures were readily achievable, however, with CPC collectors having modest concentration levels of 3-10X. With higher concentration levels, it appeared that more demanding applications such as industrial process heating and power generation could be satisfied.

Application of the CPC collector to the photovoltaic conversion of solar energy to electricity was also of interest. The use of reflective surfaces decreased the amount of silicon required for a given power output, which might allow a five- to eight-fold decrease in the cost per peak kilowatt (defined as a kilowatt at noon on a sunny day).

Initial collector arrays built and tested at ANL had demonstrated the capability to concentrate sunlight without tracking the sun, and the collection efficiency was higher than that for conventional flat-plate collectors. One of the major goals early in this program was to develop inexpensive materials and fabrication methods for the curved, reflective trough surfaces. Materials used in these studies included thermoformable plastics, foamed plastics, roll-formed metals with reflective surfaces, and silvered glass.

Several collector arrays were designed and constructed during the course of the program. A prototype thermal collector was designed, built, and operated at temperatures over 250°C. A typical design for a small, lightweight 1.5X thermal collector is shown in Fig. 4-20. This collector resembled a conventional flat-plate collector in its exterior appearance, but it required no sun-tracking or movement during use. The reflective troughs, fabricated from plastic or thin sheet metal, directed the incoming light onto an absorber located within an evacuated glass tube. A fluid flowing through tubes attached to the absorber plate recovered the thermal energy. A glass cover



Fig. 4-20. Lightweight Solar Collector

over the assembly protected the troughs from dust, snow, *etc*. Collectors of this general type would be suitable for process-heat and airconditioning applications.

prototype Three collectors were constructed: (1) a low-cost 3X concentrator having plastic mirrors and an area of about 6 sq ft, which would require repositioning four times per year, (2) a 1.5X concentrator with rolled aluminum mirrors and an area of about 8 sq ft, which would not require periodic adjustments, and (3) a 1.5X collector panel with an area of about 30 sq ft in a configuration envisioned for mass production. To expedite transfer of this technology to industry, ANL worked closely with several industrial firms, including General Electric Co., Chamberlain Mfg. Corp., Corning, Inc., and Owens-Illinois, Inc. In 1977, the 1.5X CPC cusp collector was selected by Industrial Research magazine as one of the nation's 100 most significant technological developments in that year. Two licensees of the DOE patent, Sunmaster Corp. and Energy Design Corp., began marketing commercial versions of this collector and half a dozen or so other firms also became licensees. By 1979, Sunmaster and Energy Design were selling units commercially, and a 200-ton air conditioning machine using a 13,400-sq ft collector array at the Frenchmen's Reef Hotel in St. Thomas, Virgin Islands, was started up as a demonstration project. Several CEN personnel were

instrumental in making this demonstration a success. At this point, the CPC concept had been developed and demonstrated, so the CEN staff turned mainly to modeling studies for further design optimization and materials selection. Further attention was given to process heat for industrial use.

Research and development continued on the photovoltaic application of solar concentrators. A dielectric CPC panel was designed, built, and tested. This panel, which was four feet square, produced 125 W of electrical power, and it required only 20% of the silicon needed for a conventional flatplate photovoltaic panel of equivalent power, which illustrated the potential for a major cost reduction.

As of 1978, the ANL solar energy program was an interdivisional effort in which CEN had the responsibilities for development of improved solar collectors, development of a passive cooling system based on seasonal storage of ice, and provision of technical assistance to the National Solar Energy Demonstration Program. Most of the development work had been subcontracted. As a part of the ANL program, a unique, fully instrumented facility was built for testing collectors and evaluating new designs. Figure 4-21 is a photograph of this facility, which was located in an area just south of the ANL Guest Facilities.

A new program was started in 1978 on thermal energy storage for cooling applications. This was an outgrowth of the CEN effort on the use of solar energy for cooling buildings. This concept involved a large, well-insulated tank of water buried underground near the building. Freezing units at the bottom of the tank formed and released sheets of ice, which floated upward. Refrigeration was achieved by vaporization of ammonia in the units, rising of the vapor to above-surface condensers, and gravity return of the condensate to the freezing units. Operation ceased when the air temperature rose



On the right is a 3X collector for process heat application that operates at 200°C; at the center, still covered, is an experimental 3X collector with low-cost plastic mirrors; to its left, is a 1.5X collector that operates at 150°C without tilt adjustments.

Fig. 4-21. Solar Energy Test Facility

above freezing, and the system was totally passive with no need for external power. Estimates indicated that a tank with a height and diameter of 15 ft or so could provide sufficient cooling capacity for a wellinsulated family home.

As was the case with most of the other CEN programs in the late 1970s, the DOE felt that they needed more technical and management assistance in the national program, so a substantial part of the CEN manpower was diverted to those activities.

Bill Schertz was responsible for getting the solar program underway in CEN, and for the continuing management of the CEN and other ANL solar programs. Don Webster was the cognizant Associate Division Director. Other personnel who worked on the program included John Allen, Norm Levitz, Bill McIntire, Kent Reed, Bob Rush, and Alvin Wantroba.

Fuel-Cycle Studies

With the administrative reorganizations occurring during the changeover from the AEC to ERDA and then to DOE, the confusion of the financial transition quarter in 1976, and other political wind shifts in the 1970s, the engineers and scientists working on nuclear fuel-cycle programs sometimes felt as if they were living through a chapter of The Perils of Pauline. Programs seemed to be started and then terminated or redirected suddenly more in response to current political considerations than to the long-term potential benefits of the work. Nevertheless, a sizable amount of fuel-cycle technology was generated during this period.

DEVELOPMENT OF ADVANCED FUEL RECOVERY OPERATIONS

In mid-1969, development work on pyrochemical processes, in particular, salt-transport processes, was terminated. At a reduced level of effort, a program to support the reference process for recovery of fuel from liquid metal fast breeder reactors (LMFBRs) was instituted. The reference process was a modification of the Purex solvent-extraction process, mentioned in Chapter 1, that had been developed for recovery of spent light water reactor (LWR) fuels. It was basically a chop-leach process to segment and subsequently dissolve UO₂ and PuO₂ mixed oxide ("MOX") from fast reactor fuels. Concentrations of the dissolver solution constituents were then adjusted to provide a feed solution for the solvent-extraction operation. The major effort on the development of this process was at Oak Ridge National Laboratory. The objective of CEN's work was to investigate alternative steps that might improve the reference process. The major elements of the program were the following:

- 1. Liquid metal decladding.
- 2. Fluidized-bed conversion of dissolved uranium and plutonium nitrates to solid oxides.
- 3. Adaptation of centrifugal contactors for the solvent-extraction operation.
- 4. Electrolytic reduction of tetravalent plutonium in the solution to the trivalent form.
- 5. In-line analysis of mixed oxides during fabrication.

This program capitalized on CEN's extensive experience in liquid metal and molten salt technology, centrifugal contactors, and fluidized-bed technology. It was terminated, however, in April 1973, when major reductions were made countrywide in research and development funding by the AEC in order

to concentrate financial resources on the Fast Flux Test Facility (FFTF), which was then under construction at Hanford, Washington.

Liquid Metal Decladding of Reactor Fuels. The most difficult and costly aspect of reprocessing LMFBR fuels by the Purex process was the head-end operation, which consisted of cladding removal, sodium and iodine removal, fission-product and introduction of fuel into the dissolver. The reference process for preparing fuel for dissolution called for shearing of whole fuel subassemblies to produce short pin segments, 1/4- to 1/2-in. long. Problems encountered at Oak Ridge with the shearing operation were expected to become more difficult with highly irradiated fuels. Stimulated by their extensive experience with liquid metals and molten salts, workers at CEN began an investigation of liquid metal decladding.

In liquid metal decladding, the cladding was removed by slowly immersing a subassembly, from which the end hardware had been removed, into molten zinc at 800°C. The zinc dissolved the stainless steel cladding. The uranium and plutonium oxides, which were not affected by the zinc, were collected in a basket at the bottom of the zinc pool. An overlying layer of molten salt served to collect the iodine, probably as potassium iodide, and also to restrict the rate of zinc vaporization. The amount of steel that could be removed far exceeded the solubility of iron in the zinc, indicating a corrosive, grain-boundary attack on the stainless steel. The zinc-steel slurry could be pumped to a zinc-distillation apparatus, where the zinc would be distilled for recycle, and the steel residue removed to waste.

Cladding from fuel elements could be removed in about two hours or less. Fissionproduct iodine was retained completely in the overlying salt layer. Centrifugal pumps were used successfully to transport liquid metal alloys between vessels.

In the proposed ANL head-end flowsheet, the uranium and plutonium oxides were reduced to metal by magnesium and calcium reductants dissolved in zinc. The product metals were recovered by distilling off the solvent metals or by converting them to nitrides by pumping the product solution through a bed of calcium nitride (Ca_3N_2). The uranium-plutonium product, either metal or nitride, was to be fed to a dissolver for preparing feed solution for the solventextraction steps.

Decladding by melting stainless steel cladding and allowing it to drain away from the oxide fuel columns at a temperature between 1490 and 1650°C was also investigated. Work ended at an early stage when the Advanced Fuel Processing Program was terminated in 1973.

Irv Winsch, Terry Johnson, Dean Pierce, and Bill Miller were responsible for most of the work on this program.

Fluidized Bed Conversion of U/Pu Nitrates to Oxides. Following recovery of uranium and plutonium from spent MOX fast reactor fuels, it is necessary to convert the uranium-plutonium nitrate solution from the solvent extraction process to oxides for refabrication of new fuel. The process in use at the time was a multipass batch procedure consisting of precipitation, filtration, and calcination. The presence of plutonium introduced several problems resulting from its toxicity, intrinsic gamma radiation, and need to avoid nuclear criticality. As a result, conversion and fuel-fabrication operations had to be conducted remotely in glove boxes. A need for an improved process amenable to continuous operation was apparent.

The Division investigated the use of fluidized beds, which may be operated in a continuous mode, for the nitrate-to-oxide conversion. Supporting the denitration effort was a laboratory program to characterize the properties of the oxides produced under various denitration conditions and to determine their dissolution rates in nitric acid.

A fluidized-bed pilot plant (see Fig. 4-22) was constructed and operated in the early 1970s. The major components were geometrically safe (4-in.-dia) denitrator and a fluidized-bed reduction unit (1.6-in. dia) for reduction of the UO_3 -PuO₂ product of denitration to UO_2 -PuO₂. These, plus auxiliary systems, were housed in a large glove box.

Denitration runs were performed over the temperature range of 300 to 450° C. About 25 kg of UO₂-2.2 wt% PuO₂ was prepared. (Had the program continued, products with higher plutonium concentrations would have been prepared.) A planned assessment of the sinterability of the mixed oxide product, important for the production of suitable oxide pellets, was not done because of program termination. However, oxide pellets produced in-house appeared to be satisfactory, having densities that were 84% of the theoretical value. The process was operable over the range of plutonium concentrations of interest and with plutonium nitrate alone.

This program, led by Norm Levitz, also involved Dave Grosvenor, Nick Quattropani, Gale Teats, and Sy Vogler.



Fig. 4-22. Denitration Pilot Plant

Development of Centrifugal Contactors.

Development of centrifugal contactors for use in the Purex-type solvent-extraction process for LMFBR fuels was begun in 1970. The objective was to guarantee nuclear criticality safety by developing a centrifugal contactor having a maximum diameter of four inches. Other advantages of the centrifugal contactor are high efficiency, low holdup of the organic and aqueous streams, and improved ease of operation and maintenance. Radiation damage to the organic solvent is minimized by the short time the solvent is in contact with the highly Centrifugal radioactive aqueous phase. contactors are so efficient that each unit in a bank of contactors can be counted as a theoretical stage.

Centrifugal contactors were first developed at the Savannah River Plant, where they were installed in one of the Purex lines for the extraction-scrubbing step. Their performance was outstanding. Responsible for their development was Don Webster, who was hired into the CEN Division as an Associate Director in 1967. He oversaw the CEN development of centrifugal contactors for LMFBR process applications. The principal investigator was George Bernstein, and others in the program included Dave Grosvenor, John Lenc, Dean Pierce, Nick Quattropani, and Noel Vargo. Others who became involved in applications of the centrifugal contactor were Ralph Leonard, Aldona Siczek, Janet Meisenhelder, Martin Steindler, and Tony Ziegler.

An annular mixing design was adopted for the ANL contactor (see Fig. 4-23). In this design, a large-diameter hollow rotor was employed within an outer casing. Mixing was effected by skin friction between the rotor and the casing. Rotor speeds ranged between 1,000 and 6,000 rpm; the larger the unit, the lower the speed. The mixed aqueous and organic phases flowed into the hollow rotor through a hole in the bottom and were separated efficiently by centrifugal action. The separated phases flowed through their respective ports, each going in an opposite direction to the next contactor.

Terminated in 1973, this program was resumed in 1977, and larger 25-cm (about 10-in.) diameter units were also constructed for application to LWR fuel processing. However, focus was soon restricted to the smaller units when commercial processing of LWR fuel in the United States was banned. A theoretical analysis of annular mixing in a centrifugal contactor resulted in development of a dimensionless dispersion number by which various combinations of variables (*e.g.*, rotor speed, width of annulus, residence time of fluids in the annulus) could be used to give satisfactory mixing.

Electrolytic Reduction of Plutonium in the Purex Process. Electrolytic reduction of plutonium from the tetravalent to the trivalent state, in which it is insoluble in the organic phase, was investigated in the early 1970s. This reduction is necessary to separate plutonium from uranium in the Purex process. Although chemical reductants, such as ferrous sulfamate [Fe(H₂NHSO₃)₂], are very effective, their ultimate appearance in the aqueous waste limits the waste-volume reduction by evaporation of the water. Successful electrolytic reduction of tetravalent plutonium was achieved in the presence of 0.005 M hydrazine (N_2H_4) , but difficulties were encountered in maintaining electrode performance. As the program ended, titanium and gold electrodes were being tested. John Heiberger, Mike Krumpelt, and Martin Steindler performed the electrolytic reduction studies.

In-line Analysis during Fuel Fabrication. A program for conducting in-line analyses of U/Pu mixed oxide fuel during its fabrication was partially completed at program termination in 1973. An in-line X-ray fluorescence method was developed that was capable of measuring the U:Pu ratio to within



Fig. 4-23. Annular Centrifugal Contactor

the required accuracy of 0.5%. Work on an X-ray diffraction method to measure the ratio of oxygen to plutonium plus uranium, O:(U + Pu), was underway when the program was cancelled. This work was done by Martin Steindler and Glenn Schnizlein with support from the Analytical Chemistry Laboratory.

POST-1973 FUEL-CYCLE PROGRAMS

Following termination of the large fuel-cycle programs in 1973, the Division conducted a number of smaller activities in this area during the remainder of the decade. Most of this work was done under the direction of Martin Steindler. Because of its diversity, it is difficult to give due credit for each aspect of the work, but the following individuals were involved in one way or another. Tom Gerding, Les Jardine, Ruth Juvinall, Rudolf Keller, Bob Kessie, Bruce Kullen, Romesh Kumar, Norm Levitz, Ralph Loutfy, Bill Mecham, Bob Nelson, John Parks, Wally Seefeldt, Martin Seitz, Verne Trevorrow, Charlie Wach, and Irv Winsch. Fuel Reprocessing. Beginning in October 1974, a one-year study was directed toward the reprocessing of carbide and nitride fuels. Reference flowsheets were evaluated with safety. emphasis on environmental, and of recovery materials-protection aspects integrated concept operations. An for reprocessing and remote fabrication of these advanced fuel types was developed.

Reliability of High-Level Waste Canisters. Also completed in 1975 was a one-year study to determine the reliability against failure and leakage of canisters used to contain high-level radioactive wastes in glass and calcined forms. The storage times considered for the canistered wastes were 10 years underwater at a reprocessing plant storage pool, followed by 100 years at a retrievable surface storage facility. Final emplacement would be in а geologic repository. In general, the study exposed a woeful lack of materials-property information needed for reliable analyses. Even so, canisters of 304L stainless steel showed promise of reliable storage of the wastes over the 100-year time span.

Encapsulation of Radioactive Wastes in Metal. The Division investigated incorporation of high-level waste in a metal matrix such as lead as an alternative to incorporation into glass monoliths. Considered was waste in the forms of calcined pellets and vitrified borosilicate glass beads. Dispersion of these wastes in lead produced a two-phase composite containing 60 to 70 vol% of the high-level waste. Advantages of the metalmatrix waste form compared to a glass monolith are higher thermal conductivity, mechanical strength, ductility, and impact resistance. The corrosion rate of lead in salt water is as low or lower than that of glass. Encapsulating the metal-waste composites would further delay the escape of fission products from the waste form. One centimeter of lead would be expected to reduce penetration by salt water for about 3,000 years.

Large cylindrical composites, 4-in. dia by 20 in. long, were made by pouring lead over glass beads contained in a low-carbon steel pot. Impact and leaching tests conducted on small cylindrical composites (2-in. OD by 2 in. long) revealed good impact resistance and low leach rates. A comparison of the cost of metalmatrix encapsulation with that of casting borosilicate glass monoliths showed the processing costs to be about the same within the sensitivity of the cost analyses. The program was terminated at the end of FY 1980.

Salvage of Alpha-Contaminated Structural Materials. Work was conducted to develop processes for cleanup of structural materials (e.g., piping, discarded equipment, and discarded glove boxes) contaminated by transuranic elements. The objective was to reduce the contamination level to less than 10 nCi/g, thereby permitting disposal of the materials as low-level waste or, possibly, their return to beneficial use. Melting contaminated steel materials under a fluoride slag resulted in transfer of plutonium to the slag and a reduction of the plutonium concentration in the metal to below-detectable levels. The very low rate of accumulation of plutonium in the slag would allow many batches of metal to be processed before discard or treatment of the slag for recycle would be necessary.

Storage and Disposal of Tritium. A short study was made on the management of tritium formed in light water reactors (LWRs). Tritium in spent fuel reports to the low-level aqueous waste when the fuel is dissolved and recovered by the Purex process. A conclusion of the study was that the tritium-containing waste could be disposed satisfactorily by injection of the waste into deep underground aquifers.

Consolidation Techniques for Cladding Hulls. Under the leadership of Norm Levitz, work was performed to develop methods for safe and economic management of spent fuel-subassembly hardware components (Zircaloy cladding hulls plus other items such as spacers and fittings) that result from processing LWR fuels. The objective of the program was to reduce the large volume of this waste and eliminate the hazard due to the pyrophoricity of Zircaloy. Ancillary goals were separation of the hulls from long-lived radioactive contamination and, possibly, recovery of the zirconium. The study involved an assessment of the volumes of these wastes. characterization of their composition, and a review of current experience in handling them. This study culminated in publication of tentative criteria for managing cladding hulls and other subassembly hardware.

Studies of Fission-Product Migration in Geological Formations. In the late 1970s, CEN participated in the Waste Rock Interaction Technology Program managed by Pacific Northwest Laboratories. This program concerned the disposal of fission-product wastes in deep underground rock formations, *e.g.*, granite. The geochemistry group in CEN studied transport through the granite host rock of fission-product elements released from a breached waste canister. An experimental study of the migration of cerium, sodium, and cesium through granite (saprolite) under simulated groundwater flow showed that water intrusion did not adversely affect the effectiveness of the granite host rock as a barrier. A conclusion of this study was that site-specific studies are necessary for any host material being considered for a repository (e.g., salt, basalt, or granite).

Other geochemical studies included (1) an applied program to develop well-logging techniques using a pulsed neutron source and gamma or neutron detectors to determine oil levels in the vicinity of a bore hole, and (2) a basic research program to investigate the migration of trace elements in the earth's crust on the assumption that these natural processes could be useful in the design of a repository.

Evaluation of Source Term for Exreactor Fuel Cycles. Work funded by the Electric Power Research Institute was performed to evaluate the plutonium source term for three reactor fuel cycles: LWRs fueled with uranium, LWRs fueled with plutonium, and LMFBRs (see Table 4-15). The source term is the fraction of total plutonium that escapes containment and reaches the environment. For the technology then in use, the fraction was 1×10^{-8} for processing plants and 1×10^{-9} for fabrication plants. Improvements in that technology would reduce these fractions by 100 and 1000, respectively, and it was estimated that future technology could reduce them by another factor of 1000.

LWBR Proof-of-Breeding Analytical Support. In 1978, CEN became a major participant in a program to determine the breeding ratio in the Shippingport Light Water Breeder Reactor (LWBR), which was located in Shippingport, Pennsylvania. This reactor was fueled with a $ThO_2^{-233}UO_2$ fuel. Breeding, if any, would result from generation of U-233 by the reactions

$$_{90} Th^{232} + {}_{0}n^{1} \rightarrow {}_{90} Th^{233} _{90} Th^{233} \rightarrow {}_{91} Pa^{233} + \beta^{-} _{91} Pa^{233} \rightarrow {}_{92} U^{233} + \beta^{-}$$

in which the thorium-232 absorbs a neutron to form thorium-233, which then decays by beta emission first to protactinium-233 and then to the uranium-233, which is fissionable. Our role was to analyze precisely located segments

Table 4-15. Estimated Plutonium Releases, µg Pu/GW(e)-yr

	Currently Used	Currently	Available		Anticipated	
Operation	LWR-U	LWR-U	LWR-Pu	LWR-U	LWR-Pu	LMFBR
Fabrication	-	-	0.7	-	0.0008	0.002
Processing	3450	34	72	0.003	0.008	0.027
Total	2350	34	73	0.003	0.009	0.03

of fuel rods. The results of these analyses were to be used by the Bettis Atomic Power Laboratory to calibrate an Irradiated Fuel Assay Gauge for measurement of uraniumisotope and selected fission-product concentrations in irradiated fuel rods. The fission-product concentrations were used to determine fuel burnup. The Irradiated Fuel Assay Gauge was to be used for making these measurements on hundreds of fuel rods after they had been irradiated for four years in the LWBR.

Very stringent requirements were set for analytical accuracy and precision. Process requirements included high-precision shearing of fuel rods to obtain segments at designated locations along the rod, complete dissolution of a segment, and minimal contamination on successive dissolution of the segments.

Designed and built was a shear capable of locating cuts to within 0.05 mm and of providing at least 99.7% recovery of a sheared segment. Total uranium and uranium isotopic abundance in samples of dissolver solution was determined by mass-spectrometric/ isotopic-dilution procedures. Concentrations of the fission products, Cs-137, Ce-144, and Zr-95, were determined by radiometric techniques. Analyses of fuel-rod segments provided by Bettis showed that their requirements for high analytical precision and accuracy could be met.

Charles E. Stevenson handled the negotiations for this program. Norm Levitz was the Project Leader. Don Graczyk of the Analytical Chemistry Department played a key role in devising the exacting analytical procedures that were required. Other participants in this program are listed in the next chapter.

Nuclear Fusion Energy Research

It seems paradoxical that both nuclear fission and nuclear fusion release large amounts of energy although they are reverse processes. Fission, however, occurs with large atoms

such as uranium and plutonium, which split into fission products, while fusion involves isotopes of hydrogen, which combine to form a larger atom (helium). Both nuclear reactions entail the conversion of a very small amount of mass into a very large amount of energy $(E = mc^2)$. The three isotopes of hydrogen with atomic weights of 1, 2, and 3 ($_1H^1$, $_1H^2$, and ₁H³) are called hydrogen (H), deuterium (D), and tritium (T). Natural hydrogen contains about 0.15% deuterium, which can be concentrated by fractional distillation or electrolysis of water, but many separation stages are required to produce essentially pure D_2O (heavy water). On the other hand, the supply is basically unlimited (sea water, for example). Tritium can be obtained only by nuclear reactions. It decays with a soft β emission and a half-life of about 12 years.

The two nuclear reactions that are usually considered for fusion reactors are D-D and D-T:

$$_{1}D^{2} + _{1}D^{2} \rightarrow _{2}He^{4}$$

 $_{1}D^{2} + _{1}T^{3} \rightarrow _{2}He^{4} + _{0}n^{1}$

To maintain the nuclear reactions at a "break-even" energy level requires a temperature of about 100 million degrees, and a product of plasma density and confinement time of 10^{14} sec/cm³ for the D-T reaction. The requirements are even more stringent for the D-D reaction. If a lithium blanket to absorb neutrons from the D-T reaction surrounds the high-vacuum space around the plasma, the system has a capability for breeding new tritium *via* the reactions

$$_{3}\text{Li}^{6} + _{0}n^{1} \rightarrow _{2}\text{He}^{4} + _{1}\text{T}^{3}$$

 $_{3}\text{Li}^{7} + _{0}n^{1} \rightarrow _{2}\text{He}^{4} + _{1}\text{T}^{3} + _{0}n^{1}$

The bred T is recovered and used to fuel the plasma. Natural lithium consists of about 7.42% lithium-6 in lithium-7. Most of the tritium breeding occurs by the first (lithium-6) reaction, but the second one also contributes

when the neutron energies are below about 3 MeV. The less severe requirements in operating conditions and the possibility of breeding strongly favor the D-T reaction over the D-D reaction for a practical fusion reactor. Lithium metal and its compounds are readily available from commercial sources.

Superconducting magnets are used to levitate and compress the plasma in the vacuum chamber. The best known fusion device is a toroidal or doughnut-shaped chamber, called a "Tokamak," which was used by the Russians, at Princeton University, and eventually by other laboratories. Other experimental devices included a "pinch" magnetic field (the Scyllac machine at Los Alamos) and magnetic mirrors at Livermore National Laboratory. In these devices, the plasma was introduced into the machine by a plasma gun. Another approach to fusion power involves the use of high-power lasers to heat pellets of fuel where the inertia of the material confines the plasma, but work in CEN was limited to the magnetic systems.

A highly simplified version of a fusion system is shown in Fig. 4-24, in which the vacuum chamber enclosing the plasma is called the "first wall." This wall is surrounded by a liquid lithium blanket, which serves as a coolant and neutron absorber, and the whole assembly is surrounded by superconducting magnets to confine the plasma.

Fusion power would have some compelling advantages if it could be developed into a practical technology: (1) The fuel resources, deuterium and lithium, are basically unlimited. (2) Fusion does not produce radioactive fission products, which create a serious wastedisposal problem for fission reactors. (3) There is no possibility of a catastrophic reactor excursion or explosion. The potential problems are a fire if hot liquid lithium should escape from the blanket, and confinement of tritium, which is not highly radioactive, but could be insidious and virtually impossible to recover were it to escape to the environment. The only other significant radioactivity would

be that produced by absorption of neutrons by structural materials in the reactor; the levels of this activity would be orders of magnitude lower than those of wastes from a fission reactor. The principal difficulty with fusion is that maintaining a stable plasma is a formidable problem, which has not yet been solved. In the 1950s, practical fusion power was predicted for the 1990s; and now that we are in the 1990s, it appears that another 40 or 50 years may be needed for it to achieve fruition.

Although Argonne was not recognized as one of the leading players in the fusion program of the early 1970s, it made valuable contributions to the national effort. Later on, CEN became well known for its work on the first wall and other structural hardware, blanket materials, tritium recovery, and neutron dosimetry.

LITHIUM HYDRIDE SYSTEMS

When the fusion work started at CEN, Vic Maroni, Carl Johnson, and others had already been investigating molten salt systems containing lithium hydride (LiH), partly because of the previous interest in regenerative galvanic cells based on hydride systems. This work continued to be supported by the AEC Division of Physical Research, and it was a natural fit with the fusion program when it was started at ANL.

Thermochemical Properties and Solubilities. The thermochemistry of the Li-LiH system had been characterized earlier with respect to the standard free energy of formation of LiH, Sievert's constant for dilute solutions of LiH in lithium, and the equilibrium constant for the formation of LiH. A similar study was conducted on the Li-D system by measuring equilibrium pressures of D₂ at temperatures of 705-851°C, pressures of 0.5-760 torr, and compositions of 0.5-99% LiD. The results showed a small, but measurable difference in the LiH and LiD systems. Because nitrogen



Deuterium and tritium are injected into the system by a plasma gun, where they are confined as a plasma by a magnetic field at a temperature around 100 million degrees. Nuclear fusion reactions occur, releasing large amounts of heat and high-energy neutrons, which are absorbed in a liquid lithium blanket. Helium atoms and ions, including alpha particles, are also generated. To produce useful electrical power, the lithium would be pumped through heat exchangers to convert water to steam to drive turbines. One of the greatest technical challenges, other than maintaining the fusion reaction, is to design a first wall that can withstand the high temperature differential, radiation damage from the neutrons, mechanical stresses, and corrosion by the lithium blanket, which may contain various impurities. Many of the engineering problems with fusion power stem from the enormous temperature gradients between the plasma at about 100 million degrees and the superconducting magnets, which must operate at temperatures near absolute zero.

Fig. 4-24. Simplified Representation of a Magnetic Fusion Reactor

was a potential impurity in fusion-reactor blankets, measurements were also made on the Li-Li₃N system, and the results proved to be in good agreement with existing calorimetric data.

The possibility of extracting bred tritium from a lithium blanket in a fusion reactor was explored by measuring the distribution coefficients of LiT between lithium and molten halide salts at 400-600°C. The results are given in Table 4-16, where K_d is the volumetric ratio of tritium in the salt to that in the lithium. These results showed that the distribution coefficients are favorable for such an extraction.

The solubility of LiD in liquid lithium was measured because cold-trapping was under consideration as a method of removing hydrogen isotopes from lithium blankets. The solubilities (in mol%) were 0.50, 0.84, and 2.30, respectively, at 322, 375, and 451°C. Some studies were also conducted on the ternary system, Li-Al-H, to determine the effects of an additive on the activity coefficients of lithium and hydrogen. Aluminum was of practical interest because it and its alloys were potential low-activation structural materials in fusion-reactor blankets. At low hydrogen concentrations, the equilibrium hydrogen pressure increased monotonically with concentration, indicating a homogeneous condensed phase. At higher concentrations, however, the results suggested a miscibility gap at the lower temperatures.

Table 4-16. Distribution Coefficients of LiT between Lithium and Molten Salts

Molten Salt Composition	Temp., ℃	K _d
LiCl-31 mol% LiF	550	4.1
LiCl-41 mol% KCl	600	2.6
LiBr-41 mol% RbBr	500	1.2

The solubility of oxygen, also a potential impurity in liquid lithium, was measured in a joint effort with Oak Ridge National Laboratory, and preliminary results showed that the oxygen solubility in mole percent, S, was represented by the equation

$$\ln S = 6.610 - 7140 \text{ T}^{-1}$$

where T is in degrees Kelvin.

Hydrogen Permeation Studies. Hydrogen and its isotopes are noted for their ability to diffuse through metals, especially at high temperatures. This Houdini-like behavior was of concern because of the possibility that tritium in the hot liquid lithium blanket would diffuse to the environment through the containment walls not only of the blanket itself but also the lithium pumps, the steamgenerator tubing, and other auxiliary equipment. Studies were therefore initiated on methods of decreasing tritium permeability in various metals. Some of the initial concepts involved multilayer metals, impermeable impurity coatings on the metal surfaces, and inert gas purging with a tritium-trapping capability. Test specimens were normally in the form of sheet or tubing.

The permeation rate, Φ , in units of $[cm^{3}(STP)\cdot mm]/(cm^{2}\cdot hr\cdot atm^{0.5})$, can be expressed by the equation

$$\Phi = \Phi^{\circ} \exp(-Q_{p}/RT)$$

where Φ° is a pre-exponential term, and $-Q_p/RT$ represents the activation energy, which reflects the temperature dependence of the rate. Permeation rates were measured at 10-600 torr of upstream hydrogen pressure and temperatures of 400-800°C. For copper, Types 316 and 304 stainless steel, multilayered specimens of 304-SS/Nb, 316-SS/Cu/316-SS, and 304-SS/Cu/Nb, the values of Φ° ranged between about 1,000 and 12,000, with values of Q_p falling between about 15 and 27 kcal/mol.

The hydrogen-permeation characteristics of vanadium were investigated. The permeability varied greatly, depending on activation (hydrogen firing) and deactivation of the material. At the end of a sixty-day study, an approximately 1-µm-thick surface layer containing oxygen and carbon was observed.

In 1977, permeation studies were continued with emphasis on stainless steel/aluminum bronze combinations. The permeation rates fell from that expected for pure stainless steel to a value about 30 times lower after a few weeks. Examinations of the specimens suggested that the lower rates were due to delamination and oxidation of the aluminum bronze. A similar type of effect was found in the thermal conductivity of a 304-SS/Cu/304-SS tube. The effect was attributed to a buildup of oxide layers at the metal interfaces.

Hydrogen-permeation studies were continued on candidate austenitic (316-SS), nickel (Inconel-625 and -718), and refractory metal (Ti-base) alloys at temperatures between 100 and 800°C and hydrogen driving pressures from 10^{-1} to 10^4 Pa. The objective was to provide information on the probable rate and extent of tritium migration through structural materials in fusion-reactor systems. Surface oxidation of the small amounts of aluminum in the alloys by impurities in the gas reduced the hydrogen permeation rate by a factor of about ten at low hydrogen pressures. The values of Φ ° for the stainless steel and Inconel alloys fell in the range of about $0.2-0.6 \text{ cm}^3/$ $(mm \cdot s \cdot kPa^{0.5})$, with Q values of about 13-15 kcal/mol. Titanium-base alloys were of interest because of titanium's availability, structural strength, low induced radioactivity, and resistance to radiation damage. Titanium, however, reacts with hydrogen to form a hydride, so it might be expected to have a high hydrogen-permeation rate. A study of 5621 titanium alloy (Ti-5 wt% Al-6 wt% Sn-2 wt% Zr-1 wt% Mo-0.25 wt% Si) showed hydrogen-permeation rates about a factor of 1,000 higher than those of stainless steel.

There was no obvious change in the visual appearance or the physical strength of a specimen after the tests.

LITHIUM BLANKET PROCESSING

The objectives of blanket processing in a fusion reactor are to prevent an ongoing buildup of tritium in the lithium and, in the case of a breeder, to recover the tritium for use as the reactor fuel. Two avenues were pursued for these purposes, chemical gas sparging and electrochemical evolution. In both cases, the tritium was first extracted as LiT into a molten salt such as LiF-LiCl-LiBr, which was saturated with metallic lithium from the blanket. In the experimental work, deuterium was used as a stand-in for tritium.

The gas-sparging method was investigated by circulating an argon-HCl mixture in a closed loop through molten LiF-LiCl-LiBr containing small quantities of lithium metal and LiD. The extent and rates of the HCl reactions with LiD and Li were followed by monitoring the off-gas stream for the reaction products, H_2 , HD, and D_2 , with a mass spectrometer. A typical experiment consisted of adding 5 mg LiD and 50 mg Li to about 900 g of LiF-LiCl-LiBr at 500°C while argon was bubbled through the melt. The HCl was then added to the argon to titrate out the Li and LiD. At completion of the reaction, the gas stream was passed through a hot (550°C) titanium bed, which served as a getter for the hydrogen isotopes. In all the experiments, the extraction was complete (within the experimental uncertainty) without excess HCl. The results of this work indicated that molten salt extraction with gas sparging would probably be capable of maintaining hydrogen levels at about 1 ppm by weight in lithium circuits.

The electrochemical method, which consisted simply of electrolyzing lithium hydride at a voltage below the decomposition potential of the molten salt, had the advantages that corrosive gases were not required and the dissolved lithium in the salt did not have to be oxidized. Experiments were performed in which a constant voltage was applied to the salt, and then 5 to 10 mg of LiD was added to the system. The current increased sharply as expected, and then decreased as the LiD was removed from the salt. Again, the removal of LiD was essentially complete, suggesting that this method could also maintain a hydrogen level of about 1 ppm in the lithium.

Lithium-Processing Test Loop. Work began in 1976 on the design and fabrication of a 50-gal (190-L) Lithium-Processing Test Loop (LPTL), which was started up in late 1977. The principal initial objectives were to (1) test the effectiveness of semicontinuous molten salt extraction using a single vessel as a pseudo-mixer-settler, (2) evaluate the efficiency of a high temperature zirconium getter trap and a regenerative cold trap in series for removal of non-metallic impurity elements, and (3) develop impurity control along with processing and monitoring methodology for large liquid lithium loop systems. Provisions were also made for attachment of various types of other experimental test equipment. The general layout of the LPTL, which was located in one of the shielded cells in Laboratory H-126, is shown in Fig. 4-25. A bench-scale mini loop was also constructed and operated to provide technical support for the LPTL.

By mid-1979, the LPTL had reached an operating time of 9,500 hr. At that time the initial objectives had been met, and the focus was shifted somewhat toward (1) demonstrating that the steady-state concentration of bred tritium in the blanket could be limited to about 1 ppm by a continuous tritium-recovery process, (2) developing on-line methods for monitoring tritium and impurities, (3) testing materials and equipment, and (4) providing technical input for other tritium-handling facilities.

Tests of the molten salt-extraction procedure with LiF-LiCl-LiBr showed that the

salt was highly effective in removing hydrogen, deuterium, and carbon from the lithium. Cold trapping proved effective in removing entrained salt from lithium in the extraction unit from >2,000 ppm to <300 ppm. Analyses of zirconium wires exposed to flowing lithium for about 10,000 hr indicated that refractory metals could be used to getter O, N, H, and C. An in-line meter was devised for monitoring hydrogen (and its isotopes) by coupling a hydrogen-permeation probe with a mass spectrometer. Another useful monitoring device was a four-probe electrical resistance meter to determine total lithium impurities, including the hydrogen isotopes.

In October 1979, the electromagnetic pump channel of the loop developed a leak that released 10-20 gal (~ 40-80 L) of hot liquid lithium which caught fire. The fire was well contained, and there was no significant damage beyond the pump area. Although the operators were not pleased by this event, especially since it occurred during Fire Prevention Month, it tended to lay to rest some of the prevailing fears about the severity of lithium fires and difficulties in coping with them. The loop was repaired and placed back in operation.

NEUTRON DOSIMETRY

In 1975, a Dosimetry and Damage Analysis Center (DADAC) was established at ANL as a support group to provide standardized neutrondata dosimetry and damage-correlation parameters to programs determining irradiation effects. The overall program concerned two interrelated areas. one focused on characterization of irradiation facilities in term of neutron flux, fluence, and the energy spectrum, and the other on the development of computer codes to calculate damage parameters from observed irradiation effects. Two types of irradiation facilities were involvedreactors and accelerators. Among these were Argonne's EBR-II and CP-5 reactors and the



The Lithium Processing Test Loop, located in a shielded isolation cell in Laboratory H-126, contained about 50 gal (190 L) of liquid lithium metal at a temperature of about 500°C. Stainless steel was the material of construction. The molten lithium from a reservoir was pumped electromagnetically through flowmeters, a molten salt contactor, getter traps, and cold traps to study various methods of removing hydrogen isotopes and other impurities from the liquid metal phase. Instruments such as a conductivity meter and a mass spectrometer were used to monitor impurity levels. For reasons of cost, availability, and safety, deuterium was used as a stand-in for tritium, which would be the principal isotope in an operating fusion reactor.

Fig. 4-25. Lithium Processing Test Loop

High Beam Flux Reactor at Brookhaven. The accelerator facilities included the Rotating Target Neutron Source and the Davis Cyclograaff, both at Livermore, and a Van de Graaff and research reactor at Oak Ridge. Characterization of the accelerator sources was particularly difficult due to low neutron fluxes and sensitivity of the neutron distribution to the incident angle of the neutrons at close geometries. Damage effects from neutron irradiation include displacement per atom (DPA), primary knock-on-atom distribution, gas generation rates (H and Ne), and transmutation rates. By 1979, sufficient data were available to generate computer codes that could predict radiation-damage parameters with ±10% accuracy for most irradiations. Most of this work was being done to support the Fusion Materials Irradiation Test (FMIT) facility under construction at Hanford at that time. At the end of the 1970s, CEN was serving as a nationwide center for information on dosimetry and radiation damage in fusion systems.

TRITIUM HANDLING AND CONTAINMENT STUDIES

Argonne had played an important role in parametric design and analysis studies of the Tokamak Experimental Power Reactor (TEPR) and The Next Step (TNS) reactor, and in the late 1970s it was involved in similar studies of the engineering test facility (ETF), the commercial fusion reactor (STARFIRE), and the international tokamak reactor (INTOR). The Chemical Engineering Division was responsible for tritium handling and processing systems and, in some cases, for the entire blanket and shield portions of the reactor or facility. STARFIRE was managed by ANL, ETF by ORNL, and INTOR by an International Atomic Energy Authority (IAEA)sponsored group involving USA, the

European Community, Russia, and Japan. The Division, because of the preceding experimental and design work, was able to put together a library of global computer programs with the following capabilities.

- 1. Performing comprehensive analyses of vacuum pumping, tritium handling, system costing, *etc.*, for all types of fusion reactors.
- 2. Unfolding experimental air-detritiation test data to derive tritium reaction parameters, as well as adsorption and desorption rates.
- 3. Performing broad-based thermalhydraulic calculations for a variety of first wall/blanket configurations with various coolants and structural materials.
- 4. Performing finite subsystem analyses of distillation cascades (fuel enrichment), magnetic diverter processing systems, *etc.*

The codes were updated continually as new information became available, and many were supplied to other USA and foreign fusion facilities at their request.

Vic Maroni spearheaded the fusion program of the 1970s. Wally Calaway, Ewald Veleckis, and Bob Yonco did most of the work on molten salt chemistry and blanket processing, and Erv Van Deventer conducted the hydrogen-permeation studies. Jim Weston was primarily responsible for the lithium test loop, and Larry Greenwood handled the neutron dosimetry effort. Rob Clemmer, Pat Finn, and Bali Misra performed the tritium handling and containment studies, which required extensive computer work. Norm Chellew, Bob Heinrich, Bob Land, and two students, Ralph Pelto and Ray Peterman, also contributed to this program.

Materials Chemistry and Thermodynamics

As mentioned in the previous chapter, the thermochemistry program consisted of two parts. One, which was based primarily on combustion calorimetry to measure standard enthalpies of formation $(\Delta H_{f_{298}}^{\circ})$, was under the direction of Ward Hubbard and Pat O'Hare. The other program, led by Paul Blackburn, was aimed primarily toward potential fast breeder reactor fuels and included phase studies together with determinations of higher-temperature heat capacities, enthalpies of transition, and entropies with the ultimate objective of providing a full set of thermodynamic functions for the materials of interest.

CALORIMETRY

As of 1970, fluorine combustion calorimetry had been used to obtain standard enthalpies of formation of 35 elemental fluorides and 21 other compounds. The more conventional oxygen bomb calorimetry had been used to study 15 reactions, and solution calorimetry was used for nine aqueous reactions. Empirical correlations were used to estimate enthalpies of formation of the rare earth fluorides, and work had begun on the use of theoretical calculations (extended Hückel molecular-orbital calculations and *ab initio* calculations based on the Hartree-Fock-Roothan approach), to predict thermodynamic data.

Standard enthalpies of formation were determined for the compounds shown in Table 4-17, using combustion and solution techniques.

The standard enthalpy of formation of plutonium sesquicarbide (PuC_{1.466}), measured by oxygen bomb calorimetry, was -19.4 \pm 0.7 kcal/mol. A redetermination of the enthalpy of formation of liquid HF produced a value of -72.57 \pm 0.09 kcal/mol. Because

Table 4-17.	Compounds Investigated by	
Standard Enthalphy Measurements		

As ₂ S ₃	Cs ₂ U ₂ O ₇	Pu ₂ C ₃
As_4S_4	HF	Rb ₂ MoO ₄
BaMoO₄	K ₂ UO ₄	Rb ₂ UO ₄
BaZrO ₃	Li ₂ MoO ₄	Sb ₂ S ₃
CaUO₄	Li ₂ N	SrUO ₄
Cs ₂ CrO ₄	Li ₂ O	UF ₆
Cs ₃ CrO ₄	Li_2UO_4	UN
Cs ₄ CrO ₄	MgUO ₄	U ₂ N ₃
Cs ₂ Cr ₂ O ₇	MoS ₂	VC _{0.79, 0.85}
Cs ₂ MoO ₄	Na_2C_2	XeF ₆
Cs ₂ Mo ₂ O ₇	NaHC ₂	
CsNO ₃	α -Na ₂ UO ₄	

sodium acetylides were thought to have a role in carbon transport in liquid sodium reactor coolant, the standard enthalpies of formation of Na_2C_2 and $NaHC_2$ were determined from the enthalpies of their reactions with water. The results showed the enthalpies of formation to be 4.77 \pm 0.40 kcal/mol for Na₂C₂ and 23.10 \pm 0.27 kcal/mol for NaHC₂. These values, together with estimates of the entropy and incremental enthalpy functions, suggested that the free energy of formation of Na₂C₂ would make it thermodynamically unstable with respect to graphite and sodium. As information was becoming available on the chemistry of irradiated fuels, the thermochemistry of fission-product oxides became an important subject. The fission products, generated as elements, reacted with the oxide fuel to form mixtures of oxides. Standard enthalpies of formation of Cs₂MoO₄, Cs₂UO₄, Rb₂MoO₄, $BaMoO_4$, and Li_2MoO_4 were determined. Enthalpies of formation were also obtained on compounds of interest for oxide and carbide fuels, $VC_{0.85}$, $VC_{0.79}$, NaUO₃, and α -Na₂UO₄, and other compounds of interest to the nonnuclear energy programs, Li₂S, Li₃N, CsAlO₂,

and KAlO₂. The enthalpy of formation of UF_6 was redetermined when a question arose about the previous value. In addition to the above, LaNi₅ was included because of its possible role as a hydrogen-storage medium, and, toward the end of the 1970s, measurements were started on organic compounds that constitute "building blocks" of coal constituents.

HIGH-TEMPERATURE THERMODYNAMIC STUDIES

The objective of this program was to obtain and thermodynamic physical property information on potential fast breeder reactor fuels. The work was predicated on the use of mixed uranium-plutonium oxide or possibly carbide fuel and liquid sodium coolant. Massspectrographic studies showed that the volatile species resulting from vaporization of (U_{0.8}Pu_{0.2})O_{2-x}, a typical reactor-fuel composition, were UO^+ , UO_2^+ , UO_3^+ , PuO^+ , and PuO_2^+ . The partial enthalpies of sublimation of these species were determined and their partial pressures were derived for oxygen-to-metal (O/M) ratios of 1.92 to 2.0 in the solid phase at 1968°C. To calculate more accurate pressures from the measured ion intensities, one needs to know the ionization probabilities, fragmentation patterns, and partial relative ionization cross sections. Paul Blackburn and Phil Danielson obtained most of these data experimentally, and, with minor assumptions concerning the plutonium oxides, calculated the pressures of the species. The UO_2 and UO_3 pressures were then used to calculate the oxygen pressure. Oxygen pressures or potentials in the fuel were important for several practical reasons in that they affect (1) the extent of cladding attack by oxygen at the cladding/fuel interface, (2) the extent to which sodium coolant would interact with the fuel in case of cladding failure, and (3) redistribution of fuel and fission products by vapor transport. The oxygen potential could also affect diffusion and creep rates within the fuel.

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A computer model based on these results and other U-Pu-O phase studies was developed to permit oxygen-potential calculations over a range of variables. Calculated results from the model agreed well with experimental data in the literature that had been obtained under specific conditions by various investigators.

There was concern that interaction of sodium coolant with the oxide fuel in a reactor could produce swelling and cladding rupture in the event of a leak in the cladding. Earlier studies had indicated that the equilibrium phase between sodium and UO_2 in the temperature range of 600-1000°C is Na₃UO₄. Experiments conducted with mixed oxide (UO2-19.8% PuO₂) gave an X-ray pattern similar to that of $Na_{2}UO_{4}$, indicating that the material was Na_2MO_4 , where M is (U + Pu). When attempts were made to measure Na_2UO_4 with the mass spectrometer, sodium vaporized, leading to a three-phase region believed to be NaUO₃- Na_2UO_4 - Na_2O_7 , where both sodium and oxygen could be measured. Further studies were conducted in which UO₂-20% PuO₂ in the form of powders or sintered pellets was contacted with sodium at 900°C, yielding Na_3MO_4 . X-ray diffraction showed this to be a single-phase material with a face-centered cubic structure and a lattice parameter of 4.77 Å. In another study, lattice-parameter measurements were used to determine the equilibrium O/M ratio of mixed UO₂-PuO₂ fuel as a function of temperature and the U/Pu ratio. To determine the kinetics of UO_2 -20% PuO₂ reaction with sodium, sintered pellets of the material were exposed to sodium in sealed capsules at temperatures of 500-900°C, sectioned, polished, and examined under a microscope. The unreacted UO₂-PuO₂ and the Na_3MO_4 phases were readily distinguishable, so the extent of reaction could be measured. The product was observed as a surface layer that extended into cracks near the surface, which were somewhat enlarged because the product had a lower density than the original material.

A technique called "matrix isolation spectroscopy" investigate was used to thermodynamic properties of materials at temperatures beyond the range of direct experimental measurements. For example, thermodynamic data obtained by this technique were important in determining equation-ofstate relationships used to project the outcome of design-basis accidents in a fast breeder reactor. In using this technique, a solid sample of the material of interest was heated in a Knudsen effusion cell, and the resulting molecular beam in a stream of inert gas impinged on an infrared transmitting window in a liquid helium cryostat, freezing the molecules in an inert gas lattice. These lowtemperature conditions greatly simplify interpretation of visible and infrared spectroscopic data. Construction and testing of this equipment were completed in 1970. These studies began with uranium oxides and were extended include oxides of cerium. later to europium, terbium, praseodymium, and thorium.

REACTOR FUEL STUDIES

Thermodynamic Properties. Although the high-temperature thermodynamic studies provided much of the basic information needed to evaluate the safety of fast breeder reactors and possible consequences of an accident, additional investigations were focused more specifically on this subject. For example, Len Leibowitz, Martin Chasanov, and Bob Blomquist measured the speed of sound in liquid sodium to provide data for analyses of shock-wave propagation. Further studies by these individuals plus Don Fredrickson and Don Fischer extended the results and provided additional thermodynamic data.

A variational calculation method based on thermodynamic considerations was developed to determine the effects of burnup, void volume, and starting fuel composition on the phase composition and pressure of an oxide fuel-fission product mixture produced when the fuel is heated to 3225° C. The vapor pressure was important in evaluating designbase accidents, and the phase composition was necessary for post-accident heat-removal analysis. The thermal diffusivity of UO₂ was required to evaluate safe methods of cooling an LMFBR core in case of a meltdown.

Arc-melting experiments showed that liquid phases of iron and UO, separated cleanly on solidification, and that the zirconium favored the oxide phase, as expected. Because a concrete base might be located under the core of a reactor such as FFTF, high-temperature experiments were conducted with liquid UO2concrete and molten steel. The concrete forms a liquid at about 1100°C, and at some point the liquid phase of UO₂, PuO₂, fission products, and concrete constituents (SiO2, CaO, and Al₂O₃) will rise to the surface and float on the molten steel. Information on the fissionproduct distribution between these two liquid phases is needed to estimate the heat distribution between the phases. This study was then extended to a situation in which basalt would be used as a sacrificial material that would, in case of a meltdown, dissolve the molten fuel, thereby reducing the heat flux. Experiments were performed on the distribution of representative fission products (lanthanum, cerium, niobium, molybdenum, and ruthenium) between molten iron and a 6 wt% solution of UO_2 in molten basalt. As expected from thermodynamic predictions, rare earths and niobium were found in the basalt phase, and the noble metals (ruthenium and molybdenum) were in the iron phase. During these studies, the solubility of UO_2 in basalt was found to be 5 to 7 wt% at 1550°C and 50 to 55 wt% at 2200°C.

The viscosity of liquid basalt was measured over the range 1350-1950°C, using a rotatingcup viscometer, and similar measurements were made on molten alumina over the range 2121-2469°C. Thermal-diffusivity measurements on UO₂ were also made by Bob Blomquist, Jim Haley, Jack Fischer, and Martin Chasanov.

In 1975, a study was begun on various methods of retaining an ex-vessel core after an accident. The function of the core retainer would be to prevent uncontrolled downward travel of the core debris following a breach of the reactor vessel ("China syndrome") and to remove fission-product decay heat. Although a variety of solutions had been suggested and most of them were considered in the study, the major effort was aimed at sacrificial barriers. Barrier materials under consideration included basalt, alumina, magnesia, urania, and thoria.

The post-accident heat-removal (PAHR) studies consisted of two parts. One was a comprehensive computer modeling study that incorporated the extensive physical property and thermodynamic information that was alreadv available; other the was an experimental effort to provide additional key data. The matrix-isolation method was used to generate thermodynamic functions of fuelvapor species at high temperatures. Data on UO₂ were obtained by Steve Gabelnick, Gerry Reedy, and Martin Chasanov. Dave Green and Gerry Reedy produced data on uranium nitrides, plutonium oxides, and plutonium nitrides. Joanne Fink, Martin Chasanov, and Len Leibowitz prepared a preliminary set of property values for thorium and uranium systems.

In addition to the fission-product heating in a meltdown situation, consideration must be given to heat produced by chemical reactions of the materials. One such situation was found in the modeling of post-accident heat removal in gas-cooled fast reactors, where the hightemperature (~2100°C) reaction of UO_2 , graphite, and stainless steel is exothermic. Heat evolution from this reaction must be included in the development of procedures for containing failed core material in gas-cooled fast reactors.

The Division participated in various international efforts to assess the state of

thermodynamic data for reactor safety analysis, to identify what further information was needed, and to determine the most effective ways of promulgating the existing data.

Effects of *Irradiation* on Reactor Fuels. Nuclear fuels in a reactor undergo a variety of changes due to radiation exposure, heat, contact with the coolant, and mechanical stresses. The fissile material is converted to fission products, which may react chemically with one another, with the fuel, and with the cladding. Fission gases can pressurize the fuel elements, and cladding can be embrittled or affected otherwise by the high temperatures and by coolant corrosion. The principal variables affecting the fuel are the radiation level (mainly of neutrons), the time of exposure, and the temperature. The burnup of the fuel (% of fissile material consumed) depends upon the flux and energy distribution of the neutrons and the time of exposure. The objective of these studies was to evaluate the chemical and physical effects that occurred in the fuel during irradiation.

Determination of Burnup in Fast **Reactor Fuels.** In the late 1960s, a program for measuring burnup in fast reactor fuels was based on developing analytical methods for fission products that could be used as burnup monitors, and on establishing accurate values of their fission yields. An ideal burnup monitor would be a fission product whose fission yield is insensitive to neutron energy. The primary candidates lie on the two peaks of the fissionyield curve. On the heavy element peak are the four major rare earth elements (lanthanum, cerium, praseodymium, and neodymium), plus iodine, tellurium, and barium. On the light element peak are zirconium, ruthenium, and molybdenum. Radioactive nuclides of these elements were investigated as potential burnup monitors.

The fission yield of a candidate burnup monitor was determined from the amount of

that fission-product nuclide produced from a known number of fissions. A new technique for quickly determining the number of fissions consisted of using solid-state track recorders (SSTRs) and foil activation. The technique involves placing a thin, uniform deposit (nanograms) of a fissile material in contact with a suitable dielectric such as mica. As fissions occur, the recoil fission fragments produce damage tracks in the dielectric, which, after chemical etching, are visible under a microscope. Simultaneous irradiation of an adjacent foil (approximately 300 mg) of the fissile material produces enough fissionproduct nuclides for radiochemical analysis or direct counting with a Ge(Li) detector.

Using the above technique, fission-yield determinations were made for Ce-144, Zr-95, Zr-97, Mo-99, Ru-103, I-131, Te-132, and Ba-140. Distinguishing features of these nuclides were short half-lives (1 to 65 days), fission yields greater than three percent, and well-established photon emissions (gamma rays) from disintegration. Fission yields are different for Pu-239 and U-235, but for a particular fissile material the yields vary little with neutron energy. As a result of this work, Zr-95 and Ba-140 were frequently chosen as burnup monitors.

Fast Reactor Neutron Reactions. With the cooperation of the EBR-II and the Materials Science Divisions, the CEN Division measured the capture-to-fission ratios of the principal heavy elements in fast reactor fuels, determined the extent of helium production and its possible relationship to radiation damage of cladding and structural materials, and measured the fission yield of tritium.

Capture-to-fission ratios for Pu-239, U-235, U-238, and U-233 were determined as functions of radial and axial positions in the EBR-II core. A study was made of helium production in sections of the stainless steel control and safety rod thimbles in EBR-II. Nitrogen in stainless steel diffuses from colder to hotter zones in stainless steel, where it undergoes (n,α) reactions to produce helium. Because helium acts to stabilize voids in stainless steel, it can accelerate loss of ductility of the stainless steel under irradiation. This study showed that helium generation rates could be calculated with an accuracy of 25-30%.

Knowledge of how much tritium is generated in fuel during irradiation is important in the design of reactors and processing plants. Accurate measurements of the tritium fission yield were difficult because of its low yield relative to those of other fission products, its long half-life (11 years), and the possibility that reactions other than fission could produce tritium. Experiments in CEN revealed a tritium fission yield of 2.25×10^{-4} (±20%) per fission of U-235. This value is two to three times that for the thermal yield of 0.8 to 0.9×10^{-4} tritons per fission.

A program to measure the tritium yields from fast fission of Pu-239 was begun in Early 1972. measurements showed а considerably higher yield than that for fast fission of U-235. The irradiation experiments were redesigned to accommodate the higher yield and were performed in EBR-II, but the program was canceled before the samples could be analyzed-part of the general cutback in LMFBR research and development to provide additional funding for construction of the Fast Flux Test Facility.

Dosimetry and Damage Analysis. On July 1, 1971, a dosimetry program was established in the CEN Division. The program comprised three major tasks: (1) development and application of experimental and analytical techniques for characterizing fast-neutron irradiation environments in terms of neutron flux, fluence, energy spectrum; and (2) establishment of methods for computing parameters irradiation correlation (e.g., displacements per atom) from dosimetry data; and (3) service dosimetry.

Development of Dosimetry Methods. The principal means by which dosimetry methods were developed and demonstrated was by participation in the Interlaboratory Reaction Rate program. (ILRR) The participating laboratories utilized different methods, and the results were compared through the ILRR program. The participating laboratories and their principal methods were as follows: (1) Argonne, SSTRs and foil activation, (2) Hanford Engineering Development Laboratory, foil activation, (3) National Bureau of Standards, ion chamber, (4) Aerojet Nuclear Corporation, proton recoil and neutronics calculations, (5) Los Alamos National Laboratory, neutronics calculations.

Neutron reactions comprise both fission and nonfission reactions (e.g., capture). Rates for both types of reaction were needed. The required accuracy for nonfission reactions $(\pm 5\%)$ was considered to be in hand. Additional work, however, was required to achieve a higher accuracy $(\pm 3\%)$ for fission reactions because of their use for calculating reactor power and fuel burnup, and for developing fuel behavior correlations.

Investigators at ANL exposed SSTRs and adjacent massive foils (300 mg) of U-235 in a low-power facility (the Coupled Fast Reactor Measurement Facility, at Aerojet Nuclear Corp.) to establish a factor, K, for the relationship between the counts per minute for a particular fission product (e.g., Zr-95) counted in a particular Ge(Li) detector and geometry to the number of fissions per gram established by the SSTRs. Because SSTRs could not be used in a high-flux reactor such as EBR-II, K factors were used in conjunction with foil activation in EBR-II to determine fission rates. From work in the low-power facility. K factors for four different radionuclides were shown to be constant over a wide range of neutron energies. With the foil technique, fission rates in EBR-II could be measured with an accuracy of $\pm 2.5\%$.

Radiation Damage Correlations. Correlating radiation damage effects with the neutron environments was just getting underway when the dosimetry program became a casualty of cutbacks in LMFBR research and development funding to provide additional support for construction of the Fast Flux Test Facility. The focus of the dosimetry then shifted to the Controlled Thermal Reactor (CTR) program.

Service Dosimetry. A service dosimetry program was organized to establish a capability for performing routine dosimetry measurements at ANL and EBR-II, and for coordinating ANL's overall dosimetry development program. This dosimetry program was responsible for designing the dosimetry aspects of all ANL experiments conducted in EBR-II. In the course of this and other work at EBR-II, over 600 dosimetry measurements were made.

IRRADIATED MIXED OXIDE FUELS

Studies of the chemistry of irradiated mixed oxide (UO_2-PuO_2) fuels were initiated in the late 1960s when the AEC selected mixed oxides as the fuel of choice for LMFBRs. These studies were continued throughout the 1970s. The objective was to gain an understanding of the complex chemical reactions and processes that take place in the fuels during irradiation. Knowledge of these phenomena was expected to lead to the development of methods for increasing fuel lifetime in the reactor.

Sampling and Analysis. As oxide fuels are irradiated, the temperature across the 3-mm radius varies from about 2500°C at the center to about 700°C at the cladding. This large temperature gradient produces restructuring of the fuel, an oxygen potential gradient, and a redistribution of the fission products (Fig. 4-26). In the hot central region, the